Electrochemical Reduction of CO₂ Catalyzed by Re(pyridine-oxazoline)(CO)₃Cl Complexes


†Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States
‡Department of Chemistry, Vassar College, Poughkeepsie, New York 12604, United States
§Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520, United States
∥Department of Chemistry, DePaul University, Chicago, Illinois 60614, United States
‡Chemistry Division, Energy & Photon Sciences Directorate, Brookhaven National Laboratory, Building 555A, Upton, New York 11973, United States
#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 CO₂ 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 CO₂ 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 CO₂ reduction by 1 in acetonitrile using density functional theory (DFT) supports the C-O bond cleavage step being the rate-determining step (RDS) (ΔG° = 27.2 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_cal/i_cat), 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 CO₂. Despite the fact that CO₂ 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 one-electron steps involves going through the high-energy radical anion intermediate (CO₂⁺⁻), demanding potentials as high as −1.90 V vs NHE at pH 7.⁴ Although the CO₂⁺⁻ radical can react with molecules such as olefins to produce carboxylate compounds, transition-metal catalysts capable of facile multi-electron transformations offer an alternate pathway to circumvent this undesirable high-energy intermediate.⁵–¹⁵ Among the many chemical transformations of CO₂ catalyzed by transition-metal catalysts, the reduction of CO₂ 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
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). 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 two-electron pathway. In the one-electron pathway, a net two-electron reduction of CO2 is initiated by the nucleophilic attack of the Re(0) species \([\text{Re}^0(bpy)(\text{CO})_3]^\text{-}\), which originates from the one-electron-reduced anion \(\text{fac-}[\text{Re}(\text{bpy}^\text{+})(\text{CO})_3]\text{Cl}^\text{-}\). 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. Thus, the bpy ligand plays an important “noninnocent” role during CO2 reduction by storing the first reducing equivalent in a Re(bpy+)-state, which facilitates CO2 binding through a low reorganization energy pathway. In the two-electron pathway, I is reduced by two electrons before it binds to CO2. The second reduction of I is assigned to a metal-based reduction, producing the anion \([\text{Re}(\text{bpy})(\text{CO})_3]^\text{-}\). 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 two-electron 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 CO2 more efficiently than the one-electron-reduced species \([\text{Re}^0(bpy)(\text{CO})_3]^\text{-}\). It is interesting to note that a recent report has shown that no CO2 reduction electrocatalysis is observed for Re(CO)_5 on the cyclic voltammetry time scale, as opposed to Mo(CO)_6 (M = Cr, Mo, W) precursors that are effective catalysts. 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 Re(diimine)(CO)3Cl 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, 5-methyl-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. 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. Stanton and co-workers studied the use of pyridyl N-heterocyclic carbenes (NHCs) derived from methylenimida- zolium-pyridine and showed that the rhenium complex of this ligand was capable of binding and transforming CO2 at the first reduction potential. In another example of substitution of one pyridyl in bpy, Liyanage et al. examined several other pyridyl N-heterocyclic carbenes. The rhenium complexes formed by these ligands can also efficiently reduce CO2 at the first reduction wave with \((i_{\text{cat}}/i)^\text{32}\) ranging from 1 to 3, with the tricarbonylbromorhenium(I) complex formed with the 3-(4-trifluoromethylphenyl)-1-(2-pyridyl)imidazolin-2-ylidene ligand showing the highest catalytic rate. Herein, the syntheses, structural characterization, the electrocatalytic activity, and the step-by-step mechanism calculated using density functional theory (DFT) for CO2 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, \((i_{\text{cat}}/i)^\text{32}\), up to 7 times larger than that of I.

### EXPERIMENTAL DETAILS

#### Materials

Acetonitrile, ethanol, benzene, toluene, isobutyl chloroformate, 2-chloroethoxylamine hydrochloride, potassium hydroxide, sodium sulfate, sodium sulfite, pyridine-2-carboxylic acid, 2-quino linecarboxylic acid, 2-pyridinecarboxaldehyde, 2-amino-1-phenylethanol, 2-aminobenzaldehyde, 2-amino-3-pyridinecarboxaldehyde, 2-chloro-3-quinolinecarboxaldehyde, 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-acetylpyrindine, 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 (pyrox), 5-methyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (Me-pyrox), and 5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (Ph-pyrox) were prepared according to previously reported methods.

