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Mechanistic insights into electrocatalytic CO$_2$
reduction within [Ru$^{II}$(tpy)(NN)X]$^{n+}$ architectures

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Abstract
A series of Ru$^{II}$-polypyridyl complexes of the design [Ru$^{II}$(tpy)(NN)X]$^{n+}$ (tpy = 2,2′:6,2″-terpyridine; NN = bidentate polypyridine; X = Cl$^{-}$ or CH$_3$CN; n = 1 or 2) have been synthesized and analyzed for their ability to function as electrocatalysts in the reduction of CO$_2$ to CO. Varying the electron-donating/withdrawing character of the NN polypyridyl ligand has allowed for modification of electron density at the formally Ru$^{II}$ metal center. Complexes where X = Cl$^{-}$ display ligand substitution for CH$_3$CN with differing rates of Cl$^{-}$ dissociation ($k_{-Cl}$), therefore providing a degree of insight into the electron density and thus the chemical activity at the Ru$^{II}$ center. Detailed analysis of the cyclic voltammograms under argon vs. CO$_2$ atmospheres using multiple switching potentials and scan rates ranging from $\nu$ = 25-2000 mV/s has painted a picture of how monodentate ligand lability due to NN polypyridyl electron-donating character is related to electrocatalytic CO$_2$ reduction activity of Ru$^{II}$-polypyridyl complexes. From these studies, multiple mechanistic pathways towards generating the catalytically active [Ru(tpy$^-$)(NN$^-$)CO$_2$]$^0$ species are proposed and differ via the order of electrochemical and chemical processes.
Introduction

High levels of thermodynamically stable, kinetically inert CO$_2$ within Earth’s biosphere from anthropogenic sources have forced the scientific community to develop a means for CO$_2$ fixation. Converting CO$_2$ to higher-energy species capable of providing energy in a fashion similar to fossil fuels is of great interest and importance in the quest for alternative fuel sources. An attractive approach to this issue involves the use of photochemical\textsuperscript{1-4} and/or electrochemical\textsuperscript{5,6} reductive processes to convert CO$_2$ into CO, HCOOH, CH$_3$OH, or CH$_4$. Multi-electron/proton transfer processes provide a lower thermodynamic potential compared to the one-electron reduction which generates a high energetic CO$_2$$^-•$ radical anion. Equations 1-6 show the thermodynamic formal potential ($E^\circ$) for each reductive process measured in V vs. NHE at 25°C in pH = 7 aqueous solution.\textsuperscript{7}

\begin{align*}
1. & \text{CO}_2 + 1\text{e}^- \rightarrow \text{CO}_2^-\text{•} \quad -1.90 \text{ V} \\
2. & \text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{HCO}_2\text{H} \quad -0.61 \text{ V} \\
3. & \text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O} \quad -0.53 \text{ V} \\
4. & \text{CO}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O} \quad -0.48 \text{ V} \\
5. & \text{CO}_2 + 6\text{e}^- + 6\text{H}^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad -0.38 \text{ V} \\
6. & \text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad -0.24 \text{ V}
\end{align*}

Transition metal-based catalysts are able to circumvent the energetically unfavorable CO$_2$$^-•$ radical anion by providing a lower energy pathway for CO$_2$ reduction via multi-electron processes. Of equal importance is the necessity for CO$_2$-selective reduction catalysts as protons are able to be reduced to H$_2$ at potentials more negative than −0.41 V vs. NHE. Combining the appropriate balance of electronics (provided by the ligand architecture) and the intrinsic properties of the metal center has generated several molecular architectures incorporating
cyclams (Co^{II}, Ni^{II})^{7-10}, porphyrins (Fe^{0})^{11, 12}, phosphines (Rh^{I}, Pd^{II}, Ir^{III})^{13-16}, and polypyridines (Mn^{I}, Ru^{II}, Rh^{III}, Re^{I}, Ir^{III})^{17-29} that function as electrocatalysts for CO\textsubscript{2} reduction. The utilization of electrochemical methods provides further insight into the factors that affect CO\textsubscript{2} reduction (redox potentials, electron transfer rates, chemical kinetics) and assist in elucidating mechanistic pathway(s) towards product formation. This powerful tool can therefore be used to not only compare catalysts, but also contribute to the design of future, more efficient catalysts.

Polypyridine-containing molecular architectures present a subset of CO\textsubscript{2}-reducing catalysts that are of great interest given the ability to tune the electronics \textit{via} ligand modification and the potential to store multiple reducing equivalents within the polypyridyl scaffold.\textsuperscript{23, 30} Molecular architectures of type [Ru^{II}(NNN)(NN)X]^{n+} (where NNN = tridentate polypyridyl ligand, NN = bidentate polypyridyl ligand, X = monodentate ligand) have recently been demonstrated to be viable catalysts for H\textsubscript{2}O oxidation\textsuperscript{31-38}, H\textsubscript{2}O reduction\textsuperscript{39}, and CO\textsubscript{2} reduction\textsuperscript{18, 21, 40, 41}. Incorporation of electron-donating or -withdrawing groups in the polypyridyl ligand is expected to increase or decrease electron density at the formally Ru\textsuperscript{II} reactive metal center, respectively, and drive formation of specific products (i.e. Ru-hydrido, Ru-carboxylato, Ru-formato) in the presence of various educts (i.e. H\textsuperscript{-}, H\textsuperscript{+}, CO\textsubscript{2}, H\textsubscript{2}O). As one might expect, the rate of product formation should also be affected by electron density at the Ru\textsuperscript{II} center. While numerous studies have been performed to assess the impact polypyridyl ligand modification has on H\textsubscript{2}O oxidation, surprisingly few studies report the role polypyridyl ligand modification has on CO\textsubscript{2} reduction within a Ru\textsuperscript{II} architecture.\textsuperscript{21, 40}

Reported herein are the electrochemical properties and electrocatalytic activity for a series of [Ru\textsuperscript{II}(tpy)(NN)X]^{n+} complexes 1-6 (NN = bidentate polypyridyl ligand; X = monodentate ligand) with varying degrees of electron-donating/withdrawing capabilities within the bidentate ligand...
set, Figure 1. A thorough and systematic approach to understanding the observed
electrochemical processes provides insight into the electrocatalytic activity towards CO₂
reduction and generates a picture of the factors impacting catalysis. Complexes where X = Cl⁻
(labeled [Ru¹ิ-Cl⁺]) provide a probe into monodentate ligand lability at the Ru¹ิ center as a
function of bidentate ligand electron-donating ability and are found to correlate with the
observed trend for CO₂ reduction activity. Similarly, complexes where X = CH₃CN (labeled
[Ru¹ิ-NCCCH₃]²⁺) serve as not only reference complexes for deciphering electrochemical
mechanisms within [Ru¹ิ-Cl⁺] complexes, but also to confirm observed trends in electrocatalytic
CO₂ reduction using various bidentate ligands. Electrochemical studies further suggest that CO₂
binding can occur at the one-electron reduced [Ru¹ิ-Cl]⁰ level or the two-electron reduced [Ru¹ิ-
NCCH₃]⁰ level when bidentate ligands with electron-donating character are incorporated.

