ORGANOMETALLICS

Evaluation of the Electrocatalytic Reduction of Carbon Dioxide using Rhenium and Ruthenium Bipyridine Catalysts Bearing Pendant Amines in the Secondary Coordination Sphere

Monica R. Madsen,[§] Joakim B. Jakobsen,[§] Magnus H. Rønne, Hongqing Liang, Hans Christian D. Hammershøj, Peter Nørby, Steen U. Pedersen, Troels Skrydstrup,* and Kim Daasbjerg*



AbSTRACT: Carbon dioxide utilization through electrocatalysis is a promising pathway toward a more sustainable future. In this work the electrocatalytic reduction of carbon dioxide by Re^I and Ru^{II} bipyridine complexes bearing pendant amines (N,N'-(([2,2'bipyridine]-6,6'-diylbis(2,1-phenylene))bis(methylene))bis(N-ethylethanamine) (dEAbpy)) is evaluated. In both cases, the majorreduction product is carbon monoxide accompanied by someformic acid, although the yield of the latter never reaches thepredominant level known from the corresponding Mn(dEAbpy)-(CO)₃Br complex. This demonstrates the profound effect of theidentity of the metal center, in addition to the ligand, for theproduct distribution. In this work, we report the synthesisprocedures and X-ray diffraction studies along with electro-



chemical and infrared spectroelectrochemical studies of $\text{Re}(\text{dEAbpy})(\text{CO})_3\text{Cl}$ and $\text{Ru}(\text{dEAbpy})(\text{CO})_2\text{Cl}_2$ to propose a mechanism for the CO₂ reduction reaction.

INTRODUCTION

In recent years, electrocatalytic reduction of carbon dioxide to fuels and C1 and C2 chemicals have received enormous interest.¹ In particular, this is driven by the need to identify a sustainable alternative to fuels that are currently provided from the petrochemical feedstock. Furthermore, CO₂ is regarded as a waste product which makes it a cheap and available carbon feedstock.² Electrochemical transformation of CO₂ to valueadded chemicals can therefore provide one way to close the carbon cycle.³⁻⁶ However, the electrochemical utilization of CO₂ is challenging due to the stability of the highly oxidized carbon, requiring multiple protons and electrons to obtain value-added products.⁷ Several molecular catalysts are known to catalyze the reduction of CO_2 .⁸⁻¹¹ Some of the most superior homogeneous systems are of the type Re- and $Mn(N^N)(CO)_3X$ (N^N = polypyridyl, X = halide or weakly coordinating anion), which under electrochemical conditions selectively produce CO.^{12–15} In contrast, isoelectronic Ru^{II} complexes, such as $Ru(bpy)(CO)_2X_2$ (bpy = 2,2'-bipyridine), typically polymerize under reductive conditions.¹⁶⁻¹⁸ However, it has been shown that using bulky ligands such as 6,6'dimesityl-2,2'-bipyridine (mesbpy) circumvents the polymerization and efficiently catalyzes the reduction of CO₂ to CO/ HCOO⁻, albeit with a lower turnover frequency (TOF)

compared to that of the Mn variant.^{13,19} The same Ru complex has been explored under photochemical conditions yielding CO selectively from CO_2 .²⁰ In general, Ru catalysts have been widely explored in electrochemical and photochemical systems for CO_2 reduction to CO/HCOO^- , both as the mono(bpy) and bis(bpy) carbonyl complexes and as poly(bpy) complexes.^{21–26}

As part of a continued research effort toward CO_2 utilization, we recently introduced benzylic tertiary amines in the second coordination sphere of Mn-tricarbonyl complexes. Remarkably, this modification increased the activity, prevented dimerization, and altered the product selectively from CO to formic acid in the electrochemical reduction of CO_2 .²⁷ This change in activity and selectivity was attributed to the capability of the amines to act as proton shuttles leading to the formation of an intermediate Mn–H species. We now question if using the dEAbpy ligand (Figure 1) in other metal–

Special Issue: Organometallic Chemistry for Enabling Carbon Dioxide Utilization

Received: December 1, 2019





Figure 1. (a) Metalation of dEAbpy yielding 1 and 2, and (b) molecular structures of 1, dEAbpy, and 2 obtained from single-crystal X-ray diffraction studies (Re = orange, Ru = brown, C = blue, N = orchid, Cl = green, O = red). Hydrogen atoms are omitted for clarity; thermal ellipsoids at 50% probability.



Figure 2. Cyclic voltammograms recorded on 1 mM (a) 1 and (c) 2 at a GC electrode (d = 1 mm) using $\nu = 0.1 \text{ V s}^{-1}$ along with the corresponding IR-SEC spectra of (b) 1 and (d) 2 during the course of a voltammetric cycling using $\nu = 0.05 \text{ V s}^{-1}$ in Ar saturated 0.1 M Bu₄NBF₄/MeCN. IR-SEC spectra acquired at three different potentials, i.e., at a resting potential ($\geq -1.37 \text{ V vs Fc}^+/\text{Fc}$; black), after the first reduction wave (red), and after the second reduction wave (blue).

carbonyl complexes, such as Re^I and Ru^{II}, would afford a similar effect on the activity and product selectivity. Furthermore, such an extended study would provide insight into the possible mechanistic change brought about by the incorporation of a tertiary amine in the ligand system.

RESULTS AND DISCUSSION

Synthesis and Characterization. Using $\text{Re}(\text{CO})_5\text{Cl}$ as the Re^I carbonyl precursor, it was possible to metalate dEAbpy in refluxing toluene over the course of 16 h to yield *fac*-Re(dEAbpy)(CO)₃Cl (1) as a yellow powder in 89% yield (Figure 1). Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of CH₂Cl₂ at -20 °C (see the Supporting Information).²⁸

 Re^{I} adopts a facial octahedral geometry having the bpy ligand as well as two carbonyl groups in the equatorial plane, while the chloride and one carbonyl group are in an axial position. In the solid state, the bpy plane is slightly distorted with a torsion angle of 10.2° and the phenyl rings are near orthogonal to the bpy ring system. Interestingly, both amine substituents on the phenyl rings are aligned in the Re–Cl direction. These observations are in agreement with the geometry found for the Mn counterpart (3).²⁷

Several synthesis protocols for $Ru(bpy)(CO)_2Cl_2$ are available in the literature, starting from $RuCl_3$ via "the red carbonyl solution" or from the polymeric Ru^{II} carbonyl precursor $[Ru(CO)_2Cl_2]_n$.^{17,19,29–35} However, these pathways were not viable in our hands, even when using a variety of solvents and temperatures. Gratifyingly, we found that using the dimeric precursor $[Ru(CO)_3Cl_2]_2$, the metalation of dEAbpy proceeded at 110 °C in toluene for 18 h, providing trans-Cl-Ru(dEAbpy)(CO)₂Cl₂ (2) (Figure 1) in a low yield (21%). Single-crystal X-ray crystallographic analysis was performed on yellow crystals obtained by slow evaporation of a saturated solution of 2 in CH₂Cl₂ at -40 °C (see the Supporting Information).³⁶ The flat bpy ring system is in the equatorial plane of the octahedral Ru center, while the two chloride atoms occupy the axial positions. The trans relationship is in agreement with other systems having bulky substituents in the 6,6'-position of the bpy,¹⁹ whereas other reports using the Ru-dimer as the precursor with simple bpy yield the *cis*-dicarbonyl-*cis*-dichloro isomer.^{33,37-40} The phenyl rings of complex 2 in the solid state are found to be perpendicular to the bpy rings. Furthermore, the benzylic amines are found to be on the same side of the bpy rings as reported for the corresponding Mn complex 3.27 Both complexes were characterized by ¹H NMR and ¹³C NMR spectroscopy, attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), and high-resolution ESI-MS (see the Experimental Section).

