

Exploiting Metal–Ligand Cooperativity to Sequester, Activate, and Reduce Atmospheric Carbon Dioxide with a Neutral Zinc Complex

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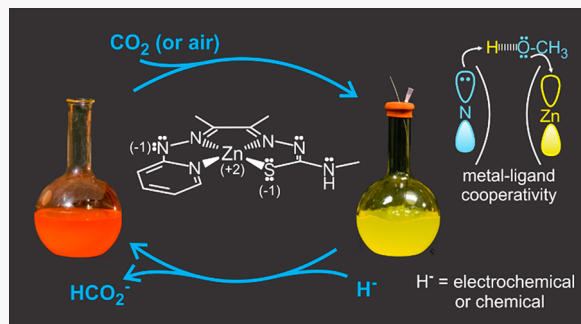


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ABSTRACT: As atmospheric levels of carbon dioxide (CO₂) continue to increase, there is an immediate need to balance the carbon cycle. Current approaches require multiple processes to fix CO₂ from the atmosphere or flue gas and then reduce it to value-added products. The zinc(II) catalyst Zn(DMTH) (DMTH = diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazonato)) reduces CO₂ from air to formate with a faradaic efficiency of 15.1% based on total charge. The catalyst utilizes metal–ligand cooperativity and redox-active ligands to fix, activate, and reduce CO₂. This approach provides a new strategy that incorporates sustainable earth-abundant metals that are oxygen and water tolerant.



INTRODUCTION

Although the degree of its effects remains in debate,¹ the current atmospheric concentration of carbon dioxide (CO₂) is in excess of 415 ppm, creating substantial impacts on climate, global temperatures, and ocean acidification. Balancing the carbon cycle by sequestering CO₂ and utilizing it as a feedstock for liquid fuels provides an ideal approach to address CO₂ levels. Currently, the initial steps of this process require one method to capture low concentrations of CO₂ from the atmosphere or flue gas^{2–5} and a second system to reduce CO₂^{6–12} to value-added products. In the current manuscript, we report the combination of these two steps for the reduction of CO₂ to formate (HCO₂[−]) from (1) pure CO₂ and (2) from air using an inexpensive catalyst containing zinc.

The two-electron reduction of CO₂ in the presence of a proton donor typically yields HCO₂[−] or carbon monoxide (CO) (Figure 1A) through common pathways that dictate the product distribution (Figure 1B).⁸ A significant limitation of these pathways is the requirement for reduction prior to CO₂ binding, which limits their ability to fix CO₂ at low pressure. To date, no catalyst following these pathways can utilize CO₂ from air or 3–13% streams commonly found in power plant exhaust.¹³ Recently, two catalysts that bind substrate prior to reduction have been reported, demonstrating the potential of alternate mechanistic approaches to improve catalytic activity. Protonation of fac-Mn([[(MeO)₂Ph]₂bpy](CO)₃(CH₃CN))-(OTf) ([[(MeO)₂Ph]₂bpy] = 6,6′-bis(2,6-dimethoxyphenyl)-2,2′-bipyridine, OTf = triflate) prior to reduction lowers the overpotential for CO₂ reduction to CO by 450 mV¹⁴ relative to that of Re(bpy)(CO)₃(X) (bpy = 2,2′-bipyridine, X = halide). The Re(bpy)(CO)₃(X) derivative developed by

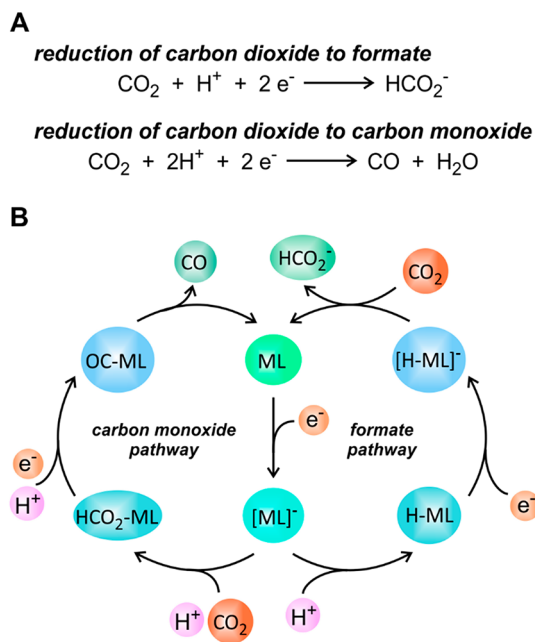


Figure 1. (A) Half-reactions for the two-electron reduction of CO₂. (B) Generalized pathways for catalytic reduction of CO₂ by two electrons with a metal-ligand (ML) catalyst.

