Homogeneous Electrochemical Reduction of CO₂ to CO by a Cobalt Pyridine Thiolate Complex

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ABSTRACT: The chemical and electrochemical reduction of CO_2 to value added chemicals entails the development of efficient and selective catalysts. Synthesis, characterization and electrochemical CO_2 reduction activity of a air-stable cobalt(III) diphenylphosphenethano-bis(2-pyridinethiolate)chloride $[{Co(dppe)(2-PyS)_2}-Cl, 1-Cl]$ complex is divulged. The complex reduces CO_2 under homogeneous electrocatalytic conditions to produce CO with high Faradaic efficiency (FE > 92%) and selectivity in the presence of water. Through detailed electrochemical investigations, product analysis, and mechanistic investigations supported by theoretical calculations, it is established that complex 1-Cl reduces CO_2 in its Co(I) state. A reductive cleavage leads to a dangling protonated pyridine arm which enables facile CO_2 binding through a H-bond



donation and facilitates the C–O bond cleavage via a directed protonation. A systematic benchmarking of this catalyst indicates that it has a modest overpotential (~180 mV) and a TOF of ~20 s⁻¹ for selective reduction of CO₂ to CO with H₂O as a proton source.

INTRODUCTION

An urgent search for alternative clean renewable energy sources has encouraged the scientific community to develop new technologies for mitigating CO₂ to value-added products through intermittent energy sources, e.g., solar, wind, and so on.^{1,2} CO₂ can be reduced to produce various products which are not only important for storing carbon but also provides a way to valorise CO₂ present in the atmosphere upon capture, e.g., CO, HCOOH, CH₄, CH₂CH₂, C₂H₆, and so on.³⁻⁵ In biological methanogenesis, CO2 is converted to CH4. Similarly, CO₂ is converted to CO industrially and hydrogenated to produce liquid fuel via Fischer-Tropsch synthesis.⁶ From the early 1980s, several complexes of first or second row transition metal complexes have been investigated for electrochemical CO_2 reduction.^{4,7} (Figure 1). Several metalo-phthalocya-nines^{8,9} and metalo-porphyrins^{10,11} as well as di- to polypyridyl complexes of rhenium,¹² ruthenium, rhodium, and iridium were developed.¹³⁻¹⁵ Apart from these, macrocyclic complexes of cobalt and nickel evolved as electrocatalysts for CO₂ reduction almost at the same time.^{16,17} Among the recent developments, Ni-cyclam,^{18,19} Fe-porphyrin,^{20–22} fac-Mn-(CO)₃(R-bpy)Br,^{23–25} and Co/Fe/Ni-polypyridine complexes^{5,26} ⁻³³ have shown promising activity for electrochemical CO₂ reduction. Some catalysts are reported to produce HCOOH selectively.^{30–32,34,35} Recently, Savéant and Robert et al. modified the Fe-porphyrin to include second sphere functionality, e.g., polymethyoxy, polyhydroxy, and trimethylammonium $(-NMe_3^+)$, and those are efficient and durable molecular catalysts for CO₂ reduction to CO.^{33,36-38} Among the polypyridyl-based catalysts, *fac*-M(CO)₃ bpy (where M = Re and Mn) are selective toward CO generation at moderate overpotentials. Structural improvisations in the bpy ligand of these catalysts, keeping the basic core of these catalysts intact, led to activation of low-energy pathways substantially lowering the overpotential (additional energy required to the thermodynamic threshold) without compromising high rates.^{24,25,39–41}

Most of the molecular catalysts reported to show 2e⁻ reduction of CO₂ with moderate to high overpotentials.^{5,28,33} Tuning the selectivity of CO₂ reduction between CO and HCOOH is a major challenge in these catalysts.^{42,43} Since CO₂ reduction requires a source of protons (CO₂ + 2e⁻ + 2H⁺ \rightarrow CO + H₂O), competitive H₂ evolution adds to the complexity of the problem and effectively bifurcates away the implemented electrons from the carbon-based products. Although the selectivity for HCOOH production against H₂ generation is explained based on the intrinsic hydricity of a metal hydride intermediate formed during catalytic turnover in combination of the choice of proton sources. Till date, the literature is lacking any rationalization to the selectivity over CO

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Figure 1. Metal thiolate complexes known via electrochemical CO_2 reduction. (top) Enzymatic active site of Mo–Cu CODH (left) and Ni–Fe CODH (right). (A–C) Some representative synthetic complexes investigated for CO_2 reduction. (A) Various kinds of first row transition metal based macrocyclic complexes; (B) different bipyridine based complexes. (C) First row transition metal based thiolate complexes.

generation vs HCOOH or H₂ production, more accurately M– CO_2^{n-} formation versus M–H formation.^{44–46} To envisage the general protocol for designing product selective catalyst, further study of new complexes is highly desirable, although some of the previous reported complexes have proved to catalyze efficiently either of these processes. However, most of these complexes can only function at sufficiently high overpotentials as well as slower rates. Hence, the search for new cheap catalysts that can catalyze the processes at lower overpotentials with higher selectivity and rates is still ongoing.