Electrochemical and Spectroscopic Characterization. The cyclic voltammetric behavior of 1 in 0.1 M Bu₄NBF₄/ MeCN was studied under an Ar atmosphere (Figure 2a). Complex 1 shows two reduction waves on the initial scan, the first one being reversible with $E^{\circ} = -1.82$ V vs ferrocenium/ ferrocene (Fc⁺/Fc). The second reduction wave is irreversible with a peak at -2.3 V vs Fc⁺/Fc. The first reduction wave is diffusion-controlled with unaltered electron stoichiometry (n =1), as evidenced from a linear relation between the peak current and square root of the sweep rate (ν) varying from 0.05–2 V s⁻¹ (Figure S1). In the same range, a unity current ratio for the two reduction waves persists, consistent with two one-electron reductions. No indication of reversibility of the second reduction wave is achievable, even at $\nu = 2$ V s⁻¹.

Infrared spectroelectrochemistry (IR-SEC) was used to monitor changes for the carbonyl bands during potential sweeping on 1 (Figure 2b). At the resting potential (≥ -1.37 V vs Fc⁺/Fc), three distinct carbonyl peaks are observed at 2021, 1918, and 1891 cm⁻¹, which is in close proximity of $\nu_{\rm CO}$ reported for $\text{Re}(t\text{Bu-bpy})(\text{CO})_3\text{Cl}$ (tBu-bpy = 4,4'-di-tertbutyl-2,2'-bipyridine).⁴¹ Once sweeping the potential to more negative values than that of the first reduction peak, these bands are down shifted by $\sim 20-30$ cm⁻¹ to 1999, 1887, and 1862 cm⁻¹. This modest IR downshift, together with the observation of a Nernstian behavior of the first electron transfer process in cyclic voltammetry, is in line with a bpy-based reduction, generating $Re^{I}(dEAbpy^{\bullet-})(CO)_{3}Cl.^{42-44}$ Complexes of this type are known to lose Cl⁻ after a ligandto-metal charge transfer (LMCT). On the longest time scale in cyclic voltammetry (using $\nu = 0.02 \text{ V s}^{-1}$), reversibility of the first reduction wave remains unperturbed, indicating that the rate constant, k_{dis} , for this first order chemical step would be <0.2 s⁻¹ assuming an E_rC_i mechanism (see the Experimental Section and Figure S2). This is further supported by potentiostatic IR-SEC measurements conducted at -1.92 V vs Fc^+/Fc , where no changes are observed during a 12 s electrolysis, implying a very slow or absent LMCT/Cl⁻ dissociation (Figure S3).

During the second reduction process at -2.37 V vs Fc⁺/Fc, an additional, but larger (~50 cm⁻¹), downshift of the carbonyl stretch bands to 1948 and 1843 (br) cm⁻¹ is

observed. Since the latter broad band most likely stems from the overlap of two very closely positioned bands, the number of carbonyl bands remain unchanged (i.e., three). The large downshift indicates that a reduction takes place at the central metal to afford a five-coordinate Re⁰ complex after a rapid loss of chloride.⁴² In this case, the value of k_{dis} must be >400 s⁻¹ due to the persistent irreversibility of the second reduction wave even at $\nu = 2 \text{ V s}^{-1}$. On this basis, we assign the doubly reduced species to Re⁰(dEAbpy[•]-)(CO)₃.

Furthermore, it should be noted that at high sweep rates in cyclic voltammetry, a new oxidation peak arises at -1.5 V vs Fc⁺/Fc, which is associated with the second reduction process. Extending the experiment to include a second voltammetric cycle, a small reduction peak at -1.6 V vs Fc⁺/Fc appears (Figure S4). These new peaks are assigned to the reversible oxidation of Re⁰(dEAbpy[•]-)(CO)₃.

In cyclic voltammetry, complex 2 shows two main reduction waves with peak potentials at -1.63 and -2.07 V vs Fc⁺/Fc together with a few smaller waves at more extreme potentials (Figure 2c). The first wave is irreversible and approximately twice as high as that of 1, recorded using the same conditions, indicating that 2 is initially reduced in a two-electron process. Bulk electrolysis of 2 at -1.77 V vs Fc⁺/Fc supports this assignment as calculated from the consumed charge in exhaustive electrolysis (Figure S5). With the linear relation observed between the peak current and square root of ν in the range from $0.05-2 \text{ V s}^{-1}$, the first reduction wave is diffusioncontrolled (Figure S6). In addition, there are no changes to the electron stoichiometry as function of ν . The wave is irreversible even at $\nu = 50 \text{ V s}^{-1}$ (Figure S7), which would be consistent with a fast cleavage of the Ru–Cl bond $(k_{dis} > 10^4 \text{ s}^{-1})$ after the first reduction (assuming an ECE mechanism). Most likely, the initial reduction is bpy-based, after which a fast LMCT takes place, forming $Ru^{I}(dEAbpy)(CO)_{2}Cl$ upon a single chloride loss. This Ru^I complex is easier to reduce than the parent complex, and Ru^I(dEAbpy^{•-})(CO)₂Cl is formed, consuming overall two electrons, following an ECE/DISPtype mechanism.¹⁸ At the second reduction potential (-2.07 V)vs Fc⁺/Fc), a metallic reduction is assumed to take place to formally afford an 18-electron complex possessing a single Cl⁻ ligand. The second reduction wave is half the size of the first one and is only partially reversible for $\nu > 1 \text{ V s}^{-1}$, which would be in line with a second Cl⁻ loss in an E_rC_i mechanism ($k_{dis} \leq$ 12 s⁻¹), thus ultimately forming $Ru^{0}(dEAbpy^{\bullet-})(CO)_{2}$.

IR-SEC was used to analyze 2 at its different redox states (Figure 2d). At the resting potential (≥ -1.37 V vs Fc⁺/Fc), two peaks at 2057 and 1994 cm⁻¹ are present, almost identical to those reported for $Ru(mesbpy)(CO)_2Cl_2$.¹⁹ When sweeping to a potential more negative than the first reduction wave, these carbonyl bands are down shifted by $\sim 50 \text{ cm}^{-1}$ to 2002 and 1940 cm⁻¹. These peaks are assigned to the complex Ru^I(dEAbpy^{•-})(CO)₂Cl. Applying a potential more negative than the second reduction peak reveals a broadening and a very large down shift of $\sim 100 \text{ cm}^{-1}$ of both carbonyl bands to 1903 and 1837 cm⁻¹. We assign these to $Ru^0(dEAbpy^{\bullet-})(CO)_2$ (i.e., a 16-electron complex with a reduced bpy ligand after the second Cl⁻ dissociation). Unfortunately, it was not possible within the time frame of IR-SEC to detect the complex before dissociation of Cl⁻. Isomerization of the CO ligands in this unsaturated complex may cause the broadening of the IR bands.

Electrochemical CO₂ Reduction. Figure 3 displays the electrocatalytic performance of 1 and 2 studied by linear sweep



Figure 3. Linear sweep voltammograms recorded on 1 mM (a) 1 and (b) 2 with varying amounts of TFE at a GC electrode (d = 1 mm) using $\nu = 0.1$ V s⁻¹ in CO₂-saturated 0.1 M Bu₄NBF₄/MeCN. A voltammogram recorded under Ar is shown as a reference.

voltammetry in CO2-saturated 0.1 M Bu4NBF4/MeCN with 2,2,2-trifluoroethanol (TFE) as proton source. Both complexes show a catalytic wave under CO2-saturation, even in the absence of a proton source (see also Figure S8). In particular, complex 1 is remarkably active for CO₂ reduction under such conditions (i.e., no TFE) reaching $i_{cat}/i_p = 6.7$ at the first plateau at -2.4 V vs Fc⁺/Fc. Here, i_{cat} defines the maximum current of the catalytic wave in the presence of CO₂ (and TFE), and i_{p} is the peak current under Ar. A further increase of i_{cat}/i_{p} to 8.4 is observed at more extreme potentials (-2.6 V vs Fc^{+}/Fc). This behavior is similar to that seen for many other $Re(N^N)(CO)_3X$ complexes, showing significant activity even in the absence of purposely added proton sources.^{45,46} This effect has previously been assigned to the ability of the [Re- $[CO_2]^-$ adducts to be reduced at these negative potentials followed by a proton abstraction from the solvent to drive the catalytic process.^{46,47}

