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Turning on the Protonation-First Pathway for Electrocatalytic CO₂ Reduction by Manganese Bipyridyl Tricarbonyl Complexes

Ken T. Ngo,[†] Meaghan McKinnon,[†] Bani Mahanti,[†] Remya Narayanan,[†] David C. Grills,^{‡*} Mehmed Z.
Ertem,^{‡*} Jonathan Rochford^{†*}

[†]Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125. [‡]Chemistry Division, Energy & Photon Sciences Directorate, Brookhaven National Laboratory, Upton, New York, 11973-5000, USA.

jonathan.rochford@umb.edu

dcgrills@bnl.gov

mzertem@bnl.gov

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ABSTRACT

Electrocatalytic reduction of CO₂ to CO is reported for the complex, {*fac*-Mn^I([(MeO)₂Ph]₂bpy)(CO)₃(CH₃CN)}(OTf), containing four pendant methoxy groups, where [(MeO)₂Ph]₂bpy = 6,6'-bis(2,6-dimethoxyphenyl)-2,2'-bipyridine. In addition to a steric influence similar to that previously established for the 6,6'-dimesityl-2,2'-bipyridine ligand in [*fac*-Mn^I(mes₂bpy)(CO)₃(CH₃CN)](OTf), which prevents Mn⁰-Mn⁰ dimerization, the [(MeO)₂Ph]₂bpy ligand introduces an additional electronic influence combined with a weak allosteric hydrogen bonding interaction that significantly lowers the activation barrier for C-OH bond cleavage from the metallocarboxylic acid intermediate. This provides access to the thus far elusive *protonation-first* pathway, minimizing the required overpotential for electrocatalytic CO₂ to CO conversion by Mn(I) polypyridyl catalysts, while concurrently maintaining a respectable turnover frequency. Comprehensive electrochemical and computational studies here confirm the positive influence of the [(MeO)₂Ph]₂bpy ligand framework on electrocatalytic CO₂ reduction and its dependence upon the concentration and p*K*_a of the external Brønsted acid proton source (water, methanol, trifluoroethanol, and phenol) that is required for this class of manganese catalyst. Linear sweep voltammetry studies show that both phenol and trifluoroethanol as proton sources exhibit the largest *protonation-first* catalytic currents in combination with {*fac*-Mn^I([(MeO)₂Ph]₂bpy)(CO)₃}⁻, saving up to 0.55 V in overpotential with respect to the thermodynamically-demanding *reduction-first* pathway, while bulk electrolysis studies confirm a high product selectivity for CO formation. To gain further insight into catalyst activation, time-resolved infrared (TRIR) spectroscopy combined with pulse-radiolysis (PR-TRIR), infrared spectroelectrochemistry, and density functional theory calculations were used to establish the ν(CO) stretching frequencies and energetics of key redox intermediates relevant to catalyst activation.

KEYWORDS CO₂ reduction, electrocatalysis, manganese, pulse radiolysis

INTRODUCTION

The security of an energy supply, its sustainability and environmental consequences are concerns both at a national and global level in our society today. It is widely accepted that the global environment cannot sustain the current rates of CO₂ uptake into the atmosphere. Having recently surpassed atmospheric CO₂ concentrations of 400 ppm our environment is progressing further into unknown territory where the consequences of such pollution are yet to be fully realized.¹ Clean and renewable alternative energy sources are therefore needed to mitigate the CO₂ issue and resolve our dependence on fossil fuels.² One approach to this problem is the catalytic transformation of CO₂ to carbon monoxide (CO), which is a key raw material alongside hydrogen gas for liquid fuel production by the Fischer-Tropsch reaction.³ The one-electron reduction of free CO₂ (Eq 1) is a thermodynamically demanding reaction, which occurs at an equilibrium potential (E_{eq}) of -1.99 V vs. the standard hydrogen electrode (SHE) in water due, in part, to the large reorganization energy involved.⁴ Through the application of bio-inspired proton-coupled electron transfer (PCET) catalysis, the thermodynamic requirements can be reduced significantly, producing, for example, CO at a more modest potential of -0.52 V vs. SHE in water at pH 7 (Eq 2, $E_{\text{eq}} = -0.11$ V vs. SHE at pH 0).⁵ More relevant to this study, the non-aqueous equilibrium potential for CO₂ to CO conversion in acetonitrile has recently been reported,⁴ where the technique of isothermal titration calorimetry was used to experimentally determine the apparent pK_a of CO₂ + H₂O in acetonitrile, allowing the previously-estimated⁶ standard potential in wet acetonitrile to be revised to -1.55 V vs. Fc^{+/0} in the presence of 1.0 M H₂O at pH 24 (Eq 3).⁴ In addition, the equilibrium potential for CO₂ to CO conversion in dry acetonitrile at pH 0 (Eq 4) was reported as -0.13 V vs. Fc^{+/0}

by Matsubara et al.⁴ and as -0.12 V vs Fc⁺⁰ by Appel and Mayer.⁷

Homogeneous transition metal-based catalysts have long been utilized for electrocatalytic CO₂ reduction^{8, 9} as the metallocarboxylate intermediate reduces the reorganization energy, and thus the required overpotential, by stabilizing a bent configuration of the carboxylate anion.¹⁰ Catalysts have varied in design using electron-rich late transition metal complexes such as cobalt and nickel cyclam or tetra-amine complexes,¹¹⁻¹⁴ cobalt and iron pincer complexes^{15, 16} and tetrapyrroles,¹⁷⁻¹⁹ polypyridyl complexes of cobalt,²⁰⁻²² rhenium,²³⁻²⁶ ruthenium,²⁷⁻³¹ osmium,³² rhodium and iridium,^{33, 34} and phosphine complexes of cobalt,³⁵ nickel,³⁶ rhodium and palladium.^{37, 38} The group VII *fac*-Re^I(N[^]N)(CO)₃X class of complexes, where N[^]N = polypyridyl ligand and X = monodentate ligand, have maintained interest for many years due to their high efficiency and selectivity for CO formation. Since the first report of photocatalytic CO₂ reduction with *fac*-Re^I(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) by Hawecker, Lehn and Ziessel, there have been many literature reports of related photo/electrocatalytic systems, with numerous reviews written on the topic.^{5, 9, 23, 39-46} A recent development in this field has been the successful application of analogous [*fac*-Mn^I(N[^]N)(CO)₃X]ⁿ complexes (where X = Br⁻ (n = 0) or X = CH₃CN (n = +1)) as electrocatalysts, taking advantage of the more abundant and economical first row transition metal, manganese. This was first reported by Bourrez et al. who used the *fac*-Mn^I(N[^]N)(CO)₃Br (N[^]N = bpy and 4,4'-dimethyl-2,2'-bipyridine (dmbpy)) electrocatalysts to demonstrate that, unlike their Re counterparts, first row [*fac*-Mn^I(N[^]N)(CO)₃X]ⁿ electrocatalysts require the presence of a Brønsted acid in the acetonitrile electrolyte solution in order to show any catalytic function.⁴⁷ This advancement has rightly been attracting significant interest of late inspiring a number of related studies on [*fac*-Mn^I(N[^]N)(CO)₃X]ⁿ systems for electrocatalytic CO₂ reduction.⁴⁸⁻⁶⁵ In fact, the same group later reported in-situ electron paramagnetic resonance evidence of a [Mn^{II}(dmbpy)(CO)₃(C(O)OH)]⁺ metallocarboxylic acid intermediate derived from the Mn⁰-Mn⁰ dimer precursor.⁵⁴ One notable example inspired by the work of Bourrez et al. is that of Sampson et al. who reported the [*fac*-Mn^I(mes₂bpy)(CO)₃(CH₃CN)](OTf) (mes₂bpy = 6,6'-dimesityl-2,2'-bipyridine)

complex where the 6,6'-dimesityl substituents on the bpy ligand sterically hinder the formation of a $\text{Mn}^0\text{--Mn}^0$ dimer complex from the five coordinate, one-electron reduced $\text{Mn}^0(\text{mes}_2\text{bpy})(\text{CO})_3$ species, thus eliminating this side reaction and enhancing catalytic turnover frequency for CO formation.⁵¹ The same group has also introduced a magnesium (Mg^{2+}) Lewis acid co-catalyst with [*fac*- $\text{Mn}^{\text{I}}(\text{mes}_2\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})$](OTf) to effect a lower overpotential pathway to generate CO and MgCO_3 using a sacrificial Mg counter electrode.^{63, 66, 67} Prior work by Fujita et al. had already demonstrated a reduction in overpotential for the $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}]^+$ electrocatalyst for CO formation in the presence of a Lewis acid.⁶⁸ Analogous work by Savéant et al. demonstrated an increase in TOF without a reduction in overpotential for a selection of Lewis acids (Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+}) with Fe^0 porphyrin-based CO_2 reduction electrocatalysts.^{66, 67} Indeed, notable work by Savéant and co-workers has demonstrated record turnover numbers (TONs) and turnover frequencies (TOFs) for electrocatalytic CO_2 to CO conversion by providing pendant Brønsted acid sites at $\text{Fe}(0)$ *meso*-tetraarylporphyrin catalysts in a DMF electrolyte.^{6, 69, 70} Inspired by the latter approach, Franco et al. reported on the introduction of a pendant 2,6-dihydroxyphenyl group in a *fac*- $\text{Mn}^{\text{I}}(\text{N}^{\wedge}\text{N})(\text{CO})_3\text{Br}$ electrocatalyst which, in the absence of an external proton source, yielded 22% Faradaic efficiency for formic acid production upon controlled potential electrolysis in acetonitrile with 70% of the Faradaic current being attributed to CO.⁵⁰ A later study by Agarwal et al. using the related asymmetrical 6-(2-hydroxyphenyl)-2,2'-bipyridine ligand demonstrated 86% Faradaic efficiency for CO evolution in a 5% H_2O /acetonitrile-based electrolyte.⁶² Interestingly, the latter two studies reported zero and insignificant catalytic activity, respectively, for their methoxy-substituted analogues in which the hydroxyl groups are replaced by methoxy groups. While both studies successfully demonstrated the participation of pendant intramolecular Brønsted acid sites in the proton-coupled reduction of CO_2 to CO, no hypothesis as to the lack of catalytic activity was put forth for their methoxy analogues. We were interested in pursuing this direction further to determine whether multiple pendant, aprotic, electron-rich methoxy ligand substituents might participate electronically and/or allosterically to promote the electrocatalytic conversion of CO_2 to CO with a [*fac*- $\text{Mn}(\text{N}^{\wedge}\text{N})(\text{CO})_3\text{X}]^{\text{n}}$ complex. Thus, in this study four pendant methoxy groups are introduced into the