The metalloenzymes like carbon monoxide dehydrogenases (CODHs), nitrogenases (N₂-ases), and formate dehydrogenases which efficiently catalyze CO₂ reduction are comprised of thiolate and sulfide ligands around the metals.^{47–54} Unfortunately, metal thiolate complexes have not been investigated for CO₂ reduction except for some synthetic Fe–S clusters which proved to be inefficient.^{55,56} Very recently, some Ni and Mo complex with synthetically

challenging bioinspired dithiolate ligands were reported to catalyze CO_2 reduction and found inefficient in terms of overpotentials as well as product selectivity.^{57–59} Our group reported a CODH inspired Co pyridine dithiolate complex that reduces CO_2 to CO selectively at very low overpotentials in the presence of water as the proton source.⁶⁰ The electronrich thiolate ligand in this complex not only contributes to activation of Co(I) state for CO_2 activation (there by lowers the overpotential) but also transfers the proton to a rate-determining Co(III)–COOH intermediate, selectively to a hydroxyl group, resulting in fast and selective CO generation.

In this manuscript, CO_2 reduction by a new cobalt(III)bis(2-thiopyridinato)-diphenylphosphenoethane chloride complex (1-Cl) is described. This complex can be synthesized from readily available chemicals. A detailed electrochemical investigation establishes that this complex, once reduced, is capable of catalyzing CO_2 reduction to CO in the presence of water as a proton source. Detailed electrochemical analysis and

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Scheme 1. Synthesis and Molecular Structure of 1-Cl^a



 $a^{(left)}$ Synthetic procedure of complex 1-Cl. (right) Molecular structure of the cationic part of 1-Cl determined by single-crystal X-ray diffraction. The H atoms and Cl⁻ counterion are omitted for clarity.

theoretical calculations help us to gain insight into the high selectivity for CO production over HCOOH and H_2 .

RESULTS AND ANALYSIS

Synthesis and Characterization. Complex 1-Cl is synthesized in two steps. Addition of a acetonitrile solution containing 2 equiv of pyridine-2-thiol to a suspension of presynthesized $Co(dppe)Cl_2$ in acetonitrile, anaerobically, results in a brown solution. Then, 2 equiv of triethyl amine was added to deprotonate the thiols. Finally, aerobic oxidation of the yellow brown solution and subsequent purification gives yellowish green crude complex 1-Cl in good yield (\sim 76%) (Scheme 1, left). The synthesis can be achieved in tetrahydrofuran (THF) as well (yield ~ 67%). A similar protocol was previously used for synthesizing tris-pyridinethiolatonickel complex by Eisenberg et al.⁶¹ Complex 1-Cl is characterized by UV-vis, ¹H NMR, ESI-MS, and single-crystal X-ray diffraction. The UV-vis spectra in CHCl₃ show absorption bands at 284, 318, 365 nm (Figure S2). The ¹H NMR data in CDCl₃ ensures that the complex is fully diamagnetic in solution (Figure S3). X-ray quality yellowish green needlelike single crystals are grown by slow diffusion of diethyl ether in a concentrated solution of 1-Cl in dichloromethane. The X-ray crystal structure is shown in Scheme 1 (right). In all the characterizations, it is confirmed that complex 1-Cl exists in monomeric octahedral Co(III) low spin form. As all of the ligands in 1-Cl are bidentate, they bind the cobalt in an η^2 -fashion. The pyridines bind *cis* to each other, whereas the thiolate ligations are trans to each other. The dppe unit completes the coordination to yield the monomeric octahedral complex. The bond distances and bond angles are given in the Table 1. The Co–S bond distances (2.24–2.28 Å)

 Table 1. Geometrical Parameters for Complex 1-Cl

 Determined by X-ray Crystallography

| bonds | bond distances (Å) | bond angles | bond angle values (deg) |
|--------|--------------------|-------------|-------------------------|
| Co1-S1 | 2.2794(19) | S1-Co1-N1 | 72.61(14) |
| Co1-S2 | 2.258(2) | S2-Co1-N2 | 72.71(15) |
| Co1-P1 | 2.222(2) | P1-Co1-P2 | 86.81(8) |
| Co1-P2 | 2.211(2) | | |
| Co1-N1 | 1.948(5) | | |
| Co1-N2 | 1.952(5) | | |

are in good agreement with other reported low spin Co(III)– thiolato complexes,⁶² and the Co–N bond distances (1.95– 1.96 Å) and N–Co–S bond angles (72.3–72.6 deg) are also in good agreement with other low-spin Fe and Ni pyridine thiolate complexes.^{63–65}