Fig. 1 Structures of Ru¹ิ-polypyridyl complexes for electrocatalytic CO₂ reduction in this study.

Experimental Section
Materials. All solvents were reagent grade and all materials were used as received unless otherwise stated. RuCl$_3$•3H$_2$O and triethylamine (TEA) were purchased from Acros Organics. 2,2′:6′,2″-Terpyridine (tpy), 4,4′-Di-tert-butyl-2,2′-bipyridine (4,4′-tBu$_2$bpy), and lithium chloride were purchased from Sigma-Aldrich. 4,4′-Dimethyl-2,2′-bipyridine (4,4′-Me$_2$bpy), 4,4′-dimethoxy-2,2′-bipyridine (4,4′-(MeO)$_2$bpy), 1,10-phenanthroline (phen), and 2,2′-bipyrimidine (bpm) were purchased from Aldrich. Ammonium hexafluorophosphate and tetrabutylammonium hexafluorophosphate (≥ 99.0%) were purchased from Fluka. CO$_2$(g) (99.998%) was purchased from Air Liquide. Glassware used for electrochemical analyses were kept in a 120°C oven until needed.

The bidentate ligand dipyrido[3,2-a:2′,3′-c]phenazine (dppz) was synthesized as previously reported. [Ru$^{II}$(tpy)(4,4′-Me$_2$bpy)NCCH$_3$](PF$_6$)$_2$ (6-CH$_3$CN) was synthesized in 65% yield. [Ru$^{II}$(tpy)(4,4′-Me$_2$bpy)Cl](PF$_6$) (0.081 g, 0.12 mmol) was heated at reflux in the dark overnight using 1:1 CH$_3$CN/H$_2$O (50 mL). The orange solution was cooled to room temperature and the volume reduced to ~20 mL which induced precipitation of an orange solid. Additional orange precipitate formed upon adding ~15 mL of 0.2 M NH$_4$PF$_6$(aq). The precipitate was filtered and washed with cold water and diethyl ether to yield a bright orange solid (0.064 g, 0.075 mmol, yield = 65%). Elemental analysis calculated for C$_{29}$H$_{26}$F$_{12}$N$_6$P$_2$Ru•1H$_2$O: C, 40.15; H, 3.25; N, 9.69. Found: C, 40.41; H, 3.24; N, 9.66. $^1$H-NMR (400 MHz, CD$_3$CN) δ 9.39 (d, $J$ = 5.7 Hz, 1H), 8.53 (d, $J$ = 8.1 Hz, 2H), 8.47 (s,
1H), 8.40 (d, $J = 8.1$ Hz, 2H), 8.27 (t, $J = 8.1$ Hz, 1H), 8.21 (s, 1H), 7.99 (td, $J = 7.9, 1.5$ Hz, 2H), 7.79 (dd, $J = 5.7, 1.2$ Hz, 1H), 7.70 – 7.66 (m, 2H), 7.39 – 7.31 (m, 2H), 7.06 (d, $J = 5.8$ Hz, 2H), 6.90 (dd, $J = 6.1, 1.3$ Hz, 1H), 2.75 (s, 3H), 2.36 (s, 3H). ESI-MS(+): [M–PF$_6$]$^+$, m/z = 703.8 (calc: m/z = 704.6); [M–2PF$_6$]$^{2+}$, m/z = 279.5 (calc: m/z = 279.8).

$[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}^{1}\text{Bu}_2\text{bpy})\text{NCCH}_3]\text{(PF}_6\text{)}_2$ (2-CH$_3$CN). The same procedure for the $[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}^{1}\text{Bu}_2\text{bpy})\text{NCCH}_3]\text{(PF}_6\text{)}_2$ was followed using $[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}^{1}\text{Bu}_2\text{bpy})\text{Cl}]\text{(PF}_6\text{)}$ (0.081 g, 0.10 mmol) to yield a bright orange solid (0.050 g, 0.054 mmol, yield = 52%).

Elemental analysis calculated for C$_{35}$H$_{38}$F$_{12}$N$_6$P$_2$Ru•1H$_2$O: C, 44.17; H, 4.24; N, 8.83. Found: C, 44.11; H, 4.22; N, 8.82. $^1$H-NMR (400 MHz, CD$_3$CN) $\delta$ 9.44 (d, $J = 6.0$ Hz, 1H), 8.59 (d, $J = 2.0$ Hz, 1H), 8.54 (d, $J = 8.2$ Hz, 2H), 8.41 (d, $J = 8.1$ Hz, 2H), 8.33 (d, $J = 1.9$ Hz, 1H), 8.31 – 8.25 (m, 1H), 8.00 (td, $J = 7.9, 1.5$ Hz, 2H), 7.94 (dd, $J = 6.0, 2.0$ Hz, 1H), 7.71 – 7.65 (m, 2H), 7.36 (ddd, $J = 7.6, 5.5, 1.3$ Hz, 2H), 7.11 (d, $J = 6.1$ Hz, 1H), 7.05 (dd, $J = 6.1, 2.1$ Hz, 1H), 1.60 (s, 9H), 1.25 (s, 9H). ESI-MS(+): [M–PF$_6$]$^+$, m/z = 787.8 (calc: m/z = 788.8); [M–2PF$_6$]$^{2+}$, m/z = 321.3 (calc: m/z = 321.9).

$[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}(\text{MeO})_2\text{bpy})\text{NCCH}_3]\text{(PF}_6\text{)}_2$ (3-CH$_3$CN). The same procedure for the $[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}(\text{MeO})_2\text{bpy})\text{NCCH}_3]\text{(PF}_6\text{)}_2$ was followed using $[\text{Ru}^{II}(\text{tpy})(4,4'\text{-}(\text{MeO})_2\text{bpy})\text{Cl}]\text{(PF}_6\text{)}$ (0.070 g, 0.095 mmol) to yield a bright orange solid (0.054 g, 0.061 mmol, yield = 64%).

