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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Asian J. 10.1002/asia.201901805

Link to VoR: http://dx.doi.org/10.1002/asia.201901805

A Journal of

ACES Asian Chemical Editorial Society

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A sister journal of Angewandte Chemie and Chemistry – A European Journal

Electrocatalytic CO₂ Reduction with Half-Sandwich Cobalt Catalyst: Selectivity towards CO

Indresh Kumar Pandey, [a]\$ Abhishek Kumar, [a]\$ and Joyanta Choudhury*[a]

Abstract: We present herein a Cp*Co(III)-half-sandwich catalyst system for electrocatalytic CO₂ reduction in aqueous acetonitrile solution. In addition to an electron-donating Cp^* ligand ($Cp^* =$ pentamethylcyclopentadienyl), the catalyst featured a protonresponsive pyridyl-benzimidazole-based N,N-bidentate ligand. Owing to the presence of a relatively electron-rich Co center, the reduced Co(I)-state was made prone to activate the electrophilic carbon center of CO2. At the same time, the proton-responsive benzimidazole scaffold was susceptible to facilitate proton-transfer during the subsequent reduction of CO₂. The above factors rendered the present catalyst active toward producing CO as the major product over the other potential 2e/2H+ reduced product HCOOH, in contrast to the only known similar half-sandwich CpCo(III)-based CO2-reduction catalysts which produced HCOOH selectively. The system exhibited Faradaic efficiency (FE) of ~70% while the overpotential for CO production was found to be 0.78 V as determined by controlled-potential electrolysis experiment.

Introduction

One of the important contemporary challenges in the context of energy and environment research is catalytic reduction of CO₂ a renewable and economical C1 feedstock - to high-value products and/or utilizable fuels.^[1] The alarming issue of escalating CO₂ concentration (>400 ppm) in the atmosphere due to consumption of fossil fuels adds renewed relevance to the above challenge. With regard to this, electrocatalytic CO2 reduction strategy holds promise in view of its suitability toward storing intermittent electrical energy and its modularity toward converting CO2 to desirable products (such as CO. HCO₂H/HCO₂⁻, C₂O₄²⁻ etc.) based on variables such as applied potential, electrocatalyst, electrolyte, pKa of the proton donor etc.^[1,2] As a result, several transition metal complexes with a wide variety of ligand scaffolds have been evolved as homogeneous molecular electrocatalysts for CO2 reduction.^[1,2] Significantly, the choice of relatively inexpensive and abundant first-row transition metals (e.g., Mn, Fe, Co, Ni) in combination with suitable ligands, is preferred over noble metal (e.g., Re, Ru, Rh, Ir)-based counterparts, considering practicality and sustainability.

An interesting point in the context of electroreduction of CO₂, is the opportunity to the selective production of CO or HCO_2H/HCO_2^- via the same net two-electron/two-proton

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(2e/2H⁺) reduction pathways as shown in Figure 1A. While HCO₂H is a well-known hydrogen-storage material.^[3] CO is used in synthesizing fuel via the Fischer-Tropsch process.^[4] However. under given reaction conditions, the competition depends crucially on the combined effect of both the metal center and the ligand backbone of the applied catalyst. A highly reduced electron-rich metal center may directly activate CO₂ forming 'M-CO2 adduct, break a C-O bond in the presence of H⁺ and liberate CO (equation i, Figure 1A). On the other hand, the metal center, after its reduction, may form hydride by reacting with H⁺. Depending on the hydricity of the generated metal hydride (M-H) species (and also on the pK_a of the proton donor), it may evolve H_2 via further reaction with H^+ (or H_2O) (equation ii, Figure 1A) or may form HCO₂⁻ via reaction with CO₂ followed by formation of HCO₂H upon protonation (equation iii, Figure 1A). In some cases, if the metal center is relatively electron-deficient, the 'M-CO2' adduct may form 'M-OCHO' intermediate upon protonation and further reduction, followed by formation of HCO₂H (equation iii, Figure 1A).^[5]