Electrochemical Investigation. Under Argon. The homogeneous cyclic voltammetry (CV) of complex 1-Cl is

performed in CH₃CN in the presence of 0.1 M ntetrabutylammonium perchlorate (TBAP) as supporting electrolyte, and the data showed a reversible 1e⁻ redox process at -1.18 V. A second irreversible 1e⁻ reduction process appeared at -1.95 V vs Fc^{+/0} (black line in Figure 2, left). The peak to peak separation of 73 mV of first reduction process compared to 67 mV of ferrocene indicate that the process at -1.18 V is a 1e⁻ redox process. We attribute that this redox process as the Co^{III/II} redox process as trispyridiniumthiolatozinc(II) complex does not show any redox event in this potential range. The reduction potential value matches well with the previously reported bipyridine analogues.⁶⁶ The second irreversible process at -1.95 V was assigned as a 1e⁻ reduction process of $Co(II) \rightarrow Co(I)$. The irreversibility of the process is attributed as the dissociation of one pyridine moiety from the metal center as the process becomes quasi-reversible at high scan rates (>300 mVs⁻¹) (Figure S5a). Similar dangling of a pyridine arm upon reduction was previously reported for nickel-pyridinethiolate complexes.^{61,67} Variation of the scan rates shows that the peak currents (I_p) associated with both of the redox events vary linearly with the square root of the scan rates (Figure S5b) and follow Randles–Sevcik diffusion equation, $I_p = 0.4463(F/RT)^{1/2}n_p^{3/2}FAD^{1/2}[C_0]\nu^{1/2}$, where I_p is the peak current, F is Faraday's constant ($F = 96485 \text{ C mol}^{-1}$), R is the universal gas constant (R = 8.314 J K⁻¹ mol⁻¹), T is temperature (T = 300K), $n_{\rm p}$ is the number of electrons transferred, A is the active surface area of the electrode, D is the diffusion coefficient of the complex, $[C_0]$ is the concentration of the catalyst, and ν is the scan rate (V/s). Using the equation, the electrochemical diffusion coefficients of 1-Cl and 1 are determined to be 4.5 \times $10^{-6}\text{--}4.2~\times~10^{-6}~\text{cm}^2~\text{s}^{-1}$ for first and second reduction processes (see the Supporting Information). An almost similar slope in the I_p versus $\nu^{1/2}$ plot for both of these processes indicates homogeneous behavior of the complex in electrolytic solution. The homogeneous electrocatalysis has been investigated in CH₃CN in the presence of H₂O. The result shows almost no change in both redox events (blue line in Figure 2, left) except for a 30 mV positive shift in $1/1^-$ redox process, which might originate from the greater solvation of anionic species due to an increase in the solvent polarity due to the addition of water.^{68,69}

*Electrochemical CO*₂ *Reduction.* The catalytic activity of complex 1-Cl is investigated in the presence of CO₂ and H₂O. The CV of complex 1-Cl almost remains unchanged in presence of CO₂ except a small increase in the current associated with Co^{II/1} process (red line in Figure 2a). We assume that the interaction of CO₂ with the Co(I) center of 1⁻ is similar to the previously reported Co(dppe)PyS₂ complex. As H₂O is added to the electrolyte solution, a faradaic process arises and saturates at around -1.5 V (green line in Figure 2a).



Figure 2. Electrochemical data for 1-Cl. (left) Overlay of the CVs of complex 1-Cl in CH_3CN under Ar (black line), CO_2 (red line), H_2O (blue line), and both together (green line). (right) Linear sweep voltammetry of 1-Cl with increasing concentration of water under CO_2 atmosphere. (Conditions: 0.5 mM of 1-Cl; 0.1 M TBAP as supporting electrolyte, glassy carbon as working electrode, Pt as counter electrode, scan rate 100 mVs⁻¹).

This catalytic process increases with addition of water (Figure 2b, right) and is not observed in the absence of CO_2 . The large positive shift of the catalytic process in the presence of CO₂ and H₂O together can be due to protonation of the pyridine which dissociates upon reduction facilitating the further reduction of 1⁻. Such ligand protonation assisted positive potential shift in a reduction process has already been observed for several pyridine thiolate complexes of Fe(II), Co(II), and Ni(II).^{60,61,70-72} Specially trispyridinethiolatoNickel(II) complex shows catalytic turnover for H⁺ reduction via pyridine protonation in presence of acetic acid ($pK_{2} = 23.5$ in CH₃CN).⁶⁷ Notably, previous reports by Morris et al. showed that depending on the solvent used the acidity of the pyridinium proton can be tuned. 73 Addition of $\rm H_2O$ in CO_2saturated acetonitrile generates H2CO3 through the equilibrium reaction $CO_2 + H_2O \leftrightarrow H_2CO_3$, that can assist the protonation of one of the pyridine ligands dissociated from the metal center providing the open site to bind the substrate, i.e., either CO₂ or H⁺. The product analysis corresponding to the catalytic process is discussed below. The process at -1.5 V vs $Fc^{+/0}$ is second-order with respect to H_2O_1 as the catalytic current (I_{cat}) varies linearly with concentration of H₂O until the concentration of H₂O reaches a limiting value of 2.4 M. Thus, we choose the H₂O concentration 2.4 M for determining the catalytic parameters and for mechanistic investigation. Different mixture of CO_2 and Ar gas is used and the data showed that the I_{cat} at -1.5 V vs $Fc^{+/0}$ varies linearly with square root of CO₂ concentration, suggestive of first-order kinetics (Figure S6). Thus, the catalytic process at -1.5 V vs $Fc^{+/0}$ is second- and first-order with respect to H₂O and CO₂ respectively. These results are crucial for mechanistic analysis of the reaction and will be discussed in a later section of the article.