Elemental analysis calculated for C$_{29}$H$_{26}$F$_{12}$N$_6$O$_2$P$_2$Ru•1H$_2$O: C, 38.72; H, 3.14; N, 9.34. Found: C, 38.52; H, 3.10; N, 9.18. $^1$H-NMR (400 MHz, CD$_3$CN) $\delta$ 9.32 (d, $J = 6.4$ Hz, 1H), 8.52 (d, $J = 8.1$ Hz, 2H), 8.40 (d, $J = 8.1$ Hz, 2H), 8.25 (t, $J = 8.1$ Hz, 1H), 8.13 (d, $J = 2.7$ Hz, 1H), 7.99 (td, $J = 7.9, 1.5$ Hz, 2H), 7.87 (d, $J = 2.8$ Hz, 1H), 7.78 – 7.72 (m, 2H), 7.52 (dd, $J = 6.5, 2.7$ Hz, 1H), 7.37 (ddd, $J = 7.6, 5.5, 1.3$ Hz, 2H), 6.97 (d, $J = 6.6$ Hz, 1H), 6.61 (dd, $J = 6.6, 2.8$ Hz, 1H), 2.36 (s, 3H).
4.18 (s, 3H), 3.83 (s, 3H). ESI-MS(+): [M–PF$_6$]$^+$, m/z = 735.7 (calc: m/z = 736.6); [M–2PF$_6$]$^{2+}$, m/z = 295.1 (calc: m/z = 295.8).

**Physical Measurements.** $^1$H-NMR spectra were measured in CD$_3$CN solvent using a JEOL 400 MHz spectrometer at 293 K. The chemical shifts given in ppm are internally referenced to the residual CH$_3$CN solvent signal (1.96 ppm). HPLC-MS data were obtained using a Dionex UltiMate 3000 system on a Phenomenex Gemini C18 column (150 x 3.0 mm, 5µm) coupled to a Thermo LCQ Deca XP Max with electrospray ionization. Solvents used for HPLC: 0.05% HCO$_2$H in H$_2$O and 0.05% HCO$_2$H in CH$_3$CN. Electronic absorption spectra were measured in CH$_3$CN solvent using a Varian Cary 50 UV-Vis spectrophotometer with 1 nm resolution. Elemental analysis (C,H,N) was performed by Analytische Laboratorien GmbH (Lindlar, Germany).

**Electrochemistry.** Cyclic voltammetry (CV) experiments were performed using a one-compartment, three-electrode configuration connected to an Autolab PGSTAT100 potentiostat controlled with GPES 4.9 software (EcoChemie). The electrode setup included a glassy carbon disc (0.071 cm$^2$) working electrode that was polished using 0.05 μM alumina prior to use, a carbon rod auxiliary electrode, and a Ag/Ag$^+$ (0.01 M AgNO$_3$ in CH$_3$CN, −0.060 V vs. Fe$^{0+/+}$; Fe$^{0+/+}$ = [Fe(C$_5$H$_5$)$_2$]) non-aqueous reference electrode. Potential values were converted to versus Fe$^{0+/+}$ by addition of 60 mV. CVs containing 1 mM of each complex were measured using 0.1 M Bu$_4$NPF$_6$ supporting electrolyte in either argon- or CO$_2$-saturated CH$_3$CN solutions at room temperature with scan rates (ν) varying from 25 to 2000 mV/s. Rate constants for Cl$^−$ dissociation ($k$−Cl) were obtained by fitting experimental CVs with simulated CVs using DigiElch™ 7 electrochemical simulation software. Overlaid simulated and experimental CVs for
complex 3-Cl, along with the fitting parameter conditions, are shown in Figure S5 in Supporting Information to provide as an example.

**Bulk Electrolysis.** Bulk electrolysis experiments were performed using a one-compartment cell, three-electrode configuration which comprised a glassy carbon rod (3.67 cm²) working electrode, carbon cloth auxiliary electrode, and Ag/Ag⁺ (0.01 M AgNO₃ in CH₃CN, −0.060 V vs. Fc⁰/⁺) reference electrode controlled by the Autolab PGSTAT100 potentiostat. Experimental conditions involved purging 0.1 M Bu₄NPF₆/CH₃CN solution (10 mL) containing 1 mM of [Ru(II)(tpy)(4,4′-Me₂bpy)(NCCH₃)]²⁺ (1-CH₃CN) with CO₂ for 30 minutes prior to applying a constant potential of −2.04 V vs. Fc⁰/⁺, providing a [CO₂] = 0.28 M. Gas samples were analyzed using a Perkin Elmer Clarus 500 series gas chromatogram (GC) equipped with a thermal conductivity detector (TCD), stainless-steel column packed with molecular sieves (60/80 mesh), and N₂ as the carrier gas (flow rate = 35 mL/min). The operating temperatures of the injection port, the oven/column, and detector were 100°C, 80°C, and 100°C, respectively. Aliquots (250 µL) of the gas headspace were injected into the GC after 10 min electrolysis to analyze the gas products formed.

**Results and Discussion**

**Synthesis.** The Ru³⁺-polypyridyl complexes were synthesized (Scheme 1) via step-wise reactions whereby the tridentate tpy ligand was first coordinated to RuCl₃•3H₂O, followed by bidentate ligand coordination to afford [Ru(tpy)(NN)Cl](PF₆) as dark maroon/purple solids. Converting the Cl⁻ substituted complexes to CH₃CN substitution was achieved by heating the complexes at reflux in CH₃CN/H₂O mixtures to afford [Ru(tpy)(NN)NCCH₃](PF₆)₂ as orange solids. Isotopic distribution patterns, obtained using ESI-MS operating in positive mode, were in
agreement with calculated spectra as mass-to-charge ratios displayed \([M−PF_6]^+\) and \([M−2PF_6]^{2+}\) for the newly reported \([\text{Ru}(\text{tpy})(4,4′\text{-Me}_2\text{bpy})\text{NCCH}_3](\text{PF}_6)_2\) (1-\text{CH}_3\text{CN}), \([\text{Ru}(\text{tpy})(4,4′-1′\text{Bu}_2\text{bpy})\text{NCCH}_3](\text{PF}_6)_2\) (2-\text{CH}_3\text{CN}), and \([\text{Ru}(\text{tpy})(4,4′-(\text{MeO})_2\text{bpy})\text{NCCH}_3](\text{PF}_6)_2\) (3-\text{CH}_3\text{CN}) complexes.