[A] 2e/2H⁺ reduction of CO₂: different possibilities



[B] Co-based catalysts for CO₂ electroreduction: previous work $[Co^m(N_x)]^{n^+}$ -type: mainly CO-selective; operates mainly via Co(0) m = formal oxidation state of Co, mainly "II"; n = charge of the complex x = number of N donors in the ligand, mainly 4 and rarely 5 and 3

[(SNS)Co^{II}(PP)]: CO-selective; operates via Co(I) [Dey, *Inorg. Chem.* **2018**, *57*, 5939]

[CpCo^{III}(PP)I]⁺-half-sandwich type: HCO₂H-selective; operates via Co(I) [Artero, *J. Am. Chem. Soc.* **2017**, *13*9, 3685]

[C] this work

[Cp*Co^{III}(NN)(solvent)]²⁺-half-sandwich type CO-selective: operates via Co(I)



Figure 1. [A] Reduction of CO₂ by $2e/2H^+$ pathways to produce CO and HCO₂H. [B] Known Co-catalysts for CO₂-to-CO conversion via Co⁰ and Co¹ states, and CO₂-to-HCO₂H conversion via Co¹ state. [C] Key features of the present work.

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Focusing on Co as the potential metal candidate in this area, primarily multidentate (commonly tetradentate, and rarely penta-/tridentate) N-donor ligand motifs, Nx (Figure 1B) were utilized extensively to design a plethora of highly efficient homogeneous molecular complexes for electrocatalytic CO₂ reduction in both organic (with proton-donor additives) and aqueous media.^[1,2] Notably, most of these Co-catalysts selectively produce CO via activating CO₂ in highly reduced state of the metal, often in formal "Co(0)" oxidation state.[1,2] In contrast, recently, Dey exploited an interesting proton-responsive SNS-donor based 2,6-dithiomethylpyridino tridentate ligand (SNS) at Co center to achieve a highly efficient CO-selective CO₂-electroreduction catalysis at dramatically low overpotential, owing to the activation and reduction of CO2 by formally "Co(I)" oxidation state (Figure 1B).^[6] On the other hand, Artero introduced a new family of half-sandwich Co(III) complexes as molecular CO2electroreduction precatalysts which were found to produce HCO₂H selectively at "Co(I)" state in dimethylformamide (DMF)water solvent mixture (Figure 1B).^[7] This class of precatalysts featured a Cp (Cp = cvclopentadienvl) ligand around Co. additionally supported with a bisphosphine chelate (PP) having pendant N-H groups. These aspects rendered the suitable electronics and hydricity of the Co center, and easy availability of the pendant protons, thus facilitating the route (iii) as shown in Figure 1A, toward selective formation of HCO₂H. Inspired by Artero's HCO₂H-selective half-sandwich Co(III)-complexes^[7] and our own interest in developing half-sandwich complex-based CO₂-reduction catalysts,^[8] we asked whether the same "Co(I)" state in this new class of half-sandwich Co(III) complexes, could be exploited toward selective electrocatalytic production of CO. To achieve the desired CO-selectivity, we relied upon a new design comprising of Cp*Co(III) center surrounded with pyridylbenzimidazole-based N,N-bidentate ligand (Figure 1C). The Cp* ligand (Cp* = pentamethylcyclopentadienyl) is relatively strong electron-donating which would facilitate the reduced Co center to bind the electrophilic carbon center of CO2, while the benzimidazole scaffold is proton-responsive which might facilitate proton-transfer step(s).

Results and Discussion

The study was initiated with synthesizing the Cp*Co(III)-based half-sandwich complex 1 as shown in Figure 2, from reaction of the cobalt precursor, [Cp*Co(CO)I₂] and the corresponding pyridyl-benzimidazole ligand in CH₂Cl₂, followed by counteranion (iodide) metathesis with aqueous NH₄PF₆ in CH₃CN (see Supporting Information for details). Complex 1 was fully characterized by ¹H, ¹³C{¹H} NMR spectroscopic, and highresolution electron-spray ionization mass spectrometric (HR-ESIMS) techniques (for details, see Supporting Information). Further, the molecular structure of 1 was determined by singlecrystal X-ray diffraction study. The crystal structure revealed a monocationic Co(III) complex having one PF₆⁻ counteranion in the molecule (Figure 3). The cobalt center consisted of the expected bidentate N.N-chelating binding mode of the pyridylbenzimidazole ligand, with the pendant benzimidazole N-H group intact. In fact, an intramolecular N-H...O hydrogenbonding interaction between this pendant benzimidazole N-H group and the OH₂ molecule (probably came from solvent during crystallization step) at a distance of 1.850 Å was evident from