\(\text{Re(ppy)}\text{Cl)}(\text{CO})_3(\text{Cl})\) (I). In a 50 mL round-bottom flask, Re(CO)_5Cl (0.2 g, 0.6 mmol), pyrox (0.08 g, 0.6 mmol), and tol uene (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)
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MHz, DMSO-\(d_6\)); 9.04 (d, 1H), 8.35 (t, 1H), 8.15 (dd, 1H), 7.89 (t, 1H), 5.02 (m, 2H), 4.31 (m, 1H), 4.11 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 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 (CH\(_3\)CN): \(m/z\) 460.1 [M – Cl + CH\(_2\)CN]. Analyzed for C\(_{12}\)H\(_8\)N\(_2\)O\(_4\)ClRe\(_{1.5}\). Found for C\(_{12}\)H\(_8\)N\(_2\)O\(_4\)ClRe\(_{1.5}\): C, 28.42; H, 2.15; N, 5.36. Calcd: C, 28.66; H, 2.39; N, 5.77.

Re[Me-pyrrxo]/[CO]/Cl (2). In a 50 mL round-bottom flask, Re(OCO)\(_2\)/Cl (0.7 g, 1.9 mmol), Me-pyrrxo (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 C\(_7\)H\(_8\) and hexanes afforded material suitable for single-crystal X-ray crystallography. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 8.99 (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). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 170.98 (s), 154.28 (s), 144.76 (s), 139.29 (s), 129.37 (s), 126.19 (s), 83.48 (s), 61.31 (s), 20.82 (s). ESI-MS (CH\(_3\)CN): \(m/z\) 474.1 [M – Cl + CH\(_2\)CN]. Analyzed for C\(_{12}\)H\(_8\)N\(_2\)O\(_4\)ClRe\(_{1.5}\)/H\(_2\)O, C, 29.76; H, 2.25; N, 5.36. Calcd: C, 29.26; H, 2.49; N, 5.77.

Re[Ph-pyrrxo]/[CO]/Cl (3). In a 50 mL round-bottom flask, Re(OCO)\(_2\)/Cl (0.25 g, 0.7 mmol), Ph-pyrrxo (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 C\(_7\)H\(_8\) and hexanes afforded material suitable for single-crystal X-ray crystallography. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 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). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 165.26 (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), 76.05 (d). ESI-MS (CH\(_3\)CN): \(m/z\) 536.1 [M – Cl + CH\(_2\)CN]. Analyzed for C\(_{17}\)H\(_{12}\)N\(_2\)O\(_4\)ClRe\(_{1.5}\): C, 29.62; H, 1.90; N, 5.36. Calcd: C, 29.43; H, 1.98; N, 5.36.

**Methods.** \(^1\)H and \(^{13}\)C 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 (CH\(_2\)CN) 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 using a Model 6012D electrochemical analyzer from CH Instruments, Inc. or DY2311 potentiostat from Digi-Fry. Cyclic voltammetry experiments were performed using the nonaqueous electrolyte mixture of acetonitrile, DMF or DMSO as solvent, and with tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) or tetrabutylammonium fluorophosphate (TBAPF\(_6\)Cl). Aved and 1 to 1 M transfer (solvation) free energy computed from the 6-311G(d) basis set of all species in solution. Thus, the free energy in solution is computed as

\[ \Delta G_{\text{sol}} = \Delta G_0 + \Delta G_{\text{R}} - \Delta G_{\text{sol}} \]  

where \(\Delta G_0\) is the free energy change associated with eq 1 (using Boltzmann statistics for the electron) and \(\Delta G_{\text{sol}}\) is taken as 0.141 V, which is required for the conversion of calculated \(E_{\text{rel}}\) versus the