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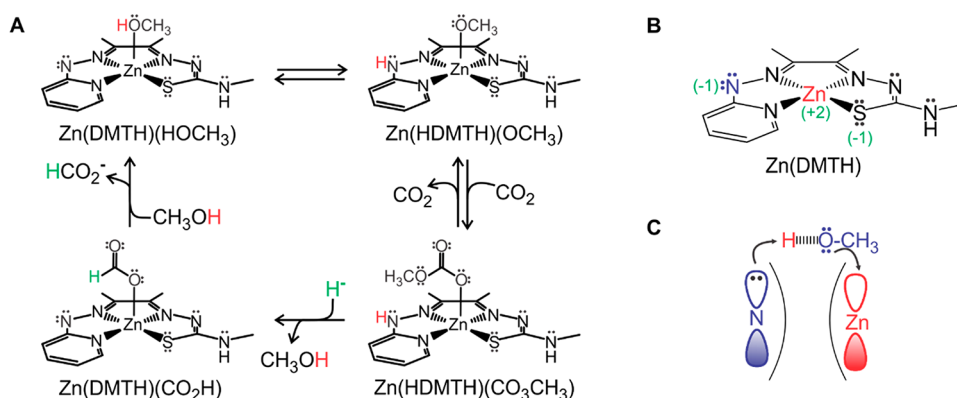


Figure 2. (A) Catalytic pathway for the reduction of CO_2 to HCO_2^- by Zn(DMTH) . The proton of the catalytic methanol is shown in red. The hydride (H^-), which can be chemical or electrochemical, is shown in green. All noncoordinating lone-pair electrons are shown. (B) Representation of Zn(DMTH) highlighting the frustrated Lewis pair-like interaction between the noncoordinating Lewis base (blue) and Lewis acid (red). Formal charges are shown in green. (C) Addition of methanol to Zn(DMTH) via metal–ligand cooperativity.

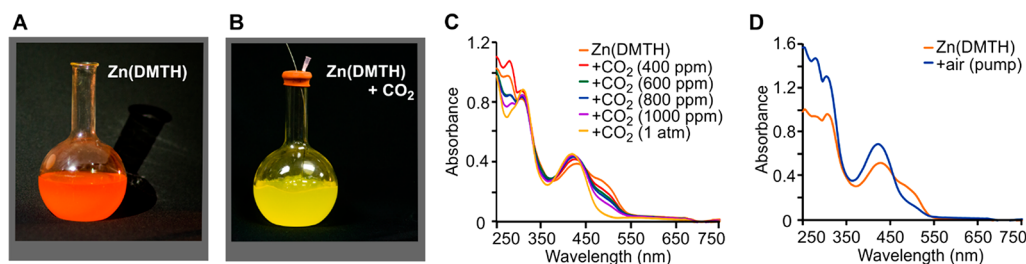


Figure 3. (A) Photograph of a 3 mM solution of Zn(DMTH) in methanol under ambient conditions. (B) Photograph of a 3 mM solution of Zn(DMTH) in methanol, while bubbling with CO_2 . (C) UV–visible spectra of a 0.1 mM solution of Zn(DMTH) in methanol under varying concentrations of CO_2 gas. (D) UV–visible spectra of a 0.1 mM solution of Zn(DMTH) in methanol before and after bubbling the solution with untreated air from the laboratory using an air pump.

Ishitani and co-workers, where X is a deprotonated triethanolamine, facilitates CO_2 binding from air without prior reduction.¹⁵ Similar complexes with Ru¹⁶ and Mn¹⁷ also sequester low levels of CO_2 , but only the Re derivative has been reported to catalytically reduce CO_2 .¹⁸ The Ishitani catalyst underscores the necessity to bind CO_2 first in order to reduce CO_2 at low concentrations. Previously, Ito reported CO_2 fixation that yielded zinc-alkylcarbonate complexes ($\text{Zn-CO}_3\text{R}$) from air with alcohol solutions of N_4 macrocycles, such as $\text{Me}_4[14]\text{aneN}_4$, containing Zn(II) and base.¹⁹ Building upon these ideas, we developed Zn(DMTH) (DMTH = diacetyl-2-(4-methyl-3-thiosemicarbazone)-3-(2-pyridinehydrazonato)) as a sustainable catalyst for the reduction of CO_2 to formate from air.