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2 (R = H); **2-Me** (R = Me)

Figure 2. Synthesis of complexes 1, 2 and 2-Me.





Figure 3. (Top) X-ray structure of 1 (*CCDC* 1973864). Selected bond lengths (Å) and bond angles (°): N1–Co1 = 1.973(9); N3–Co1 = 1.992(8); I1–Co1 = 2.599(19); N1-Co1-N3= 81.8 (3). (Bottom) X-ray structure of 2 (*CCDC* 1973865). Selected bond lengths (Å) and bond angles (°): N2–Co1 = 1.986(3); N1–Co1= 1.975(2); N4–Co1 = 1.933(3); N2-Co1-N1= 81.33 (10). In structure 1 Cp*-H and in 2 Cp*-H as well as CH₃CN hydrogens are omitted for clarity.

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the solid-state structure of the complex. The Cp* ligand was coordinated via η^5 mode, resulting in a three-legged piano-stool geometry around Co, with the sixth coordination site occupied by the iodo ligand. The N_{bim} -Co- N_{p} bite angle in 1 was found to be 81.8(3)°, while the Co-N_{bin}, Co-N_p and Co-I distances were 1.992(8) Å, 1.973(9) Å, and 2.599(19) Å respectively. At this stage, anticipating a plausible interference from the iodide ligand during future electrochemical and catalytic studies, due to its reversible dissociation in polar solvent, we synthesized a new complex 2, which is the iodo-free solvato version of complex 1 (Figure 2). Thus, the cobalt precursor, [Cp*Co(CO)I₂] was stirred with 1.1 equiv. of the corresponding pyridyl-benzimidazole ligand in the presence of 3 equiv. of the halide abstracting agent, AgOTf in CH₃CN solution at ambient temperature for 24 h. The solution eventually changed its color to red with concomitant formation of a precipitate of Agl. Upon filtering out the precipitate followed by evaporation of the resulting filtrate, a brick-red solid was obtained which upon further purification by recrystallization from a mixture of CH₃CN/diethvlether furnished pure complex 2 as dicationic triflate salt. Notably, the corresponding N-Me version of the complex 2 (2-Me) was also synthesized for comparative control study (Figure 2). Full characterization of both 2 and 2-Me was accomplished via similar NMR and HR-ESIMS techniques (see Supporting Information). Furthermore, the crystal structure of 2 disclosed a dicationic Co(III) complex supported with two $CF_3SO_3^-$ counteranions in the molecule (Figure 3). The coordination geometry around the Co center was similar to that found in complex 1, except the sixth coordination site which contained now a CH₃CN ligand instead of the iodo ligand. Additionally, in this case also, the intramolecular N-H-O interaction hydrogen-bonding between the pendant benzimidazole N-H group and the CF₃SO₃⁻ counteranion at a distance of 1.945 Å was evident. Finally, the complex 2 featured the $N_{\text{bim}}\text{-}\text{Co-}N_{\text{p}}$ bite angle of 81.33(10)°, and the Co– $N_{\text{bim}},$ Co– N_{p} and Co-N_{CH3CN} distances of 1.975(2) Å, 1.986(3) Å, and 1.933(3) Å respectively.