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**X-ray Crystallography.** X-ray diffraction data were collected on a Bruker APEX DUO CCD platform diffractometer (Mo K\(\alpha (\lambda = 0.71073\) A) 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 \(P\) with SHELXL (Version 2008). 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 displacement parameters (SIMU) and rigid bond 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 an 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 model for acetonitrile as the solvent. The Stuttgart \[8s7p6d2f|ECP60MWB\] contracted pseudopotential basis set was used for Re and the 6-31G(d) basis set for all other atoms. Nonanalytical integrals were evaluated using the integral = (grid = ultrfine) 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. The nature of all stationary points was verified by analytic vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 cm\(^{-1}\) replaced by 50 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. 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(2d,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. 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

\[ \text{O(soln) + ne}^{-}(g) \rightarrow \text{R(soln)} \]  

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 \(E_{\text{OR}}\) relative to SCE was computed as

\[ E_{\text{OR}} = -\frac{\Delta G_{\text{OR}}}{nF} - \Delta E_{\text{rel}} \]  

where \(\Delta G_{\text{OR}}\) is the free energy change associated with eq 1 (using Boltzmann statistics for the electron) and \(\Delta E_{\text{rel}}\) is taken as 0.141 V, which is required for the conversion of calculated \(E_{\text{rel}}\) versus the
normal hydrogen electrode (NHE) in aqueous solution ($E_{\text{NHE}} = -4.281 \, \text{V}$)\textsuperscript{57} to $E_{\text{SCE}}$\textsuperscript{58} versus the saturated calomel electrode (SCE) in acetonitrile ($E_{\text{SCE}} = -4.422 \, \text{V}$).\textsuperscript{59} We obtained reduction potentials referenced to the ferrocene/ferrocenium couple by using a shift of $-0.384 \, \text{V}$ from $E_{\text{SCE}}$ to SCE.

Benchmark Calculations. Benchmark calculations at the M06-L, B3LYP,\textsuperscript{59} M06,\textsuperscript{41,42,50} MP2, domain based local pair natural orbital (DLPNO) based single- and double-excitation coupled-cluster (DLPNO-CCSD),\textsuperscript{51,52} and DLPNO-CCSD with perturbative inclusion of triple excitations (DLPNO-CCSD(T))\textsuperscript{53} levels of theory were performed using the def2-TZVPP basis set\textsuperscript{54} on all atoms and the Hamiltonian.\textsuperscript{55} Atom-pairwise dispersion correction to the DFT energies with Becke–Johnson damping has been applied for B3LYP density functional.\textsuperscript{56} The activation energies were accounted for using the zeroth-order regular approximation (ZORA) Hamiltonian.\textsuperscript{57–58} Atom-pairwise dispersion correction to the DFT energies with Becke–Johnson damping has been applied for B3LYP density functional.\textsuperscript{59} The activation energies were computed using the optimized geometries at the M06-L level of theory (see above for full description).

\section{RESULTS}

Syntheses and Characterization of the Re(I) Complexes. The synthesis of complex 1 was carried out by treating Re(CO)$_5$Cl with the corresponding ligand in refluxing toluene under N$_2$ 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 $^1$H and $^{13}$C 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.\textsuperscript{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 $\nu_{\text{CO}}$ values for these compounds do not differ significantly from each other (see below). In addition, the C–Re–C angles for the three complexes range from 88.1 to 90.8$^\circ$ and are similar to the reported structures for other Re diimine complexes.\textsuperscript{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

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
Complex & X-ray & M06-L \\
\hline
Re–N1 & 2.199(2) & 2.271 \\
Re–N2 & 2.164(2) & 2.189 \\
Re–Cl & 2.4833(6) & 2.546 \\
Re–C1 & 1.918(3) & 1.908 \\
Re–C2 & 1.912(2) & 1.919 \\
Re–C3 & 1.921(2) & 1.900 \\
N1–Re–N2 & 74.12 & 72.90 \\
\hline
\end{tabular}
\end{table}

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.