Controlled Potential Electrolysis (CPE) and Product Analysis. As discussed earlier, there are two cathodic processes in the presence of both CO_2 and H_2O . A series of electrolysis experiments are performed at different potentials between -1.1 to -1.6 V vs Fc^{+/0} having an interval of 0.1 V between each applied potential using a Hg-pool electrode with 2.7 cm² electrode surface area, and the head space gas is analyzed by gas chromatography (GC) using a thermal conductivity detector (TCD) to identify the product (Figure S7). The background catalysis is monitored under the same conditions without adding the complex in the electrolyte solution prior to performing the electrolysis. The results show that without the complex Hg-pool electrode itself produces very little CO or H₂ at these potentials even after 20 min electrolysis. The amount of charge consumed is substantially higher compared to the background when complex 1-Cl is added in the electrolyte solution. Electrolysis at -1.1 or -1.2 V does not yield CO (in GC) more than the background after 20 min electrolysis. Similarly, it does not show any peak corresponding to HCOOH in the ¹H NMR (or in ion chromatography (IC)), so the process at -1.1 V is not catalytic. The peak intensities of CO and H_2 in GC increase when a potential of -1.3 V was applied. Even within 5 min of electrolysis at -1.3 V, substantial production of CO is observed. These data suggest that the second catalytic process is responsible for CO₂ reduction. As the applied potential is further lowered, the amount of charge consumed over bulk electrolysis (BE) experiments at same duration increases almost linearly. The results showed that the amount of H₂ release also increased at more cathodic potential. The ratio of CO/H_2 changes from 17.3:1 to 6.5:1 on changing the potential from -1.3 to -1.6 V (Figure S8). The faradic yield (FY) for the electrocatalytic process is determined by the displacement of water in an inverted buret set up from electrolysis at -1.5 V over 2 h of electrolysis and is $91 \pm 6\%$ (Table S2). The electrolyzed solution is analyzed by ¹H NMR, and no chemical shift value corresponding to HCOOH is observed. These results clearly suggest that complex 1-Cl is a very efficient catalyst for CO₂ reduction to CO in the presence of H₂O as proton source. The electrolysis is performed with glassy carbon plate electrode as well at -1.5 V for 2 h, a total FY of 92 \pm 4% is obtained (Figure S10). To determine the product selectively, the head space is analyzed at the end of electrolysis and it shows ~12:1 ratio of CO/H_2 at the end of 2

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Figure 3. Catalytic Tafel plot using TOF_{max} value obtained from scan rate dependent on CVs under optimized catalytic conditions. The catalytic parameters are compared with other reported CO producing catalysts and other thiolate catalysts. Other catalysts or composites are represented with respective colors. Proton source used during the catalysis are mentioned in the figure with the same color code. TFE = trifluoroethanol.

h of electrolysis, so complex 1-Cl catalyzes CO_2 reduction to CO with high selectivity irrespective of the electrode used. The high selectivity for CO production is very similar to the previously reported cobalt-pyridinethiolate catalyst⁶⁰ and very different from other reported metal thiolate catalyst, i.e., $[Ni(qpdt)_2]^{1-}$ catalyst, which is more selective for CO_2 reduction to HCOOH.⁵⁸ A rinse test experiment was performed on the glassy carbon electrode after 1 h of electrolysis in a CO_2 -saturated wet acetonitrile solution containing 2.4 M H₂O without the catalyst showed no catalytic wave which indicates that the catalytic activity is originating from soluble complex 1-Cl (Figure S11).