RESULTS

The reduction of CO_2 to HCO_2^- by Zn(DMTH) follows an unprecedented mechanism employing metal–ligand cooperativity (Figure 2A).²⁰ The catalyst contains a frustrated Lewis pair²¹ (FLP)-like interaction between the Zn(II) ion (Lewis acid) and a close proximity noncoordinating nitrogen of the 2-pyridinehydrazonato group (Lewis base) (Figure 2B). The metal–ligand cooperativity facilitates deprotonation of methanol (CH_3OH) to generate the active catalyst $\text{Zn(HDMTH)-(OCH}_3\text{)}$ in equilibrium with $\text{Zn(DMTH)(HOCH}_3\text{)}$ (Figure 2C). As previously reported for other metal-alkoxides,^{16,17,22} insertion of CO_2 into the Zn-OCH_3 bond yields a stable methylcarbonate intermediate $\text{Zn(HDMTH)(CO}_3\text{CH}_3\text{)}$. The methylcarbonate provides an activated form of CO_2 that is susceptible to reduction by hydride generating HCO_2^- and

CH_3OH . The hydride source can be chemically (NaBH_4) or electrochemically generated from Pt or Zn(DMTH) . The electrochemical hydride is generated in a similar method presented for the HER of Zn(DMTH) .²³ Ligand substitution of CH_3OH for HCO_2^- regenerates $\text{Zn(DMTH)(HOCH}_3\text{)}$ to complete the cycle. It should be noted an alternate route via C–O isomerization cannot be completely ruled out.²⁴

A critical feature of our system is the ability of Zn(DMTH) to bind CO_2 prior to reduction. In methanol, $\text{Zn(DMTH)-(CH}_3\text{OH)}$ yields a bright orange solution (Figure 3A) that changes to bright yellow upon bubbling with CO_2 (Figure 3B) (see the Supporting Information, Movie S1). The solution returns to the original orange color when sparged with an inert gas (N_2 or Ar) (see Supporting Information, Movie S2). The reversible CO_2 binding to $\text{Zn(DMTH)(CH}_3\text{OH)}$ can also be observed by changes in cyclic voltammetry (CV). In methanol, the CV of $\text{Zn(DMTH)(CH}_3\text{OH)}$ displays an irreversible reduction event with peak cathodic current (E_{pc}) at -1.77 V and an irreversible oxidation with peak anodic current (E_{pa}) at -0.06 V, vs Fc^+/Fc , at a scan rate of 200 mV/s. Introduction of CO_2 shifts the reduction peak anodically to -1.66 V and a prepeak develops at -1.23 V (Figure S1). Analysis of the peak currents at -1.23 V and -1.66 V as a function of catalyst concentration shows that both are first order with respect to the catalyst (Figures S3 and S4), indicating that $\text{Zn-(HDMTH)(CO}_3\text{CH}_3\text{)}$ formation occurs via CO_2 insertion into $\text{Zn(DMTH)(CH}_3\text{OH)}$ through internal proton rearrangement. Sparging with an inert gas restores the initial CV confirming that CO_2 fixation is reversible.

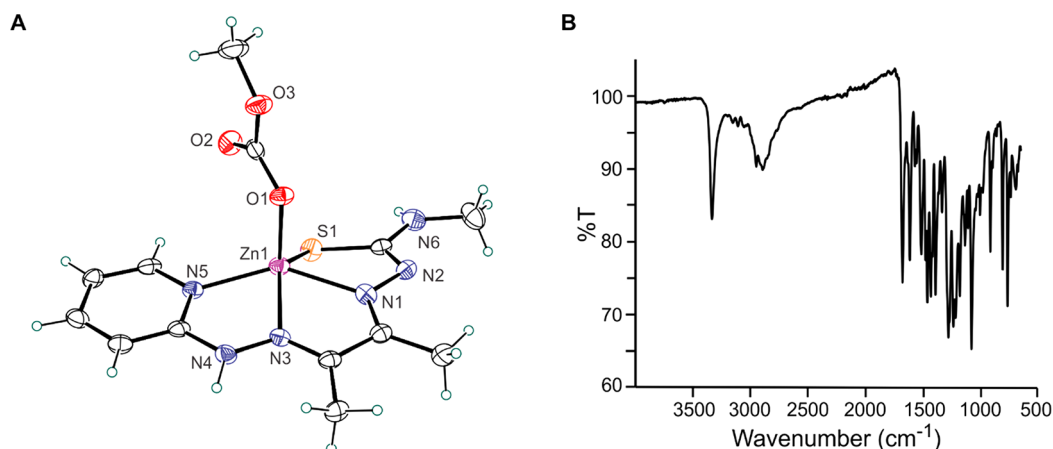


Figure 4. (A) ORTEP²⁷ representation of [Zn(HDMTH)(CO₃CH₃)]. (B) FT-IR of [Zn(HDMTH)(CO₃CH₃)] from single crystals.