second coordination sphere of a manganese catalyst for the first time in $\{fac-Mn^I([(MeO)_2Ph]_2bpy)(CO)_3(CH_3CN)\}(OTf)$ (**1-CH₃CN⁺**, Chart 1). In addition to establishing the Brønsted acid dependence of catalytic current evolution and product selectivity, most remarkable is how voltammetry conditions can be manipulated for this new catalyst to strongly turn on the hitherto elusive *protonation-first* CO₂ reduction pathway at low overpotential.⁷¹ Bulk electrocatalytic CO₂ reduction is also described for **1-CH₃CN⁺** relative to $[fac-Mn^I(mes_2bpy)(CO)_3(CH_3CN)](OTf)$ (**2-CH₃CN⁺**) under both low overpotential (*protonation-first*) and high overpotential (*reduction-first*) conditions, with CO:H₂ product distributions reported. Insight into the catalytic pathways was also gained through density functional theory (DFT) calculations. Furthermore, voltammetry studies are presented for a $[fac-Mn(N^{\wedge}N)(CO)_3X]^n$ complex for the first time in a buffered electrolyte system in order to quantitatively evaluate the true catalytic overpotential under known non-aqueous pH conditions.

Chart 1. Molecular structures of complexes investigated.

RESULTS AND DISCUSSION

Synthesis

The [(MeO)₂Ph]₂bpy ligand was prepared by Suzuki coupling of 6,6'-dibromo-2,2'-bipyridine in the presence of excess 2,6-dimethoxyphenyl boronic acid under microwave reflux conditions. The synthesis

of **2-CH₃CN⁺** was recently reported via bromide/triflate metathesis of the *fac*-Mn^I(mes₂bpy)(CO)₃Br precursor with silver triflate in acetonitrile followed by column chromatography.⁵¹ To avoid chromatography, an alternative synthesis was employed for both *fac*-Mn^I[(MeO)₂Ph]₂bpy)(CO)₃(OTf) (**1-OTf**) and *fac*-Mn^I(mes₂bpy)(CO)₃(OTf) (**2-OTf**) that involved using the Mn^I(CO)₅(OTf) precursor and refluxing with one equivalent of [(MeO)₂Ph]₂bpy or mes₂bpy in diethyl ether. Mn^I(CO)₅(OTf) was synthesized according to the literature procedure.⁷² It should be kept in mind that both **1-OTf** and **2-OTf** undergo facile solvation in acetonitrile (vide infra) due to the weak binding strength of the triflate anion.⁷³ Thus, the [*fac*-Mn^I(R₂-bpy)(CO)₃(CH₃CN)]⁺ cations are generated when **1-OTf** and **2-OTf** are dissolved in acetonitrile solution, and are hereafter referred to as **1-CH₃CN⁺** and **2-CH₃CN⁺**, respectively (Chart 1).

FTIR spectroscopy

Using FTIR spectroscopy, characteristic $\nu(\text{CO})$ ligand vibrational stretching modes are observed for **1-CH₃CN⁺** and **2-CH₃CN⁺** consistent with their facial tricarbonyl geometries (Fig. 1).⁷⁴ The solvated complex, **1-CH₃CN⁺** exhibits *pseudo*-C_s symmetry with a sharp $\nu(\text{CO})$ symmetric A'(1) stretching mode at 2038 cm⁻¹ and two lower-frequency A'(2) and A'' asymmetric $\nu(\text{CO})$ stretching modes at 1954 cm⁻¹ and 1941 cm⁻¹, respectively. Consistent with the Mn(I) centers of **1-CH₃CN⁺** and **2-CH₃CN⁺** being isoelectronic, **2-CH₃CN⁺** exhibits an almost identical sharp $\nu(\text{CO})$ symmetric A(1) stretch at 2039 cm⁻¹. However, the lower-energy asymmetric stretches appear as a single A(2) broad $\nu(\text{CO})$ band suggesting *pseudo*-C_{3v} symmetry for **2-CH₃CN⁺**. Computed IR spectra at the M06 level of theory confirm these assignments (see computational methods for details).

Figure 1. Experimental FTIR spectra of **1-CH₃CN⁺** (top) and **2-CH₃CN⁺** (bottom) recorded in acetonitrile displaying characteristic $\nu(\text{CO})$ stretching modes for their facial (*fac*) tricarbonyl geometries. Computed IR spectra at the M06 level of theory are overlaid for comparison (frequency scaling factor = 0.960).

Cyclic voltammetry under 1 atm argon

Prior to catalysis studies, electrochemical characterization was conducted under an inert argon atmosphere in the absence of an external Brønsted acid to characterize the fundamental redox properties of both **1-CH₃CN⁺** and **2-CH₃CN⁺**. It was recently established⁵¹ that the bulky mes₂bpy ligand has a strong influence on the redox properties of **2-CH₃CN⁺** relative to less-bulky complexes, such as [*fac*-Mn^I(bpy)(CO)₃(CH₃CN)]⁺, which are prone to Mn⁰–Mn⁰ dimerization upon one-electron reduction. For example, the Mn⁰ radical, *fac*-Mn^I(dtbpy)(CO)₃ (where dtbpy = 4,4'-^tBu₂-bpy) exhibits a Mn⁰–Mn⁰ dimerization rate-constant of $2k_{\text{dim}} = 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁴⁹ In contrast, a reversible two-electron reduction wave is observed for the reaction, **2-CH₃CN⁺** + 2 e[−] ⇌ **2[−]** + CH₃CN ($E = -1.60 \text{ V vs Fc}^{+/0}$) where **2[−]** is the five-coordinate, 18 valence electron, two-electron reduced [*fac*-Mn(mes₂bpy)(CO)₃][−] anion. This

redox reaction follows an electrochemical-chemical-electrochemical (*ECE*) mechanism whereby, after one-electron reduction, the acetonitrile ligand dissociates followed by rapid one-electron reduction of the neutral Mn(0) intermediate, *fac*-Mn(mes₂bpy)(CO)₃, to generate **2**⁻. A subsequent third irreversible reduction wave is observed at -3.01 V vs Fc⁺⁰ (Fig. S3). A cyclic voltammogram of **1-CH₃CN**⁺ recorded in dry acetonitrile with 0.1 M Bu₄NPF₆ as the supporting electrolyte under 1 atm of argon at a glassy carbon disc working electrode and 100 mV s⁻¹ scan rate is presented in Figure 2.

Figure 2. Cyclic voltammogram of **1-CH₃CN**⁺ recorded in acetonitrile containing 0.1 M Bu₄NPF₆ at a glassy carbon disc working electrode with a scan rate (ν) of 100 mV s⁻¹ under 1 atm argon.

The profile of the current-voltage response for **1-CH₃CN**⁺ shown in Figure 2 is almost identical to that of **2-CH₃CN**⁺, suggesting that a similar quasi-reversible two-electron *ECE* mechanism is occurring to generate the **1**⁻ anion at $E = -1.63$ V vs Fc⁺⁰. This is consistent with a narrow peak-to-peak separation of $\Delta E = 40$ mV (compared to $\Delta E = 39$ mV for **2-CH₃CN**⁺) and is confirmed by both computational analysis and controlled potential FTIR spectroelectrochemistry (*vide infra*). Scan rate dependence of the current response for the two-electron reduction of **1-CH₃CN**⁺ to **1**⁻ confirms quasi-reversible behavior

analogous to **2-CH₃CN⁺** as the anodic-cathodic peak separation increases with scan rate (Figs. S5 – S6). Similar to **2-CH₃CN⁺**, there is no evidence of Mn⁰–Mn⁰ dimerization and a linear Randles-Sevcik plot confirms the inertness of **1[–]** in acetonitrile under an argon atmosphere. Similarly, a third irreversible one-electron reduction is observed at -3.10 V vs. Fc^{+/⁰}. For the record, an irreversible one-electron oxidation of **1-CH₃CN⁺** is also observed at +0.91 V vs. Fc^{+/⁰}. However, as this oxidation is irrelevant for reductive catalysis it will not be discussed any further here.

Table 1. Electrochemical data recorded by cyclic voltammetry for **1-CH₃CN⁺** and **2-CH₃CN⁺** in acetonitrile reported vs. the non-aqueous ferrocenium/ferrocene (Fc^{+/⁰}) pseudo reference.

	<i>E</i> vs. Fc ^{+/⁰}		
1-CH₃CN⁺	+0.91 ^a	-1.63 ^b	-3.10 ^c
2-CH₃CN⁺	+0.85 ^a	-1.60 ^b	-3.01 ^c

^a irreversible, *E*_{pa} reported. ^b quasi-reversible two-electron couple ^c irreversible, *E*_{pc} reported. *Conditions:* 1 mM sample concentration; 3 mm diameter glassy carbon working electrode; Pt wire counter electrode; Ag/AgPF₆ non-aqueous reference electrode; 0.1 V s⁻¹ scan rate.