**Scheme 1** Synthetic scheme for the step-wise assembly of \([\text{Ru}^{II}(\text{tpy})(\text{NN})\text{X}]^{n+}\) complexes.

**Electrochemical Properties.** Electrochemistry provides insight into the redox-active nature of \([\text{Ru}^{II}(\text{tpy})(\text{NN})\text{X}]^{n+}\) complexes, their electron affinities and chemical stability(Figure 2; Figures S6-S11). The redox potentials of electrochemical processes are summarized in Table 1 and displayed in Figure 3. Anodic scans display a reversible, one-electron \(\text{Ru}^{II/III}\) oxidation that is strongly influenced by the nature of the monodentate ligand (Cl\(^-\) vs. \text{CH}_3\text{CN}) and, to a lesser degree, the electron-donating/withdrawing ability of the bidentate ligand set. The \([\text{Ru}^{II-\text{Cl}}]^+\)
complexes are oxidized at fairly mild potentials (+0.44 V to +0.66 V vs. Fe$^{0/+}$), with the complexes containing electron-donating ligands (1-Cl, 2-Cl, 3-Cl) being easier to oxidize than those containing electron-withdrawing ligands (5-Cl, 6-Cl). This trend is expected as increased electron density at Ru$^{II}$ shifts the Ru-based HOMO to higher energy. Substituting the stronger π-donor Cl$^-$ by a weaker π-donor CH$_3$CN to generate [Ru$^{II}$-NCCH$_3$]$^{2+}$ species stabilizes the Ru(dπ) orbital set. Consequently, Ru$^{II/III}$ couple is observed at ~0.50 V more positive potentials, indicative of a decrease in electron density at the Ru center.
Fig. 2 Cyclic voltammograms of 1 mM solutions of 
[Ru$^{II}$ (tpy)(NN)Cl]$^+$ (A) and 
[Ru$^{II}$ (tpy)(NN)NCCH$_3$]$^{2+}$ (B) complexes (NN = 4,4′-(MeO)$_2$-bpy, bpm, or dppz) in Ar-saturated 
CH$_3$CN using 0.1 M Bu$_4$NPF$_6$ supporting electrolyte at $\nu$ = 200 mV/s.

![Cyclic voltammograms of 1 mM solutions of Ru$^{II}$ complexes](image)

Fig. 3 Reduction and oxidation potentials of [Ru$^{II}$ (tpy)(NN)X]$^{n+}$ complexes (NN = bidentate ligand; X = Cl$^-$ or CH$_3$CN). Energy values represent measured $E_{1/2}$ potentials which were obtained using cyclic voltammetry. Black and red lines correspond to complexes where X = Cl$^-$ and CH$_3$CN, respectively.

Table 1 Redox Potentials for [Ru$^{II}$ (tpy)(NN)X]$^{n+}$ Complexes$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>[Ru-X]$^{(n+1)/n}$</th>
<th>[Ru-X]$^{(n)/(n-1)}$</th>
<th>[Ru-X]$^{(n-1)/(n-2)}$</th>
<th>$k_{Cl}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{1/2}$, V ($\Delta E_p$, mV)</td>
<td>$E_{1/2}$, V ($\Delta E_p$, mV)</td>
<td>$E_{1/2}$, V ($\Delta E_p$, mV)</td>
<td>($s^{-1}$)</td>
</tr>
<tr>
<td>1-Cl</td>
<td>0.502 (82)</td>
<td>-1.709 (91)</td>
<td>$b$</td>
<td>1.1</td>
</tr>
<tr>
<td>1-CH$_3$CN</td>
<td>0.996 (90)</td>
<td>-1.546 (81)</td>
<td>-1.882 (110)</td>
<td>$b$</td>
</tr>
<tr>
<td>2-Cl</td>
<td>0.511 (83)</td>
<td>-1.696 (82)</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>2-CH$_3$CN</td>
<td>0.985 (91)</td>
<td>-1.555 (73)</td>
<td>-1.884 (95)</td>
<td>$b$</td>
</tr>
<tr>
<td>3-Cl</td>
<td>0.443 (81)</td>
<td>-1.731 (94)</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>3-CH$_3$CN</td>
<td>0.855 (90)</td>
<td>-1.573 (81)</td>
<td>-1.896 (101)</td>
<td>$b$</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.547 (77)</td>
<td>-1.690 (84)</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>4-CH$_3$CN</td>
<td>1.055 (81)</td>
<td>-1.537 (81)</td>
<td>-1.838 (72)</td>
<td>$b$</td>
</tr>
</tbody>
</table>
5-Cl  0.659 (81)  -1.412 (84)  -1.811 (79)  1 x 10^{-3}
5-CH\textsubscript{3}CN  1.181 (81)  -1.303 (81)  -1.658 (72)
6-Cl  0.582 (80)  -1.280 (79)  -1.759 (87)  5 x 10^{-4}
6-CH\textsubscript{3}CN  1.082 (81)  -1.240 (81)  -1.600 (81)

\(a\) Measurements performed using 1 mM of Ru\textsuperscript{II} complex in an argon-saturated CH\textsubscript{3}CN solution with 0.1 M Bu\textsubscript{4}NPF\textsubscript{6} supporting electrolyte at \(\nu = 200\) mV/s. Values reported are measured vs. Fe\textsuperscript{0/+}. Values in parentheses correspond to the cathodic and anodic peak potential separation for each redox couple. The value of \(n = 1+\) and \(2+\) for X = Cl\textsuperscript{-} and CH\textsubscript{3}CN complexes, respectively. \(b\) Reduction corresponding to [Ru\textsuperscript{II}-Cl]\textsuperscript{0/-} is not observed up to 2000 mV/s, only reduction for CH\textsubscript{3}CN-substituted species. \(c\) Rate constant for Cl\textsuperscript{-} dissociation following first reduction of [Ru\textsuperscript{II}-Cl]\textsuperscript{+} complexes calculated using DigiElch\textsuperscript{TM} software by fitting experimental CVs with simulated CVs.