Determination of Catalytic Efficiency. The efficiency of electrocatalysts depends on their overpotential, inherent turn over frequencies (TOFs, cycles completed in a second), turn over numbers (TONs, maximum number of cycles possible from 1 mol of catalyst during controlled potential electrolysis), and rate of the catalysis, i.e., maximum TOF (TOF_{max}). I_{cat}/I_p is a direct estimate of the TOF although more detailed analysis is required for a more accurate determination of TOF.³⁶ The TOF_{max} can be determined from catalytic response obtained at various scan rates. If the catalytic currents do not vary at different scan rates, which is the case here (Figure S12), then the TOF_{max} can be determined from the equation I_{cat}/I_p = 4.484(RT/F)^{1/2}(TOF_{max})^{1/2} $\nu^{-1/2}$.^{25,30} Accordingly, the TOF_{max} for the second catalytic process, i.e., CO₂ reduction is determined to be 27 ± 3 s⁻¹, which is substantially lower

than our previously reported cobalt-pyridinedithiolate catalyst, but it functions almost at same potentials as the previous one.⁶⁰ Moreover the TOF from CPE experiment is determined to be 17.6 s^{-1} (see the Supporting Information) which is in reasonable agreement with the TOF_{max} determined from CV. The determination of the overpotential is complicated for CO_2 reduction in the presence of H₂O. Recently, Mayer and Appel et al. derived an easy way to determine $E_{\rm CO_2/CO}^{\rm standard}$ from the thermodynamic cycle of the reductive process which is given by $E_{\rm CO_2/CO}^{\rm standard} = E_{\rm CO_2/CO}^0 - 0.059 \times pK_a$ vs Fc^{+/0.74} Assuming that the source of the proton under the electrochemical condition is *in situ* generated H_2CO_3 (pK_a = 17.03), as described by Artero, Fontecave, and co-workers,⁷⁵ the standard reduction potential for CO₂ to CO production is determined to be $E_{CO_2/CO}^{standard}(H_2CO_3, CH_3CN) = -1.12 \text{ V}$ vs $Fc^{+/0}$. Using these values, the lowest overpotential for complex 1-Cl is determined to be 180 mV as CO is detected even at -1.3 V. This value is almost at the same range as some of the best-known molecular catalysts for electrochemical reduction of CO₂ to CO.⁶⁰ The cationic -NMe₃⁺ substituted iron porphyrin catalyst shows 100-280 mV overpotential to reach optimal activity.³⁸ The quaterpyridine cobalt or iron complex works at 200–400 mV overpotentials.⁷⁶ The bioinspired thiolato complex $[Ni(qpdt)_2]^{1-}$ catalyst needs 500 mV overpotential to catalyze CO₂ reduction to produce HCOOH as a major product along with CO and H₂ as minor



Figure 4. Kinetic dependence of complex 1-Cl. (left) Overlay of the linear sweep scan at increasing concentration of H_2O and D_2O in CO_2 saturated CH₃CN with 0.5 mM of 1-Cl. The *x*-axis is offset by 1.2 V for D_2O for clarity. (right) I_{cat}/I_p vs concentration of Bronsted acid plot (here H_2O or D_2O).

Scheme 2. DFT Computed Potential Energy Surface for the Reduction of CO₂ to CO by the Co(I) State of Complex 1-Cl



products.⁵⁸ To directly compare the catalytic activity of 1-CI with other metal thiolate complexes, we determine the catalytic Tafel Plot (Figure 3). The plot shows that 1-Cl compares well with the best known first row transition metal catalysts in terms of overpotential. To determine the stability of the catalyst, we determined the limiting TON from the CPE at -1.5 V to be 75 ± 4 over 2 h of electrolysis with Hg-pool electrodes (2.7 cm²) and almost 22% of the complex is degraded (Figure S13) (likely due to high affinity of Hg for thiols; see the Supporting Information). However, with a glassy carbon plate electrode, only 4% degradation of 1-Cl was observed (Figure S14) and hence TON is determined to be much higher (>1 × 10⁵). These data support that complex 1-Cl is a sustainable catalyst for CO₂ reduction to CO at very low overpotential at fast rates.

Mechanistic Consideration. From Electrochemistry. The rate of CO₂ reduction increases with increasing concentrations of the catalyst (Figure S15) and it shows a linear dependence. $I_{\rm cat}$ is related to its catalytic components by the equation $I_{\rm cat}$ = $n_{cat}FA[cat](DK_{sub}[sub])^{1/2}$ ([sub] denotes the substrate concentration). Hence, the catalytic activity is first-order with catalyst concentration. As mentioned earlier, the catalytic current varies linearly with the square-root of CO₂ partial pressure, suggesting a first order kinetic dependence of CO₂. Also, the current varies linearly with the concentration of H₂O as is expected for a second order rate dependence.³⁰ Taken together, the rate of CO_2 reduction can be expressed as rate = $k \times [\text{catalyst}] \times [\text{CO}_2] \times [\text{H}_2\text{O}]^2$, where k is the rate constant. To get further insight into the rate-determining step (rds, which is the slowest step during catalytic turnover), the catalytic activity is determined in D₂O instead of H₂O. The data show that the catalysis proceeds at slower rates and shows a second-order dependence on D_2O (Figure 4). Primary kinetic isotope effect $(k_{\rm H}/k_{\rm D})$ of 6.28 \pm 0.5 is determined (Figure S16) indicating that a proton is directly involved in the rds.^{30,60} In analogy to the CodppePyS₂ complex, it could be proposed that either the formation of Co-COOH intermediate or the second protonation of the Co-COOH species could be the rds.⁶⁰ As the first faradaic process around -1.1 to -1.2 V has already proved to be noncatalytic, this reduction process is likely associated with pyridine protonation to generate a Co(II)-PyH⁺ (which we denote as 1-H) species. Such ligand protonation associated noncatalytic increment of current was also previously observed by nickel-pyridine thiolate complex or nickel-amido complex catalyzed electroreduction of proton to H2.⁷⁰ We conclude that first reduction to Co(II) species which follows the pyridine protonation by the in situ generated H_2CO_3 facilitates the further reduction to Co(I) to more positive potential. Then, the CO₂ interacts with the Co(I) center and gets reduced to CO. Hence, this catalytic process can be represented as an ECEC mechanism. For detailed insights into the mechanistic steps involved density functional theory (DFT) calculations are performed and are presented in the next section.