Electrocatalysis

A thorough description of the electroanalytical methods used to extract accurate values of TOF from voltammetry data is beyond the scope of this manuscript, however a recent perspective article published by Dempsey and co-workers deals with this topic in depth.⁷⁵ The reader is also recommended to consult the relevant literature by Savéant and co-workers dealing specifically with electrocatalytic CO₂ reduction.^{70, 76-79} Briefly, prior to calculation of the maximum electrocatalytic turnover frequency (TOF_{max}), steady-state experimental conditions must be established with respect to the rates of catalyst activation & consumption. This is typically identified by a characteristic S-shaped catalytic wave or scan-rate independence of the peak catalytic current (*i*_{cat}). Steady state conditions were here achieved by increasing the scan rate to achieve pure kinetic conditions such that CO₂ consumption within the diffusion layer at the electrode surface did not hinder access to a peak catalytic current.^{80, 81} Subsequently, TOF_{max} was determined from the ratio of *i*_{cat} versus the non-catalytic Faradaic current (*i*_p)

using an established method according to Eq 5,^{82, 83} where F is the Faraday constant, R is the gas constant, T is temperature, v is the scan rate, n_p is the number of electrons involved in the non-catalytic Faradaic response (2 electrons for both **1-CH₃CN⁺** and **2-CH₃CN⁺**), and n_{cat} is the number of electrons required to complete a single catalytic cycle (2 electrons as shown in Scheme 1 or Scheme 2).

$$TOF_{max} = 0.1992 \left(\frac{Fv}{RT} \right) \left(\frac{n_p^3}{n_{cat}^2} \right) \left(\frac{i_{cat}}{i_p} \right)^2 \quad (5)$$

Where steady-state conditions could not be confirmed, foot-of-the-wave-analysis (FOWA) was necessary to estimate TOF_{max} using Eq. 6^{75, 84}

$$\frac{i_{cat}}{i_p} = \frac{2.24 \sqrt{\left(\frac{RT}{Fv} \right) TOF_{max}}}{1 + \exp \left[\left(\frac{F}{RT} \right) (E - E_{P/Q}^0) \right]} \left(\frac{n_{cat}}{n_p^{3/2}} \right) \quad (6)$$

where $E_{P/Q}^0$ represents the standard reduction potential of the active catalyst recorded under non-catalytic conditions (Table 1). Also, in the interests of comparison to other literature catalysts, the simple ratio of i_{cat}/i_p is also highlighted; importantly it should be kept in mind that the latter is scan rate dependent and is reported throughout this manuscript only at a scan rate of $v = 0.5 \text{ V s}^{-1}$ for consistency unless stated otherwise. A complete collection of linear sweep voltammetry data for both **1-CH₃CN⁺** and **2-CH₃CN⁺** is provided in the supporting information (Figs. S9 – S15). A first-order rate dependence of the TOF_{max} was also independently confirmed for each Mn complex concentration and CO₂ concentration for both **1-CH₃CN⁺** and **2-CH₃CN⁺** (Figs. S7 & S8). It should also be pointed out that CO was not observed during bulk electrolysis control experiments in the absence of a manganese catalyst.

Electrocatalysis with H₂O as a proton source

For many years it was believed that manganese polypyridyl tricarbonyl complexes were inactive for catalytic CO₂ reduction, unlike their isoelectronic rhenium counterparts. However, Bourrez et al. established that the proton concentration is rate limiting for manganese polypyridyl-mediated CO₂ reduction electrocatalysis, and that in the presence of a Brønsted acid, efficient catalytic reduction of

CO₂ to CO occurs.⁴⁷ Riplinger et al. have since established that, in contrast to their rhenium analogues, protonation is required for the binding of CO₂ to the two-electron reduced active manganese catalyst.^{52, 71} Thus, before entering the catalytic cycle, two-electron reduction is required to generate the five-coordinate anionic active catalyst, e.g., [*fac*-Mn(mes₂bpy)(CO)₃][−] (**2**[−]), in situ (Scheme 1 intermediate i). The **2**[−] anion then reacts with CO₂ in the presence of a proton source to generate the neutral six-coordinate *fac*-Mn(mes₂bpy)(CO)₃(CO₂H) metallocarboxylic acid intermediate (Scheme 1 intermediate ii). To facilitate rapid hydroxide abstraction from the metallocarboxylic acid intermediate and subsequently generate the desired *fac*-Mn(mes₂bpy)(CO)₄ tetracarbonyl intermediate (Scheme 1 intermediate iv), one-electron reduction to the [*fac*-Mn(mes₂bpy)(CO)₃(CO₂H)][−] metallocarboxylic acid anion (Scheme 1 intermediate iii) occurs. It is this latter step that provides the *reduction-first* label to this catalytic pathway. Subsequent protonation, resulting in C–OH bond cleavage and H₂O ejection, is rate limiting (Scheme 1 intermediates iii-iv) and requires a minimum concentration (pK_a dependent) of weak Brønsted acid in solution to proceed. Thus, the catalytic cycle, proposed by Kubiak⁵¹ and further corroborated computationally by Riplinger and Carter⁶⁰, demonstrates a mandatory two-electron reduction of the Mn(I) polypyridyl complex merely to enter the catalytic cycle and that an implicit overpotential is required to overcome the *reduction-first* and rate-determining *protonation-second* steps to generate the tetracarbonyl intermediate (Scheme 1 intermediate iv) prior to reductive CO loss and catalyst regeneration (Scheme 1 intermediates iv-i).^{51, 52, 71}

Scheme 1. Catalyst activation and the *reduction-first* catalytic cycle for electrocatalytic reduction of CO₂ to CO by manganese polypyridyl catalysts (rds = rate-determining step).

With this knowledge in hand, the electrocatalytic properties of both catalytic precursors, **1-CH₃CN⁺** and **2-CH₃CN⁺**, were probed by linear sweep voltammetry in acetonitrile using H₂O as the sacrificial Brønsted acid. To demonstrate the *reduction-first* pathway described in Scheme 1, linear sweep voltammetry of **1-CH₃CN⁺** under 1 atm CO₂ in the presence of 6.33 M H₂O (optimized for maximum catalytic current) is presented in Figure 3 at a variety of scan rates. In all cases a significant growth of catalytic current is observed in the region of -2.3 V, cathodic of the two-electron reduction wave to produce **1⁻** by -0.7 V (Fig. 3, top), with a corresponding TOF_{max} of 258±11 s⁻¹ (*i*_{cat}/*i*_p = 5.9). This observation is consistent with the *reduction-first* pathway requiring an additional overpotential to drive the rate-determining protonation/H₂O abstraction steps described above in Scheme 1 (intermediates ii-

iii-iv). Upon repeating this experiment with **2-CH₃CN⁺**, a similar catalytic current is observed, peaking at 5.95 M H₂O concentration with a decreased TOF_{max}, relative to **1-CH₃CN⁺**, of $93 \pm 1 \text{ s}^{-1}$ ($i_{\text{cat}}/i_p = 3.5$) (Fig. 3, bottom). For both **1-CH₃CN⁺** and **2-CH₃CN⁺**, scan rate independence of TOF_{max} was only observed in the range of $\nu = 0.25$ to 1.0 V s^{-1} as illustrated in plots of TOF vs scan rate (Fig. 3).

Figure 3. Linear sweep voltammetry of **1-CH₃CN⁺** (top) and **2-CH₃CN⁺** (bottom) recorded in acetonitrile containing 0.1 M Bu₄NPF₆ and the specified concentrations of H₂O, under 1 atm CO₂ at a glassy carbon disc working electrode over a scan rate (ν) range of 0.1 to 1.0 V s^{-1} . In both cases, the H₂O concentration was optimized for maximum catalytic current. The y-axis current (i) is normalized with respect to the non-catalytic Faradaic current (i_p) to allow a direct comparison of i_{cat}/i_p ratios for each combination of catalyst and proton source where $n = 2$ is the electron stoichiometry of the i_p

Faradaic *ECE* event under 1 atm argon. Alongside are plots of TOF vs scan rate, with an inset of $i_{\text{cat}}/i_{\text{p}}$ vs inverse square root of the scan rate, to demonstrate steady state conditions at faster (0.5 and 1.0 V s⁻¹) scan rates.

The pendant methoxy groups of **1-CH₃CN**⁺ clearly have a positive influence on the TOF_{max}, giving rise to a 2.8-fold increase relative to **2-CH₃CN**⁺ under optimized H₂O concentration conditions. It is worth noting that a common practice in the literature for electrocatalytic CO₂ to CO conversion has been to solely employ 5% v/v H₂O in 0.1 M Bu₄NPF₆ acetonitrile electrolyte. As a point of reference, this corresponds to a concentration of only 2.77 M H₂O. Based upon the weak catalytic current observed for the tetramethoxy catalyst **1**⁻ at this concentration of H₂O it is unsurprising, in hindsight, that negligible catalytic activity was observed for a previously reported analogous monomethoxy substituted catalyst under such conditions.⁶² Whether the influence of the pendant methoxy groups is purely electronic or involves a second coordination sphere hydrogen bonding effect is difficult to confirm. Computational studies do show evidence of non-covalent hydrogen bonding (discussed further below) between the C–OH of the metallocarboxylic acid and the pendant methoxy groups during C–OH bond cleavage. However, an inductive electronic influence of the pendant methoxy groups cannot be ruled out.

Electrocatalysis with a non-aqueous proton source

Of significant note in the voltammogram of **1-CH₃CN**⁺ under 1 atm CO₂ in the presence of 6.33 M H₂O (Figure 3) is the observation of a weak catalytic current growing in at -1.6 V upon generation of **1**⁻. In contrast, this behavior is not observed upon in-situ generation of **2**⁻. This prompted us to explore electrocatalysis with stronger Brønsted acids. In addition to water ($pK_{\text{a(DMSO)}} = 31.4^{85}$; $pK_{\text{a(CH₃CN})}$ not reported, n.r.), methanol (MeOH, $pK_{\text{a(DMSO)}} = 29.0^{85}$; $pK_{\text{a(CH₃CN})}$ n.r.), trifluoroethanol (TFE, $pK_{\text{a(DMSO)}} = 23.5^{86}$; $pK_{\text{a(CH₃CN})} = 35.4$ est.⁶¹), and phenol (PhOH, $pK_{\text{a(DMSO)}} = 18.0^{87}$; $pK_{\text{a(CH₃CN})} = 29.1^{88}$) were also chosen to study the Brønsted acid concentration dependence of the electrocatalytic TOF for both **1**-

CH_3CN^+ and $2\text{-CH}_3\text{CN}^+$. $\text{p}K_{\text{a}}$ data in acetonitrile are not available for each Brønsted acid employed. However, $\text{p}K_{\text{a}}$ data reported in DMSO are often assumed to be representative of the trend in acetonitrile. The actual Brønsted acid $\text{p}K_{\text{a}}$ values will be influenced by dissolved CO_2 (~ 0.28 M at 1 atm), especially when using water⁴, so the reported non-aqueous $\text{p}K_{\text{a}}$ values should be used with caution. From a qualitative perspective however, there is ample evidence from this study and previous reports that the trend of non-aqueous $\text{p}K_{\text{a}}$'s in acetonitrile follows as $\text{H}_2\text{O} > \text{MeOH} > \text{TFE} > \text{PhOH}$.^{51, 89} This is clearly evident in Figure 4 where linear sweep voltammograms are presented for both $1\text{-CH}_3\text{CN}^+$ at optimized concentrations of the four Brønsted acids, determined by careful addition of H_2O and the non-aqueous Brønsted acids at incrementing concentrations (Fig. S15) to optimize the observed catalytic current. Analogous data for $2\text{-CH}_3\text{CN}^+$ are presented in Figure S16.

