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## Activation of Co(I) State in a Cobalt-Dithiolato Catalyst for Selective and Efficient CO<sub>2</sub> Reduction to CO

Subal Dey,<sup>†</sup> Md Estak Ahmed,<sup>†</sup> and Abhishek Dey\*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700032, India

## **Supporting Information**



**ABSTRACT:** Reduction of  $CO_2$  holds the key to solving two major challenges taunting the society—clean energy and clean environment. There is an urgent need for the development of efficient non-noble metal-based catalysts that can reduce  $CO_2$ selectively and efficiently. Unfortunately, activation and reduction of  $CO_2$  can only be achieved by highly reduced metal centers jeopardizing the energy efficiency of the process. A carbon monoxide dehydrogenase inspired Co complex bearing a dithiolato ligand can reduce  $CO_2$ , in wet acetonitrile, to CO with ~95% selectivity over a wide potential range and 1559 s<sup>-1</sup> rate with a remarkably low overpotential of 70 mV. Unlike most of the transition-metal-based systems that require reduction of the metal to its formal zerovalent state for  $CO_2$  reduction, this catalyst can reduce  $CO_2$  in its formal +1 state making it substantially more energy efficient than any system known to show similar reactivity. While covalent donation from one thiolate increases electron density at the Co(I) center enabling it to activate  $CO_2$ , protonation of the bound thiolate, in the presence of  $H_2O$  as a proton source, plays a crucial role in lowering overpotential (thermodynamics) and ensuring facile proton transfer to the bound  $CO_2$ ensuring facile (kinetics) reactivity. A very covalent Co(III)-C bond in a Co(III)-COOH intermediate is at the heart of selective protonation of the oxygen atoms to result in CO as the exclusive product of the reduction.

## **INTRODUCTION**

An ongoing, exhaustive, and urgent search for clean and sustainable energy sources has progressively shifted the focus of the scientific community toward the development of efficient ways for the mitigation of  $CO_2$ , the "greenhouse gas", to useful chemicals.<sup>1-3</sup>  $CO_2$  can be reduced electrochemically through two-, four-, six-, and eight-electron reduction pathways in gaseous and solution phases to useful gaseous as well as liquid fuels like carbon monoxide (CO), formic acid or formate (in basic solution), oxalic acid or oxalate (in basic solution), ethane, methane, ethanol, and methanol.<sup>4-6</sup> In nature  $CO_2$  is reduced by  $8e^-$  and  $8H^+$  to methane (CH<sub>4</sub>), through a process called methanogenesis, which can, in principle, be used as a fuel to derive energy from.<sup>7</sup>  $CO_2$  can also be reduced to CO, and further reduction, by hydrogenation, can produce liquid fuels by Fischer–Tropsch synthesis.<sup>8</sup>

Homogeneous transition-metal-based catalysts have been utilized since 1970s for  $CO_2$  reduction.<sup>9–11</sup> Cobalt or nickel phthalocyanines were shown to have electrocatalytic  $CO_2$  reduction properties. Later on sulfonated cobalt or nickel

phthalocyanines<sup>10</sup> or porphyrins<sup>11</sup> were studied for the same purpose with limited chemical analysis of the reduction product. Fischer and Eisenberg used Co and Ni complexes of various tetra-azamacrocycle as an electrocatalyst and got CO as the major product along with H<sub>2</sub> as a minor product.<sup>12</sup> Molecular systems utilizing rare-earth metals for  $CO_2$  reduction were utilized as well.<sup>13–15</sup> Recent years have seen a rapid growth in reports of CO<sub>2</sub> reduction by transition-metal complexes.<sup>4,16–19</sup> Among these the first-row transition metals (e.g., Mn, Fe, Co, Ni) have been in the focus recently. Most of the first-row transition-metal catalysts reported in the literature can activate  $CO_2$  only in their formal "0" or "(-) ve" oxidation states  $(M^{0/n-})$ . Initial reports demonstrated that Ni(cyclam) can reduce CO<sub>2</sub> to CO in aqueous solution on Hg cathode as a working electrode with high selectivity.<sup>20,21</sup> The two-electron reduced Ni(cyclam) is the active species for the catalysis, with 0 (M<sup>0</sup>) formal oxidation state of the nickel center. It was

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Figure 1. Active site structure of CODH (left). Schematic presentation of the 2,6-dithiolatomethylpyridine-dppe cobalt(II) complex (1) (middle) and its X-ray crystallographically determined structure (right).