Cathodic scans under an argon atmosphere present varied electrochemical properties throughout the [Ru\textsuperscript{II}-Cl]\textsuperscript{+} and [Ru\textsuperscript{II}-NCCH\textsubscript{3}]\textsuperscript{2+} series that are strongly influenced by bidentate ligand identity. Each series of complexes possess sequential, one-electron, ligand-based reductions with NN = Me\textsubscript{2}bpy, tBu\textsubscript{2}bpy, (MeO)\textsubscript{2}bpy, and phen complexes 1-4 possessing a tpy(\(\pi^*\))-based first reduction. Conversely, NN = bpm and dppz complexes 5 and 6 possess a NN(\(\pi^*\))-based first reduction due to the strong electron-accepting capability of the pyrimidine and phenazine subunits. This orbital inversion assignment is supported by comparing the 1\textsuperscript{st} reduction potential of the respective tris homoleptic complexes (\(E_{1/2}([\text{Ru(tpy)\textsubscript{2}}]^{2+/+}) = -1.67\) V vs. Fe\textsuperscript{0/+}; \(E_{1/2}([\text{Ru(bpm)}\textsubscript{3}]^{2+/+}) = -1.38\) V vs. Fe\textsuperscript{0/+}; \(E_{1/2}([\text{Ru(dppz)}\textsubscript{3}]^{2+/+}) = -1.35\) V vs. Fe\textsuperscript{0/+})\textsuperscript{51-53}, as well as a previously reported assignment for [Ru\textsuperscript{II}(tpy)(bpm)Cl](PF\textsubscript{6}).\textsuperscript{46} Switching scan direction following the first reduction displays the chemical reactivity in [Ru\textsuperscript{II}-Cl]\textsuperscript{+} complexes 1-4. As representatively shown in Figure 4A, the reverse scan in the CV of [Ru\textsuperscript{II}(tpy)(4,4'-MeO\textsubscript{2}bpy)Cl]\textsuperscript{+} (3-Cl) displays two anodic waves (\(E_p\))\textsuperscript{8}, one at -1.68 V for the expected [Ru\textsuperscript{II}-Cl]\textsuperscript{0/+} oxidation, and a second oxidation at -1.53 V for the ligand-exchanged [Ru\textsuperscript{II}-NCCH\textsubscript{3}]\textsuperscript{3+/2+} oxidation. Similar chemical reactivity is observed for NN = Me\textsubscript{2}bpy, tBu\textsubscript{2}bpy, and phen complexes, Figure S12. Varying the scan rate from 25-2000 mV/s allows for
measuring the rate of Cl⁻ dissociation \(k_{-Cl}\) within these systems, providing a degree of insight into monodentate ligand lability as a function of electron-donating ability from the bidentate ligand to the formally Ru²⁺ metal center. DigiElch™ electrochemical simulation software was used to generate simulated CVs and fit those with experimentally obtained CVs by varying parameters such as the reduction potential (E), the rate constant for heterogeneous electron transfer \(k_s\), and the equilibrium constant and rate constant for a chemical reaction (i.e. Cl⁻ dissociation). The calculated \(k_{-Cl}\) values range from \(5 \times 10^{-4}\) to \(1.1 \text{ s}^{-1}\) depending on electron-donating character of the bidentate ligand, Table 1. Chloride ligand lability is not observed in the one-electron reduced bpm or dppz-containing [Ru²⁺-Cl]⁺ complexes 5-Cl and 6-Cl (Figure 4B and Figure S12, respectively) in which the injected electron is localized on the electron-deficient bidentate ligands that are evidently electronically isolated from the Ru-Cl bond. The decreased electron density at Ru²⁺ of 5 and 6 suppresses Cl⁻ ligand dissociation at the applied potentials and therefore predicts 5 and 6 to function poorly as efficient catalysts for metal-centered, reductive catalysis. [Ru²⁺-NCCH₃]²⁺ complexes, regardless of bidentate ligand identity, display a reversible one-electron, ligand(π*)-based reduction as CH₃CN dissociation is slow on the electrochemical time scale at the applied potentials (Figure S13). The potential difference between the anodic and cathodic waves \(\Delta E_p \approx 80 \text{ mV}\) and the ratio of anodic to cathodic current \(i_p^a/i_p^c \approx 0.9\) remain constant at all measured scan rates, indicating electrochemical and chemical reversibility within [Ru²⁺-NCCH₃]²⁺ complexes. When comparing \(\Delta E_{1/2}\) values between [Ru²⁺-Cl]⁺/⁰ and [Ru²⁺-NCCH₃]²⁺⁺⁺, the \(E_{1/2}\) shifts to more positive potential by \(-110\text{-}160 \text{ mV}\) upon CH₃CN coordination for all complexes except NN = dppz. The observed \(\Delta E_{1/2}\) value of only 40 mV indicates the very strong electron-withdrawing nature of the phenazine component, as
CH$_3$CN substitution has a minimal affect and suggests some degree of electronic isolation between the bipyridine and phenazine portions of the dppz ligand.

Fig. 4 Cyclic voltammograms of [Ru$^{II}$](tpy)(4,4′-(MeO)$_2$bpy)Cl]$^+$, 3-Cl (A) and [Ru$^{II}$](tpy)(bpm)Cl]$^+$, 5-Cl (B) complexes with $\nu$ ranging from 25 mV/s (black line) to 2000 mV/s (purple line). The 1$^{st}$ reduction at $\nu = 200$ mV/s (green dashed line) for [Ru$^{II}$](tpy)(4,4′-(MeO)$_2$bpy)NCCH$_3$$^+$, 3-CH$_3$CN (A) and [Ru$^{II}$](tpy)(bpm)NCCH$_3$$^+$, 5-CH$_3$CN (B) complexes are included as a reference. [Ru$^{II}$-Cl] and [Ru$^{II}$-NCCH$_3$] labels correspond to the presence of Cl$^-$ or CH$_3$CN bound species.