To quantify the CO₂ binding affinity, UV–visible spectra were recorded using different concentrations of CO₂ (Figure 3C). In the absence of CO₂, the UV–visible spectrum of Zn(DMTH)(CH₃OH) shows a peak at 424 nm and a peak at 309 nm with a shoulder at 500 nm. Bubbling with 100% CO₂ results in a shift of the lower energy peak to 420 nm and loss of the shoulder at 500 nm. At lower CO₂ concentrations (400–1000 ppm), the intensity of the shoulder at 500 nm varies as a function of CO₂ concentration. Analysis of the data (see Supporting Information sample calculations and Table S1) to determine a CO₂ binding constant (*K*) of $(6.9 \pm 1.8) \times 10^3$, which is similar to the value of 1.7×10^3 reported for the Ishitani catalyst.¹⁵ Based on our measured value of *K*, Zn(DMTH) should be able to bind CO₂ from air (~415 ppm) in methanol. To confirm this, an air pump was used to introduce nonpurified air from the surroundings into solutions of the complex (Figure 3D). The results clearly demonstrate the ability of Zn(DMTH) to sequester CO₂ from the atmosphere without first reducing the catalysts or pretreating the air sample.

The CO₂ bound complex was identified as the methylcarbonate intermediate, Zn(HDMTH)(CO₃CH₃), by single-crystal X-ray diffraction (Figure 4A). The Zn(II) ion sits in a distorted square pyramidal arrangement with the N₃S donors of (HDMTH)-chelate in the equatorial plane and a methylcarbonate in the apical position. The hydrogen atom H4N on the 2-pyridinehydrazonato nitrogen N4 was located in the electron difference map. The metric parameters are similar to previously reported structures of [Zn(HDMTH)(OH₂)]·NO₃, [Zn(HDMTH)(OAc)] (OAc = acetate), and Zn(DMTH)(HOCH₃)^{23,25,26} (see the Supporting Information). The methylcarbonate is coordinated to Zn through the formally anionic O1 with a Zn–O1 distance of 1.991(3) Å, which is similar to the distance of 1.965(3) Å in [Zn(Me₄[14]aneN₄)(CO₃CH₃)] (ClO₄).²² The planarity of the carbonate carbon, C12, is consistent with a change in hybridization to sp² from sp in CO₂. The infrared spectrum of Zn(HDMTH)(CO₃CH₃) crystals further confirms the fixation of CO₂ as a methylcarbonate with concomitant protonation of the 2-pyridinehydrazonato nitrogen (Figure 4B). The infrared spectra of monoalkylcarbonato zinc(II) complexes display characteristic ν₁ and ν₂ stretching vibrations near 1650 and 1300 cm⁻¹, respectively, and an out-of-plane bending mode (π) at ~810 cm⁻¹.¹⁹ These bands are present in the spectrum of Zn(HDMTH)(CO₃CH₃) as an

intense band at 1681 cm⁻¹, a shoulder at 1298 cm⁻¹, and a peak at 814 cm⁻¹. The protonation of the 2-pyridinehydrazonato nitrogen is confirmed by the appearance of a broad N–H stretch at 2889 cm⁻¹, which is similar to the acetate bound species, 2937 cm⁻¹.

Next, we evaluated the reactivity of Zn(HDMTH)-(CO₃CH₃) with hydride sources to complete the reduction of CO₂ to HCO₂⁻. Previously, Ito established the nucleophilic character of zinc-methylcarbonate complexes in reactions with alkylsulfonates (FSO₃R),¹⁹ which has been further exploited for epoxide copolymerization.^{28,29} However, to our knowledge the reactivity of zinc-methylcarbonate complexes with nucleophiles has not been previously evaluated. First, the reaction of a chemical source of hydride, NaBH₄, with Zn(HDMTH)(CO₃CH₃) was examined. In a typical experiment, the Zn(HDMTH)(CO₃CH₃) complex was generated from the parent complex in methanol under constant bubbling of CO₂. An excess of NaBH₄ was added, and the reaction was stirred for 30 min. Analysis of the reaction mixture by ¹H NMR confirmed the formation of HCO₂⁻ with 170 turnovers. Since NaBH₄ is known to produce formate under CO₂ in ethanol,³⁰ control experiments in the absence of Zn(DMTH)-(CO₃CH₃) were conducted, yielding 62 turnovers for the uncatalyzed reaction. The results confirm Zn(DMTH)-(CH₃OH) is able to fix CO₂ from a gaseous stream and catalyze its reduction to HCO₂⁻ with hydride.