Scheme 1<sup>a</sup>



a'(top) Synthetic procedure for 2,6-dithiolatomethylpyridinium hydrochloride (L1). (below) Synthetic procedure for 2,6-dithiolatomethylpyridinedppe cobalt(II) complex (1).

determined that in the case of Ni(cyclam), CO release from  $[Ni(cyclam)(CO)]^+$  is the rate-determining step.<sup>21</sup> Later, another Ni(macrocycle) was used during the electrocatalysis as a CO scavenger to increase the catalytic current.<sup>21</sup> Manganese bipyridyl tricarbonyl complexes could also reduce CO<sub>2</sub> to CO in the presence of Lewis acid in organic medium, and these complexes are generally active in their formal -1(M<sup>-I</sup>) oxidation state in monomeric form.<sup>22,23</sup> Metalloporphyrins (Fe, Co) can reduce CO<sub>2</sub> in organic and aqueous medium to useful chemicals in the presence of phenol as a proton source.<sup>24-27</sup> Recently an iron porphyrin complex with four quaternary alkyl ammonium moiety have been reported to achieve  $1 \times 10^6 \text{ s}^{-1}$  turnover frequency (TOF) at 220 mV overpotential when a mildly acidic phenol is used as proton donors, and this complex likely represents the most active homogeneous CO2 reduction electrocatalyst.<sup>28</sup> However, all of these porphyrinato complexes reduced CO2 at formal 0 oxidation state.

The key challenges involved in  $CO_2$  reduction are (a) the binding of  $CO_2$  to a metal center via the C atom instead of the more Lewis acidic O atom and (b) weakening (activating) the strong C–O bonds by backbonding into the C–O  $\pi^*$ orbitals.<sup>29</sup> Reduced transition-metal centers are known to bind  $CO_2$  through the carbon atom, where the high-energy filled d-orbitals of the metal activate  $CO_2$  by back bonding as well. However, the high electron density needed to do so requires the metal to be reduced to low formal oxidation states

(generally 0 or lower), which requires substantially more energy to reduce CO<sub>2</sub> than what is thermodynamically required.<sup>30</sup> Thus, the  $CO_2 + 2H^+ + 2e^- = CO + H_2O$  process with an  $E^0_{CO2/CO} = -0.52$  V versus normal hydrogen electrode (NHE) can only be achieved at potentials lower than -1.0 to -1.5 V. This additional energy in an electrocatalytic system is referred to as the overpotential. Large overpotentials are detrimental to the efficiency of the catalytic process and have deterred development of good CO<sub>2</sub> reduction catalysts. Alternatively, the large electron density on the reduced metal center, necessary for CO<sub>2</sub> binding and activation, also makes it susceptible to protonation by H<sup>+</sup>, which is also needed for the reduction of  $CO_2$ , resulting in H<sub>2</sub> formation.<sup>31,32</sup> Protonation of a reduced metal center produces a metal-hydride species that tends to reduce  $CO_2$  to HCOOH, another  $2e^-/2H^+$  reduction product of  $CO_2$ .<sup>33–36</sup> Thus, control over the competitive metal hydride formation pathway, which will lead to H<sub>2</sub> or HCOOH, becomes a necessary, albeit daunting, task and has presented itself as a formidable challenge in the area. Spectroscopic investigations established the presence of at least two intermediates in the reaction of iron(0) porphyrins with CO<sub>2</sub>,<sup>37</sup> namely, an Fe<sup>II</sup>–CO<sub>2</sub><sup>2–</sup> species, stabilized by hydrogen bonding, followed by an Fe<sup>II</sup>-COOH species. While the proton transfer to the Fe<sup>II</sup>-CO<sub>2</sub><sup>2-</sup> species can be achieved by methanol, heterolytic C-O bond cleavage of the Fe<sup>II</sup>-COOH species can only be achieved by a relatively stronger proton donor like PhOH or organic acids, and weak proton source



Figure 2. (a) Overlay of the CV at different conditions (0.5 mM of 1 in CH<sub>3</sub>CN, scan rate: 0.2 V/s, GC working electrode, 0.1 M nBu<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte). The black one is in dry acetonitrile; purple one is in the presence of 0.11 M H<sub>2</sub>O in acetonitrile; green one is in the presence of CO<sub>2</sub> in dry acetonitrile; and the blue one is in the presence of both 0.11 M H<sub>2</sub>O and CO<sub>2</sub>. (b) CVs of Co(II/I) redox process of complex 1 at different scan rate (2 mM in dry CH<sub>3</sub>CN). (inset)  $i_p$  versus square root of scan rate plot. (c) Linear sweep voltammetry of 0.5 mM solution of 1 in CO<sub>2</sub>-saturated CH<sub>3</sub>CN with increasing concentration of H<sub>2</sub>O (scan rate: 0.2 V/s, GC working electrode). (d) Overlay of the CVs at different concentration of CO<sub>2</sub> in wet acetonitrile (scan rate: 0.2 V/s, GC working electrode. (inset) Catalytic peak current vs square root of % of CO<sub>2</sub> plot.