Next, electrochemical characterization of the complexes were performed using cyclic voltammetric technique. The cyclic voltammograms (CVs) of **1**, **2** and **2-Me** were recorded in an argon-saturated CH₃CN solution using a glassy carbon working electrode and 0.1 M [$^{n}Bu_{4}N$][PF₆] as supporting electrolyte under argon atmosphere (Figure 4A). All of the CVs featured two reversible redox couples in the cathodic region. For the complexes **1** and **2**, the first peak appeared at $E_{1/2}$ values of

-0.95 V and -0.89 V vs. ferrocene/ferrocenium (Fc/Fc+), respectively. The second redox peak for 1 appeared at -1.89 V vs Fc/Fc⁺ while for 2 it was at -1.87 V vs Fc/Fc⁺. Comparing the electrochemical responses of similar 'Cp*Co^{III}(LL)'-based complexes (LL = bidentate ligands) reported in literature,^[9] the observed two peaks in 1 and 2, were characterized for Coll/Coll and Co^{II}/Co^I redox couples. For the N-Me version 2-Me, the corresponding two couples were quasi-reversible, and were observed at -0.93 V and -1.98 V vs Fc/Fc⁺ respectively. Notably, the proposed Co^{II}/Co^I potential was more negative in 2-Me than that in 1 and 2, suggesting inefficient stabilization of highly reduced Co^I state by the relatively more electron-rich N-Me ligand. Finally, as per the Randles-Sevcik equation, the relationship between the peak currents (i_p) with the square root of the scan rate ($v^{1/2}$) was evaluated for both the redox peaks (Co^{III}/Co^{II} and Co^{II}/Co^I) in case of complex 2 (Figures 4B,C and Supporting Information). The observed linear plot in the wide

range of scan rates, 25 mVs⁻¹–500 mVs⁻¹ under argon, suggested a diffusion-controlled process.



Figure 4. [A] CVs of complexes 1, 2, and 2-Me at a scan rate of 50 mVs⁻¹. [B] Scan-rate (25 mVs⁻¹ – 500 mVs⁻¹) dependent CVs of complex 2. [C] Variation of cathodic peak currents corresponding to the Co^{III}/Co^{II} and Co^{III}/Co^{II} redox responses of complex 2 vs square root of the scan rate. Experiment conditions: concentration of complexes = 1 mM in CH₃CN, supporting electrolyte = 0.1 M solution of "Bu₄NPF₆ in CH₃CN, working electrode= glassy carbon (3 mm diameter), counter electrode= a Pt wire, reference electrode= Ag/AgCI). Ferrocene (E_{1/2}, Fc/Fc⁺ = 0.46 V vs. Ag/AgCI) was used as an external calibration standard for the CV experiments.

Complex 2 was next investigated toward the proposed activity for electrocatalytic CO₂ reduction. The CV trace of 2 measured in CO₂-saturated dry CH₃CN solution under CO₂ atmosphere exhibited interesting property. The first reduction peak essentially did not show any change but the second reduction showed a positive (anodic) shift in comparison to the CV of 2 in Ar-saturated dry CH₃CN, followed by a small catalytic wave (red trace vs black trace, Figure 5A). The shape of the peak at this potential was associated with the loss of reversibility as well. This observation near the Co^{II}/Co^I reduction, suggested interaction of the reduced Co¹ catalyst with CO₂ to form a plausible activated "Col-CO2" species followed by a weak catalysis to convert CO2.[10] The catalysis was facilitated next by adding H₂O as proton (H⁺) source to the test solutions (Figure 5B). Thus, the CV recorded in CO2-saturated 5% H2O/CH3CN (v/v) mixed solvent clearly showed a large enhancement of catalytic current, achieving a current density of approx. 13.5 mA/cm² (Figure 5B, blue trace). The large enhancement of current density was corresponding to the catalytic reduction of CO₂ to CO which was verified by bulk electrolysis and follow-up product characterization by gas chromatography (GC) (see below, and Supporting Information). Significantly, when the CV was run in Ar-saturated 5% H₂O/CH₃CN (v/v) in the absence of CO₂, the corresponding H⁺-reduction catalysis was observed but at higher negative potential than the potential for catalytic CO2reduction (Figure 5C, red trace vs blue trace). Notably, the y N-H proton of the benzimidazole ligand in complex 2 seemed to play an important role in the required proton transfer step for CO₂ reduction during catalysis in line with the previously reported local-proton effect,[11] because the complex 2-Me did not show any catalytic CO2-reduction current under similar