Continued cathodic scanning presents further varied electrochemical properties and chemical reactivity. [Ru$^{II}$-Cl]$^+$ complexes 1-Cl to 4-Cl do not display a [Ru$^{II}$-Cl]$^{0/-}$ reduction under argon due to Ru-Cl bond labilization and CH$_3$CN coordination upon further applied negative bias. Therefore, only the reduction corresponding to [Ru$^{II}$-NCCH$_3$]$^{+/0}$ is observed, Figure 5A and Figure S14. As expected, return anodic scans display only re-oxidations that arise from the CH$_3$CN-bound complexes. Electron-withdrawing ligands as in 5-Cl and 6-Cl stabilize the [Ru$^{II}$-Cl]$^0$ species which exhibit a [Ru$^{II}$-Cl]$^{0/-}$ reduction that is tpy($\pi^*$)-based at $E_p^c = -1.85$ V (bpm) and −1.80 V (dppz). For 5-Cl, two-electron reduction forms [Ru$^{II}$tpy]$^-$(bpm$^-$)Cl]$^-$ which is quasi-stable as the presence of both [Ru$^{II}$-Cl]$^0$ and [Ru$^{II}$-NCCH$_3$]$^{0+/}$ re-oxidations are observed at $E_p^a = −1.77$ V and −1.62 V, respectively, Figure 5B. Re-oxidation of both one-electron
reduced species, [Ru$^{II}$-Cl]$^{0/+}$ and [Ru$^{II}$-NCCH$_3$]$^{+/2+}$, is only observed when the potential has been scanned past two reductive couples, indicating that Ru-Cl bond labilization for NN = bpm requires two electrons. Complex 6-Cl is able to undergo two-electron reduction to form [Ru$^{II}$((tpy)$^-$(dppz)$^-$)Cl]$^-$ with the Cl$^-$ ligand remaining coordinated to Ru$^{II}$ at $\nu = 200$ mV/s (Figure 2A). This lack of Cl$^-$ lability emphasizes the impact strongly electron-withdrawing ligands have on chemical reactivity at the sixth coordination site within this architecture which requires ligand dissociation prior to formation of a catalytically active species. Assignments for each redox couple within the Cl$^-$ series of complexes are justified by using the synthesized [Ru$^{II}$((tpy)(NN)NCCH$_3$)]$_{2+}$ complexes as a reference given the observed redox couples will only correspond to [Ru$^{II}$-NCCH$_3$] species.

**Fig. 5** Cyclic voltammograms (including the 2$^{nd}$ reduction) of [Ru$^{II}$((tpy)(4,4′-(MeO)$_2$bpy)Cl)]$^+$, 3-Cl (A) and [Ru$^{II}$((tpy)(bpm)Cl)]$^+$, 5-Cl (B) complexes with $\nu$ ranging from 25 mV/s (black line) to 2000 mV/s (purple line). The CVs of [Ru$^{II}$((tpy)(4,4′-(MeO)$_2$bpy)NCCH$_3$)]$^{2+}$, 3-CH$_3$CN (A) and [Ru$^{II}$((tpy)(bpm)NCCH$_3$)]$^{2+}$, 5-CH$_3$CN (B) at $\nu = 200$ mV/s (green dashed line) are included as a reference. [Ru$^{II}$-Cl] and [Ru$^{II}$-NCCH$_3$] labels correspond to the presence of Cl$^-$ or CH$_3$CN bound species.
While the synthesized [Ru\textsuperscript{II}-NCCH\textsubscript{3}] complexes are expected to display chemical stability upon multi-electron reduction, two trends were observed. The complexes containing NN = bpm (5-CH\textsubscript{3}CN) or dppz (6-CH\textsubscript{3}CN) displayed two reversible, one-electron reductions (Figure S15). However, complexes where NN = Me\textsubscript{2}bpy (1-CH\textsubscript{3}CN), \textsuperscript{1}Bu\textsubscript{2}bpy (2-CH\textsubscript{3}CN), or (MeO)\textsubscript{2}bpy (3-CH\textsubscript{3}CN) deviate substantially from chemical reversibility for the second reduction as CH\textsubscript{3}CN dissociation is observed at scan rates as low as 200 mV/s (Figure S15). This assignment is in direct agreement with a previous observation for [Ru\textsuperscript{II}(tpy)(bpy)NCCH\textsubscript{3}]\textsuperscript{2+}.\textsuperscript{54} Substitution of CH\textsubscript{3}CN for a substrate, such as CO\textsubscript{2}, is therefore expected to be favorable due to ligand lability at the sixth coordination site in complexes containing electron-donating substituents (methoxy, tert-butyl, or methyl). Complexes containing strong, electron-withdrawing subunits (pyrimidines or phenazines) are expected to display minimal-to-negligible reactivity towards CO\textsubscript{2} substitution as ligand reduction does not greatly labilize the Ru-X bond. Complexes where NN = phen (4-Cl and 4-CH\textsubscript{3}CN) present an intermediary regime as the phenanthroline ligand contains appropriate electron-donating ability to labilize the Ru-Cl bond upon one-electron reduction for [Ru\textsuperscript{II}-Cl]\textsuperscript{+}, but also possesses sufficient electron-withdrawing character to minimize CH\textsubscript{3}CN dissociation upon two-electron reduction for [Ru\textsuperscript{II}-NCCH\textsubscript{3}]\textsuperscript{2+} complexes (Figure S15).

**Electrocatalytic Properties.** Cyclic voltammograms were obtained under a CO\textsubscript{2} atmosphere to assess the capabilities of [Ru\textsuperscript{II}(tpy)(NN)X]\textsuperscript{n+} complexes for electrocatalytic CO\textsubscript{2} reduction. Bulk electrolysis of a CO\textsubscript{2}-saturated solution of 1-CH\textsubscript{3}CN was performed and the headspace analyzed by gas chromatography to confirm the formation of CO as the major product, Figure S16, as well as measuring reference gas samples to identify retention times. Anodic scans did not alter the redox-active nature, chemical stability, or potential of the Ru\textsuperscript{II/III} couple in any complexes, indicating that Cl\textsuperscript{-} or CH\textsubscript{3}CN do not dissociate at applied positive bias and CO\textsubscript{2} is
unable to coordinate. However, performing cathodic scans at multiple scan rates and switching potentials provided insight into the mechanism of catalytic CO$_2$ reduction and the electronic factors impacting catalysis. **Scheme 2** summarizes the proposed electrochemical and chemical processes that lead to catalytic CO$_2$ reduction. **Figure 6** shows cathodic scans of $[\text{Ru}^{II}(\text{tpy})(4,4'$-$(\text{MeO})_2\text{bpy})X]^{n+}$ (3-Cl and 3-CH$_3$CN) in Ar- and CO$_2$-saturated acetonitrile solutions with cathodic current enhancements visible at potentials more negative than $-1.74$ V vs Fc$^{0/+}$ under a CO$_2$ atmosphere. Qualitatively similar voltammograms are obtained for complexes 1, 2, and 4 (Figures S17-S19). While previous reports using $[\text{Ru}^{II}(\text{tpy})(\text{bpy})\text{NCH}_3]^2+$ ascribe this cathodic current enhancement to multiple electron transfer steps within the catalytic cycle for CO$_2$ reduction to CO,$^{18,21}$ the present study gives a more intimate picture of the order of chemical and electrochemical steps, as well as the impact NN ligand donor strength has on catalytic activity.
**Fig. 6** (A) CVs displaying the cathodic region of [Ru^{II}(tpy)(4,4′-(MeO)_2bpy)Cl]⁺ under Ar (solid black line) and CO₂ (dashed black line) atmospheres at ν = 200 mV/s. Inset: Isolation of 1st reduction process under Ar (solid) and CO₂ (dashed) atmospheres. (B) CVs displaying the cathodic region of [Ru^{II}(tpy)(4,4′-(MeO)_2bpy)NCCH₃]^{2+} under Ar (solid red line) and CO₂ (dashed red line) atmospheres at ν = 200 mV/s. Inset: Isolation of 1st reduction process under Ar (solid) and CO₂ (dashed) atmospheres.