leads to HCOOH.<sup>37</sup> Unfortunately, use of very strong acid protonates the Fe(0) center and catalyzes competitive hydrogen evolution.<sup>38</sup> A few factors have thus been deemed to be important in determining the selectivity of CO<sub>2</sub> reduction, for example, back-donation capacity and hydricity of the metal centers,  $pK_a$  of the acid source, and the site of protonation of a M-COOH intermediate.<sup>33,38,39</sup> Choice of metal to tune the selectivity is as essential as ligand framework.

In nature, CO<sub>2</sub> to CO reduction is catalyzed by the thiolateligated Ni center in the active site (Figure 1, left) of carbon monoxide dehydrogenase (CODH).<sup>7,40</sup> CODH works near the thermodynamic potential (-0.52 V vs standard hydrogen electrode (SHE)) of CO<sub>2</sub> reduction.<sup>40–42</sup> The nickel center of the C-cluster binds CO<sub>2</sub> at Ni(0) state, and the adjacent iron weakens the C-O bond to facilitate C-O bond cleavage.<sup>40,43</sup> Thus far, no first-row transition-metal thiolate catalyst has been shown to activate CO<sub>2</sub> in its formal +1 oxidation state and/or utilize a bound thiolate ligand acting as a proton source in CO<sub>2</sub> reduction. A nickel complex containing a NiS<sub>4</sub> motif, mimicking the molybdopterin, has been recently reported, which can reduce CO2 to formate with minor amounts of carbon monoxide and hydrogen with an overpotential of 340 mV in acetonitrile.44 The paramount importance of thiolate protonation in reactivity and redox potential is well-established in several natural enzymes like hydrogenases and ferredoxins. 45-47 In this present report a bioinspired 2,6-dithiomethylpyridino cobalt(dppe) (dppe = bis(diphenylphosphinoethane)) complex (1) was synthesized, and this complex is capable of efficient

reduction of CO<sub>2</sub> to CO under mildly acidic conditions. In the absence of  $H_2O$  the complex does not show any catalytic activity in CO<sub>2</sub>-saturated acetonitrile solution. But when  $H_2O$  is added, a large catalytic current is observed, which suggests the catalytic CO<sub>2</sub> reduction in the presence of a Lewis acid. A substantial amount of potential advantages is observed due to activation of Co(I) state, which could be quite impressive to further catalyst design.

#### RESULTS AND ANALYSIS

Synthesis and Characterization. The synthetic scheme of the ligand and the complex is given in Scheme 1. The ligand 2,6-dithiolmethylpyridinium hydrochloride (L1) is synthesized separately from 2,6-dihydroxymethylpyridine by previously reported procedures (Scheme 1, top).48 L1 is deprotonated with sodium methoxide in tetrahydrofuran (THF) and then is added to a suspension of Co(dppe)Cl<sub>2</sub> in THF to immediately result in a reddish-brown homogeneous solution. After 4 h of stirring, filtration and removal of the solvent yields the complex 1. The purity of the complex is checked by elemental analysis, and the <sup>1</sup>H NMR shows that it is a paramagnetic species as may be expected for a Co(II) compound in solution (Figure S1). The X-ray quality single crystals were grown from slow diffusion of THF and hexane. The single-crystal X-ray diffraction (XRD) data show that the complex 1 crystallized in Co(II) form in a slightly distorted square pyramidal geometry with an open coordination site. The Co-S  $(2.229^{\circ})$  and Co–N  $(1.967^{\circ})$  bond distances are in good



Figure 3. (left) FOW plot of complex 1 to determine the second-order rate at the kinetic region. (right) Catalytic Tafel plot using the  $TOF_{max}$  value obtained from scan-rate-dependent CVs under optimized catalytic conditions. The red stars designate the TOF determined from BE.

agreement with other high-spin cobalt(II) thiolate complexes known in the literature (Table S1).<sup>49</sup>