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Figure 5. [A] CV of 1 mM solution of complex 2 in (black) Ar-saturated dry CH₃CN under Ar, and (red) CO₂-saturated CH₃CN under CO₂. [B] Effect of addition of H₂O (1%, 3% and 5%) to CH₃CN (v/v) for 2-catalyzed CO₂ reduction. [C] Comparative CVs of 2 in Ar- and CO₂-saturated 5% H₂O/CH₃CN (v/v) solvent system. [D] Comparative CVs of 2 (blue) and 2-Me (red) in CO2saturated CH₃CN containing 5% H₂O (v/v) under CO₂. Experimental conditions: concentration of complexes = 1 mM in CH₃CN, supporting electrolyte = 0.1 M solution of ⁿBu₄NPF₆ in CH₃CN, working electrode= glassy carbon (3 mm diameter), counter electrode= a Pt wire, reference electrode= Ag/AgCl), scan rate = 50 mVs⁻¹. Ferrocene ($E_{1/2}$, Fc/Fc⁺ = 0.46 V vs Ag/AgCl) was used as an external calibration standard for all the CV experiments. [E] CV plots for complex 2 (0.1 mM) at different scan rates (50 mVs⁻¹-300 mVs⁻¹). [F] Plot of normalized catalytic current (i_{cat}/i_p) vs (scan rate)^{-1/2} for the catalytic process by complex 2. Experimental conditions were same as mentioned above. [G]. Plot of charge consumed vs time during the bulk electrolysis with complex 2 (1 mM) at -2.19 V vs Fc/Fc+ using Hg pool electrode in CO2 saturated CH₃CN solution containing 5% H₂O (v/v).

conditions in CO₂-saturated 5% H₂O/CH₃CN (Figure 5D). H⁺transfer from the hydrogen-bonding assisted H₂O molecules to Co-bound CO₂ might be a plausible scenario in line with Xiao's proposal with similar γ N–H-containing ligands around Ir center.^[12] The maximum turnover frequency, TOF_{max} of this catalytic system was roughly estimated from the linear relationship between the normalized peak catalytic current (i_{cat}/i_p) derived from scan-rate variable catalytic CV data and inverse square root of scan rate ($1/\nu^{1/2}$) according to the formula reported in literature (Figures 5E,F).^[7] The TOF_{max} was found to

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be 164 s⁻¹. A controlled potential electrolysis (CPE) experiment was performed at -2.19 V (vs Fc/Fc⁺) using a 1 mM solution of catalyst 2 and 0.1 M solution of ["Bu₄N][PF₆] as supporting electrolyte in CO₂-saturated CH₃CN solvent containing 5% (v/v) H₂O under CO₂ atmosphere (Figure 5G). GC analysis of the produced gas mixture revealed the presence of CO and H₂ in a ratio of 83:17. Similar electrolysis at -2.39 V (vs Fc/Fc⁺) resulted in the CO:H₂ ratio of 79:21, while the catalysis at a lower potential of -1.99 V (vs Fc/Fc⁺) led to the formation of traces of H₂ only without any CO generation. For the electrolysis at -2.19 V (vs Fc/Fc⁺), only traces of formic acid were detected in the liquid phase, when analysed by ¹H NMR spectroscopy and ionexchange chromatography. A Faradaic efficiency (FE) of ~70% was obtained in this experiment. The overpotential for the present catalytic CPE results obtained by 2 was calculated to be 0.78 V. A detailed study would be undertaken to optimize the same through catalytic Tafel plots.