To test if the reduction of CO₂ to HCO₂⁻ can be achieved electrocatalytically, controlled potential coulometry (CPC) was conducted using a platinum (Pt) working electrode. Pt electrodes are known to catalyze the hydrogen evolution reaction (HER) via a Pt-hydride intermediate with no observed CO₂ reduction in the absence of a cocatalyst.^{31,32} To test if Zn(HDMTH)(CO₃CH₃) could intercept the Pt–H intermediate to generate HCO₂⁻, a solution of the cocatalyst was prepared in methanol under constant bubbling of CO₂. A potential of −2.00 V vs ferrocenium/ferrocene (Fc⁺/Fc) was applied for 24 h during which 55.8 C of charge was consumed. Analysis of the reaction mixture by ¹H NMR confirmed the presence of HCO₂⁻ with a total of 8.70 turnovers. The relatively low number of turnovers as compared to the NaBH₄ study results from the fact that catalytic turnover in electrochemical reaction only occurs in the diffusion layer, whereas the chemical reaction occurs throughout the bulk. The faradaic efficiency for CO₂ reduction based on the total charge is 30.1%. A substantial portion of the charge is associated with

hydrogen evolution at Pt, which was found to account for 38.6 C in control experiments in the absence of our cocatalyst. Of the additional 17.2 C consumed upon addition of Zn(DMTH)(CH₃OH), 97.8% is associated with HCO₂[−] production.

To determine if Zn(DMTH)(CH₃OH) is able to catalyze CO₂ reduction in the absence of external hydride sources, CV experiments using a glassy carbon working electrode were performed. Recently, we reported Zn(DMTH) as an electrocatalyst for ligand-centered HER in acetonitrile upon addition of acetic acid.²³ The CV of Zn(DMTH) in acetonitrile/methanol (9:1) at a scan rate of 200 mV/s shows an irreversible reduction ($E_{pc} = -2.12$ V vs Fc⁺/Fc) and two irreversible oxidations ($E_{pa1} = -0.27$ and $E_{pa2} = -0.13$ V) (Figure 5 black). Upon addition of CO₂, a new peak attributed

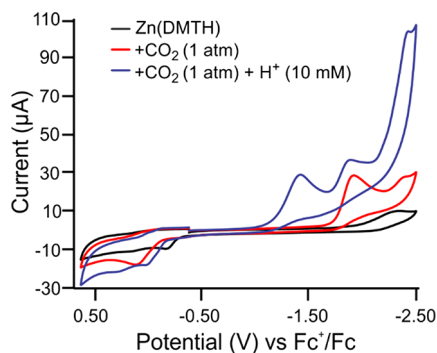


Figure 5. Cyclic voltammograms of Zn(DMTH) recorded at a scan rate of 200 mV/s in 9:1 acetonitrile/methanol solution containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte with a glassy carbon working electrode, platinum counter electrode, and a Ag/AgCl reference electrode. Potentials are scaled to an internal Fc⁺/Fc standard. Traces shown are Zn(DMTH) (black), Zn(DMTH) + 1 atm CO₂ (red), and Zn(DMTH) + 1 atm CO₂ and then +10 mM acetic acid (blue). All scans are from −0.48 V to −2.5 to 0.60 V to −0.48 V and background corrected.

to the reduction of Zn(HDMTH)(CO₃CH₃) is observed at −1.87 V with a small catalytic peak at −2.37 V (Figure 5 red). Addition of acetic acid results in a substantial increase in the current of the catalytic peak at −2.37 V and an additional reduction event at −1.40 V (Figure 5 blue). The peak at −1.40 V is attributed to the [Zn(H₂DMTH)(CO₃CH₃)]^{+/0} couple resulting from the protonation of the hydrazone nitrogen of the thiosemicarbazone group. This event is shifted by +470