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–C1 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–C1 1.915(3), Re–C2 1.926(2), Re–C3 1.926(3).
Cotton–Kraihanzel method (Table 1). The interaction constants, $k_0$, for 1–3 are very similar to those calculated for 1

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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>15.44</td>
</tr>
<tr>
<td>3</td>
<td>15.60</td>
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indicating similar weak σ bonding between the α-dimine ligands and the tricarbonylrhenium fragments, in agreement with the similar Re–N 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). This assignment is supported by the significant bathochromic shift on going from polar to less polar solvents (Δν_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 solvatochromatic effect due to the diminished polarity difference between ground and excited states. In addition, the MLCT bands for compounds 1–3 are broad, with Δν_max ≈ 6900 cm⁻¹. Although a number of factors can influence the width of an absorption band, the broader MLCT bands observed for the rhenium pyridine-oxazine 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 ππ* LC transitions, as similar transitions are also observed in the spectra of the free ligands.

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 Fe⁺/⁻³, 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, $i_r/i_p$, increases progressively with the scan rate (Figures S17 and S18 in the Supporting Information), indicating that an irreversible 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 Fe⁺/⁻³) in comparison to 1 (−2.2 vs Fe⁺/⁻³). Due to the similar potentials at which the first reduction wave appears for 1 and 1–3, it is likely that it represents a pyridine-based reduction of the starting complex to form the radical complex [Re(pyroxa)n⁺(CO)₃(Cl)]⁻. Since the complexes undergo facile halide loss on reduction, an anodic peak appears at −1.6 V corresponding to the [Re(pyroxa)₃(CO)₃(solvent)]⁺/²⁺ couple. This behavior is consistent with the ECE reduction behavior of 1 and similar rhenium species.

<table>
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<tr>
<th>catalyst</th>
<th>1st reduction potential (V vs Fc⁺/⁻³)</th>
<th>2nd reduction potential (V vs Fc⁺/⁻³)</th>
<th>$j$ (mA/cm²)</th>
<th>$i_r/i_p$</th>
<th>$\eta$ (V)</th>
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</table>

*Cyclic voltammograms were recorded in acetonitrile solution (1.0 mM in catalyst) with 0.1 M [Bu₄N]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. Current densities, $j$, and overpotentials were determined at the potential of $E_{1/2}$. Calculated as described in ref 66. Reference 30.
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 \( \frac{(i_{cat}/i_p)^2}{\text{current density}} \), obtained from cyclic voltammetry, was used. It has been proposed that \( \frac{(i_{cat}/i_p)^2}{\text{current density}} \), being proportional to the turnover frequency (TOF), provides a useful quantity to compare relative TOFs. On the basis of such analysis, catalyst 1 shows a higher performance in comparison to 1. 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 \( \frac{(i_{cat}/i_p)^2}{\text{current density}} \). The current densities for the three catalysts are higher than that of 1; 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 S22 and Table S23 in the Supporting Information). The addition of the more acidic proton donor, methanol (Figure S21 in the Supporting Information), the quantity \( \frac{(i_{cat}/i_p)^2}{\text{current density}} \), 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 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 \([\text{Re(pyroxa})(\text{CO})_4](\text{OTf})\) (4) was synthesized similarly to a reported procedure for \([\text{Re(bpy})(\text{CO})_4](\text{OTf})\).\(^{69}\) Compound 4 was characterized by elemental analysis and FT-IR spectroscopy (Figure 6) as well as \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. The cation is likely to be a product formed during the reduction of CO₂ 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 \([\text{Re(bpy})(\text{CO})_4](\text{OTf})\),\(^{69}\) we hypothesized that the release of CO from \([\text{Re(pyroxa})(\text{CO})_4](\text{OTf})\) requires additional reducing equivalents.\(^{69,70}\) When a solution of 4 in acetonitrile under an inert atmosphere was exposed to a stoichiometric amount of Na–Hg amalgam (0.1–0.2 equiv, blue) in acetonitrile.