Electrochemical Investigations and Product Analysis. The cyclic voltammogram (CV) of 1 using glassy carbon (GC) electrode shows two quasi-reversible redox processes at -1.65 V ( $\Delta E_p = 240 \text{ mV}$ ) and -2.12 V ( $\Delta E_p = 270 \text{ mV}$ ) versus Fc<sup>+/0</sup>, which corresponds to Co(II/I) and Co(I/0) redox processes in acetonitrile (0.1 M nBu<sub>4</sub>NClO<sub>4</sub> supporting electrolyte; Figure 2a, black). The CV corresponding to Co(II/I) process was recorded at higher concentration (2 mM) of 1 to obtain data at different scan rates (Figure 2b), and the current versus square root of scan rate shows a linear relationship (Figure 2b, inset) as expected, and the diffusion coefficient is determined to be  $1.2 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> using Randles-Sevcik eq (Figure S2). Addition of CO<sub>2</sub> and H<sub>2</sub>O (0.11 M) separately in the electrolytic solution shows a very little change on Co(I/0) process but no effect on the Co(II/I) process (Figure 2a, purple & green). However, when the CV of 1 is recorded in a CO<sub>2</sub>-saturated acetonitrile solution in the presence of 0.11 M  $H_2O$ , the redox event at -1.65 V shifts to -1.27 V versus  $Fc^{+/0}$ (Figure 2b blue). The 380 mV positive shift in the first cathodic process in the presence of CO<sub>2</sub> and H<sub>2</sub>O is likely due to protonation of the Co(I) bound electron-rich thiolate ligand due to the formation of H2CO3 in CO2-saturated wet acetonitrile (Figure 2a, blue).<sup>50</sup> Similar positive shift in Co(II/I) potential due to thiolate protonation has been reported for cobalt-dithiolene complexes by Eisenberg et al. and later supported by theoretical calculations.<sup>51-53</sup> Upon addition of more water into the CO2-saturated electrolytic solution, a steady increase in the electrocatalytic current  $(I_{cat})$  is observed with an onset of -1.17 V (where  $I_{cat}/I_p > 1$ ), which saturates at -1.46 V (half peak potential,  $E_{cat}^{1/2} = -1.29$  V) with current density  $\sim 1.1 \text{ mA/cm}^2$  (Figure 2c). This current is attributed to the electrocatalytic  $CO_2$  reduction by the Co(I)state of the complex. The catalytic current shows linear correlation with the concentration of water (Figure 2c) as well as with the concentration of  $CO_2$  (Figure 2d, inset). The same current is observed when bicarbonate and equivalent amount of trifluoroacetic acid is used as the source of  $CO_2$  (Figure S3). These results suggest that complex 1 activates  $CO_2$  in Co(I)state and reduces it. The process at -1.46 V saturates at 2.1 M H<sub>2</sub>O concentration, and further H<sub>2</sub>O addition only enhances a catalytic current at -2.2 V representing electrochemical CO2 reduction by complex 1 in its Co(0) state, which reaches up to a current density of greater than 10  $mA/cm^2$  at 3.6 M  $H_2O$ (Figure S4). Thus, the complex 1 can reduce  $CO_2$  in both its Co(I) and Co(0) states.

Headspace gas analysis was performed by gas chromatography (GC) fitted with thermal conductivity detector (TCD) in a sealed electrochemical cell containing CO2-saturated 0.5 mM solution of 1 on Hg-pool electrode with surface area of 27  $\text{cm}^2$ . The chromatograms obtained from GC after electrolyzing the solution at -1.6 V (Figure S5) and -2.2 V (Figure S6) versus  $Fc^{+/0}$  suggest that the complex 1 reduces  $CO_2$  to CO at both potentials. Trace amounts of  $H_2$  (3–5%) were also observed in both cases. To further characterize the electrocatalytic process, bulk electrolysis is performed over a range of potential from -1.2 to -1.6 V versus Fc<sup>+/0</sup> for the same duration of time (Figure S7, left), and the data suggest that the complex 1 reduces CO<sub>2</sub> to CO (Figure S7, right) with a faradaic yield of  $95 \pm 2\%$  (Table S2) at all potentials, and the data indicate that CO<sub>2</sub> to CO reduction rate (volume of CO produced) increases on lowering the applied potential (Figure S7, right). No  $H_2$  was detected at lower overpotentials, and only at higher overpotential could minor amounts of H<sub>2</sub> be detected (Figure S7, right). Similarly, no HCOOH was detected in Fourier transform infrared (FTIR) measurements performed with the electrolytic solution after bulk electrolysis experiments (Figure S8). Thus, the results confirm that the  $CO_2$  is reduced to CO predominantly by complex 1 in both Co(I) and Co(0) states. Since the electrocatalysis of the Co(I) state has much lower overpotential, the rest of the investigation is focused on that. The shift of the Co(II/I) potential at low  $H_2CO_3$  concentration and reduction of  $\mathrm{CO}_2$  at higher concentration is attributed to thiolate-assisted protonation first CO<sub>2</sub> reduction mechanism as reported for polymethoxy-bipyridyl manganese tricarbonyl complex by Carter et al.<sup>31,32,54</sup> Control potential electrolysis of a solution of complex 1, CO<sub>2</sub>, and H<sub>2</sub>O in CH<sub>3</sub>CN using both Hg-pool (Figure S9) and GC electrode (Figure S10) indicates that the complex is stable through the duration of the electrolysis experiment. Slight decay of current is observed in the case of Hg-pool electrode, which suggests decay of the catalyst likely due to the higher affinity of the thiol groups present in the ligand for Hg. Rinse test experiment performed after 30 min of electrolysis in a CO<sub>2</sub>-saturated wet acetonitrile solution without the catalyst showed no catalytic wave indicating that the catalyst does not get absorbed on the GC electrode (Figure S11).