Figure 4. Linear sweep voltammetry of $1\text{-CH}_3\text{CN}^+$ recorded in acetonitrile containing 0.1 M Bu_4NPF_6 with optimized Brønsted acid concentrations at a glassy carbon disc working electrode with a scan rate (ν) of 0.5 V s^{-1} under 1 atm CO_2 . Voltammetry under 1 atm argon in the absence of Brønsted acid is also included for reference.

The *reduction-first* TOF_{max} for **2-CH₃CN⁺** is already established⁵¹ to increase with decreasing $\text{p}K_{\text{a}}$ of the Brønsted acid employed for H₂O, MeOH and TFE, as observed here. A *reduction-first* TOF_{max} of $910 \pm 4 \text{ s}^{-1}$ ($i_{\text{cat}}/i_{\text{p}} = 10.8$) is here reported for **2-CH₃CN⁺** in the presence of 2.03 M PhOH as a proton source. This decreased significantly in the presence of TFE (2 M) and MeOH (2.09 M) to $453 \pm 5 \text{ s}^{-1}$ ($i_{\text{cat}}/i_{\text{p}} = 7.7$) and $115 \pm 2 \text{ s}^{-1}$ ($i_{\text{cat}}/i_{\text{p}} = 3.8$), respectively. Electrocatalysis for **2-CH₃CN⁺** has previously been reported⁵¹ with significantly higher TOFs for the *reduction-first* pathway, however we were unsuccessful at reproducing these results (Fig. S17, Table S1). A similar trend was observed for the *reduction-first* pathway of **1-CH₃CN⁺** with TOFs of $1257 \pm 26 \text{ s}^{-1}$ ($i_{\text{cat}}/i_{\text{p}} = 12.6$) in the presence of 1.37 M PhOH, $694 \pm 7 \text{ s}^{-1}$ ($i_{\text{cat}}/i_{\text{p}} = 9.4$) in the presence of 1.35 M TFE and 259 s^{-1} ($i_{\text{cat}}/i_{\text{p}} = 5.7$) with 2.09 M MeOH. Consistent with the H₂O data presented in Figure 3 above, **1-CH₃CN⁺** outperforms **2-CH₃CN⁺** when using either PhOH, TFE or MeOH. Moreover, **1-CH₃CN⁺** is capable of reaching its optimum catalytic turnover at a reduced PhOH concentration of 1.37 M relative to that for **2-CH₃CN⁺** at 2.03 M. This overall trend is effectively illustrated in scatter plots of ' $i_{\text{cat}}/i_{\text{p}}$ vs Brønsted acid concentration' for both **1-CH₃CN⁺** and **2-CH₃CN⁺** (Fig. S15).

Outstanding among these Brønsted acid $\text{p}K_{\text{a}}$ and concentration dependence studies, is the evolution of a strong catalytic wave for **1-CH₃CN⁺**, growing in at reduced overpotential directly from the two-electron reduced active catalyst **1⁻**, as illustrated in Figure 4, especially in the presence of TFE and PhOH as proton sources. This catalytic wave is here assigned to the hitherto elusive *protonation-first* mechanistic pathway as theoretically predicted by Riplinger and Carter.⁷¹ While the *protonation-first* catalytic cycle may result in a lower TOF_{max} , due to a decreased electrochemical driving force for CO₂ activation, it is much desired over the *reduction-first* pathway due to the opportunity for a significant saving in overpotential which may benefit in terms of increased catalyst stability, higher turnover numbers, and opening up the possibility to drive this cycle efficiently by photochemical means. As with the *reduction-first* pathway, the active catalyst is again the two-electron reduced, five-coordinate anion, e.g., **1⁻** {*fac*-Mn^I[(MeO)₂Ph]₂bpy)(CO)₃}⁻ (Scheme 2 intermediate i). Similarly, the **1⁻** anion is then

predicted to react with CO₂ and a proton source to generate the neutral six-coordinate *fac*-Mn^I([(MeO)₂Ph]₂bpy)(CO)₃(CO₂H) metallocarboxylic acid intermediate **1-CO₂H** (Scheme 2 intermediate ii). At this juncture the *protonation-first* pathway takes over where the rate-determining step of C–OH bond cleavage and H₂O ejection is facilitated by the pendant methoxy groups of **1-CO₂H**, through weak hydrogen bonding, generating the six-coordinate tetracarbonyl cation intermediate, {*fac*-Mn^I([(MeO)₂Ph]₂bpy)(CO)₄}⁺ (Scheme 2 intermediate iii). By generating the positively charged intermediate, **1-CO⁺** (Scheme 2 intermediate iii), the *protonation-first* pathway enables a facile *reduction-second* step, significantly anodic of the *reduction-first* pathway, to generate the six-coordinate neutral tetracarbonyl intermediate, {*fac*-Mn^I([(MeO)₂Ph]₂bpy)(CO)₄} (**1-CO**, Scheme 2 intermediate iv), which eliminates the CO product upon another one-electron reduction event, regenerating the active catalyst, **1^{•−}** (Scheme 2 intermediates iv-i).

Scheme 2. Catalyst activation and the *protonation-first* catalytic cycle for electrocatalytic reduction of CO₂ to CO by manganese polypyridyl catalysts (rds = rate-determining step).

As shown in Figure 4, linear sweep voltammetry of **1-CH₃CN⁺** under 1 atm CO₂ in the presence of 1.37 M optimized PhOH concentration shows an excellent growth of *protonation-first* catalytic current maximizing at around -1.85 V (estimated by multiple-peak deconvolution; the true maximum is difficult to ascertain due to overlap with the *reduction-first* catalytic response). This overlap of catalytic peaks renders the application of Eq. 5 impossible to ascertain TOF_{max} as the peak catalytic current (i_{cat}) is not obtainable. Thus, in the case of the *protonation-first* pathway we have employed foot-of-the-wave analysis (FOWA) to estimate accurate TOF_{max} values using Eq. 6 under appropriate experimental conditions. An example of FOWA is presented for **1-CH₃CN⁺** in the presence of 1.37 M PhOH where, due to the underlying onset current from the overlapping *reduction-first* catalytic wave, the experimental fit exhibits a positive hysteresis with respect to the theoretical linear FOWA fit (Fig. 5)

Figure 5. (left) Linear sweep voltammograms of the *protonation-first* catalytic wave for **1-CH₃CN⁺** in the presence of 1.37 M PhOH recorded at various scan rates plotted against $E-E_{P/Q}$. (right) Foot-of-the-wave analysis under equivalent experimental conditions with a linear fit (dashed line) extrapolated from an $E-E_{P/Q}$ range of 0.35 to -0.20 V. For clarity only FOWA at faster scan rates is presented.

Using FOWA a TOF_{max} of $138 \pm 4 \text{ s}^{-1}$ is estimated for the *protonation-first* pathway for **1-CH₃CN⁺** in the presence of 1.37 M PhOH. Although this represents an order of magnitude drop in TOF_{max} relative to the *reduction-first* catalytic pathway under identical conditions it does come with the benefit of saving 0.55 V in overpotential. Consistent with its weaker acidity, a TOF_{max} of 82 ± 2 is estimated for **1-CH₃CN⁺** in the presence of 2.13 M TFE (Fig. S18). As very weak catalytic currents were observed for the *protonation-first* pathways of **1-CH₃CN⁺** combined with MeOH or H₂O, or **2-CH₃CN⁺** combined with PhOH or TFE, accurate values of TOF_{max} could not be determined in these cases by FOWA. Suffice to say, catalysis was very slow ($< 5 \text{ s}^{-1}$), however bulk electrolysis studies could still be conducted in each case (*vide infra*).

An overlaid scatter plot of the ‘*protonation-first* pathway $i_{\text{cat}}/i_{\text{p}}$ vs Brønsted acid concentration’ is presented in Figure 6 following the growth of the *protonation-first* catalytic wave for both **1-CH₃CN⁺** and **2-CH₃CN⁺** with respect to PhOH and TFE concentrations. Importantly, this plot clearly distinguishes the superior kinetic performance of **1-CH₃CN⁺** relative to **2-CH₃CN⁺** for the *protonation-first* pathway when using either PhOH or TFE as a proton source. Brønsted acids MeOH and H₂O are less effective at promoting the *protonation-first* pathway for **1-CH₃CN⁺**, whereas **2-CH₃CN⁺** shows no catalytic activity at low overpotential under these conditions, most likely due to the higher $\text{p}K_{\text{a}}$ values of these acids (Figs. 3, S9-S14). A complete summary of all electrocatalysis potential and kinetic data derived from linear sweep voltammetry experiments of **1-CH₃CN⁺** and **2-CH₃CN⁺** with various Brønsted acids is provided in Table 2.

Figure 6. Plots of ‘protonation-first pathway $i_{\text{cat}}/i_{\text{p}}$ vs. Brønsted acid concentration’ determined by linear sweep voltammetry of **1-CH₃CN⁺** and **2-CH₃CN⁺** in acetonitrile containing 0.1 M Bu₄NPF₆ and varying concentrations of PhOH and TFE, at a glassy carbon disc working electrode recorded at a scan rate (ν) of 0.01 V s⁻¹ under 1 atm CO₂. All data were monitored at the indicated potentials.