Upon addition of TFE, an increase in current is seen for complex 1. Ultimately, this leads to a two-electron reduction wave and an ECE process, where the proton donor assists in the dissociation of Cl⁻ and formation of Re⁰(dEAbpy[•])-(CO)₃, the same intermediate as formed at the second reduction wave in the absence of TFE. Further addition of TFE increases the electrocatalytic performance at the second wave, reaching its maximum activity of $i_{cat}/i_p = 9.4$ with 0.4 M TFE. For complex 2, the first reduction wave already follows an ECE mechanism with fast Cl⁻ dissociation and consumption of two electrons. This process is, by and large,

not changed by addition of TFE and/or CO₂. However, a significantly higher activity is observed at the second reduction wave, reaching its maximum at $i_{cat}/i_p = 15$ with 1.0 M TFE. Table 1 reports the catalytic potentials for both complexes determined as the half wave potential, $E_{cat/2}$,⁴⁸ along with the values of i_{cat}/i_p determined at the TFE concentration yielding the highest activity and the maximum turnover frequency (TOF_{max}).

Equation 1 shows the relationship between TOF_{max} and $i_{\text{cat}}/i_{\text{p}}$, where n_{p} is the number of electrons transferred to the catalyst in the first reduction wave in absence of CO₂, n_{cat} is the number of electrons in the catalytic transformation, F is Faraday's constant, R the universal gas constant, and T is the temperature.^{50–52} According to the electrochemical characterization under Ar, $n_{\text{p}} = 1$ for complex 1 and $n_{\text{p}} = 2$ for complex 2. In both cases, two electrons are involved in the catalytic reduction of CO₂ (i.e., $n_{\text{cat}} = 2$). A good estimation of TOF_{max} is only obtainable when the catalytic voltammograms are S-shaped with well-defined plateaus. Unfortunately, the waves of 1 and 2 are peak-shaped (see Figure 3) which may lead to an underestimation of TOF_{max}.

$$\text{TOF}_{\text{max}} = \frac{F\nu n_{\text{p}}^3}{RT} \left(\frac{0.4463}{n_{\text{cat}}}\right)^2 \left(\frac{i_{\text{cat}}}{i_{\text{p}}}\right)^2 \tag{1}$$

Figure 4 shows the product distribution obtained after 1 h bulk electrolysis at various potentials for complexes 1 and 2, following the experimental procedure reported previously by our group.²⁷ Both complexes show a good faradaic efficiency (FE) for CO (~80% in most cases) with smaller, but still significant, amounts of H_2 (<2% for 1; 3–6% for 2) and HCOOH (5-12%) detected. Complex 1 was tested at low $(-1.87 \text{ V vs Fc}^+/\text{Fc})$ and highly overpotentials (-2.27 V vs) $Fc^+/Fc)$ in the presence of 0.3 M TFE, resulting in the latter case in a slight increase in FE_{HCOOH} and FE_{H_2} . With the observation in cyclic voltammetry of a significant current increase at even higher overpotentials in the presence of CO₂ and in the absence of TFE, we conducted an electrolysis at -2.37 V vs Fc⁺/Fc without addition of a proton source. FE_{HCOOH} now increases to 11.8 \pm 3.5%, while FE_{CO} drops to $56 \pm 0.4\%$. In comparison, complex 2 was tested at a narrower potential interval close to $E_{cat/2}$ as only a small pre-peak at low overpotentials was present. FE_{HCOOH} (7.5–8.7%) is found to be independent of the potential, while FE_{CO} increases and FE_{H2} decreases at higher overpotentials. The total FE is significantly lower than 100% at -1.87 V; it has not been possible to account for the remaining charge in this case.

To evaluate the stability of the two catalysts, 4 h electrolysis experiments were conducted on complexes 1 and 2 (Figure S9). In accordance with the observations in linear sweep voltammetry, complex 2 shows the highest initial current density. However, it decreases rapidly during the first hour, after which it stabilizes at $1-3 \text{ mA cm}^{-2}$. In contrast, complex

Table 1. Key Figure of Merits for Complexes 1 and 2 in the Electrochemical Reduction of CO₂

	$E_{\rm cat/2}$ (V vs Fc ⁺ /Fc)	$[TFE] (M)^a$	$i_{\rm cat}/i_{\rm p}$	TOF _{max} ^b
1	-2.12	0.4	9.4	17
2	-2.08	1.0	15	340

"At maximal activity. ^bMay be underestimated due to the lack of a plateau in the catalytic voltammograms.⁴⁹



Figure 4. Product distribution after 1 h of electrolysis at different applied potentials in CO_2 -saturated solutions of (a) 1 mM 1 and 0.3 M TFE and (b) 1 mM 2 and 1.0 M TFE in 0.2 M Bu₄NBF₄/MeCN. No TFE was present in the electrolysis conducted at -2.37 V vs Fc⁺/Fc (*).

1 starts at a lower current density, but it remains fairly stable and decreases only slightly during the course of the experiment.

In Table S1, the performance of 1 and 2 is compared to that of similar bipyridinic Re and Ru catalysts with respect to turnover number (TON), TOF_{max} and FE. The activity of complex 1 is relatively low compared to that of other Re bpy catalysts, both with respect to TON and TOF_{max} . The lower performance can, most likely, be attributed to the bulky dEAbpy ligand, shielding the metal center, while the other Re complexes have substituents pointing away from the metal center. Nevertheless, 1 stands out by being the only catalyst capable of producing significant amounts of HCOOH. Complex 2 shows similar TON and TOF_{max} as those of the reported Ru catalyst.¹⁹ However, 2 is distinguished by its ability to produce HCOOH in a large potential window, while the reported Ru(mesbpy) complex only produces a detectable amount of HCOOH at low overpotentials.

Comparison of IR-SEC experiments in the presence and absence of CO₂ reveals some interesting features about the reactivity of the individual species. First, no differences in the recorded spectrum of 1 are observed, until the second reduction potential at -2.37 V vs Fc⁺/Fc is reached (in the absence of TFE, Figure S10). Complex 1 usually shows peaks at 1948 and 1843 cm⁻¹ at this potential, which are assigned to $\operatorname{Re}^{0}(\operatorname{dEAbpy}^{\bullet-})(\operatorname{CO})_{3}$ (Figure 2b, blue). However, once CO_{2} is introduced, these peaks are gone, indicating a fast reaction between $\text{Re}^{0}(\text{dEAbpy}^{\bullet-})(\text{CO})_{3}$ and CO_{2} . Instead, a new carbonyl band at 2008 cm⁻¹, accompanied by overlapping bands in the range 1950-1850 cm⁻¹, appears. A distinct band at 1684 cm⁻¹ is assigned to formate,²⁷ while the peaks at 1999, 1892, and 1866 cm^{-1} are close to those found for the singly reduced complex (Figure 2b, red). The peak at 2008 cm⁻ could be indicative of a metal-carboxylate complex, which is a known intermediate in the CO₂-to-CO reduction.²

Similarly, complex 2 shows the same IR signals in the presence (Figure 2d) and absence of CO₂ (Figure S11) at neutral and mildly reducing conditions (> -1.92 V vs Fc/Fc⁺), while differences are observed at more negative potentials (-2.27 V vs Fc/Fc⁺). In the presence of CO₂, new peaks at 2018 and 1956 cm⁻¹ appear together with bands associated with Ru^I(dEAbpy^{•-})(CO)₂Cl (\sim 2000 and \sim 1945 cm⁻¹). The major band seen at 1678 cm⁻¹ is assigned to catalytically formed formate (*vide supra*). The exact structure(s) of the

complex(es) giving rise to the remaining $\nu_{\rm CO}$ stretches is uncertain, as different constitutional isomers can be formed upon Cl⁻ loss.^{17,19}

