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Electrocatalytic Dihydrogen Production by an Earth-Abundant Manganese Bipyridine Catalyst

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Supporting Information

ABSTRACT: Earth-abundant manganese bipyridine complexes have been extensively studied as homogeneous electrocatalysts for proton-coupled CO_2 reduction. To date, these manganese complexes have not been examined as catalysts for the reduction of other small molecules. We report electrocatalytic H_2 production by $[Mn(mesbpy)(CO)_3(MeCN)](OTf)$. In acetonitrile, this manganese electrocatalyst displays a turnover frequency (TOF) of 5500 s^{-1} at an overpotential of 0.90 V (at $E_{cat/2}$) for the reduction of protons to H_2 using trifluoroacetic acid (TFA) as the acid source. These findings show the flexibility of these manganese bipyridine complexes to serve as catalysts for a variety of small molecule reductions.

A dramatic increase in global fuel consumption coupled with unsustainable emissions of carbon dioxide (CO_2) has led to one of the biggest challenges of our modern era: the development of renewable, CO_2-neutral fuels.[1] In recent years, efforts have been made to develop technologies for solar and wind power; however, the energy sources for these technologies suffer from intermittent availability. Therefore, research in energy storage, particularly storage in chemical bonds, is essential to the sustainability of these technologies. To counteract the intrinsic availability problem of solar and wind energy, electricity generated from these sources can be stored in chemical fuels, such as dihydrogen (H_2).[2] Platinum is considered an excellent electrocatalyst for the H_2 evolution reaction (HER); however, the high cost of this material limits its economic viability. The necessity to find viable HER electrocatalysts has led to significant research on molecular complexes based on earth-abundant metals.[3]

Of the homogeneous catalysts studied for HER, including numerous examples of those based on earth-abundant metals nickel, iron, and cobalt, few catalysts have been developed based on manganese. Sparse research on homogeneous manganese HER catalysts is surprising, especially considering that the $Mn^{I}(CO)_3$ fragment is isolobal with the $Fe^{II}(CO)(CN)_2$ fragment found in the active site of [NiFe]hydrogenases.[4] The majority of manganese HER catalysts studied to date are binuclear complexes ([NiMn]- and $Mn_2(CO)_6$-type complexes).[5] To our knowledge, there have only been two reports of mononuclear manganese catalysts,[6] and they both suffer from very low activity.

$Mn(bpy)(CO)_3X$ complexes (bpy = 2,2′-bipyridine; X = halogen or solvent molecule with counteranion) have garnered significant interest in recent years as CO_2 reduction catalysts. Specifically, work by Deronzier[7] and our own group[8] have shown that these systems reduce CO_2 to carbon monoxide (CO) with comparable activities to the well-studied $Re(bpy)(CO)_3X$ catalysts[9] in the presence of weak Brønsted acids. Not only are these manganese catalysts more earth-abundant than their rhenium analogues, they also operate at considerably lower overpotentials (i.e., less energy is needed to drive the catalytic reactions). Although these manganese and rhenium complexes have been extensively studied for CO_2 reduction, they have not been investigated as H^+ reduction catalysts, mainly because of the high overpotentials necessary to access their doubly reduced states.[10] Recently, our group reported electrocatalytic CO_2 reduction by a manganese complex with a bulky bpy ligand, $[Mn(mesbpy)(CO)_3(MeCN)](OTf)$ (**1**; mesbpy = 6,6′-dimesityl-2,2′-bipyridine; MeCN = acetonitrile; OTf = trifluoromethanesulfonate; structure in Figures 1 and S1 in the Supporting Information, SI).[8b] In contrast to typical $Mn(bpy)(CO)_3X$ complexes, **1** does not dimerize after one-electron reduction, which significantly lowers the potential necessary for two-electron reduction (by 0.30 V). Because **1** possesses a relatively moderate reduction potential, we have investigated the ability for **1** to function as a HER electrocatalyst.