Conclusions

In summary, a new design of Cp*Co(III)-based half-sandwich catalyst system was presented in this work for electrocatalytic CO₂ reduction in aqueous acetonitrile solution promoted by the Co(I) state, driving the selectivity toward CO as the major product. The Co(III) center in the catalyst was supported with an electron-donating Cp* ligand and a proton-responsive pyridylbenzimidazole-based N,N-bidentate ligand. In effect, the electron-rich reduced Co(I)-state expectedly preferred to activate the electrophilic carbon center of CO₂, and convert it to CO. The proton-responsive benzimidazole motif probably facilitated the required proton-transfer during the 2e/2H⁺ reduction of CO₂ to CO. Thus, for the present catalyst system, CO was the major product over the other potential 2e/2H⁺ reduced product HCOOH, in contrast to the only known similar half-sandwich CpCo(III) catalysts which produced HCOOH selectively. The present catalyst showed the Faradaic efficiency (FE) of ~70% while the overpotential for CO production was found to be 0.78 V as determined by controlled-potential electrolysis experiment. Detailed investigation including mechanistic insight will focus on optimizing the catalyst's structure as well as the catalytic conditions to improve the efficiency and selectivity further.

Experimental Section

Procedure for synthesis of complexes 1, 2, and 2-Me

Synthesis of Complex 1:

Step-1: Synthesis of ligand precursor: The ligand precursor was synthesized by a slightly modified method reported in literature.^[13] A ortho-phenylenediamine 2-pyridine mixture (2.3 mmol), carboxaldehyde (2.3 mmol) and NH₄Cl (0.70 mmol) were refluxed in 5 mL of ethanol for 5 h. After that the reaction mixture was cooled to room temperature, followed by addition of cold water to it. Upon stirring the mixture, a yellow precipitate appeared which was filtered off and washed with water. Recrystallization of the crude product with a minimum amount of ethanol containing 5 to 10 drops of water afforded the pure product as light-yellow needle-like crystals (yield 80%).1H NMR (500 MHz, CDCl₃): δ 11.09 (s, 1H), 8.68 - 8.59 (m, 1H), 8.46 (d, J = 7.9 Hz, 1H), 7.87 (ddd, J = 9.0, 6.7, 2.9 Hz, 1H), 7.45 (dd, J = 6.2, 2.7 Hz, 1H), 7.37 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 7.32 - 7.27 (m, 1H) ppm. Step-2: Synthesis of Complex 1: The reaction mixture of ligand precursor (22.5 mg, 0.115 mmol) and Cp*Co(CO)I₂ (50.0 mg, 0.105 mmol) in dry dichloromethane was refluxed

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under Ar atmosphere for 12 h. After 12 h, solvent was fully evaporated and the crude solid obtained was dissolved in minimum amount of acetonitrile followed by the addition of NH₄PF₆ (3 equiv. of solid crude). Further 2 mL of H₂O was added to precipitate the desired complex. The dark purple coloured precipitate obtained was washed with diethylether for further purification (yield 51.3 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ:9.23 (d, J = 5.50 Hz, 1H), 8.22 (d, J = 7.87 Hz, 1H), 7.84 (d, J = 7.64, 1H), 7.80 (m, 1H), 7.73 (d, J = 7.91 Hz, 1H), 7.31 (t, J = 6.48, 1H), 7.20 (dd, J = 9.04, 16.97 Hz, 2H), 1.53 (s, 15H). ¹³C{¹H} NMR (101 MHz, $CDCI_3$): $\delta = 156.19, 149.17, 148.67, 141.17, 140.52, 136.34, 126.99, 126.9$ 126.64, 125.65, 124.86, 118.12, 94.78, 29.81, 11.46. HRMS (ESI, positive ion): 516.0345 (calcd 516.0346 for [C22H24N3Col]+.

Synthesis of Complex 2:

The above-mentioned ligand precursor (22.5 mg, 0.115 mmol) as prepared during the synthesis of complex 1, was dissolved in dry acetonitrile in a Schlenk tube. Next, AgOTf (80.9 mg, 0.315 mmol) and Cp*Co(CO)I₂ (50.0 mg, 0.105 mmol) were mixed to it under argon atmosphere. After 5-10 min, a yellow-colored precipitate appeared. At the same time, the solution changed to red. The reaction mixture was kept for stirring at room temperature for next 24 h. After 24 h, the reaction mixture was filtered through Celite, and all volatiles were removed under reduced pressure. The complex was obtained as a brick-red solid by precipitation from CH_3CN and Et_2O (yield 49.7 mg, 65%). ¹H NMR (400 MHz, CD₃CN) δ : 9.38 (d, J = 5.5 Hz, 1H), 8.55 (d, J = 7.9 Hz, 1H), 8.15 (TD, J = 7.8, 1.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.78 (dd, J = 9.6, 3.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 1.96 (s, 3H), 1.30 (s, 15H).¹³C{¹H} NMR (101 MHz, CD₃CN): δ = 206.43, 154.88, 153.10, 152.80, 145.37, 143.07, 140.86, 126.57, 122.98, 122.13, 119.69, 118.54, 115.84, 97.97, 29.74, 9.13.HRMS (ESI, positive ion): 538.08 (calcd 538.0817 for [C23H24F3N3O3SC0]+.

Synthesis of Complex 2-Me:

Step-1: Synthesis of ligand precursor: The ligand precursor was synthesized by following the reported procedure.^[13] ¹H NMR (500 MHz, DMSO-d6) δ: 8.76 (d, J = 4.28 Hz 1H), 8.31 (d, J = 7.90 Hz 1H), 8.01 (td, J = 1.77, 7.78 Hz 1H), 7.73 (d, J = 7.92 Hz 1H), 7.65 (d, J = 8.07 Hz 1H), 7.52 (ddd, J = 1.04, 4.81, 7.50 Hz 1H), 7.34 (m, 1H), 7.28 (m, 1H), 4.24 (s, 3H). Step-2: Synthesis of complex 2-Me: Complex 2-Me was synthesized by following the previously described procedure. ¹H NMR (500 MHz, CD₃CN) δ :9.59 (d, J= 5.45 Hz 1H), 8.52 (d, J= 8.08 Hz 1H), 8.41 (td, J= 1.32, 7.92 Hz 1H), 8.10 (d, J= 9.21 Hz 1H), 8.00 (m, 1H), 7.89 (d, $\not=$ 9.34 Hz 1H), 7.69 (m, 2H), 4.29 (s, 3H), 1.32 (s, 15H). $^{13}\text{C}\{^{1}\text{H}\}$ NMR (101 MHz, CD_3CN) δ = 157.18, 151.73, 149.55, 142.47, 139.91, 139.29, 129.28, 127.32, 126.48, 126.27, 118.89, 114.09, 100.06, 34.04, 10.38. HRMS (ESI, positive ion): 552.096 (calcd 552.097 for [C24H26F3N3O3SC0]+.

Procedure for electrochemistry and electrocatalysis

All the electrochemical experiments were performed using CHI 620E Electrochemical Analyzer. The electrochemical setup contained a customized four-neck electrochemical cell, glassy carbon electrode (3 mm diameter) as working electrode, Pt wire as counter electrode and Ag/AgCI (saturated KCI) as reference electrode. The electrochemical cell was evacuated and filled with Ar or CO2 gas before respective experiments. A 0.1 M "Bu4NPF6 solution was used as supporting electrolyte in dry acetonitrile (or water/acetonitrile as mentioned). The solutions were saturated with CO2 gas (or Ar gas) for 90 min prior to each experiment. The glassy carbon electrode was polished before each CV run. For controlled potential electrolysis (CPE) experiment, a customized four-neck two-compartment electrochemical cell was used. The gas evolved in bulk electrolysis experiment was detected by using a gas chromatograph (GC) instrument (7890B) equipped with thermal conductivity detector (TCD).

Acknowledgements

This work was financially supported by DST-SERB (grant nos. EMR/2016/003002 and SERB/EMR-II/080063) and IISER Bhopal. I.K.P. thanks DST-SERB for NPDF and A.K. thanks IISER Bhopal for IPhD fellowship. The authors sincerely thank Professor Abhishek Dey (Indian Association for the Cultivation of Science, Kolkata, India) and his group for help in conducting a

few experiments including CPE, as well as helpful discussions. We thank the reviewers for insightful comments.

Keywords: CO2 reduction • electrocatalysis • cobalt • halfsandwich • CO.

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