Figure 5a shows the effect of adding TFE to the CO₂ containing electrolyte solutions of 1. Noteworthy, once the potential is stepped to the second reduction wave, strong bands at 1708 and 1680 cm⁻¹ are increasing with time. The former is assigned to $CF_3CH_2OC(O)O^-$, being an alkyl carbonate formed during a reaction between TFE and CO_2 , and the latter to formate.²⁷ The remaining part of the IR-SEC spectra seems to be a superposition of the parent complex (i.e., $\text{Re}^{\text{I}}(\text{dEAbpy})(\text{CO})_{3}\text{Cl}$ with $\nu_{\text{CO}} = 2021$, 1918, and 1891 cm⁻¹) and the singly reduced complex (i.e., $Re^{I}(dEAbpy^{\bullet-})(CO)_{3}CI$ with ν_{CO} = 1999, 1887, and 1862 cm⁻¹). The ratio of these two complexes changes only slightly during the 60 s electrolysis (Figure S12), although an additional peak at 2008 cm^{-1} slowly grows at the expense of the one at 2021 cm⁻¹. As previously discussed, the peak at 2008 cm⁻¹ could indicate the presence of a metal-carboxylate, which is formed upon oxidative addition of CO₂ to the active catalyst, Re⁰(dEAbpy^{•-})(CO)₃. During the CO₂ insertion and subsequent protonation, the molecules diffuse away from the electrode. However, two electron transfers are required to drive the electrochemical reduction of CO₂. If these electrons are provided by the singly reduced complex, $Re^{I}(dEAbpy^{\bullet-})(CO)_{3}Cl$, instead of the electrode, then this complex itself is oxidized, explaining the presence of IR bands corresponding to the parent complex at



Figure 5. IR-SEC spectra recorded of (a) 1 mM 1 and 50 mM TFE at -2.37 V vs Fc⁺/Fc and (b) 1 mM 2 and 70 mM TFE at -2.07 V vs Fc⁺/Fc in the presence of CO₂ (half-saturated) in 0.1 M Bu₄NBF₄/MeCN. The potential was kept at -1.37 V vs Fc⁺/Fc for 5 s before applying the denoted potential.



Figure 6. Proposed catalytic cycle involving complexes 1 and 2 in the electrochemical reduction of CO_2 to CO and HCOOH. "H⁺" most likely is present as the alkyl carbonate (i.e., $CF_3CH_2OC(O)OH$), and "e" can indicate heterogeneous as well as homogeneous electron transfers.

2021, 1918, and 1891 cm⁻¹. Immediately after stopping the electrolysis, IR signals from the singly reduced complex decrease rapidly (half-life ~ 2 s), while the intensity of peaks originating from the parent complex increases. This substantiates that $\text{Re}^{I}(\text{dEAbpy}^{\bullet-})(\text{CO})_{3}\text{Cl}$ indeed is oxidized to form $\text{Re}^{I}(\text{dEAbpy})(\text{CO})_{3}\text{Cl}$ (Figure S12). In addition, the observation of IR bands from the parent complex indicates that the reduction potential of the metal-carboxylate is not far from the first standard potential of 1. A similar electron-mediating role of another Re bipyridine complex has been reported in the photocatalytic reduction of $\text{CO}_{2}^{.54}$

Figure 5b displays the corresponding IR-SEC spectra recorded for complex 2. Here, the initial reduction at -2.07 V vs Fc⁺/Fc yields new IR peaks at 2001 and 1941 cm⁻¹, which after a few seconds change to 2042, 2017, 1992, 1978, and 1945 cm⁻¹. In general, the peaks are less well-defined, making it difficult to do specific assignments. Some of these peaks slightly shift during the electrolysis, and a new peak at 1890 cm⁻¹ slowly grows. Interestingly, the position of these peaks is close to peaks reported for a Ru(mesbpy)-complex after reduction at its second reduction peak in the presence of CO₂ and phenol.¹⁹ The authors hypothesize that the species giving rise to these peaks are isomers of the type [Ru^{II}(mesbpy)·(η^1 -OCOH)(CO)₂X]ⁿ or [Ru^I(mesbpy)(η^1 -OCOH)(CO)₂X]ⁿ

where X is Cl or a solvent molecule and n is the charge. Such complexes are formed via CO_2 insertion in a Ru–H species, and complex 2 might follow a similar mechanism to form a formato-intermediate.

Evaluating the Effect of Different Metal Centers. Using 1 and 2 as electrocatalysts in the reduction of CO_2 , the major product is CO (FE > 50%), accompanied by some formic acid formation with FE's of 11.8 \pm 3.5% at -2.37 V vs Fc⁺/Fc for 1 (without proton source) and 8.7 \pm 0.1% at -1.97 V vs Fc⁺/Fc for 2 (with 1.0 M TFE present). In comparison, the corresponding Mn complex, 3, gives almost exclusively HCOOH as reported recently by us.²⁷ The formation of HCOOH is suggested to go through a manganese hydride as a key intermediate, as it could be detected by IR-SEC during the reduction process in the presence of TFE. With 1 there was no sign of Re-H, which was further confirmed by a control experiment using deuterated TFE (TFE-OD), giving no additional changes to the IR spectrum (Figure S13).⁵⁵ Overall, this is in accordance with the low yield of HCOOH in this case.

Figure 6 outlines the mechanism suggested for the electrochemical CO_2 reduction using complexes 1 and 2. For both complexes initial reductions are required before the catalytically active complex $M^0(dEAbpy^{\bullet-})(CO)_2X$ (A) is

formed. This complex may react with either CO_2 or H⁺ to afford the metal-carboxylate (\mathbf{B}) or metal-hydride species (\mathbf{D}) , respectively, noting at the same time that the presence of the ammonium moiety (in C), serving as a proton shuttle, is a key to the formation of the latter. The competition between these two pathways will decide the product selectivity of CO/ HCOOH. Computational studies on $[Re(bpy)(CO)_3]^-$ has shown that CO₂ binding is exergonic $(-3.4 \text{ kcal mol}^{-1})$, whereas it is slightly endergonic $(2.2 \text{ kcal mol}^{-1})$ for the corresponding Mn complex.⁵⁶ Assuming the same trend is valid for our complexes, we suggest that the reaction between Re and CO_2 is faster than the reaction between Mn and CO_2 . The protonation of the tertiary amines is most likely equally fast for 2 and 3; hence, the proton shuttling to form a metal hydride must be crucial when differentiating the two pathways. Since binding of CO₂ to Re is thermodynamically favored, we hypothesize that this reaction is faster than the formation of a Re-H, explaining the selectivity toward CO rather than HCOOH. This is, furthermore, consistent with the selectivity observed for other Re electrocatalysts (Table S1). Following the same analogy, we believe CO_2 binding is slower for Mn complex 3, meaning that Mn-H is formed instead of a metalcarboxylate. This pathway was evaluated computationally in our previous work, and the presence of Mn-H was evidenced using IR-SEC and NMR.²

In the case of 2, the IR characterization under catalytic conditions implied formation of a formato-intermediate, although the competitive formation of a metal-carboxylate cannot be ruled out. Hence, we suggest that active catalyst A is protonated, yielding ammonium intermediate C, which can rearrange and transfer the proton to the Ru metal center, forming Ru-H (i.e., D). CO₂ is inserted herein, after a reduction, to give the formato-intermediate (E). Since CO is quantified as the major CO₂ reduction product and E is key to formate production, we propose an interconversion to a hydroxyl-carbonyl adduct (F), as also suggested for other Ru complexes.^{19,25,57,58} The tricarbonyl complex (G) is then formed upon protonation followed by expulsion of water, and the catalytic cycle is closed with a final reduction, releasing CO. If the reduced hydride reacts with H^+ instead of CO_{22} then hydrogen is formed in a competing reaction. Hence, the significant amounts of H₂ produced in electrolysis experiments support the presence of a Ru-H intermediate. To support the rearrangement from E to F, a bulk electrolysis with complex 2, TFE, and excess HCOOH instead of CO₂ was conducted at -2.07 V vs Fc⁺/Fc. The experiment showed that CO was produced together with substantial amounts of H₂. While hydrogen evolution can be explained by the lack of a competing CO_2 insertion, by which protons react with the hydride, CO production is explained by the interconversion of the formato-intermediate (E) to the hydroxylcarbonyl adduct (\mathbf{F}) . However, it should be underlined that the metalcarboxylate (B) pathway may be partially responsible for the production of CO when CO₂ is present in the solution.