A mutual electronic/H-bonding influence of the pendant methoxy groups in **1-CH₃CN⁺** is here proposed to lower the activation barrier for C–OH bond cleavage from the metallocarboxylic acid intermediate when stronger proton sources, e.g., trifluoroethanol, and phenol, are used, thus promoting a lower overpotential *protonation-first* catalytic pathway for CO₂ to CO conversion. This proposed mechanisms is discussed in more detail in the Theoretical Investigation section below.

Table 2. Summary of electrocatalysis data derived from linear sweep voltammogram experiments for both the *protonation-first* and *reduction-first* pathways.^a

	1-CH₃CN⁺				2-CH₃CN⁺			
	PhOH	TFE	MeOH	H ₂ O	PhOH	TFE ^c	MeOH ^c	H ₂ O ^c
<i>protonation first</i> (E_{max} , V)	–1.85	–1.85	–1.70	–1.85	–1.75	–1.65	~	~

$E_{\text{cat}/2}$ (V)	-1.64	-1.63	-1.57	-1.63	-1.60	-1.58	~	~
[HA] (M) ^d	1.37	2.13	2.09	6.33	2.03	2.00	~	~
TOF max (s ⁻¹) ^e	138±4	82±2	< 5	< 1	< 3	< 1	~	~
<i>reduction first</i> (E_{max} , V)	-2.40	-2.36	-2.36	-2.34	-2.77	-2.32	-2.26	-2.25
$E_{\text{cat}/2}$ (V)	n.o. ^b	n.o. ^b	-2.07	-2.08	-2.29	-2.11	-2.10	-2.11
[HA] (M) ^d	1.37	2.13	2.09	6.33	2.03	2.00	2.09	5.95
$i_{\text{cat}}/i_{\text{p}}$ (0.5 V s ⁻¹)	12.6	9.4	5.7	5.9	10.8	7.7	3.8	3.5
TOF max (s ⁻¹) ^f	1257±26	694±7	259±4	258±11	910±4	453±5	115±2	93±1

^a All potentials are reported versus the ferrocenium/ferrocene pseudo reference recorded at 0.5 V s⁻¹. ^b $E_{\text{cat}/2}$ is not observable (n.o.) due to overlap of both protonation- and reduction-first catalytic waves. ^c Catalytic current is negligible for the protonation-first pathway of **2-CH₃CN**⁺ with MeOH or H₂O as a proton source. ^d [HA] refers to the bulk concentration of weak Brønsted acid in the electrolyte and should not be confused with [H⁺]. ^e reported as an average with standard deviation from foot-of-the-wave-analysis, hence $i_{\text{cat}}/i_{\text{p}}$ not reported. ^f reported as an average with standard deviation recorded at steady state conditions from scan rate-dependent studies, typically 0.25 – 1 V s⁻¹.

Bulk electrolysis

With a fast-growing interest in molecular catalysts for electrocatalytic CO₂ conversion, it is critical to appreciate that the simple observation of catalytic current in a voltammogram alone is not sufficient to demonstrate CO₂ reactivity.⁹⁰ Thus, quantitative in-situ gas chromatography analysis has been completed for both **1-CH₃CN**⁺ and **2-CH₃CN**⁺ in the presence of optimized Brønsted acid concentrations under 1 atm CO₂ during controlled potential electrolysis at various applied potentials (derived from voltammetry studies). For example, it is demonstrated that some of the TOF's here reported actually incorporate current density from competitive proton reduction via the hydrogen evolution reaction. It should also be highlighted that formic acid could not be detected in any case by ¹H NMR studies. A summary of Faradaic yields for CO and H₂ evolution under a variety of bulk electrolysis conditions is provided in Table 3 for both **1-CH₃CN**⁺ and **2-CH₃CN**⁺.

Table 3. Summary of controlled potential electrolysis data. Experimental conditions: 5 mL of 1 mM catalyst in 0.1 M Bu₄NPF₆ acetonitrile supporting electrolyte with stated Brønsted acid concentration [HA] under 1 atm CO₂.

	1-CH₃CN⁺			2-CH₃CN⁺		
	[HA] ^a	Potential (V vs. Fc ⁺⁰)	Faradaic yield CO : H ₂ (%)	[HA] ^a	Potential (V vs. Fc ⁺⁰)	Faradaic yield CO : H ₂ (%)
PhOH	1.37 M	-1.64 ^b	88 : 5	2.03 M	-1.75	74 : 21
		-2.40	85 : 6		-2.77	91 : 0
TFE	2.13 M	-1.63 ^b	88 : 13	2.00 M	-1.65	97 : 2
		-2.36	100 : 0		-2.32	80 : 8
MeOH	2.09 M	-2.36	99 : 0	2.09 M	-2.26	80 : 6
H ₂ O	6.33 M	-2.34	61 : 38	5.95 M	-2.25	73 : 27

^a [HA] refers to the bulk concentration of Brønsted acid in the electrolyte and should not be confused with [H⁺]. ^b controlled potential electrolysis was conducted at $E_{cat/2}$ to ensure only protonation-first catalysis.

It should be clarified that the data in Table 3 are single point analyses reported after 1h of electrolysis for each experiment. A more detailed summary of the real-time CO:H₂ product evolution is provided in the supporting information (Figs. S19 – S31) including product turnover numbers (TONs). In general, TONs are very low across the board for both **1-CH₃CN⁺** and **2-CH₃CN⁺**, leaving little merit to their discussion. Unfortunately, this is a common problem across the literature with [*fac*-Mn^I(N[^]N)(CO)₃X]ⁿ electrocatalysts for CO₂ conversion due to their propensity to undergo hydrolytic decomposition. In fact, the maximum reported TON for a manganese-based polypyridyl CO₂ reduction electrocatalyst is 471 over 4 hours for nafion-supported *fac*-Mn^I(bpy)(CO)₃Br at a glassy carbon electrode in a pH 7 phosphate buffer electrolyte.⁹¹ The highest reported TON for a homogeneous [*fac*-Mn^I(N[^]N)(CO)₃X]ⁿ electrocatalyst is just 30 for **2-CH₃CN⁺** in acetonitrile in the presence of Mg²⁺ as a Lewis acid co-catalyst.⁶³ The true merit of investigating [*fac*-Mn^I(N[^]N)(CO)₃X]⁺ catalysts for CO₂ conversion at this

stage of their development is their very low overpotential, high TOFs and high product selectivity. Taking Faradaic yields for CO production alone into account, **1-CH₃CN⁺** performs very well via the *protonation-first* pathway exhibiting an 88% Faradaic yield for CO in the presence of either 1.37 M PhOH or 2.13 M TFE. Competing H₂ evolution, albeit weak, is observed in both of the latter cases with 5% and 13% Faradaic yields for PhOH and TFE, respectively. The CO product selectivity of **1-CH₃CN⁺** is reduced slightly to 85% upon application of a greater overpotential via the *reduction-first* pathway in the presence of 1.37 M PhOH. However, when using 2.13 M TFE or 2.09 M MeOH as a proton source **1-CH₃CN⁺** exhibits superior product selectivity with 100% and 99% selectivity for CO evolution. For both **1-CH₃CN⁺** and **2-CH₃CN⁺** the large concentration of H₂O required to optimize the catalyst TOF results in a significant drop in catalyst selectivity with significant H₂ evolution observed in both cases, 38% and 27% Faradaic yields respectively. In comparison to **2-CH₃CN⁺**, catalyst **1-CH₃CN⁺** performs equally well at the *reduction first* pathway in the presence of optimized concentrations of PhOH, TFE and MeOH with Faradaic yields in the range of 80 – 91 % for CO evolution. Thus, while there is certainly motivation to use a stronger Brønsted acid to overcome the rate-determining step of either catalytic pathway (Scheme 1 intermediates ii-iii-iv or Scheme 2 intermediates i-ii-iii), this study emphasizes that extreme care must be exercised to identify optimum conditions for selective CO evolution (if that is the desired product), precluding any competitive side reactions, e.g. hydrogen evolution or formate production (not observed here). For example, TFE and MeOH as proton sources demonstrate superior selectivity for CO formation in combination with **1-CH₃CN⁺** via the *reduction-first* catalytic pathway, albeit with a slightly lower TOF than when using an optimum concentration of PhOH.

Electrocatalysis with a buffered electrolyte

Conducting electrocatalysis in the presence of excess weak Brønsted acid prevents determination of the electrolyte pH, thus precluding knowledge of the standard CO₂ reduction potential under the same conditions. The use of a buffered electrolyte system with an established pH is recommended⁹² for

determining the true overpotential (η) of a catalytic system. This requires knowledge of the CO₂ to CO equilibrium potential ($E_{\text{CO}_2/\text{CO}}$) under identical pH conditions. Using the method of Appel and Helm⁹², a convenient way to compare the overpotentials (η) required for efficient catalysis with various homogeneous catalysts, is to define η as the difference between the equilibrium potential $E_{\text{CO}_2/\text{CO}}$ (the standard potential $E_{\text{CO}_2/\text{CO}}^0$ applies at pH = 0) and the catalytic peak half-wave potential ($E_{\text{cat}/2}$) as shown in Eq 7.^{4, 92}

$$\eta = |E_{\text{CO}_2/\text{CO}} - E_{\text{cat}/2}| \quad (7)$$

It is imperative to appreciate here that the equilibrium potential $E_{\text{CO}_2/\text{CO}}$ is pH-dependent (Eqs. 2 & 4). As such, the standard reduction potential of $E_{\text{CO}_2/\text{CO}}^0 = -0.13$ V vs Fc⁺⁰ reported by Matsubara et al.⁴ (or the almost identical value of -0.12 V vs Fc⁺⁰ reported by Appel and Mayer⁷) for the reduction of CO₂ to CO in dry acetonitrile (Eq 4), represents a very specific reaction condition. Fortunately, by using a buffered Brønsted acid with an established $\text{p}K_{\text{a}}$ in acetonitrile it is possible to correct $E_{\text{CO}_2/\text{CO}}^0$ using the pH-dependent Nernst equation for the two-electron/two-proton reduction of CO₂ (Eq. 8), thereby allowing calculation of η where the pH is buffer-stabilized:

$$E_{\text{CO}_2/\text{CO}} = E_{\text{CO}_2/\text{CO}}^0 - \left(\frac{2.303RT}{2F} \right) \cdot 2 \text{ pH} \quad (8)$$