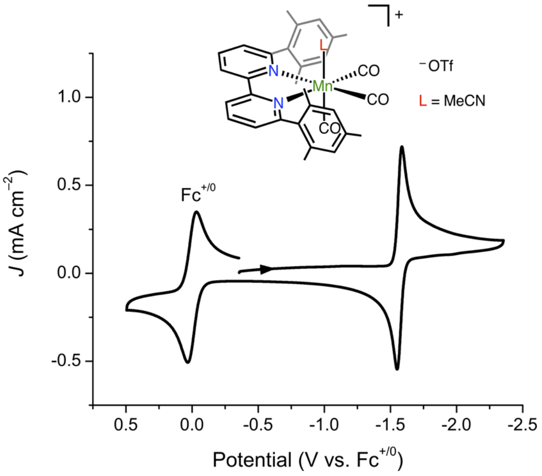

Figure 1. CV of 1 mM complex **1** in MeCN (0.1 M $TBAPF_6$) under a N_2 atmosphere (ν = 0.1 V s^{-1}).

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The cyclic voltammogram (CV) of **1** in dry MeCN with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte under an inert atmosphere is shown in Figure 1 and has been previously described.[8b] The CV of **1** displays a single reversible, two-electron reduction wave at −1.55 V vs $Fc^{+/0}$. The addition of TFA (pK_a = 12.7 in MeCN)[11] to electrochemical solutions of **1** results in an increase in the current near this two-electron reduction, as shown in Figure 2. This current increase corresponds to the electrocatalytic reduction of H^+ from TFA to H_2, as verified by controlled potential electrolysis experiments, with 100% Faradaic efficiency (Figures S5−S7 in the SI). Higher concentrations of TFA resulted in further increased current densities in electrocatalysis experiments (Figures 2 and S3 in the SI). For reference, a CV of TFA in the electrolyte solution (without added catalyst) is shown in Figure S2 in the SI.

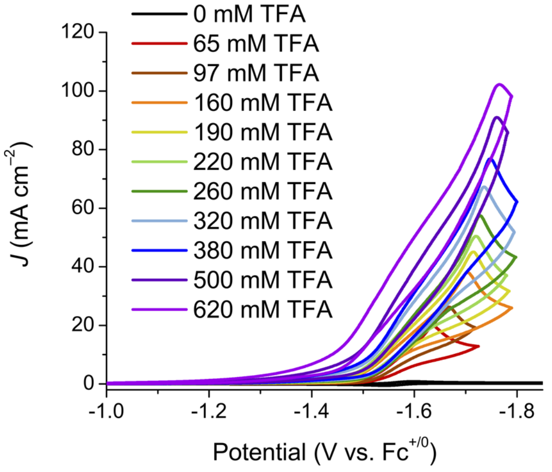

Figure 2. CVs of 1 mM complex **1** with varying [TFA]. Conditions: 0.1 M $TBAPF_6$/MeCN; under N_2; ν = 0.1 V s^{-1}.

For HER, the overpotential (η) is defined as the difference between the thermodynamic potential for the reduction of H^+ (E_{H^+}) and the potential at half of the catalytic current ($E_{cat/2}$).[12] For many acids, such as TFA, homoconjugation of acid/base pairs is a known problem, which lowers the accuracy of calculating E_{H^+}.[12] TFA has a relatively large homoconjugation constant in MeCN (7.6×10^3 M^{-1}),[13] which significantly lowers the effective pK_a of the acid in MeCN. Artero et al. accurately measured E_{H^+} for TFA, taking into account homoconjugation of the acid at various concentrations.[14] At 0.1 M TFA, E_{H^+} = −0.65 V vs $Fc^{+/0}$,[14] and, thus, η = 0.90 V using $E_{cat/2}$ = −1.55 V vs $Fc^{+/0}$ (see the SI, Figure S8). The η for **1**, although far from ideal, is comparable to many previously reported HER electrocatalysts.[4,15]

The peak-shaped current response in our catalytic CVs can be attributed to a variety of "side-phenomena" that cause local perturbations in the diffusion layer and have been previously discussed.[16] Additionally, peak-shaped current responses are typical for electrocatalysis involving TFA due to issues involving homoconjugation.[14,17] At high concentrations of TFA, the catalytic current response splits into two features. The first feature shifts to more positive potentials as the concentration of TFA is increased, whereas the second feature shifts to more negative potentials. Artero et al. have previously described this phenomenon as follows: the wave at more positive potentials corresponds to the reduction of TFA to H_2 by **1**, resulting in the formation of the homoconjugate adduct of TFA, and the wave at more negative potentials corresponds to the reduction of the homoconjugate adduct, [TFA-H-TFA], by **1** (into H_2 and TFA^-).[14]