The high selectivity toward HCOOH using the dEAbpy ligand seems to be unique for the Mn complex (i.e., 3): One of the reasons is the less favorable interaction with CO_2 , leading to formation of the ammonium intermediate, that then further protects the metal center from attack by CO_2 , and favors the Mn–H adduct formation. For 3, there is no evidence of a hydroxylcarbonyl interconversion after CO_2 insertion, as was the case for 2. Whereas the HCOOH that we observe for both 1 and 2 underlines the significance of the second-sphere amine

as a proton shuttle for the formation of the metal-hydride species, it is also clear that even more specific proton shuttle ligands would be necessary to achieve the same control toward HCOOH formation for Re and Ru as for Mn.

CONCLUSION

The synthesis and electrochemical characterization of two CO₂-reducing catalysts, Re(dEAbpy)(CO)₃Cl and Ru- $(dEAbpy)(CO)_2Cl_2$, were described. The two complexes have the same bipyridine-modified ligand, where two benzylic amines are positioned in the second coordination sphere of the metal center. This ligand was earlier studied with Mn as the catalytic center, where a high selectivity toward HCOOH in the electrochemical CO₂ reduction was observed. However, with either Re or Ru as the metal center, the amounts of HCOOH produced, were at most $11.8 \pm 3.5\%$ and $8.7 \pm 0.1\%$, respectively. The major CO₂ reduction product was CO, but minor amounts of H₂ were produced as well. Evidence for a metal-carboxylate was found for the Re complex and a formato-intermediate was proposed for the Ru-catalyst, using IR-SEC. Although formato-intermediates often are involved in CO2-to-HCOOH reductions, rearrangement to a hydroxylcarbonyl adduct is believed to take place, yielding CO as the major product. These studies highlights not only the unique selectivity of the Mn catalyst toward HCOOH formation but also that by a combined tuning of both the metal center and the ligand it will be possible to control the product selectivity.

EXPERIMENTAL SECTION

General Methods. All commercially available reagents and analytical-grade solvents were purchased from Fluorochem, Sigma-Aldrich, or TCI Chemicals and used as received, unless otherwise noted. Dry solvents were obtained from a MBRAUN MB SP-800 purification system, and further drying was performed over 3 Å molecular sieves. All air-sensitive reactions were either performed in an Ar-filled glovebox or using standard air-free techniques.

Bu₄NBF₄ was synthesized by mixing sodium tetrafluoroborate (98%, Fluka) and tetrabutylammonium hydrogensulfate (Chemische Fabrik Berg) in a 1:1 molar ratio. High purity CO₂ (99.999%) was supplied by Air Liquide. ATR FTIR was recorded with a PerkinElmer Spectrum Two instrument (abbreviation of intensity assignments: w, weak; m, medium; s, strong). Quantification of gaseous products generated during bulk electrolysis was performed on an Agilent 7890B Gas Chromatograph equipped with TCD and FID detectors. The liquid phase was analyzed using a Dionex ICS-1100 Ion Chromatography System. NMR spectra were recorded using a Bruker 500 MHz spectrometer running at 500 MHz for ¹H NMR and 126 MHz for ¹³C NMR. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent signals (CD₃CN, 1.94 ppm for ¹H NMR; CD₃CN, 118.26 ppm for ¹³C NMR; CD₂Cl₂, 5.32 ppm for ¹H NMR; CD₂Cl₂, 54.00 ppm for ¹³C NMR). Abbreviations used to indicate the multiplicity in NMR spectra are as following: s, singlet; d, doublet; t, triplet; m, multiplet. ¹³C NMR spectra were acquired in broad band decoupled mode. High-resolution mass spectra were recorded using electrospray ionization (ESI⁺) (referenced to the mass of the charged species) on a Bruker Maxis Impact mass spectrometer. The obtained data were analyzed using Data Analysis by Bruker Daltonics to give the mSigma value as a measure for the isotope pattern. Thin-layer chromatographic analysis (TLC) was performed using precoated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by UV radiation or KMnO₄ stain.

Cyclic Voltammetry. Cyclic voltammograms were recorded with a CH Instrument (601D) potentiostat using 0.1 M $Bu_4NBF_4/MeCN$ as electrolyte and a three-electrode setup. The working electrode (WE) was a homemade glassy carbon disk electrode (Sigradur G, HTW, diameter = 1 mm, unless otherwise stated) embedded into an epoxy resin similar to our previous studies.²⁷ As reference electrode (RE), a nonaqueous Ag/AgI electrode was used, and the potentials were referred to the ferrocenium/ferrocene (Fc⁺/Fc) redox couple using Fc as an internal reference. A Pt wire was employed as the counter electrode (CE).

Bulk Electrolysis. An Autolab PGSTAT302 potentiostat was employed. Electrolysis experiments were conducted in a homemade two-chamber cell with a glass frit separating the two chambers as described elsewhere.²⁷ Carbon paper (Toray Paper 060 from FuelCellStore) was used as WE, and the desired electroactive area $(0.5 \text{ cm} \times 0.27 \pm 0.02 \text{ cm})$ was demarcated using Teflon tape. The RE was a saturated Ag/AgCl, attached to the WE with Teflon tape during electrolysis to maintain the same distance in all experiments. A Pt mesh served as CE. Each chamber was equipped with a magnetic stir bar and 0.2 M Bu₄NBF₄/MeCN. The catalyst was added in 1 mM concentration to one of the chambers, while TFE (0.3 M with complex 1 and 1.0 M with complex 2) was added to both chambers. The final volume in each chamber was 5 mL. The cell was equipped with electrodes and sealed. The WE/RE assembly was placed in the catalyst-containing chamber, while the CE was placed in the chamber without catalyst. The electrolyte was saturated with CO₂ by purging with the gas for 10-15 min prior to electrolysis. The electrochemical cell was placed in a water bath at room temperature during the 1-4 h electrolysis to avoid overheating of the membrane, and the solutions were stirred during experiment.

Infrared Spectroelectrochemistry. A Nicolet 6700 (Thermo Fisher Scientific) instrument was used for recording IR spectra, and a CH Instruments (601C) potentiostat controlled and monitored the electrochemical processes during the experiments. The IR-SEC cell used herein was described in detail in our previous work.²⁷ The WE was a 5 mm glassy carbon disk, which was surrounded by a Pt wire functioning as CE. A commercial Ag/AgCl RE was positioned in between the WE and CE. The electrolyte was 0.1 M Bu₄NBF₄/ MeCN, which also was used for background subtractions. A catalyst concentration of 1 mM was used in all experiments. Half-saturation of CO₂ was obtained by equal mixing of Ar and CO₂ with the use of two variable area flow meters (Key Instruments). In electrolysis experiments, the potential was kept at -1.37 V vs Fc⁺/Fc for 5 s before stepping to the denoted potential. For cyclic voltammetric experiments in this part the sweep rate was 0.05 V s⁻¹.