mV relative to the [Zn(HDMTH)(CO₃CH₃)]^{0/−} couple at −1.87 V. It should be noted the presence of both peaks indicates an equilibrium between [Zn(HDMTH)(CO₃CH₃)] and [Zn(H₂DMTH)(CO₃CH₃)]. The catalytic peak at −2.39 V is associated with the further reduction of Zn(H₂DMTH)(CO₃CH₃), which is the proposed hydride source based on prior HER studies.^{23,33} Analysis of the catalytic peak under scan rate independent conditions with 10 mM acetic acid yields a turnover frequency (TOF) of 73.4 s^{−1} with an overpotential of 0.86 V.^{34,35} Since Zn(DMTH) is known to adhere to glassy carbon under extended catalytic conditions, data were analyzed from CV traces on fresh electrode surfaces.²³ Notably, if acetic acid is added to Zn(DMTH) prior to CO₂ fixation, only catalytic HER is observed. This is attributed to protonation of the 2-pyridylhydrazone N, which is the internal base required for CO₂ fixation. Under turnover conditions, the insertion of CO₂ into Zn(DMTH)(CH₃OH) is kinetically preferred to protonation at acetic acid concentrations of 10 mM or less. At acetic acid concentrations above 10 mM in 9:1 acetonitrile/methanol only catalytic HER is observed at −3.29 V vs Fc⁺/Fc.²³ Attempts using phenol (96.8 mM) as a weaker acid showed no catalytic wave above background catalyst and CO₂ (Figure S35).

To quantify the product of CO₂ reduction with Zn(DMTH) at a glassy carbon electrode, a series of CPC experiments were performed in the presence of acetic acid and slow bubbling of CO₂ for 24 h (Table 1) at a potential of −2.30 V vs Fc⁺/Fc. The current remained constant over the course of the experiment with no sign of catalyst degradation. In all cases, including control experiments, H₂ was observed as a product in the headspace via gas chromatography. Analysis of the reaction solution via ¹H NMR revealed the production of formate or formic acid, depending on the reaction solvent, when Zn(DMTH) was present as a catalyst. No formate or formic acid was detected in control experiments in the absence of Zn(DMTH). The highest average charge and best average faradaic efficiencies were observed with Zn(DMTH) in 9:1 acetonitrile/methanol solution saturated with a stream of CO₂ at a glassy carbon electrode. Based on total charge consumed, these solutions yielded a faradaic efficiency of 29.2% for formic acid with a total of 16 turnovers. Notably, formic acid production accounts for 95.5% of the charge in excess of the background.

The subtraction of the background activity allows evaluation of the faradaic efficiency for the homogeneous catalyst.^{36–38} In methanol solution, Zn(DMTH) at a glassy carbon electrode

Table 1. Compilation of Average Faradaic Efficiencies for the Reduction of Carbon Dioxide to Formate by Zn(DMTH) under Various CPC Conditions^a

working electrode	solvent	CO ₂ source ^b	charge consumed (C)		faradaic efficiency (%)	
			total	corrected ^c	overall	corrected ^d
Pt	MeOH	1 atm	49.7–55.8	11.1–17.2	15.6–30.1	70.3–97.8
GC	MeCN/MeOH	1 atm	102.7–101.1	29.4–31.4	27.7–29.2	93.9–95.6
GC	MeOH	1 atm	98.0–98.3	24.6–24.9	18.7–24.1	75.0–95.0
GC	MeOH	air	51.9–63.3	15.7–27.1	14.3–15.8	36.9–47.6

^aAll experiments conducted for 24 h; CPC = controlled potential coulometry, Pt = platinum electrode, GC = glassy carbon electrode, MeOH = methanol, MeCN = acetonitrile (MeCN). ^b1 atm CO₂ was obtained from a CO₂ cylinder (99.9%), gas was passed through a drying tube prior to introduction to the cell; CO₂ from air was obtained by using an air pump to introduce laboratory air into the solution with no pre-purification. ^cThe corrected charge is the total charge obtained in the presence of substrate and Zn(DMTH) minus the charge obtained under identical substrate conditions without Zn(DMTH). ^dThe overall faradaic efficiency is calculated based on the quantity of formate produced relative to the total charge consumed; the corrected faradaic efficiency is calculated using the corrected charge.

provided a total of 12 turnovers with a faradaic efficiency of 24.1% based on total charge under a stream of CO₂. Variation of the acid concentration shows optimal HCO₂[−] production between 8.3 and 10 mM acetic acid (Figure S34). At lower acid concentrations, significantly less HCO₂[−] is detected, while higher concentrations favor HER. To confirm that HCO₂[−] is derived from CO₂, isotopic labeling studies with ¹³CO₂ were conducted. The resulting experiment showed a doublet centered at 8.44 ppm (*J* = 139 Hz) for H¹³CO₂[−] and a singlet at 8.44 ppm for H¹²CO₂[−] (Figure S36).³⁹ The singlet intensity for H¹²CO₂[−] is attributed to CO₂ generated by oxidation of solvent at the anode. Remarkably, when the reaction was repeated using air pumped into solution from the surroundings in place of a CO₂ stream, reduction to HCO₂[−] was observed with a total of 4 turnovers. The optimal faradaic efficiency is 15.8% based on total charge consumed and 47.6% for background corrected charge. To our knowledge, this is the first reported electrocatalytic reduction of CO₂ to HCO₂[−] from air.