**Kinetic and Thermodynamic Parameters.** The catalytic parameters for CO<sub>2</sub> reduction for the first cathodic process is determined at -1.46 V, where the faradic current has an S shape. The pseudo-first-order rate of the catalysis (TOF<sub>max</sub>) is determined by the equation  $I_{cat}/I_p = 4.484 \times (RT/F)^{1/2}(TOF_{max})^{1/2} \nu^{-1/2}$ .<sup>33</sup> The TOF<sub>max</sub> for CO<sub>2</sub> reduction to CO is determined from the scan rate dependence and found to be  $1559 \pm 8 \text{ s}^{-1}$  (Figure S12). The second-order rate of the same process is also determined by foot-of-the-wave (FOW) analysis (Figure 3, left) to be  $2.53 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (Figure



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Figure 4. (left) Linear sweep voltammetry of 0.5 mM solution of 1 in  $CO_2$ -saturated  $CH_3CN$  with increasing concentration of  $D_2O$ . (right) Concentration of Bronsted acid vs catalytic current plot for the first catalytic process.

S13).<sup>19,27</sup> The rate of this complex, which utilizes water as a source of proton, thus compares quite favorably to those reported for the best iron porphyrin complex using water as a source of proton.<sup>38</sup> The stability of the complex is checked before and the after electrolysis by UV–vis spectroscopy (Figure S14). On a glassy carbon working electrode no decay is observed after 1 h of bulk electrolysis (BE), and a turnover number (TON)  $\gg 1 \times 10^6$  is estimated. After 2 h of electrolysis with Hg-pool electrode ~27% of the complex decays (likely due to high affinity of Hg for thiols) yielding a TON of only 300 (detailed calculation in Supporting Information).

The determination of the overpotential for the electrocatalytic CO<sub>2</sub> reduction in the presence of water in organic solvents (e.g., acetonitrile) is nontrivial.<sup>55</sup> Addition of  $H_2O$  in  $CO_2$ -saturated acetonitrile generates  $H_2CO_3$  (p $K_a = 17.03$  in  $CH_3CN$ ), which plays the role of proton donor <sup>27,33</sup> Hence,  $E^{0}_{CO2/CO}$  can be determined by the equation  $E^{0} = -0.12$  –  $0.059 \times pK_a$  as developed by Appel & Mayer, to be ca. -1.12 V versus  $\text{Fc}^{+/0.56}$  Thus, according to the Appel and Mayer estimates, complex 1 is able to generate CO at very high rates with as low as 340 mV overpotential (peak maximum at -1.46vs  $Fc^{+/0}$ ). Note that the thermodynamic potential of  $CO_2$  to CO conversion can also been determined by Savéant et al. by considering the thermodynamic cycle for the conversion of CO2 into CO in a solvent S and in the presence of an acid HA. With this approach, the standard thermodynamic potential determined in CH<sub>3</sub>CN solvent in the presence of H<sub>2</sub>O is  $E^{0}_{CO2/CO,CH3CN} = -0.650 \text{ V}$  versus NHE<sup>27</sup> or -1.41 V versus Fc<sup>+/0</sup> ( $E_{Ag/AgCl} = 0.210 \text{ V}$  vs NHE and  $E_{CH3CN}$  (Fc<sup>+/0</sup>) = 0.550 V vs Ag/AgCl).<sup>57</sup> According to this complex 1 can reduce CO<sub>2</sub> to CO at only 50 mV overpotential. In any case, we can conclude that complex 1 can produce CO from CO<sub>2</sub> with very low overpotential.