Single-Crystal X-ray Diffraction. Crystallographic single-crystal X-ray data for 1 and 2 was collected using an Oxford Diffraction Supernova instrument equipped with a Mo microfocus X-ray source, an Atlas charge-coupled device detector, and a four-circle goniometer. The crystal was cooled to 100(1) K using an Oxford Cryosystems liquid nitrogen Cryostream device. The intensities were empirically corrected for absorption using SCALE3 ABSPACK implemented in CrysAlisPRO.⁵⁹ The unit cell parameters were determined, and the Bragg intensities were integrated using CrysAlisPRO. Crystallographic single crystal X-ray data for N,N'-(([2,2'-bipyridine]-6,6'-diylbis(2,1phenylene))bis(methylene))bis(N-ethylethanamine) (dEAbpy) was collected on a Bruker Kappa Apex2 diffractometer equipped with a Ag source. Absorption correction was done with SADABS. Cell refinement and data reduction were done in SAINT-plus.⁶⁰ All structures were solved and refined with SHELXT and SHELXL, respectively, in Olex2.61-

Determination of Rate Constants. For an E_rC_i mechanism, the rate constant was determined using $\lambda = k_{dis}RT/nF\nu$, where k_{dis} is the rate constant for the chemical reaction, *n* is the number of electrons involved, ν is the sweep rate, and *R*, *T*, and *F* are the universal gas constant, the temperature, and Faraday's constant, respectively. The value of λ was estimated from the shape of the cyclic voltammograms by comparing with simulated voltammograms of known λ values.^{64,65} A reversible voltammogram indicates that $\lambda < 0.3$ and $k_{dis} < 12\nu_{min}$, whereas a completely irreversible voltammogram indicates that $\lambda > 5$ and $k_{dis} > 200\nu_{max}$. Likewise, for $E_rC_iE_r$ or DISP mechanisms, a two-electron irreversible wave will be indicative of $\lambda > 5$ and $k_{dis} > 200\nu_{max}$.

Synthesis of Starting Materials. Ligand dEAbpy. $N_{N}N'$ -(([2,2'-Bipyridine]-6,6'-diylbis(2,1-phenylene))bis(methylene))bis(N-ethylethanamine) was synthesized according to a known procedure.²⁷ All

spectroscopic data were in accordance with literature data.²⁷ A crystal suitable for X-ray crystallographic analysis was obtained by layering a saturated CH_2Cl_2 solution with heptane at -20 °C. The crystals were obtained as slightly tainted colorless hexagonal crystals.

fac-Re(dEAbpy)(CO)₃Cl (1). In a 50 mL round-bottomed flask equipped with a magnetic stir bar Re(CO)₅Cl (123 mg, 0.34 mmol, 1.0 equiv) and dEAbpy (163 mg, 0.34 mmol, 1.0 equiv) were dissolved in toluene (25 mL) and degassed with Ar. The solution was heated to reflux for 16 h under an Ar atmosphere. Hereafter, the solvent was removed by rotatory evaporation and the residue was redissolved in CH₂Cl₂ (0.5 mL). The product was crystallized by vapor diffusion of pentane at -18 °C. After 16 h, additional pentane (3 mL) was added and the solution was cooled at $-20 \degree$ C for 1 h. The product was collected by vacuum filtration and washed with pentane $(3 \times 5 \text{ mL})$ yielding the pure Re complex as a yellow powder (236 mg, 89%). ¹H NMR (500 MHz, CD₃CN) (δ) ppm: δ 8.47 (dd, J = 8.2, 1.2 Hz, 2H)*, 8.12 (t, J = 8.1 Hz, 2H)*, 7.68-7.28 (m, 10H), 3.64-3.26 (m, 4H), 2.57-2.16 (m, 8H), 0.90 (t, J = 7.1 Hz, 12H)*. ¹³C NMR (126 MHz, CD₃CN) (δ) ppm: 194.3 (2C), 191.8, 163.3 (2C), 158.3 (2C), 142.7 (2C), 139.7 (2C), 139.1 (2C), 131.4 (2C), 130.8 (2C), 130.4 (2C), 128.3 (2C), 127.2 (2C), 124.2 (2C), 56.5 (2C), 47.5 (4C), 12.1 (4C). HRMS(ESI⁺) m/z: Calcd for C₃₅H₃₉ClN₄O₃Re [M + H]⁺: 785.2255. Found: 785.2275 (mSigma = 14.9). IR (ATR, cm⁻¹) $\tilde{\nu}$ = 2957 (m), 2932 (m), 2808 (m), 2012 (s), 1879 (s), 1606 (m), 1557 (m), 1458 (m), 1412 (w), 1384 (w), 1227 (w), 803 (w), 765 (m), 633 (w), 532 (w). For peaks marked with "*", 2-3 additional minor peaks with the exact same splitting were observed next to or underneath these peaks, presumably due to rotamers

trans-Cl-Ru(dEAbpy)(CO)₂Cl₂ (2). In an Ar-filled glovebox [Ru-(CO)₃Cl₂]₂ (54 mg, 0.21 mmol, 0.5 equiv), dEAbpy (100 mg, 0.21 mmol, 1.0 equiv), and dry toluene (5 mL) were charged into a flamedried Schlenk tube equipped with a magnetic stir bar. The tube was transferred out and fitted with a reflux condenser, and the mixture was stirred at reflux overnight shielded from light and under an atmosphere of Ar. After 18 h the tube was transferred to the glovebox, and approximately half of the red solvent was removed in*vacuo*. The flask was placed at -35 °C for 20 h. After this time, a pale yellow solid had precipitated which was isolated by vacuum filtration and washed with pentane $(3 \times 1 \text{ mL})$ to give the complex as a pale yellow solid (31 mg, 21%). Adding pentane to the filtrate allowed a pale red solid to crash out, from which further product could be obtained by recrystallization from heptane. ¹H NMR (500 MHz, CD_2Cl_2 (δ) ppm: δ 8.28 (t, J = 8.2 Hz, 2H), 8.05 (t, J = 8.0 Hz, 2H), 7.66-7.33 (m, 10H), 3.77-3.31 (m, 4H), 2.55-2.23 (m, 8H), 0.87 (t, $J = 7.1 \text{ Hz}, 12 \text{ H})^*$. ¹³C NMR (126 MHz, CD₂Cl₂) (δ) ppm: 191.2 (2C), 163.9 (2C), 156.6 (2C), 142.2 (2C), 139.4 (2C), 138.3 (2C), 132.2 (2C), 130.9 (2C), 130.6 (2C), 130.5 (2C), 127.1 (2C), 123.1 (2C), 56.4 (2C), 47.2 (4C), 12.2 (4C). HRMS (ESI⁺) m/z: Calcd for $C_{34}H_{38}Cl_2N_4O_2Ru [M + H]^+: 707.1488$. Found: 707.1496 (mSigma = 22.3). IR (ATR, cm⁻¹) $\tilde{\nu}$ 3062 (w), 2964 (m), 2050 (vs), 1987 (s), 1568 (m), 1459 (m), 1229 (m), 803 (m), 766 (s), 729 (m), 581 (m), 531 (m). For peaks marked with "*", one additional minor peak with the exact same splitting was observed next to or underneath these peaks, presumably due to rotamers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00815.

Additional figures (Figures S1–S13), including additional cyclic voltammograms, IR-SEC data, and electrolysis data; comparison of catalyst performances (Table S1); NMR data (Figures S14–S17); and X-ray crystallographic data (Tables S2–S4) (PDF)

Organometallics

Accession Codes

CCDC 1966625, 1967469, and 1968075 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data request/cif, or by emailing data request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Troels Skrydstrup - Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; orcid.org/0000-0001-8090-5050; Email: ts@chem.au.dk

Kim Daasbjerg - Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; © orcid.org/0000-0003-0212-8190; Email: kdaa@ chem.au.dk

Authors

- Monica R. Madsen Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; [®] orcid.org/0000-0002-2903-7419
- Joakim B. Jakobsen Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; orcid.org/0000-0003-4369-3858
- Magnus H. Rønne Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; © orcid.org/0000-0001-7603-968X
- Hongqing Liang Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark
- Hans Christian D. Hammershøj Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark
- **Peter Nørby** Center for Materials Crystallography (CMC), Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; o orcid.org/0000-0002-4904-2813
- Steen U. Pedersen Carbon Dioxide Activation Center (CADIAC), Interdisciplinary Nanoscience Center, Department of Chemistry, Aarhus University, Aarhus C 8000, Denmark; orcid.org/0000-0002-8919-2576

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.9b00815

Author Contributions

[§]M.R.M. and J.B.J. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the Danish National Research Foundation (grant nos. DNRF-93 and DNRF-118), NordForsk (grant no. 85378), and Aarhus University.