The turnover frequency (TOF) of **1**-catalyzed TFA reduction can be estimated from CVs by comparing the peak catalytic current (i_{cat}) to the peak current of the reversible redox wave under an inert atmosphere (i_p), as described in the SI. Because of the complications of homoconjugation, i_{cat} values were determined from catalytic current values at $E_{cat/2}$ = −1.55 V vs $Fc^{+/0}$. In order to make this analysis, the catalytic reaction must be at steady state. Scan rate studies indicate that the catalytic current response is at steady state despite the peak-shaped current responses (Figure S4 in the SI). The addition of 620 mM TFA results in a peak i_{cat}/i_p = 59.3 and a TOF = 5500 s^{-1} (Figure 2). This calculated TOF is likely an underestimation in the overall catalyst activity due to **1**-catalyzed reduction of [TFA-H-TFA] at higher overpotentials (described above). However, a small amount of current at $E_{cat/2}$ results from TFA reduction by the glassy carbon electrode, further complicating the true activity of **1**. The TOF of **1** is comparable to the widely studied nickel bis(diphosphine) complexes bearing pendant amines, arguably the most active family of HER electrocatalysts to date (see the SI).[15e,18]

Catalytic Tafel plots, along with a determination of η at $E_{cat/2}$, provide a cohesive method for comparing electrocatalysts at different experimental conditions.[19] A "good" electrocatalyst is defined to have a high TOF, low η, and high stability. Catalytic Tafel plots assess the later two of these parameters in a single plot, allowing for catalyst benchmarking independent of variable experimental conditions. For this analysis, we assume an EECC-type catalytic mechanism (see SI for mechanistic details), which leads to the catalytic Tafel plots shown in Figure 3 (see SI, Figures S9 and S10). Recently, Artero and Savéant have compared the Tafel plots of widely studied HER electrocatalysts.[19] With log TOF_{max} = ∼4.0, **1** displays a maximum activity similar to that of $Co(dmgH)_2$. Catalyst **1** has a lower TOF_0 (TOF at η = 0) than $Co(dmgH)_2(py)$, $[Ni(P^{Ph}{}_2N^{Ph})_2]^{2+}$, and Fe(TPP).[19]

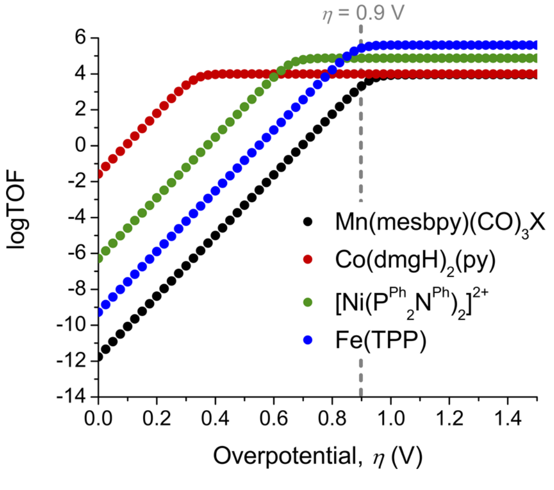

Figure 3. Catalytic Tafel plots for **1**, $Co(dmgH)_2(py)$, $[Ni(P^{Ph}{}_2N^{Ph})_2]^{2+}$, and Fe(TPP) with 1.0 M H^+.

We have investigated the ability for the earth-abundant manganese complex **1** to perform HER using TFA as a H^+ source. Upon two-electron reduction, **1** displays remarkably high activity for HER, reaching a TOF of 5500 s^{-1}. We utilize two complementary methods to benchmark catalyst **1** with other HER catalysts in the literature. These findings provide a new example of catalytic small-molecule reduction by these well-studied manganese bpy catalysts, which to date have been primarily investigated with regard to CO_2 reduction. Future studies will include exploring the ability for catalyst **1** to produce a tunable syngas ratio (H_2/CO) using acids under a CO_2 atmosphere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, determination of η, TOF, and Tafel plots. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01080.

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Notes

The authors declare no competing financial interest.

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