DFT Calculations and Structure–Function Correlation. Geometry-optimized DFT calculations are performed to elucidate the energy and barriers in the different steps involved in the catalytic cycles and presented in Scheme 2. Furthermore, structure-function correlations are developed to explain the selectivity. To test the reliability of the method, an optimization of the cationic part for 1-Cl is performed, and the optimized structural parameters show good agreement with the crystal structure (Table S3). From the experimental data and previous literature reports, it is evident that one of the pyridine ligands opens up on the reduction of 1 to 1⁻ state, and the electrochemical data also suggest that all the components are important for the activity. From the reversible nature of Co(III/II) redox couple even after scanning beyond the irreversible second reduction process, it can be assumed that the resting structure of 1^+ is regenerated upon completion of the redox cycles. This is also confirmed from the unchanged UV-vis data after CPE indicating that 1⁺ remains unaltered even after catalytic turnovers. The redox-triggered dangling pyridine moiety provides the binding site for exogeneous CO_2 ,and after completion of catalytic turnover, it comes back to the original oxidized form. Note that for further discussions, it is assumed that all the Co(I) and Co(II) intermediates involved during the catalytic turnovers are high-spin and Co(III) intermediates are low-spin.

The catalysis begins with the interaction of CO_2 with $[1_{open}$ -NH] species (Scheme 2) that is generated by 1e⁻ reduction of the protonated Co(II) species in the presence of *in situ* generated H₂CO₃ as discussed earlier. A similar protonation feature was observed before for a Ni-imidothiol complexes in the presence of proton source.

To initiate the CO₂ reduction, CO₂ is allowed to bind the open site in [1_{open} -NH] which leads to the formation of [1-COO-NH] species, and this step is endergonic by 11.6 kcal/ mol. Substantial bending of O-C-O bond angle (131.5°) in this metal-bound CO₂ bound entity is suggestive of a strong charge transfer from reduced Co(I) center to one of the π^* orbital of CO₂ molecule. Additionally, the H-bonding donated by protonated pyridine to one of the oxygen atoms of the CO₂ moiety should help the CO₂ binding through the C center to

the metal by stabilizing the electron-rich oxygen atoms of CO₂. A similar bisdithiolato complex has been recently shown to be very efficient and selective for CO₂ reduction where protonation of the thiolate arm was proposed.⁶⁰ A similar protonation of the thiolates here leads to a CO_2 binding energy of 26.8 kcal/mol which is much higher than the CO₂ binding energy of the pyridyl protonated complex and is unlikely to be catalytically active. The CO₂ binding step is followed by proton transfer from the pyridyl nitrogen to the oxygen atom of the bound CO_2 in the [1- CO_2 -H] species which is computed to be uphill by 4.5 kcal. The transition state (TS1, Scheme 2) for the process is very low energy and involves one imaginary mode at 571 cm⁻¹ which involves transfer of the proton from the pyridyl nitrogen to the CO₂ oxygen with simultaneous shortening of the Co-C bond. The Co-C bond shortens from 1.98 Å in $[1-CO_2-H]$ to 1.95 Å in [1-COOH]. The Mulliken charge on the C atom of the [1-COOH] moiety is 0.38, and on O atoms, the charges are -0.34 and -0.57, respectively. This ascertains the second protonation on the O atom of the elongated C-O bond facilitating the release of a H₂O molecule and precludes any possibility of isomerization to produce HCOOH. The mode of binding and the ensuing protonation step has been proposed to be key to the observed product selectivity, i.e., only CO and no HCOOH.⁶⁰