REFERENCES

(1) De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.; Sargent, E. H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? Science 2019, 364, eaav3506.

(2) Aresta, M. Carbon Dioxide: Utilization Options to Reduce its Accumulation in the Atmosphere. In Carbon Dioxide as Chemical Feedstock; Aresta, M., Ed.; Wiley-VCH: Weinheim, 2010; p 1-13.

(3) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. Chem. Soc. Rev. 2009, 38, 89-99.

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

(5) Malik, K.; Singh, S.; Basu, S.; Verma, A. Electrochemical reduction of CO₂ for synthesis of green fuel. WIREs Energy Environ. 2017, 6, No. e244.

(6) Grills, D. C.; Ertem, M. Z.; McKinnon, M.; Ngo, K. T.; Rochford, J. Mechanistic aspects of CO₂ reduction catalysis with manganese-based molecular catalysts. Coord. Chem. Rev. 2018, 374, 173-217.

(7) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. Nat. Commun. 2015, 6, 5933. (8) Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M. Molecular polypyridine-based metal complexes as catalysts for the reduction of CO₂. Chem. Soc. Rev. 2017, 46, 761-796.

(9) Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO₂ Reduction. ACS Catal. 2017, 7, 70-88.

(10) Francke, R.; Schille, B.; Roemelt, M. Homogeneously Catalyzed Electroreduction of Carbon Dioxide - Methods, Mechanisms, and Catalysts. Chem. Rev. 2018, 118, 4631-4701.

(11) Jiang, C.; Nichols, A. W.; Machan, C. W. A look at periodic trends in d-block molecular electrocatalysts for CO₂ reduction. Dalton Trans. 2019, 48, 9454-9468.

(12) Costentin, C.; Robert, M.; Savéant, J.-M. Catalysis of the electrochemical reduction of carbon dioxide. Chem. Soc. Rev. 2013, 42, 2423-2436.

(13) Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. Manganese Catalysts with Bulky Bipyridine Ligands for the Electrocatalytic Reduction of Carbon Dioxide: Eliminating Dimerization and Altering Catalysis. J. Am. Chem. Soc. 2014, 136, 5460-5471.

(14) Smieja, J. M.; Benson, E. E.; Kumar, B.; Grice, K. A.; Seu, C. S.; Miller, A. J.; Mayer, J. M.; Kubiak, C. P. Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO. Proc. Natl. Acad. Sci. U. S. A. 2012, 109, 15646-15650.

(15) Wong, K.-Y.; Chung, W.-H.; Lau, C.-P. The effect of weak Brönsted acids on the electrocatalytic reduction of carbon dioxide by a rhenium tricarbonyl bipyridyl complex. J. Electroanal. Chem. 1998, 453, 161-170.

(16) Chardon-Noblat, S.; Cripps, G. H.; Deronzier, A.; Field, J. S.; Gouws, S.; Haines, R. J.; Southway, F. Synthesis, Structure, and Physicochemical Characterizations of a New Cationic Ruthenium(I)-Ruthenium(I) Tetracarbonyl Bipyridine Dimer Precursor for the Electrochemical Synthesis of an Organometallic Ruthenium(0) Polymer. Organometallics 2001, 20, 1668-1675.

(17) Chardon-Noblat, S.; Deronzier, A.; Ziessel, R.; Zsoldos, D. Selective Synthesis and Electrochemical Behavior of trans(Cl)- and cis(Cl)-[Ru(bpy)(CO)₂Cl₂] Complexes (bpy = 2,2'-Bipyridine). Comparative Studies of Their Electrocatalytic Activity toward the Reduction of Carbon Dioxide. Inorg. Chem. 1997, 36, 5384-5389.

(18) Collomb-Dunand-Sauthier, M.-N.; Deronzier, A.; Ziessel, R. Electrocatalytic Reduction of Carbon Dioxide with Mono(bipyridine)carbonylruthenium Complexes in Solution or as Polymeric Thin Films. *Inorg. Chem.* **1994**, *33*, 2961–2967.

(19) Machan, C. W.; Sampson, M. D.; Kubiak, C. P. A Molecular Ruthenium Electrocatalyst for the Reduction of Carbon Dioxide to CO and Formate. *J. Am. Chem. Soc.* **2015**, *137*, 8564–8571.

(20) Kuramochi, Y.; Itabashi, J.; Fukaya, K.; Enomoto, A.; Yoshida, M.; Ishida, H. Unexpected effect of catalyst concentration on photochemical CO_2 reduction by $trans(CI)-Ru(bpy)(CO)_2Cl_2$: new mechanistic insight into the CO/HCOO⁻ selectivity. *Chem. Sci.* **2015**, 6, 3063–3074.

(21) Gao, C.; Wang, J.; Xu, H.; Xiong, Y. Coordination chemistry in the design of heterogeneous photocatalysts. *Chem. Soc. Rev.* 2017, 46, 2799–2823.

(22) Kuramochi, Y.; Ishitani, O.; Ishida, H. Reaction mechanisms of catalytic photochemical CO_2 reduction using Re(I) and Ru(II) complexes. *Coord. Chem. Rev.* **2018**, 373, 333–356.

(23) Luo, Y.-H.; Dong, L.-Z.; Liu, J.; Li, S.-L.; Lan, Y.-Q. From molecular metal complex to metal-organic framework: The CO_2 reduction photocatalysts with clear and tunable structure. *Coord. Chem. Rev.* **2019**, 390, 86–126.

(24) Rodrigues, R. R.; Boudreaux, C. M.; Papish, E. T.; Delcamp, J. H. Photocatalytic Reduction of CO_2 to CO and Formate: Do Reaction Conditions or Ruthenium Catalysts Control Product Selectivity? ACS Appl. Energy Mater. **2019**, *2*, 37–46.

(25) Ishida, H.; Tanaka, K.; Tanaka, T. Electrochemical CO_2 Reduction Catalyzed by Ruthenium Complexes $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)Cl]^+$. Effect of pH on the Formation of CO and HCOO⁻. Organometallics **1987**, *6*, 181–186.

(26) Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. Formation of a Metal-Hydride Bond and the Insertion of Carbon Dioxide. Key Steps in the Electrocatalytic Reduction of Carbon Dioxide to Formate Anion. *Inorg. Chem.* **1991**, *30*, 86–91.

(27) Rønne, M. H.; Cho, D.; Madsen, M. R.; Jakobsen, J. B.; Eom, S.; Escoudé, É.; Hammershøj, H. C. D.; Nielsen, D. U.; Pedersen, S. U.; Baik, M.-H.; Skrydstrup, T.; Daasbjerg, K., Ligand Controlled Product Selectivity in the Electrochemical Carbon Dioxide Reduction Using Manganese Bipyridine Catalysts. *J. Am. Chem. Soc.*, **2020** DOI: 10.1021/jacs.9b11806.

(28) The X-ray crystal structure of 1 has been deposited as CCDC no. 1967469.

(29) Kingston, J. V.; Jamieson, J. W. S.; Wilkinson, G. Octahedral ruthenium (II) carbonyl complexes with nitrogen, sulphur and tin donor ligands. *J. Inorg. Nucl. Chem.* **1967**, *29*, 133–138.