**Mechanistic Analysis.** The linear correlation of the electrocatalytic CO<sub>2</sub> reduction current with H<sub>2</sub>O concentration (Figure 4, right) implies that H<sub>2</sub>O (or H<sub>2</sub>CO<sub>3</sub>) is involved in the transition state of the rate-determining step (rds). The catalyst concentration (Figure S15) and CO<sub>2</sub> concentration-dependent catalysis (Figure 2d) suggest that the catalysis is first-order with respect to both. To obtain further insight, CO<sub>2</sub> reduction is performed under varying concentration of D<sub>2</sub>O. As may be expected, the CO<sub>2</sub> reduction current increases linearly with increasing D<sub>2</sub>O concentration (Figure 4, left). The slope of the line is proportional to the rate constant (kinetic isotope effect (KIE) =  $k_{CO2, H}/k_{CO2, D}$  = (slope<sub>H2O</sub>/slope<sub>D2O</sub>)<sup>2</sup>) and is much lower in D<sub>2</sub>O than in H<sub>2</sub>O (Figure 4, right) implying that there is a H/D isotope effect on the rate. The  $k_H/k_D$  ratio is

estimated from the relative slopes to be 5.41  $\pm$  0.4 (Figure S16). Thus, the rds of CO<sub>2</sub> reduction catalyzed by 1 involves protonation.

The CV and UV-vis absorption data of 1 in the presence of  $\mathrm{CO}_2$  or  $\mathrm{H}_2\mathrm{O}$  do not show any change implying that  $\mathrm{CO}_2$  and  $H_2O$  by themselves do not interact with either Co(II) or Co(I)state of 1 (Figure 1a, purple & green lines, and Figure S17). Yet, when both CO<sub>2</sub> and H<sub>2</sub>O are present in solution, the Co(II/I) CV shifts by more than 300 mV. This implies that 1 gets protonated in the presence of  $H_2O$  and  $CO_2$  in its Co(I)state. Since H<sub>2</sub>O and CO<sub>2</sub> forms H<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN, and the lone pairs on the bound thiolates are available in 1, it is likely that the H<sub>2</sub>CO<sub>3</sub> formed protonates the thiolates. Similar shift in the Co(II/I) process is observed in the presence of trifluoroacetic acid (TFA) in case of electrocatalytic proton reduction (Figure S18). Of course, in the presence of TFA, there is no CO<sub>2</sub> reduction, and H<sub>2</sub> evolution is observed instead. The results suggest that the CO<sub>2</sub> does not bind Co(I) on its own; it binds only when the thiolate(s) is(are) protonated.

Theoretical Structure-Function Correlation to Reactivity. Geometrically optimized density functional theory (DFT) calculations are used to model the CO<sub>2</sub> binding to Co(I) state of 1. The optimized geometry of 1 agrees quite well with the crystal structure (Table S1). The calculations indicate that  $CO_2$  binding to a Co(I) state leads to dissociation of the phosphine arm (Figure 5a, Co···P =  $3.3^{\circ}$ ) trans to CO<sub>2</sub>. On the contrary when one of the thiolates is protonated a stable minimum is observed, where the  $CO_2$  is bound to the Co(I)center (Figure 5b). The proton is localized on one of the oxygen atoms of the bound CO<sub>2</sub> in this structure. The optimized Co–C and C–O bond lengths are  $1.98^{\circ}$  and  $2.30^{\circ}$ , and the O–C–O angle of 118° shows substantial bending from  $180^{\circ}$  in CO<sub>2</sub> and is close to that of free formate suggesting electron transfer to the bound CO<sub>2</sub> from the Co(I) center resulting in a Co(III)-COOH electronic structure. Note that there is a strong H-bonding between the bound -COOH and the thiolate sulfur (S···O =  $2.96^{\circ}$ ). There are two bonding interactions between the Co and the bound  $CO_2$ ; a  $\sigma$ -bonding between an empty Co  $d_{z^2}$  and a filled C sp<sup>2</sup> orbital (Figure 5c) and a  $\pi$ -backbonding interaction between the occupied Co  $t_2$ orbital and an unoccupied C=O  $\pi^*$  (Figure 5d).