CONCLUSION

In conclusion, Zn(DMTH) catalyzes the sequestration, activation, and reduction of CO₂ to HCO₂[−] on its own or in tandem with a hydride source. While Zn(DMTH) can generate HCO₂[−] at GC, it also serves as a cocatalyst at Pt where HCO₂[−] is achieved at a lower overpotential. Notably, Zn(DMTH) maintains its activity at low pressure in the presence of oxygen and water allowing for direct capture and reduction of CO₂ from air. The unprecedented activity of Zn(DMTH) results from the inclusion of a FLP-like interaction for CO₂ fixation in a redox-active ligand framework that facilitates CO₂ reduction at a nonredox active Zn(II). Further, Zn(DMTH) is a stable catalyst that incorporates a sustainable earth-abundant metal in an oxygen- and water-tolerant complex that can be synthesized from inexpensive chemical reagents. Our ligand-centric approach that combines features to fix and reduce CO₂ at a single redox nonactive metal site is different from all other CO₂ reduction catalysts and provides a new strategy to mitigate global CO₂ levels.

EXPERIMENTAL SECTION

Materials and Methods. All reagents were obtained from commercially available sources and used as received unless otherwise noted. Solvents were dried and purified using an MBraun solvent purification system, except methanol which was dried using magnesium and iodide and then stored over molecular sieves. The complexes in this study are air and water stable as solids and were handled on the benchtop with no required protection from the atmosphere unless noted. Zn(DMTH) was synthesized and characterized by previously reported methods,²⁵ with slight modifications. The solid was collected as the dihydrate and placed under vacuum to dry. The container of Zn(DMTH) was subjected to flame drying prior to storage and use. It is important to note the solid is red in color after flame drying, while its initial color is orange.

All experiments with pure CO₂ were conducted by passing CO₂ through a drying column filled with CaSO₄. For experiments using air as the CO₂ source, a Unicliffe air pump UL40 purchased from Amazon was used. The pump has two ports, one of which was sealed with parafilm. The other port was connected to a piece of tygon tubing first sealed with parafilm and then fitted with a nozzle containing a needle that was inserted into the septum on the reaction vessel. The pump was operated at its highest setting for all experiments.

Physical Methods. All ¹H NMR spectra were obtained using DMSO-*d*₆ as a solvent on a 500 MHz Bruker NMR spectrometer. Infrared spectra were recorded on a freshly prepared crystalline

sample using a Nicolet 360 FT-IR with a smart iTR attachment. UV–vis spectra were obtained for 0.1 mM solutions of Zn(DMTH) in dry methanol using a Variant Cary 50 Bio instrument with fast scan capabilities. To determine the equilibrium binding constant, various concentrations of CO₂ were bubbled through the solutions for 30 min prior to recording the spectra. Acid titration studies were conducted using 0.1 M acetic acid in methanol.