(30) Black, D.; Deacon, G.; Thomas, N. Ruthenium carbonyl complexes. I. Synthesis of $[Ru(CO)_2(bidentate)_2]^{2+}$ complexes. *Aust. J. Chem.* **1982**, 35, 2445–2453.

(31) Kelly, J. M.; O'Connell, C. M.; Vos, J. G. Synthesis and Spectroscopic Characterisation of $[Ru(bpy)_2(CO)_2](PF)_6)_2$. Inorg. Chim. Acta 1982, 64, L75–L76.

(32) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C. Designed Synthesis of Mononuclear Tris(heteroleptic) Ruthenium Complexes Containing Bidentate Polypyridyl Ligands. *Inorg. Chem.* **1995**, *34*, 6145–6157.

(33) Haukka, M.; Kiviaho, J.; Ahlgren, M.; Pakkanen, T. A. Studies on Catalytically Active Ruthenium Carbonyl Bipyridine Systems. Synthesis and Structural Characterization of $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$, $[Ru(bpy)(CO)_2Cl]_2$, and $[Ru-(bpy)(CO)_2ClH]$ (bpy = 2,2'-Bipyridine). Organometallics **1995**, 14, 825–833.

(34) Spiccia, L.; Deacon, G. B.; Kepert, C. M. Synthetic routes to homoleptic and heteroleptic ruthenium(II) complexes incorporating bidentate imine ligands. *Coord. Chem. Rev.* **2004**, *248*, 1329–1341.

(35) Balducci, G.; Iengo, E.; Demitri, N.; Alessio, E. New Insight into a Deceptively Simple Reaction: The Coordination of bpy to Ru^{II} -Carbonyl Precursors – The Central Role of the *fac*-[Ru(bpy)-Cl(CO)₃]⁺ Intermediate and the Chloride Rebound Mechanism. *Eur. J. Inorg. Chem.* **2015**, 2015, 4296–4311. (36) The X-ray crystal structure of **2** has been deposited as CCDC no. 1966625.

(37) Eskelinen, E.; Luukkanen, S.; Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. Redox and photochemical behaviour of ruthenium-(II) complexes with H₂ dcbpy ligand (H₂ dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid). J. Chem. Soc., Dalton Trans. 2000, 2745–2752. (38) Haukka, M.; Hirva, P.; Luukkanen, S.; Kallinen, M.; Ahlgrén, M.; Pakkanen, T. A. Reactions of Ruthenium Bipyridine Catalyst Precursors: Synthetic, Structural, and Theoretical Studies on Ruthenium Mono(bipyridine) Carbonyls in Ethylene Glycol Solutions. Inorg. Chem. 1999, 38, 3182–3189.

(39) Homanen, P.; Haukka, M.; Luukkanen, S.; Ahlgrén, M.; Pakkanen, T. A. Selective Formation of cis(X)- and trans(X)-Ru(dmbpy)(CO)₂X₂ Complexes (X = Cl, Br, I, SCN) from Monomeric and Dimeric Ru-mono(dmbpy) Carbonyl Complexes (Dmbpy = 4,4'-Dimethyl-2,2'-bipyridine). *Eur. J. Inorg. Chem.* **1999**, 1999, 101–106.

(40) Homanen, P.; Haukka, M.; Pakkanen, T. A.; Pursiainen, J.; Laitinen, R. H. Ruthenium(II) Bipyridine Complexes: Synthesis and Characterization of $Ru(bpy)(CO)_2(SCN)_2$, $Ru(dmbpy)(CO)_2Cl_2$, and $Ru(dmbpy)(CO)_2(NCS)H$ (bpy = 2,2'-Bipyridine; dmbpy = 6,6'-Dimethyl-2,2'-bipyridine). Organometallics **1996**, 15, 4081–4084. (41) Machan, C. W.; Sampson, M. D.; Chabolla, S. A.; Dang, T.;

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

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

(43) Sullivan, B. P.; Bolinger, C. M.; Conrad, D.; Vining, W. J.; Meyer, T. J. One- and two-electron pathways in the electrocatalytic reduction of CO_2 by *fac*-Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine). *J. Chem. Soc., Chem. Commun.* **1985**, 1414–1416.

(44) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. Electrocatalytic Reduction of CO_2 Using the Complexes [Re(bpy)- $(CO)_3L$]ⁿ (n = + 1, L = P(OEt)_3, CH₃CN; n = 0, L = Cl⁻, Otf⁻; bpy = 2,2'-Bipyridine; Otf⁻ = CF₃SO₃) as Catalyst Precursors: Infrared Spectroelectrochemical Investigation. *Organometallics* **1996**, *15*, 3374–3387.

(45) Haviv, E.; Azaiza-Dabbah, D.; Carmieli, R.; Avram, L.; Martin, J. M. L.; Neumann, R. A Thiourea Tether in the Second Coordination Sphere as a Binding Site for CO_2 and a Proton Donor Promotes the Electrochemical Reduction of CO_2 to CO Catalyzed by a Rhenium Bipyridine-Type Complex. J. Am. Chem. Soc. **2018**, 140, 12451–12456.

(46) Clark, M. L.; Cheung, P. L.; Lessio, M.; Carter, E. A.; Kubiak, C. P. Kinetic and Mechanistic Effects of Bipyridine (bpy) Substituent, Labile Ligand, and Brønsted Acid on Electrocatalytic CO_2 Reduction by Re(bpy) Complexes. ACS Catal. **2018**, 8, 2021–2029.

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

(48) Appel, A. M.; Helm, M. L. Determining the Overpotential for a Molecular Electrocatalyst. *ACS Catal.* **2014**, *4*, 630–633.

(49) Lee, K. J.; Elgrishi, N.; Kandemir, B.; Dempsey, J. L. Electrochemical and spectroscopic methods for evaluating molecular electrocatalysts. *Nat. Rev. Chem.* **2017**, *1*, 0039.

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

(51) Costentin, C.; Savéant, J.-M. Multielectron, Multistep Molecular Catalysis of Electrochemical Reactions: Benchmarking of Homogeneous Catalysts. *ChemElectroChem* **2014**, *1*, 1226–1236.

(52) Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. Turnover Numbers, Turnover Frequencies, and Overpotential in Molecular Catalysis of Electrochemical Reactions. Cyclic Voltammetry and Preparative-Scale Electrolysis. J. Am. Chem. Soc. **2012**, 134, 11235– 11242.

Article

(53) Sampson, M. D.; Froehlich, J. D.; Smieja, J. M.; Benson, E. E.; Sharp, I. D.; Kubiak, C. P. Direct observation of the reduction of carbon dioxide by rhenium bipyridine catalysts. *Energy Environ. Sci.* **2013**, *6*, 3748–3755.

(54) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. Development of an Efficient Photocatalytic System for CO₂ Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies. *J. Am. Chem. Soc.* **2008**, *130*, 2023–2031.

(55) Kaesz, H. D.; Saillant, R. B. Hydride Complexes of the Transition Metals. *Chem. Rev.* **1972**, *72*, 231–281.

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

(57) Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. Ligand Effects of Ruthenium 2,2'-Bipyridine and 1,10-Phenanthroline Complexes on the Electrochemical Reduction of CO₂. J. Chem. Soc., Dalton Trans. **1990**, 2155–2160.

(58) Ishida, H.; Tanaka, K.; Morimoto, M.; Tanaka, T. Isolation of Intermediates in the Water Gas Shift Reactions Catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$. Organometallics 1986, 5, 724–730.

(59) CrysAlisPRO; Oxford Diffraction /Agilent Technologies UK Ltd.: Yarnton, England.

(60) APEX2, SAINT, and SADABS; Bruker AXS Inc.: Madison, WI, 2014.

(61) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

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

(63) Sheldrick, G. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.

(64) Nicholson, R. S.; Shain, I. Theory of Stationary Electrode Polarography. Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems. *Anal. Chem.* **1964**, *36*, 706–723.

(65) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Application*, 2nd ed.; John Wiley & Sons, Inc., 2001; pp 496-497.