The buffer system, benzoic acid:tetrabutylammonium benzoate, [BzOH]:[Bu₄N][BzO], was studied with equimolar acid:base concentrations (1:1; 0.10 M in acetonitrile), ensuring that the electrolyte pH was equal to the $\text{p}K_{\text{a}}$ of BzOH in acetonitrile, i.e., pH = 21.5.⁹³ These conditions correlate to an equilibrium potential of $E_{\text{CO}_2/\text{CO}} = -1.40$ V vs. Fc⁺⁰ upon application of Eq. 8. It was observed that under both 0.10 M [BzOH]:[Bu₄N][BzO] acid-base buffer and 0.10 M [Bu₄N][BzO] electrolyte conditions, the benzoate anion is strongly coordinating to form the neutral **1-BzO** and **2-BzO** complexes in-situ. This was confirmed by variable scan rate analysis in 0.10 M [Bu₄N][BzO] electrolyte under 1 atm argon where the concerted two-electron reduction peaks for both **1-CH₃CN⁺** (-1.63 V) and **2-CH₃CN⁺** (-1.60 V) are

shifted cathodically to -1.97 V and -1.87 V for **1-BzO** and **2-BzO**, respectively (Figs. S32 & S33). It is noteworthy that both **1-BzO** and **2-BzO** show quasi-reversible behavior but only corresponding to one-electron equivalent for the reverse anodic peak (Figs. S32 & S33). Cyclic voltammetry of **1-BzO** in 0.10 M [BzOH]:[Bu₄N][BzO] (1:1) acetonitrile buffer under 1 atm CO₂ is presented in Figure 6 with analogous data provided for **2-BzO** in the supporting information (Fig. S34). For control conditions, to record i_p under 1 atm of argon, 0.10 M [Bu₄N][BzO] electrolyte was used in acetonitrile. Also, linear sweep voltammetry of **1-CH₃CN⁺** and **2-CH₃CN⁺** recorded in 0.10 M Bu₄NPF₆ acetonitrile supporting electrolyte under 1 atm of CO₂ upon addition of benzoic acid alone (unknown pH) is provided for comparison in the supporting information (Fig. S35).

Figure 7. Cyclic voltammetry of **1-BzO** recorded in acetonitrile containing 0.10 M [BzOH]:[Bu₄N][BzO] (1:1) buffer electrolyte under 1 atm CO₂ (pH = 21.5) and 0.10 M [Bu₄N][BzO] electrolyte under 1 atm argon. Both scans were recorded at a glassy carbon disc working electrode with a scan rate (ν) of 10 mV s⁻¹.

A consequence of BzO^- coordination is the inherent cathodic shift for both **1-BzO** and **2-BzO**, which adds an overpotential for BzO^- dissociation prior to generation of the two-electron reduced active catalysts **1**⁻ and **2**⁻. Nonetheless, the *protonation-first* overpotential for the electrocatalytic reduction of CO_2 by **1-BzO** at pH 21.5 in acetonitrile under 1 atm CO_2 in 0.10 M $[\text{BzOH}]:[\text{Bu}_4\text{N}][\text{BzO}]$ electrolyte is calculated as $\eta = 0.42$ V (TOF = 10 s^{-1}) in accordance with equation 7, where $E_{\text{CO}_2/\text{CO}} = -1.40$ V and $E_{\text{cat}/2} = -1.82$ V (Fig. 6). In contrast, **2-BzO** has a slightly higher overpotential at 0.45 V with a lower TOF of 3 s^{-1} (Fig. S34). Furthermore, bulk electrolysis experiments confirmed CO as the sole product for both **1-BzO** and **2-BzO** under these conditions.

FTIR spectroscopy of reactive intermediates relevant to catalyst activation and the catalytic CO_2 reduction cycle

We have used pulse radiolysis combined with time-resolved infrared (TRIR) spectroscopy (PR-TRIR) to characterize the intermediate species generated upon one-electron reduction of the two precatalysts under investigation. In a previous PR-TRIR study on the related $\text{MnBr}(\text{}^t\text{Bu}_2\text{-bpy})(\text{CO})_3$ complex in acetonitrile,^{49, 94} we made use of formate (HCO_2^-) as an additive to scavenge solvent-derived radicals generated upon pulse radiolysis. It was found that the formate anion replaced the Br^- ligand, resulting in formation of the Mn-HCO_2 complex before pulse radiolysis. However, upon one-electron reduction, the HCO_2^- ligand was rapidly ejected on the nanosecond timescale to produce the Mn-based radical, $^*\text{Mn}(\text{}^t\text{Bu}_2\text{-bpy})(\text{CO})_3$ that was found to dimerize with a rate constant of $2k_{\text{dim}} = 1.3 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$.⁴⁹ Similarly, in the current experiments HCO_2^- ligated the precatalysts, resulting in **1-HCO₂** and **2-HCO₂** as starting materials for the PR-TRIR experiments. Here, we have used a new PR-TRIR detection method, namely time-resolved step-scan FTIR spectroscopy, details of which are provided in the Experimental Section.

Figure 8 shows a TRIR spectrum recorded 3 μs after pulse radiolysis of **1-HCO₂**. An analogous TRIR spectrum for **2-HCO₂** is included in the Supporting Information (Fig. S36). The first species observed in

the PR-TRIR experiments is the product of formate ejection following the one-electron reduction of **1-HCO₂** and **2-HCO₂**. In the case of **1**, this species has two $\nu(\text{CO})$ IR bands at 1947 and 1846 cm^{-1} (Figure 7), while for **2**, they occur at 1950 and 1848 cm^{-1} (Figure S36). These are very similar to the two $\nu(\text{CO})$ bands of $^{\bullet}\text{Mn}(\text{tBu}_2\text{-bpy})(\text{CO})_3$ that were previously observed at 1955 and 1853 cm^{-1} ,⁴⁹ leading us to assign the initial products of one-electron reduction and formate ejection as the five-coordinate Mn-based radicals, $^{\bullet}\{\text{Mn}^{\text{I}}[(\text{MeO})_2\text{Ph}]_2\text{bpy})(\text{CO})_3\}$ (**1[•]**) and $^{\bullet}\text{Mn}(\text{mes}_2\text{bpy})(\text{CO})_3$ (**2[•]**). Kubiak and co-workers have shown^{51, 63} that Mn complexes with bulky substituents in the 6,6' positions of a bpy ligand do not dimerize due to extreme steric hindrance. Our PR-TRIR data agree with this observation, as we saw no evidence for the dimerization of **1[•]** or **2[•]** into **1–1** or **2–2** on the micro- to millisecond timescale.

Figure 8. TRIR spectrum of the five-coordinate one-electron reduced species **1[•]** (top) recorded 3 μs after pulse radiolysis of acetonitrile solutions of **1-HCO₂** containing 0.025 M $[\text{Bu}_4\text{N}][\text{HCO}_2]$ under 1 atm argon. An FTIR spectrum (bottom) of the solution prior to pulse radiolysis is included for reference.

The two-electron reduced five-coordinate active catalyst species **1⁻** and **2⁻** were investigated by the technique of FTIR spectroelectrochemistry under 1 atm argon in 0.10 M tetrabutylammonium hexafluorophosphate electrolyte. Two $\nu(\text{CO})$ IR bands are observed for **2⁻** at the lower stretching frequencies of 1907 and 1806 cm^{-1} (within 2 cm^{-1} of those previously reported⁵¹) consistent with greater

back-bonding onto the CO π^* orbitals. Similarly, **1**[−] displays two $\nu(\text{CO})$ IR bands at 1904 and 1805 cm^{-1} , again consistent with the two-electron reduced five coordinate assignment as predicted by DFT calculations (Fig. S37). By taking advantage of the weakly coordinating OTf[−] anion in **1** and **2** we hypothesized that under 1 atm of CO gas in a non-coordinating solvent, such as dichloromethane, the tetracarbonyl species **1-CO**⁺ and **2-CO**⁺ may be generated in-situ. Complex **1-CO**⁺ is of specific interest as the immediate product/intermediate following the rate-determining C–O bond cleavage step in the *protonation first* pathway (Scheme 2 intermediate iii). Indeed, the six coordinate tetracarbonyl cation **1-CO**⁺ was formed quantitatively under these conditions. Furthermore, upon removal of the dichloromethane solvent **1-CO**⁺ remained stable in acetonitrile solvent for comparable FTIR analysis displaying four $\nu(\text{CO})$ IR bands at 2113, 2038, 2008, and 1967 cm^{-1} (Fig. S37). Although the *protonation first* pathway is not favored for **2**[−] it is worthy to note that the analogous **2-CO**⁺ intermediate could also be characterized in situ displaying four $\nu(\text{CO})$ IR bands at 2106, 2026, 2015(sh), and 1983 cm^{-1} (Fig. S38).

Table 4. FTIR absorption data in acetonitrile for all complexes, summarizing $\nu(\text{CO})$ stretching frequencies.