![Figure 6](image)

**Table 4. Results of Bulk Electrolysis in Acetonitrile**

<table>
<thead>
<tr>
<th>compound</th>
<th>potential (V) vs Fe⁺/⁻</th>
<th>Faradaic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−2.8</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>−2.8</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>−2.8</td>
<td>30</td>
</tr>
</tbody>
</table>

*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 1, the reaction is likely to proceed as CO₂ + 2e⁻ + 2H⁺ → CO + H₂O. We also performed a bulk electrolysis experiment at a lower potential for 1 (at −2.3 V vs Fe⁺/⁻) 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 CO₂ reduction products (bulk electrolysis in the absence of CO₂ produced a trace amount of CO (1% Faradaic efficiency). Notably, solid formation was observed over the course of bulk electrolysis experiments under CO₂, which supports this hypothesis.

We also performed a controlled-potential electrolysis of 1 in the presence of CO₂ 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 CO₂ 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 H₂. Under CO₂, reduction of CO₂ shifted to lower potentials, with a larger increase in current observed for the more acidic proton donor, methanol (Figure 6). The addition of the more acidic proton donor phenol (pKₐ 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 of the complexes 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).
Mechanism of CO2 reduction by [Re(pyroxa)(CO)3]−

Figure 7. Infrared spectelectrochemistry spectra of the reduction of 1 in acetonitrile under Ar with 0.1 M TBAPF6 as a supporting electrolyte. [Re(pyroxa)(CO)3]− 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, [Re(pyroxa)(CO)3]− forms. The second reduction of the complex leads to the five-coordinate anion [Re(pyroxa)(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 Electrolyte46

<table>
<thead>
<tr>
<th>compound</th>
<th>signal (cm−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2023, 1913, 1894</td>
</tr>
<tr>
<td>[Re(pyroxa)(CO)3]Cl−</td>
<td>2010, 1894, 1873</td>
</tr>
<tr>
<td>[Re(pyroxa)(CO)3]Cl−</td>
<td>1981, 1867, 1852</td>
</tr>
<tr>
<td>[Re(pyroxa)(CO)3]−</td>
<td>1979, 1850</td>
</tr>
</tbody>
</table>

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

[Re(pyroxa)(CO)3]−. 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 [Re(pyroxa)(CO)3]0 species can then be reduced by one more electron to the active anion [Re(pyroxa)(CO)3]−. The IR spectra for [Re(pyroxa)(CO)3]− possesses signals that are similar to, but more positive than, those of the corresponding [Re(bpy)(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 Fe3+/2+, 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°) 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°) of 12.5 kcal/mol, generating the highly basic [Re-CO2]− (pKac = 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., H2O). The optimized transition state structure with H2O (Figure 8) as the proton source features a ΔG° value of 27.9 kcal/mol and is followed by a reduction step with an associated computed potential of E = −1.63 V vs Fe3+/2+ to generate [Re-CO]. On the other hand, the reduction-first pathway starts with the reduction of [Re-CO2H] to [Re-CO2H]− with a computed potential of E = −2.00 V vs Fe3+/2+, followed by C−OH bond cleavage with ΔG° = 27.2 kcal/mol with H2O as the proton source. Both the protonation-first and reduction-first pathways result 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 Fe3+/2+ 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 (∼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
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 $\Delta E^\ddagger$ 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 $[\text{Re}^I(\alpha\text{-diimine})^\ddagger(\text{CO})_3\text{Cl}]^-$ and not as $[\text{Re}^0(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]^-$, similarly to $\text{I}^-$ and other "18 + δ" rhenium complexes containing α-diimine ligands. 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 $[\text{Re}^I(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]^-$ is ligand-centered.
and generates $[\text{Re}^\alpha(\text{α-diimine}^{2-})(\text{CO})_3\text{Cl}]^-$ (Figures S26–S28 in the Supporting Information). However, the dissociation of chloride ion proceeds with a relatively low $\Delta G^\dagger$ 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 $[\text{Re}^\alpha(\text{α-diimine}^{2-})(\text{CO})_3\text{Cl}]^-$ species. Further, the product of the second reduction could be assigned as $[\text{Re}^\alpha(\text{α-diimine}^{2-})(\text{CO}^\alpha)_3]^-$ 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 1, 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 CO$_2$, 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 ($i_{\text{cat}}/i_p$), are larger for 1 and 2 in comparison to 1, 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 ($i_{\text{cat}}/i_p$)$^2$ 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 CO$_2$ reduction with the Pd complex [Pd-(triphosphine)solvent)](BF$_4$)$_2$ 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 CO$_2$ reduction was calculated using eq 3.