Further protonation of the pyridyl arm of [1-COOH] from bulk proton generates [1-COOH-H]⁺ intermediate that is exothermic by -16.4 kcal/mol relative to the [1-CO₂-H] intermediate. This $[1-COOH-H]^+$ intermediate releases H_2O to give $[1-CO]^+$. The H₂O elimination step passes through a transition state (TS2) which is 12.9 kcal/mol uphill. The TS2 involves a single imaginary frequency at 342 cm⁻¹ which involves a proton transfer from the pyridyl arm to the C-OH oxygen with subsequent cleavage of the C-OH bond. The computed TS2 barrier of 12.9 kcal/mol compares reasonably well with the 13.8 kcal/mol barrier estimated from the experimental rate of 122 s⁻¹ using Eyring equation. We invoke that this step is the rate-determining step because it fits all the experimental data, i.e., rate linear with CO₂ and H₂O and a $k_{\rm H}$ / $k_{\rm D}$ of 6.28 ± 0.5. Finally, CO release and regeneration of the oxidized catalyst is required for catalytic turn overs. Our calculation suggests that CO release from [1-CO]⁺ species is spontaneous and exothermic by -10.2 kcal/mol to regenerate 1⁺ which can re-enter the catalytic cycle. The possibility that the pyridyl arm may also translocate proton from bulk solvent cannot be eliminated.

In conclusion, complex 1-Cl is an active electrocatalyst for CO_2 reduction to CO with high selectivity that operates at low overpotentials. The redox triggered hemilability of the pyridine ligand provides a local proton source and dictates the CO_2 binding to the reduced metal center through carbon center to produce CO. The anionic thiolate ligands increase the electron density on the Co(I) and effectively catalyzes the CO_2 reduction. Benchmarking of this catalyst proved that it functions at low overpotential with high rates. The mechanistic investigations reveal the following: (a) Protonation of the pyridine moiety shifts the $Co^{II/I}$ potential more positive without compromising the electron density on the metal-dithiolate unit required to activate CO_2 which effectively lowers the overpotential. (b) The Co–COOH bond covalency plays a role in determining the selectivity for CO_2 reduction. (c) Low barrier (computed) proton transfer from the pyridine

moiety selectively to the oxygen results in facile (experimental) C-OH bond cleavage to form CO. These features impart cobalt **1-Cl** complex with the ability to reduce CO_2 to CO selectively, at very low overpotential with high rates.

EXPERIMENTAL DETAILS

General Procedure. Electrochemical investigations were performed under inert atmosphere in a N₂ Glove Box from MBRAUN. All the solvents used were purchased and used after distillation over drying agents. Hexahydrated cobalt chloride (CoCl₂.6H₂O) was purchased from Spectrochem Pvt. Ltd. (India). Bis-(diphenylphosphinoethane) (dppe) and 2-pyridinethiol were bought from Sigma-Aldrich. Glassy carbon, Pt, and Ag/AgCl (saturated KCl) electrodes were purchased from Pine Instruments. The supporting electrolyte n-tetrabutylamonium perchlorate salt was bought from Sigma-Aldrich and used without purification. Caution: As perchlorate salts are explosive, they should be handled with care. UV-vis absorption data were recorded in an Agilent technologies spectrophotometer model 8453 fitted with a diode-array detector. All the NMR spectra were recorded on the Bruker DPX-400 or DPX-500 spectrometer at room temperature. The mass spectra are recorded by QTOF Micro YA263 instrument. X-ray single-crystal data were collected at 100 K on a Bruker D8VENTURE Microfocus diffractometer equipped with PHOTON II Detector, with Mo K α radiation (λ = 0.710 73 Å), controlled by the APEX3 (v2017.3-0) software package. Raw data were integrated and corrected for Lorentz and polarization effects using the Bruker APEX II95/APEX III program suite. Absorption corrections were performed using SADABS. All the structures were solved by direct methods and were refined against all data in the reported 2θ ranges by full-matrix least-squares on F^2 with the SHELXL program suite98 using the OLEX 299 interface. Hydrogen atoms at idealized positions were included during the final refinements of each structure. The OLEX 2 interface was used for structure visualization, analysis of bond distances and angles, and drawing ORTEP100,101 plots. The CO and H₂ gases evolved during controlled potential electrolysis were detected on a GC instrument (model no. 7890B (G3440B), serial no. CN14333203) fitted with a TCD.

ELECTROCHEMICAL MEASUREMENTS

Cyclic Voltammetry. All electrochemical experiments were performed using a CH Instruments (model CHI710D Biopotentiostat Electrochemical Analyzer). Reference electrodes waswere purchased from CH Instruments. A Pt wire was used as a counter electrode and was purchased from CH Instruments. The measurements were made against a leak-proof Ag/AgCl aqueous reference electrode (saturated KCl). Anaerobic experiments were performed either in glove box or within a 4-necked custom-made electrochemical cell by thoroughly degassing the whole set up with Ar/N_2 gas depending on availability. The glassy carbon electrode was used as working electrode and was freshly polished to get rid of all the contaminations out before each single use.