On the basis of the experimental evidence a plausible mechanism for  $CO_2$  reduction can be forwarded, where  $CO_2$  binds the protonated Co(I) complex, produced upon reduction at the electrode, and gets reduced to CO after a subsequent protonation from  $H_2CO_3$ . The CO then dissociates and results in the Co(III) complex, which is then reduced again at the electrode to resume the catalytic cycle (Figure 6, left). The rate-



**Figure 5.** DFT-optimized structure of the (a) Co(I)-CO<sub>2</sub> complex and (b) thiol-protonated Co(I)-CO<sub>2</sub> complex, (c)  $d_z^2$  orbital of the Co(III)-COOH complex, and (d) occupied Co  $t_2$  orbital backbonding to the unoccupied C=O  $\pi^*$ .

determining step is likely to be the protonation of the Co(III)-COOH, which has a H/D isotope effect of  $\sim$ 5.41. The site of protonation of the Co(III)-COOH is crucial in determining the selectivity between HCOOH and CO as products. In the absence of a preorganized second sphere network ascertaining protonation of either the C or the O, the greater than 93% Faradaic yield for CO is apparently surprising. However, normal population analysis of the ground-state wave function of the DFT-optimized Co(III)-COOH species reveals that the carbon center bears a charge of 0.38, whereas the oxygen centers bear -0.34 and -0.29 e<sup>-</sup> charges, respectively. The strong covalent bonding between the Co(III) and the C depletes the latter of electron density, which is localized on the more electronegative oxygen centers of the bound anionic COOH ligand (Figure 6, right). Logically the next protonation happens on the oxygen resulting in CO and not on the C, thereby precluding the formation of HCOOH. Thus, the strong covalent bonding between Co(III) and carbon center of the Co(III)-COOH intermediate imparts selectivity to CO<sub>2</sub> reduction resulting in almost exclusive formation of CO. The proposed mechanism for CO<sub>2</sub> reduction by complex 1 is, in essence, similar to that of cyanocobalamin, where the Co(I) state binds the incoming  $CH_3^+$  group, reduces it by two electrons to  $CH_3^-$ , and then transfers it to an incoming acylium electrophile.

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In conclusion, a Co complex bearing thiolate ligands predominantly reduces  $CO_2$  to CO in its Co(I) state resulting in less than 100 mV overpotential. The two electron-rich thiolates play dual role in the process. One of the thiolates increases electron density at the Co center allowing Co(I) state to bind CO<sub>2</sub> by backbonding. The other is protonated under natural experimental conditions  $(H_2O + CO_2)$ , raises the formal potential of the Co(II/I) process lowering the overpotential of CO<sub>2</sub> reduction, and helps the reduction of CO<sub>2</sub> by acting as a local proton source. The large covalent charge transfer from the -COOH to the Co(III) in a proposed Co(III)-COOH intermediate species prohibits protonation of the carbon center precluding the formation of HCOOH. Rather the protonation of the OH center of this intermediate leading to CO release is likely to be the rate-determining step with a  $k_{\rm H}/k_{\rm D}$  value of ~5.4. Using a dithiolate ligand framework to both increase electron density on the metal and act as a proton source may be a general strategy to catalyze lowpotential redox reactions that require multiple protons and multiple electrons.

## METHODS

**General Procedures.** Syntheses and electrochemical investigations were performed under inert atmosphere or Ar glove box. All the solvents, cobalt chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ ), and HBr (48% in  $H_2O$ ) were purchased from local vendors and used after purification whenever it was required. Bis(diphenylphosphinoethane) (dppe) and potassium thioacetate were bought from Sigma-Aldrich. 2,6-Pyridinedimethanol was purchased from Across Chemicals. These chemicals were used as obtained. The electrodes used for homogeneous electrochemistry were purchased from Pine Instruments and used after polish for every use. Further experimental details and characterization details are given in the Supporting Information.

Electrochemical Measurements. Cyclic Voltammetry. All electrochemical experiments were performed using a CH Instruments



Figure 6. (left) Proposed mechanistic cycle of  $CO_2$  reduction by complex 1. (right) Charge distribution contour of S-protonated COOH bound Co(III) form.

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(model CHI710D Bipotentiostat Electrochemical Analyzer). Reference electrodes and Teflon plate material evaluating cell (ALS Japan) were purchased from CH Instruments. A Pt wire electrode was used as a counter electrode. The measurements were made against a leakproof Ag/AgCl aqueous reference electrode (saturated KCl). Anaerobic experiment was performed in glove box or within a custom-made fourneck electrochemical cell by thoroughly degassing the whole setup with Ar gas. The glassy carbon electrode was used as working electrode, which was freshly polished to get rid of all the contaminations before each single use.