Electrochemical Methods. All cyclic voltammetry (CV) and controlled potential coulometry (CPC) measurements were recorded using a Gamry Interface potentiostat/galvanostat connected to a glassy carbon working electrode (3.0 mm diameter, surface area = 0.071 cm²), a platinum auxiliary electrode, and a Ag/AgCl reference electrode. Before use, the working electrode was polished using an aqueous alumina slurry. The working and counter electrodes were rinsed with ethanol, acetone, DI water, and finally methanol or methanol/acetonitrile, followed by sonication for 15 min in methanol or methanol/acetonitrile. CV experiments were conducted using a five-neck electrochemical cell. Separate necks were used for the three electrodes. The remaining necks were used to maintain a constant Ar or CO₂ atmosphere during data acquisition and to introduce solids, acids, and adjust solvent levels. Solutions were purged with Ar gas to remove oxygen and prior to recording initial voltammograms of the complex. CO₂ was then bubbled through the solutions for 15 min prior to recording voltammograms for each experiment. All data presented are background subtracted. CPC measurements were conducted to determine faradaic efficiencies and were performed using a U-shaped tube containing a frit to separate the two compartments. The working compartment contained a glassy carbon or platinum electrode and an Ag/AgCl reference electrode. The counter electrode compartment was fitted with a platinum wire. All CV and CPC measurements were performed using solutions containing 0.1 M Bu₄NPF₆ in methanol or 9:1 acetonitrile/methanol and 1 mM Zn(DMTH). Ferrocene was used as an internal standard and added at the end of each experiment. For concentration-dependent studies, a fresh solution for each concentration of complex was used. Prior to each CPC study a cyclic voltammogram of the complex was recorded. Potentials were then chosen from the potential of the catalytic peak. Following CPC studies, 100 μL of the reaction solution was transferred to an NMR tube containing 10 μL of DMF (standard solution which is calibrated to 30 mM) as an internal standard and 600 μL of DMSO-*d*₆. NMR spectra were recorded at a minimum of 128 scans with a 2 s relaxation delay. It should be explicitly noted that CO₂ or air was always added prior to the addition of acid in catalytic studies.

All calculations of overpotential and turnover frequency were done in the manner described by Haddad et al.³⁴ and Fourmond et al.³⁵ The faradaic efficiency for formation of formate was confirmed by ¹H NMR, and the millimole quantity generated was determined based on integration against a 30 mM DMF standard. The total number of coulombs passed during CPE was corrected by subtracting the coulombs associated with a blank solution and was used to determine the theoretical amount of formate that should be produced (in mM). The following formula was used to determine the faradaic efficiency.

$$\text{faradaic efficiency} = \frac{\text{actual moles of HCO}_2^-}{\text{theoretical moles of HCO}_2^-} \times 100\%$$

For isotopic labeling studies, a 5 L tank of ¹³CO₂ was purchased from Cambridge Isotopes. This tank was connected with Swagelok fittings and a regulator to the airtight electrochemical cell containing 0.1 M NBu₄PF₆ and 1.0 mM Zn(DMTH) in methanol. This cell contained a working glassy carbon and a Ag/AgCl reference. The flow rate was adjusted to 10.0 cc/min, and the cell was purged with the ¹³CO₂ for 15 min. Then, 8.3 mM acetic acid was added to the solution and it was stirred. The counter compartment containing 0.1 M NBu₄PF₆ in methanol and a platinum mesh electrode was placed as close to the working cell as possible. The solution was held at −2.30 V vs Fc/Fc⁺ for 2 h using a Biologic SP200. A 500 μL aliquot of this solution was removed and added to 100 μL of DMSO-*d*₆, and a ¹H NMR spectrum was recorded.

Crystallographic Studies. An h-tube was flame-dried prior to addition of 0.004 g (0.012 mmol) of Zn(DMTH), and the tube was sealed with a septum and then wired with copper. Ten milliliters of a 50:50 mixture of dried methanol and acetone was added to the tube to dissolve Zn(DMTH). Great care was taken to ensure that the solution stayed in the vertical portion of the h-tube, and solvent levels did not go larger than the shoulder of the h. CO₂ was passed through a drying tube prior to bubbling in the Zn(DMTH) solution for 15 min. Further, the headspace of the tube was filled with pure CO₂, which was the portion after the shoulder of the h-tube was submerged in an ice bath (Figure S33). This ice bath was changed every 24 h, and yellow X-ray quality crystals of Zn(HDMTH)(CO₃CH₃) were obtained after 5 days.

Reaction of Zn(DMTH) with CO₂ and NaBH₄ in MeOH. Zn(DMTH) (0.0066g, 2.0 mM) was added to a 50 mL round-bottom flask. This flask was then flame-dried and filled with 10 mL of dry methanol. The methanol solution was stirred for 5 min to make sure all of the Zn complex had dissolved. Then, the solution was bubbled with dry CO₂ for 15 min to ensure saturation. In a second flame-dried flask, 0.3783 g (10.00 mmol) of NaBH₄ was dissolved in 2 mL of MeOH. The solution was transferred to the flask containing the Zn complex using a syringe, and the mixture was stirred for 30 min under a stream of CO₂. A control was conducted in the absence of Zn(DMTH).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00121>.

Sample calculations, electrochemical data, crystallographic details, and FT-IR and NMR results (PDF)

Movie S1: CO₂ binding and release (MP4)

Movie S2: CO₂ binding and release (MP4)

Accession Codes

CCDC 1941623 contains 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.

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Notes

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