Comparing the reductive waves for complexes 1-4 in the absence and presence of CO₂ allows the detection of processes that arise from CO₂-related chemistry. Analysis of the Cl⁻ substituted...
complex under CO$_2$ is presented first. As shown in the inset of Figure 6A, switching scan direction after the one-electron reduction of [Ru$^{II}$-Cl]$^{+/0}$ (I) reveals only [Ru$^{II}$-Cl]$^{0/+}$ oxidation and an absence of the [Ru$^{II}$-NCCH$_3$]$^{+/2+}$ oxidation that was observed in the voltammograms obtained under Ar. This observation is significant and suggests [Ru$^{II}$-NCCH$_3$]$^+$ that is partially formed in the one-electron reduction of [Ru$^{II}$-Cl]$^+$ either reacts further in the presence of CO$_2$, or that CO$_2$ binds directly to a five-coordinate [Ru]$^+$ intermediate that arises from Cl$^-$ dissociation (Scheme 2). Either way, we ascribe the absence of the anodic wave associated with [Ru$^{II}$-NCCH$_3$]$^+$ oxidation to the formation of a one-electron reduced, CO$_2$-adduct [Ru$^{II}$-CO$_2$]$^+$. The only remaining feature in the anodic scan following [Ru$^{II}$-Cl]$^{+/0}$ reduction originates from trivial [Ru$^{II}$-Cl]$^{0/+}$ re-oxidation to regenerate the original species. Current enhancement beyond −1.80 V (cathodic to the reduction wave) should correspond to [Ru$^{II}$-CO$_2$]$^{+/0}$ reduction, while the small current magnitude indicates this to be a minor pathway towards formation of the two-electron reduced [Ru$^{II}$-CO$_2$]$^0$ complex. The potential range that is observed for the reduction of the CO$_2$-bound species (via the carbon atom) is plausible, as it can be expected to occur at more positive potential than that of the analogous CH$_3$CN-bound species given the $\delta^+$ character of the CO$_2$ carbon atom. The broad current response between −1.80 V and −2.00 V (II) corresponds to slow conversion of the [Ru$^{II}$-Cl]$^0$ species to [Ru$^{II}$-CO$_2$]$^+$ and subsequent reduction to [Ru$^{II}$-CO$_2$]$^0$. The lack of a large catalytic wave at −1.89 V, as seen for the [Ru$^{II}$-NCCH$_3$]$^{2+}$ complexes (vide infra), also suggests that a significant portion of [Ru$^{II}$-Cl]$^+$ is stable under the reaction conditions. More negative applied potential induces a large catalytic wave at −2.09 V (III) that corresponds to a second reduction to [Ru$^{II}$-Cl]$^-$, followed by Cl$^-$ dissociation, CO$_2$ coordination and further reduction processes of the thereby generated [Ru$^{II}$-CO$_2$]$^0$ species to produce CO and to regenerate the [Ru$^{II}$-NCCH$_3$]$^{n+}$ pre-catalyst.\textsuperscript{18,21}
In contrast to the behavior observed for \([\text{Ru}^{\text{II}}\text{-Cl}]^+\), the CVs for the one-electron reduction of \([\text{Ru}^{\text{II}}\text{-NCCH}_3]^2+\) (I) are identical in the presence and absence of CO\(_2\) (Figure 6B inset). This finding indicates that the one-electron reduced \([\text{Ru}^{\text{II}}\text{-NCCH}_3]^+\) is not sufficiently electron rich to initiate CH\(_3\)CN substitution by CO\(_2\). Continued negative scanning past −1.74 V displays a catalytic wave at −1.89 V (II) whereby the potential and normalized current response vary with scan rate. This process is labeled as a second, one-electron reduction to form \([\text{Ru}^{\text{II}}\text{-NCCH}_3]^0\) followed by CH\(_3\)CN dissociation and CO\(_2\) coordination to form \([\text{Ru}^{\text{II}}\text{-CO}_2]^0\) (Scheme 2). Given the large, yet unequal, current response between complexes 1-CH\(_3\)CN to 4-CH\(_3\)CN, some degree of catalysis is occurring. Peak potential corresponding to this catalytic wave varies from −1.93 V for the electron-donating complexes (NN = (MeO)\(_2\)bpy, Me\(_2\)bpy, tBu\(_2\)bpy) to −1.83 V for the intermediary complex (NN = phen) to −1.77 V for the electron-withdrawing complex (NN = bpm). The large catalytic wave at −2.09 V (III) in complexes 1-4 is attributed to further complex reduction and ensuing catalysis, as is observed for the \([\text{Ru}^{\text{II}}\text{-Cl}]^+\) complexes. The varied current response at waves II and III between complexes (\(i_{\text{cat}}\)) indicate that NN ligand donor strength impacts catalysis, with electron-donating ligands enhancing catalysis. Consequently, complexes possessing stronger electron-donating ligands require a larger negative applied bias for reduction to occur; therefore the expected overpotential (\(\eta\)) for CO\(_2\) reduction will be larger.

Recent work by Savéant and co-workers has illustrated the intimate relationship between turnover frequency (TOF) of the catalyst and the overpotential for substrate reduction.\(^5\)

Assuming wave II to contain catalytic activity further supports this statement as CH\(_3\)CN-substituted complexes with stronger donating NN ligands (1-3) are reduced at more negative potential and display larger \(i_{\text{cat}}\) than NN = phen (4) or bpm (5) complexes.
Scheme 2 Proposed mechanisms and intermediate species of the electrochemical and chemical processes prior to catalysis in the absence and presence of CO$_2$ for complexes where the first reduction is tpy($\pi^*$)-based (complexes 1-4). The specified potentials (vs. Fe$^{0/+}$) correspond to 3-Cl and 3-CH$_3$CN complexes as an illustrative example and the synthesized complexes are shown in italics.