Homogeneous Electrochemistry. Anaerobic solution (0.5 mM) of complex 1 (in ACN) with 0.1 M tetrabutylammonium perchlorate (TBAP) was taken in a four-neck two-compartment electrochemical cell that was degassed by Ar gas prior to electrochemical experiment. Then  $CO_2$  gas was bubbled into the solution for 1–1.5 h, and then the electrochemical data were collected. To determine the diffusion constant of complex 1, a 2 mM solution was used. The experiments were done in different solvents like dimethylformamide (DMF), dichloromethane (DCM), THF, and different working electrodes (GCE and Pt), and very similar data were obtained. Rinse test was performed after bulk electrolysis experiments and did not show any adsorbed material on the electrode. The catalyst was fully soluble in 3 M H<sub>2</sub>O in CH<sub>3</sub>CN up to concentrations less than or equal to 3 mM.

**Bulk Electrolysis and Gas Collection.** The bulk electrolysis (BE) experiment for gas analysis was done in a custom-made twocompartment water jacket three-electrode electrochemical cell brought from PINE with 27 cm<sup>2</sup> Hg-pool working electrode, which was connected to an inverted buret for potential dependent product analysis. The gas evolved during BE was collected into the buret by vertical displacement of water. The amount of gas evolved was measured from the volume of water displaced during the experiments. To check the stability of the catalyst BE was performed on a 2.8 cm<sup>2</sup> Hg-pool electrode or a 0.1 cm<sup>2</sup> GCE in the custom-made four-neck two-compartment electrochemical cell with  $CO_2$ -saturated 10 mL of 0.5 mM CH<sub>3</sub>CN solution of the complex 1 containing 2.1 M H<sub>2</sub>O.

**Gas Detection by Gas Chromatography.** The gas evolved during BE was detected by using GC instrument of model no. 7890B (G3440B), fitted with thermal conductivity detector (TCD). Gas (400  $\mu$ L) was syringed out by a gastight Agilent Gold Standard Syringe and was injected into the inlet of the GC.

2, 6-Dithiolatomethylpyridine-dppe Cobalt(II) Complex. Co(dppe)Cl<sub>2</sub> was synthesized by previously reported procedure, where CoCl<sub>2</sub>·6H<sub>2</sub>O was used instead of anhydrous CoCl<sub>2</sub>.<sup>58</sup> To a dark green solution of Co(dppe)Cl<sub>2</sub> (341.2 mg, 0.65 mmol) in 20 mL of dry THF 2,6-dithiolmethylpyridinium hydrochloride (134.2 mG, 0.65 mmol) was added. After the solution was stirred for 15 min, NaOMe (175.6 mg, 3.25 mmol) was added to the mixture. After few minutes the color was changed from dark green to light brown to dark brown. The resulting mixture was stirred under Ar atmosphere for additional 4 h. Then, the resulting mixture was filtered off to remove all the side product, and then the solvent was evaporated to get the brown solid. The brown solid was dissolved in acetonitrile and again filtered out to remove all the residual part. The acetonitrile was evaporated to yield (230 mg, 53%) the final product as a dark brown solid. The X-ray quality single crystals were grown from slow diffusion of THF/hexane. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.79–7.697 (9H, br d); 7.448–7.255 (14H, br s); 2.706-2.516 (4H, br d); 1.249 (4H, br s) MALDI-TOF  $(M+H)^+$  = 642.852; Calculated mass (m/z) = 642.1018 Elemental Analysis (found): C, 63.39; H, 6.71; N, 1.83; (calculated) C, 63.85; H, 6.06; N, 1.96%.

**Computational Details.** The geometries were optimized in Gaussian 03 software<sup>59</sup> using the B3LYP functional<sup>60,61</sup> and 6-311g\* basis set. Frequency calculations were performed to ensure the presence of a minimum. The single-point calculations were calculated using the same functional but a 6-311+g\* basis set and a  $1 \times 10^{-10}$  convergence criteria. The contour diagrams are plotted in Gausview 5.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00450.

Additional cyclic voltammetry data, control experiments, NMR data, and optimized coordinates (PDF)

#### Accession Codes

CCDC 1582073 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.

## AUTHOR INFORMATION

**Corresponding Author** 

\*E-mail: icad@iacs.res.in.

#### ORCID 0

Abhishek Dev: 0000-0002-9166-3349

#### Author Contributions

<sup>†</sup>S.D. and M.E.A. contributed equally to this work.

#### Notes

The authors declare no competing financial interest.

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