$$i_c = nF[A\text{[cat.]}(Dk[CO_2])^{1/2}]$$

Terms include $i_c$ for the catalytic current observed in the voltammograms, $n$ for the number of electrons (2 for the reduction of CO$_2$ 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 $^1$H 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 ± 6 M$^{-1}$ 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 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 CO$_2$ 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 reaction$^{80}$ 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

<table>
<thead>
<tr>
<th>compound</th>
<th>ACN</th>
<th>DMF</th>
<th>DMSO</th>
<th>ACN</th>
<th>DMF</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>203 ± 6</td>
<td>5.3 ± 0.1</td>
<td>2 ± 0.3</td>
<td>11.9</td>
<td>14.0</td>
<td>14.6</td>
</tr>
<tr>
<td>2</td>
<td>157 ± 24</td>
<td>4.4 ± 0.1</td>
<td>3.3 ± 0.1</td>
<td>12.0</td>
<td>14.1</td>
<td>14.3</td>
</tr>
<tr>
<td>3</td>
<td>66 ± 10</td>
<td>12 ± 2</td>
<td>12 ± 2</td>
<td>12.5</td>
<td>13.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>

$^*\text{Calculated assuming the pre-exponential factor } A = 10^{11}$ and using the rate constants from the reactions in acetonitrile, DMF, or DMSO.$^{76}$

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 ■); 3 (blue ▲). Donor numbers for acetonitrile, DMF, and DMSO are 14.1, 26.6, and 29.8, respectively.
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 (ΔE ≈ 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‡ 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‡ values from reactant complexes but ΔG‡ values from separated reactants are also reported in Table S10. The computed ΔG‡ 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‡ 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‡ 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)3H] (or [Re(CO)3H]+) 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 CO2 to CO, a rhenium complex of the form [Re(diimine)(CO)3] ‡ 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)3]‡ 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 liberation of a carbonyl ligand, similar to the behavior of the analog [Re(bpy)(CO)3] ‡, regenerating the active species.

In comparison with I and other analogues such as Re(1-bppy)(CO)3Cl (1-bppy = 4,4′-di-tert-buty1-2,2′-bipyridine), 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. Re(2-bppy)(CO)3Cl is the fastest catalyst with a reported second-order rate constant of 650 M−1 s−1,30 3 times the rate constant of I, the fastest catalyst in the series presented here. I is, nevertheless, more active than other Re(bpy)(CO)3Cl derivatives containing electron-withdrawing substituents or electron-donating substituents on the 2,2′-bipyridine ligand, namely –CO2H, –CH3, and –OCH3.30 The better activity of Re(2-bppy)(CO)3Cl in comparison to other analogues of I 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 I 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(pyridine-oxazoline)(CO)3Cl, which were demonstrated to electrocatalytically reduce CO2 to form CO. Two of our new catalysts display relative turnover frequencies, (i1/i2)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 pyridine-oxazoline 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‡ 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.inorgchem.6b02384.

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

## AUTHOR INFORMATION

Corresponding Authors
*E-mail for K.A.G.: kgrice1@depaul.edu.
*E-mail for M.Z.E.: mzertem@bnl.gov.
*E-mail for A.M.A.-B.: alfredo.angeles-boza@uconn.edu.

ORCID
Carlos Pacheco: 0000-0002-5607-5517
Victor S. Batista: 0000-0002-3262-1237
Alfredo M. Angeles-Boza: 0000-0002-5560-4405

Present Addresses
*Universidad San Ignacio de Loyola, Av. La Fontana 550, La Molina, Lima, Peru.

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