Decreased electron-density at Ru$^{II}$ via bpm or dppz incorporation diminishes CO$_2$ coordination and subsequent catalytic activity as evidenced by the lack of substantial current enhancement in the presence of CO$_2$. Figure S20 and S21. The minimal-to-negligible catalytic activity for this strongly electron-withdrawing architecture emphasizes the need for appropriate energetics to efficiently drive catalysis.

Thorough analysis of all the collected data presents a complex picture as to how electron density at the Ru$^{II}$ center affects the lability and catalytic activity at the sixth coordination site within this molecular architecture. Complexes where the first reduction is primarily tpy($\pi^*$)-
based (1-4) contain NN ligands with a greater degree of electron-donating character as opposed to complexes 5 and 6 where the first reduction is NN(π*)-based. As described above, the rate constant for Cl\(^-\) dissociation correlates well with the degree of electron-donating/withdrawing character, providing knowledge as to how the polypyridyl ligand set influences the lability at the formally Ru\(^{II}\) metal center. From a CO\(_2\) reduction viewpoint, complexes with increased electron density at Ru\(^{II}\) (Cl\(^-\) complexes 1-3) displayed much larger current enhancement ratios when measured under a CO\(_2\) atmosphere vs. an Ar atmosphere \((i_{\text{cat}}/i_p)\) than complexes with decreased electron density at Ru\(^{II}\) (Cl\(^-\) complexes 5 and 6). Complex 4-Cl\(^-\) displayed an intermediate current enhancement value compared to the two extremes, as well as possessing a balance of electron-donating and withdrawing character. This observation of catalytic activity as a function of electron density at the formally Ru\(^{II}\) metal center is in direct correlation with the rate of Cl\(^-\) dissociation through the first reductive couple in [Ru\(^{II}\)(tpy)(NN)Cl]\(^+\) complexes. By plotting current enhancement under a CO\(_2\) atmosphere \((i_{\text{cat}}/i_p)\) vs. the rate constant for Cl\(^-\) dissociation \((k_{-\text{Cl}})\), Figure 8, the effect of how electron-donating character of the bidentate ligand impacts chemical reactivity and catalytic activity can be seen. Strongly electron-donating polypyridyl ligands increase electron density at Ru\(^{II}\) and labilize the Ru-Cl or Ru-NCH\(_3\) bond, thereby producing a coordinatively unsaturated, electron-rich Ru\(^{II}\) metal center to coordinate with CO\(_2\). Electron-withdrawing ligands are expected to decrease electron density at Ru\(^{II}\) and inhibit efficient reductive, metal-based catalysis.
**Fig. 8** Plot depicting catalytic current enhancement in the presence of CO$_2$ ($i_{cat}/i_p$) vs. the rate constant for Cl$^-$ ligand dissociation ($k_{Clt}$) in [Ru$^{II}$(tpy)(NN)Cl]$^+$ complexes where the degree of electron-donating ability of NN varies. Using the chloro-substituted complexes, the $i_{cat}$ values were obtained from the large current response at −2.10 V vs. Fe$^{0/+}$ in the presence of CO$_2$ and the $i_p$ values were obtained from the current response of the 2$^{nd}$ cathodic wave near −2.0 V vs. Fe$^{0/+}$ in the absence of CO$_2$.

**Conclusions**

The relative ease of synthesis and purification for this [Ru$^{II}$(tpy)(NN)X]$^{n+}$ molecular architecture permitted generation of a small library of complexes with varying degrees of electron-donating/withdrawing ability to study their electrochemical and electrocatalytic properties. Isolating the redox couples throughout the cathodic region for [Ru$^{II}$-Cl]$^+$ and [Ru$^{II}$-NCCH$_3$]$^{2+}$ complexes display how the rate of monodentate ligand dissociation is directly related to electron density at the formally Ru$^{II}$ metal center through electron donation from the bidentate ligand. This observation is in direct correlation with the reactivity at the sixth coordination site on Ru$^{II}$ as catalytic activity for CO$_2$ reduction (measured by the ratio of current response in presence and absence of CO$_2$, $i_{cat}/i_p$) correlates well with the rate constant for Cl$^-$ ligand dissociation.
dissociation \(k_{-Cl}\). As shown, complexes 1-3 where the bidentate ligand contains electron-donating substituents (methyl, tert-butyl, methoxy) possess a much larger value for \(k_{-Cl}\) and \(i_{cat}/i_p\) compared to analogous complexes (5 and 6) containing electron-withdrawing components (pyrimidines, phenazine). The phenanthroline-containing complex 4 presented intermediate values for \(k_{-Cl}\) and \(i_{cat}/i_p\) which indicates the unique properties of the phenanthroline ligand that does not appear to function as either a strong electron-donating or withdrawing species. Interestingly, [Ru\(^{II}\)-Cl]\(^+\) complexes where the first reduction was \(\text{tpy}(\pi^*)\)-based (1-4) showed that after one-electron reduction under CO\(_2\) atmosphere, none of the corresponding CH\(_3\)CN-bound species was present upon switching scan direction. While the CH\(_3\)CN-bound complex was observed under an argon atmosphere, this lack of [Ru\(^{II}\)-NCCH\(_3\)]\(^{1/2+}\) oxidation upon scan direction reversal suggests that CO\(_2\) is able to coordinate after one-electron reduction of [Ru\(^{II}\)-Cl]\(^+\). This unique finding proposes that at least two mechanistic pathways towards CO\(_2\) reduction are present within this architecture and differ by the order of electrochemical vs. chemical steps (i.e. EC vs. CE processes). Such observations of varying mechanisms towards catalysis have been shown to exist for proton and CO\(_2\) reduction using various transition metal-based catalysts.\(^{56, 57}\) Ongoing studies within the lab involve incorporating this architecture into heterogeneous systems for electrocatalysis, as well as utilizing the strong light absorbing nature and catalytic activity for CO\(_2\) reduction of this [Ru\(^{II}\)(NNN)(NN)X]\(^{n+}\) motif for photocatalytic systems.

**Supporting Information.** Electronic absorption spectra, cyclic voltammograms, and \(^1\)H-NMR spectra of complexes. This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes

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Synopsis and TOC

Modifying the electron density within a Ru$^{II}$-polypyridyl molecular architecture via electron-donating/withdrawing character of the bidentate ligand set has provided insight into the electronic requirements for catalytic CO$_2$ reduction.