Complex	$\nu(\text{CO})$ (cm^{-1})
1-CH₃CN ⁺	2038, 1954, 1941
1 [•]	1947, 1846
1 [−]	1904, 1805
1-CO ⁺	2113, 2038, 2008, 1967
2-CH₃CN ⁺	2039, 1948 (br)
2 [•]	1950, 1848
2 [−]	1907, 1806
2-CO ⁺	2106, 2026, 2015(sh), 1983

Theoretical Investigation of the CO₂ Reduction Mechanism

Density functional theory (DFT) calculations at the M06 level of theory⁹⁵ coupled with the SMD continuum solvation method⁹⁶ were employed to study the reaction mechanism of CO₂ reduction by **1-CH₃CN⁺** (*see computational methods in SI for details*). Results for the initial activation and reduction steps of the catalyst are reported in the supporting information and are in good agreement with the electrochemical results discussed above (Scheme S1). The computed free energy changes and activation energy for formation of the metallocarboxylic acid **1-CO₂H** from the active catalyst **1⁻** and TFE are provided in Scheme S2. For brevity, only the *protonation-first* and *reduction-first* CO₂ reduction pathways are presented in Scheme 3 below. The initial species in Scheme S2 is the 18-electron **1⁻** complex generated via the two-electron-reduction of **1-CH₃CN⁺**. The first step of the proposed mechanism involves binding of CO₂ to **1⁻**, which proceeds with a free energy of activation ($\Delta G^\ddagger$) of 10.5 kcal/mol, and the formation of the resulting metallocarboxylate intermediate, **1-CO₂⁻**, is uphill by 8.5 kcal/mol. The protonation of **1-CO₂⁻** to generate **1-CO₂H** ($pK_a^{\text{calc}} = 26.1$) is favorable for PhOH with $\Delta G = -3.6$ kcal/mol and slightly uphill for TFE with $\Delta G = 6.1$ kcal/mol.

Upon formation of the metallocarboxylic acid intermediate **1-CO₂H** the subsequent steps involve C–OH bond breakage to ultimately evolve CO by either the *protonation-first* or *reduction-first* pathways (Scheme 3).⁷¹ The *protonation-first* pathway starts with cleavage of the C–OH bond in **1-CO₂H** with a Brønsted acid as the proton source (*e.g.*, H₂O, MeOH, PhOH, or TFE). The optimized transition state structure with TFE (Figure 9) as the proton source features a $\Delta G^\ddagger$ of 25.1 kcal/mol. This protonation step is uphill with $\Delta G = 16.3$ kcal/mol, and is followed by a reduction step with an associated computed potential of $E = -1.73$ V to generate **1-CO**. On the other hand, the initial step of the *reduction-first* pathway is the reduction of **1-CO₂H** to **1-CO₂H⁻** with a computed potential of $E = -2.07$ V, followed by protonation and C–OH bond breakage with $\Delta G^\ddagger = 19.0$ kcal/mol with TFE as the

proton source. Both the *protonation-first* and *reduction-first* pathways converge at the neutral tetracarbonyl species **1-CO** from where reduction to form **1-CO⁻** involves a computed potential of $E = -2.54$ V. However, reduction of **1-CO** with simultaneous evolution of CO is more favorable, requiring a potential of only $E = -1.83$ V and regenerates the active catalyst **1⁻**, completing the catalytic cycle.

Scheme 3. A thermodynamic comparison of both *protonation-first* and *reduction-first* mechanisms of CO₂ reduction by the active catalyst **1⁻** in acetonitrile obtained at the M06 level of theory. Calculated reduction potentials (E) are reported in units of volts vs Fc⁺⁰.

Figure 9. Optimized transition state structures for C–OH bond cleavage for (a) *protonation-first* and (b) *reduction-first* pathways. Color code: Mn, ochre; C, gray; N, blue; O, red, H, white.

For both pathways, cleavage of the C–OH bond is predicted to be rate-determining so this step was examined more closely with different Brønsted acids as the proton source (Table 5). First of all, the computed activation free energies ($\Delta G^\ddagger$) decrease with increasing acidity ($\text{H}_2\text{O} < \text{MeOH} < \text{TFE} < \text{PhOH}$) as expected from the nature of the chemical step. Secondly, the reduction of **1**- CO_2H to **1**- CO_2H^- facilitates the C–OH bond breakage as a decrease in $\Delta G^\ddagger$ s is observed for all four Brønsted acids examined and becomes especially significant in the case of TFE and PhOH (Table 5). The $\Delta G^\ddagger$ s associated with H_2O and MeOH are significantly higher for the *protonation-first* pathway, which is in line with the experimental observations that H_2O and MeOH are less effective at promoting the *protonation-first* pathway for **1**- CH_3CN^+ . Furthermore, we also compared the C–OH bond cleavage step for **1**- CH_3CN^+ versus **2**- CH_3CN^+ . The computed $\Delta G^\ddagger$ s are found to be consistently higher for **2**- CH_3CN^+ compared to **1**- CH_3CN^+ for both *protonation-first* and *reduction-first* pathways (Table 5), which again is in good agreement with the measured TOFs and the fact that the promotion of the *protonation-first* pathway is enhanced for **1**- CH_3CN^+ compared to **2**- CH_3CN^+ . A comparison of the key geometrical features of the optimized transition states for the *protonation-first* pathway (Table S2)

indicates earlier TS structures for **1-CH₃CN⁺** compared to **2-CH₃CN⁺**, as expected from lower $\Delta G^\ddagger$ s, and also shows that the ligand framework remains essentially the same (Fig. S39). However, there is a significant change in the position and orientation of the Brønsted acids (*e.g.*, TFE) as a result of the C–OH---OMe hydrogen bonding interaction in **1-CH₃CN⁺** complexes (C–OH---OMe hydrogen bond length for the optimized transition states ranges from 1.98 to 2.06 Å). Based on these observations, the difference in reactivity of **1-CH₃CN⁺** compared to **2-CH₃CN⁺**, especially for the *protonation-first pathway*, is proposed to stem from a combination of an inductive electronic influence of the pendant methoxy groups of **1-CH₃CN⁺** and additional stabilization of the C–OH bond cleavage TS via noncovalent hydrogen bonding interactions between C–OH and the pendant methoxy groups.⁹⁷ Finally, we performed benchmark calculations at the DLPNO-CCSD(T) level of theory for the $\Delta G^\ddagger$ s associated with the *protonation-first* pathway for **1-CH₃CN⁺** and **2-CH₃CN⁺** to assess the performance of a set of selected density functionals and found that all the levels of theory employed provide the same qualitative conclusions discussed above (Table S3) and quantitatively the M06-L functional provides the best agreement with the DLPNO-CCSD(T)⁹⁸ level of theory (see computational methods and supporting information for further details).

Table 5. Summary of computed free energies of activation ($\Delta G^\ddagger$) in units of kcal/mol at the M06 level of theory for the C–OH bond cleavage step in both the *protonation-first* and *reduction-first* pathways.

	1-CH₃CN⁺				2-CH₃CN⁺			
	PhOH	TFE	MeOH	H ₂ O	PhOH	TFE	MeOH	H ₂ O
<i>protonation-first</i>	21.0	25.1	29.6	33.2	26.8	30.7	34.1	35.4
<i>reduction-first</i>	16.6	19.0	27.5	32.9	17.7	23.9	28.1	33.1

Conclusions

Electrochemical and computational studies have been utilized to characterize the incipient *protonation-first* pathway of electrocatalytic reduction of CO₂ to CO for a $[fac\text{-Mn}^I(\text{N}^{\wedge}\text{N})(\text{CO})_3\text{X}]^n$ class of catalyst. Evolution of the *protonation-first* catalytic pathway, versus the more thermodynamically demanding *reduction-first* pathway, by **1-CH₃CN⁺** exhibits a strong dependence upon the concentration, pK_a and hence identity of the external weak Brønsted acid proton source in an acetonitrile-based electrolyte; with trifluoroethanol and phenol being the most successful. Efficient access to the sought after *protonation-first* pathway is thus granted not only by the $[(\text{MeO})_2\text{Ph}]_2\text{bpy}$ ligand in **1-CH₃CN⁺** but in combination with the appropriate Brønsted acid proton source. A maximum saving of up to 0.55 V in overpotential is exhibited by the *protonation-first* pathway for **1-CH₃CN⁺** relative to the *reduction-first* pathway in the presence of 1.37 M PhOH as a Brønsted acid proton source. Access to the *protonation-first* pathway for **1-CH₃CN⁺** has been corroborated by computational studies and is ascribed to a net inductive electronic influence of the pendant methoxy groups of the $(\text{MeO}_2\text{Ph})_2\text{bpy}$ ligand in combination with additional stabilization of the C–OH bond cleavage transition state via noncovalent hydrogen bonding interactions between C–OH and the pendant methoxy groups. In addition to its enhanced catalytic efficiency at lower overpotential, controlled potential bulk electrolysis studies demonstrate that **1-CH₃CN⁺** also maintains excellent product selectivity for CO evolution in the presence of non-aqueous Brønsted acid proton sources, MeOH, TFE and PhOH. To probe catalyst activation, the technique of time-resolved infrared spectroscopy combined with pulse-radiolysis (PR-TRIR) was used to cleanly observe the $\nu(\text{CO})$ vibrational frequencies of the neutral, one-electron reduced, 5-coordinate precatalyst species **1[•]** (1947, 1846 cm⁻¹) and **2[•]** (1950, 1848 cm⁻¹). FTIR spectra of the anionic, two-electron reduced, 5-coordinate active catalyst species **1⁻** (1904, 1805 cm⁻¹) and **2⁻** (1907, 1806 cm⁻¹) were obtained by spectroelectrochemistry and $\nu(\text{CO})$ vibrational frequencies of the key cationic, six-coordinate tetracarbonyl catalytic intermediates **1-CO⁺** (2113, 2038, 2008, 1967 cm⁻¹) and **2-CO⁺** (2106, 2026, 2015(sh), 1983 cm⁻¹) have also been reported. Finally, based on the standard potential for the reduction of CO₂ to CO in dry acetonitrile at pH 0, it has been possible to report the

true electrocatalytic overpotential for both active catalysts **1**[−] and **2**[−] in acetonitrile in the presence of an acid-base buffer at a pH of 21.5.