Homogeneous Electrochemistry. A 0.5 mM anaerobic solution of complex 1-Cl (in freshly distilled acetonitrile) with 0.1 M TBAP were taken in a 4-necked two-compartment electrochemical cell which was degassed by N_2 gas prior to electrochemical experiment. Then, CO_2 gas was bubbled into the solution for 0.5–1 h, and the electrochemical data were collected. The H₂O dependence was done by incremental addition of degassed deionized H₂O in the electrochemical solution by an air-tight syringe.

Controlled Potential Electrolysis and Gas Collection. The CPE experiment was done in a custom-made two-compartment, three-electrode electrochemical cell with a 2.7 cm^2 Hg-pool working electrode which was connected to an inverted buret for gas collection. The gas evolved during BE was collected into the buret by vertical displacement of water during long-term electrolysis, ca. 1-2 h. The amount of gas evolved was measured from the volume of water displaced during the experiments. For short-term electrolysis (20

min), the sample was collected directly from head space. Throughout the electrolysis period, the electrochemical solution was stirred.

Gas Detection by Gas Chromatography. The gas evolved during BE was detected by using a GC instrument (model no. 7890B (G3440B), serial no. CN14333203) fitted with a TCD; 400 μ L of gas was syringed out by a gas-tight syringe and was injected into the inlet of the GC.

CO₂ Percentage Dependence Using Mass Flow Meter. The CO₂ partial pressure dependence experiments were done by using CVG Technocrafts India mass flow meter purchased from Chemix. Mass flow rate of the gases were controlled manually during the experiments using a gas regulator. In this experiment we used two different gas flow meters with full setup (one for CO₂ and another for Ar). The outlet from these two flow meters were passed through degassed bulk CH₃CN in a closed vessel tightened with a rubber septum. The outlet coming from this closed vessel was connected to the electrochemical cell. During the CO₂ concentration dependence experiment, different CO2/Ar gas mixtures were used. During the experiments, the defined gas mixture is purged through the electrochemical solution for 20 mints before recording data. Once the data are collected, the solution is purged again with N₂ for 30 min to remove the dissolved CO₂ and then another portion of the gas mixture is purged.

DFT Calculations. The geometry of all compounds is optimized in gradient-corrected BP86 Functional in unrestricted formalism using Gaussian 03 version C03. All the atoms are optimized using 6-31G(d) basis set. An energy minimum is confirmed by performing frequency calculation on the fully optimized structure using the same basis set used for optimization to ensure no imaginary mode is present for all these compounds. The transition states show only one imaginary frequency along the reaction coordinates. The final energy calculations were performed using 6- 311+G(d) basis set on all atoms in PCM model using acetonitrile as a solvent and convergence criterion of 10^{-10} Hartree. The energies reported are Gibbs free energies which were calculated for all the hypothetical models from the final optimized geometries and frequencies and are corrected for zero-point energies.

Preparation of Bis(diphenylphosphino)ethane Dichloro Cobalt(II). To a solution of anhydrous cobalt(II) dichloride (1.29 g, 10 mmol) in THF (40 mL) was added a solution of bis(diphenylphosphino)ethane (3.99 g, 10 mmol) in THF (40 mL). The color of the reaction mixture changed rapidly from blue to dark green, and the resulting reaction mixture was stirred overnight. The dark green suspension was filtrated and washed with diethyl ether. After a long time under vacuum, a green powder was obtained (4.94 g, 9.3 mmol). Yield 93%.

Preparation of Cobalt(III)-bis(2-thiopyridinato)-diphenylphosphenoethane Chloride Complex. To a suspension of $Co(dppe)Cl_2(530 mg, 1 mmol)$ in acetonitrile was added a solution of pyridine-2-thiol (222.32 mg, 2 mmol) in acetonitrile in N2 atmosphere, and the resulting mixture was stirred for few minutes. Then, triethylamine (280 μ L, 2 mmol) was added to the brown mixture. The yellowish brown color solution was stirred in aerobic condition. After 4 h, the solvent was evaporated by rotary evaporator to reduce the volume to 10 mL. Diethyl ether was added to the mixture to crash out the compound, and the mixture was filtered and then dried to obtain a solid precipitate. The desired yellowish green solid compound (575 mg, 0.766 mmol) was obtained in good yield. ¹H NMR (CDCl₃): δ 8.19 (2H, d), 7.52 (10H, s), 7.30 (4H, t), 7.12 (8H, m), 6.85 (2H, t), 6.33 (2H, d), 2.19 (4H, s). ESI-MS data (M)⁺ = 722.108 (m/z). Elemental Analysis: Found: C, 61.92; H, 5.51; N, 3.64. Calcd: C, 61.78; H, 5.45; N, 3.69.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03056.

Experimental details, characterization data, additional electrochemical data and DFT optimized coordinates (PDF)

Accession Codes

CCDC 1960041 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

The authors declare no competing financial interest.

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