Experimental

Materials and Methods

The following chemicals were purchased from Sigma Aldrich; bromopentacarbonylmanganese(I) (98%), silver trifluoromethanesulfonate (>99%), 2,4,6-trimethylphenylboronic acid, 2,6-dimethoxyphenylboronic acid, tetrabutylammonium hexafluorophosphate (>99%), tetrabutylammonium benzoate (>99%), benzoic acid (>99%), potassium carbonate (>99%), tetrabutylammonium trifluoromethanesulfonate (>99%), trifluoromethanesulfonic acid (>99%), methanol (spectrophotometric grade), D₂O (99.9% D), 2,2,2-trifluoroethanol (>99%), phenol (>99.9%), acetonitrile (electronic grade, 99.999%). Tetrakis(triphenylphosphine)palladium(0) (99%) and 6,6'-dibromo-2,2'-bipyridine (>95%) were purchased from Strem and TCI America, respectively. Tetrabutylammonium hexafluorophosphate was recrystallized thrice from ethanol and dried under vacuum prior to electrolyte preparation. Gas cylinders were ordered from Airgas containing pre-mixed ratios of Ar:CO₂ (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100). FTIR spectra were recorded on a Thermo Nicolet 670 FTIR spectrophotometer in spectrophotometric grade acetonitrile. NMR spectra were recorded on an Agilent spectrometer operated at 399.80 MHz for ¹H and 100.54 MHz for ¹³C nuclei. Deuterated solvents *d*₆-DMSO and CD₃CN were used as received from Sigma Aldrich and their residual ¹H and ¹³C solvent signals⁹⁹ used as internal references for reporting the chemical shift (δ). ¹H-NMR of **2-CD₃CN**⁺ and FTIR of **2-CH₃CN**⁺ were consistent with literature reports.⁵¹ LC-MS of [(MeO)₂Ph]₂bpy was performed on an Agilent 2100 system using atmospheric pressure chemical ionization (APCI) mode. Mobile phases consisted of methanol and water both containing 0.05% trifluoroacetic acid. A linear gradient was used to increase from 25:75 v/v methanol/water to 100% methanol over 7.0 min at a flow rate of 0.7 mL/min with a C18 (5.0 μm, 6.0 x 50 mm) column. UV

detection of the eluent was conducted at 210 nm, 254 nm and 365 nm. Voltammetry and bulk electrolysis were carried out on a CH Instruments 620E potentiostat. A custom three electrode cell was used for both voltammetry and bulk electrolysis experiments allowing airtight introduction of working, counter and reference electrodes as well as septa for gas purging. For cyclic voltammetry, glassy carbon (3 mm diameter) and Pt wire were used as working and counter electrodes, respectively, with 0.1 M Bu₄NPF₆ in spectrophotometric grade acetonitrile as the supporting electrolyte. A non-aqueous reference electrode was used to minimize ohmic potential drop at the solvent interface. This consisted of a Ag wire in 0.10 M Bu₄NPF₆ acetonitrile supporting electrolyte isolated by a Vycor frit and was calibrated in-situ using the ferrocenium/ferrocene redox couple as a pseudo reference. Redox potentials (E) were determined from cyclic voltammetry as $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively. Where E could not be calculated due to irreversible behavior, E_{pc} or E_{pa} are reported accordingly. For electrocatalysis studies, all observed currents were corrected for a dilution factor upon addition of various volumes of each Brønsted acid. For controlled potential bulk electrolysis experiments a vitreous carbon (Structure Probe, Inc.) working electrode soldered to a copper wire was used. A Pt gauze counter electrode was used, isolated from the main compartment by a fine porosity Vycor tube+frit to minimize mass transfer resistance. Gas chromatography data were recorded on a custom Shimadzu GC-2014 instrument where a Ni “methanizer” catalyst was used to convert CO to CH₄ prior to quantification of CH₄ by the thermal conductivity detector (TCD detectors have poor sensitivity for CO and high sensitivity for CH₄). H₂ was simultaneously monitored by a flame ionization detector during the same injection. The GC was precalibrated for CO and H₂ quantification by mimicking bulk electrolysis conditions (i.e. 5 mL supporting electrolyte in the same cell, with electrodes, under 1 atm CO₂). Standard curves for H₂ and CO were generated using this cell where known volumes of the analyte gas (H₂ or CO) were injected and the solution stirred for 30 min to allow equilibration of the analyte between the electrolyte and headspace prior to GC injection.

Synthesis

6,6'-bis(2,6-dimethoxyphenyl)-2,2'-bipyridine [(MeO)₂Ph]₂bpy

100 mg of 6,6'-dibromo-2,2'-bipyridine (0.312 mmol) and 144 mg of (2,6-dimethoxyphenyl)boronic acid (0.936 mmol, 3 equiv.) were added to a 5 ml microwave tube. 1 ml of 2 M aqueous Na₂CO₃ and 1 ml of toluene were added to the reaction tube, and the mixture was purged with argon for 5 minutes. 18 mg of tetrakis(triphenylphosphine)palladium(0) (0.0156 mmol, 0.05 equiv.) was added to the reaction tube followed by 1 ml of ethanol with further argon purging. The reaction tube was sealed and irradiated with microwaves at 120°C for 1 hour. Upon completion, the reaction mixture was extracted with dichloromethane. The combined organic layer was washed with brine solution and dried with MgSO₄. The volume of dichloromethane was reduced under vacuum to approximately 0.5 ml, 20 ml of methanol was added, and the mixture was cooled in the freezer for 1 hour. A white solid precipitated and was collected by vacuum filtration. The product was washed with cold methanol and dried under vacuum overnight realizing 120 mg (90% yield) of pure product. LC-MS predicted (M+1) = 429.2 m/z; observed (M+1) = 429.2 m/z. ¹H NMR [(CD₃)₂SO]: δ = 8.18 (d, 2H, 3,3'-bpy-H, *J* = 8 Hz), 7.87 (t, 2H, 5,5'-bpy-H, *J* = 8 Hz), 7.39 (t, 2H, 4,4'-bpy-H, *J* = 8 Hz), 7.27 (d, 2 para H, phenyl-H, *J* = 8 Hz), 6.79 (d, 4H, 4 meta H phenyl-H, *J* = 8 Hz), 3.68 (s, 12H, 4 ortho OCH₃). ¹³C NMR [(CD₃)₂SO]: δ = 158.17, 155.66, 154.37, 137.30, 130.24, 129.38, 126.59, 119.46, 104.99, 56.30 ppm.

fac-Mn^I([(MeO)₂Ph]₂bpy)(CO)₃(OTf) **1-OTf** Following a reported procedure for the synthesis of *fac*-Mn(CO)₅(OTf)⁷², bromopentacarbonylmanganese(I) (67.6 mg, 0.241 mmol) was added to 25 ml of dichloromethane in a 50 ml round bottom flask under 1 atm argon. Silver triflate (62.6 mg, 0.241 mmol) was added and the reaction mixture was allowed to stir in the dark. After three hours, the reaction mixture was filtered through a celite plug by vacuum filtration to remove the resulting AgBr precipitate. The filtrate was dried by rotary evaporation, quantitatively yielding *fac*-Mn(CO)₅(OTf) as a yellow solid confirmed by FTIR spectroscopy⁷². This product was dissolved in 25 ml of diethyl ether in a 50 ml round bottom flask, and the ligand 6,6'-bis(2,6-dimethoxyphenyl)-2,2'-bipyridine (76 mg, 0.181 mmol) was added under 1 atm of argon. The reaction mixture was refluxed in the dark for three hours and

cooled to room temperature. The yellow precipitate was collected by vacuum filtration, washed with cold diethyl ether and dried under vacuum overnight in a sealed round bottom flask, yielding 97 mg (75%). ^1H NMR of **1-CD₃CN⁺** (CD₃CN): δ = 8.43, 8.41 (dd, 2H, 3,3'-bpy-H, J = 1, J_d = 2), δ = 8.19 (t, 2H, 5,5'-bpy-H, J = 2), δ = 7.50 (m, 4H, 4,4'-bpy-H and para H phenyl), δ = 6.79 (dd, 4H, meta H phenyl, J_d = 2), δ = 3.76 (s, 6H, 2 OCH₃), δ = 3.68 (s, 6H, 2 OCH₃). FTIR of **1-CH₃CN⁺** in CH₃CN $\nu(\text{CO})$: 2038, 1954, 1941 cm^{-1} . Anal. Calcd. for **1** C₃₀H₂₄F₃MnN₂O₁₀S: C, 50.29; H, 3.38; N, 3.91. Found: C, 50.11; H, 3.32; N, 3.84.

Pulse Radiolysis Step-Scan FTIR Experiments

The pulse radiolysis experiments were conducted at the 2 MeV Van de Graaff (VdG) electron accelerator located in the Chemistry Division at Brookhaven National Laboratory. A commercial step-scan FTIR spectrometer (Bruker, IFS 66/S) equipped with an external fast risetime HgCdTe IR detector was placed on an air-stabilized optical bench close to the VdG's electron beam line exit window, with the electron beam passing directly through a homemade, air-tight IR flow cell (0.7 mm pathlength) equipped with 0.5 mm thick CaF₂ windows. A 25 mL CH₃CN solution containing 1.5 mM of the Mn complex and 0.025 M tetrabutylammonium formate (synthesized according to a reported procedure⁴⁹) was prepared inside a glovebox and placed into a sealed reservoir vessel. The vessel was then inserted into a gas-tight recirculating flow system containing a magnetically-coupled gear pump (Micropump). The tubing was evacuated and refilled with argon several times before saturating the solution with 2 atm argon and flowing. The VdG can produce electron pulses of increasing dose by increasing the electron pulsewidth up to a maximum of 4 μs . In these experiments, we used 1 μs electron pulses at a repetition rate of 5 Hz. Since our experiments were not quantitative, we did not measure the absorbed dose. The time-resolved step-scan FTIR measurements were performed in a manner similar to those previously reported¹⁰⁰ for laser flash photolysis, except in this case a digital delay generator (Stanford Research Systems, DG535) was used to trigger the electron pulses in synchronization with the data collection. A 1

MHz preamplifier (Stanford Research Systems, SR560) was used to amplify the detector signal prior to digitization. In a typical experiment, data were collected at 6 cm⁻¹ spectral resolution with an optical band pass filter that resulted in 252 interferogram mirror positions. Either 4 or 8 averages were acquired at each mirror position, leading to a total of either 1008 or 2016 electron pulses impinging on the flowing sample. FTIR spectra recorded after the experiment showed very little overall sample decomposition (< 5 %).

Supporting Information. NMR spectra, additional voltammetry, FTIR, bulk electrolysis, computational and Cartesian coordinate data. This material is available free of charge via the internet at <http://pubs.acs.org>.

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