Supporting Information

Electrocatalytic CO_2 Reduction to Formate by a Cobalt Phosphino-Thiolate Complex

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General

All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a dual manifold Schlenk line. The glassware was oven-dried prior to use. All solvents were degassed with nitrogen and passed through activated alumina and were purchased from commercial vendors and used without further purification.

Physical Methods.

Single-crystal X-ray Diffraction

An opaque black plate specimen was mounted for the X-ray crystallographic analysis, with approximate dimensions of 0.58 × 0.383 × 0.209 mm^3. The X-ray intensity data were measured on a XtaLAB Synergy, Dualflex, HyPix system equipped with a micro-focus sealed tube (Cu Kα λ = 1.54184 Å), a goniometer (4-axis kappa with telescopic detector sled), and a detector (HPC HyPx-6000HE 77.5 × 80.3 mm^2). Data was collected on CrysAlisPro 1.171.41.122a (Rigaku OD, 2021) and a total of 2584 frames were collected and integrated. The SHELXT 2014/5 Software Package was used to determine the structure solution with direct methods. The SHELXL Software Package was used for refinement by full-matric least-squares on F2. OLEX2-1.5 program was used for both structure solution and refinement.

Calculation of angular structural parameter τ

Calculation of the angular structural parameter, τ, was performed according to established protocol (Eq S1).[1] In Eq. S1, β and α are the two largest angles of the coordination center, where β > α. When τ approximates 0 this corresponds to the metal complex displaying a square pyramidal geometry, whereas when τ approximated 1, this corresponds to a trigonal bipyramidal geometry.

$$\tau = \frac{360° - (\beta + \alpha)}{360° - 2\cos^{-1}\left(-\frac{1}{3}\right)} \qquad \textbf{Equation S1}$$

NMR Spectroscopy

Proton NMR spectra were acquired at room temperature using Varian (Mercury 400 2-Channel, VNMRS-500 2-Channel, VNMRS-600 3-Channel, and 400-MR 2-Channel) spectrometers and referenced to the residual ^{1}H resonances of the deuterated solvent and are reported as parts per million (ppm) relative to tetramethylsilane (^{1}H: CH_3CN-d_3, δ 1.94 ppm). ^{31}P resonances are reported as parts per million relative to an external sample of 85% H_3PO_5, which is set as 0 ppm.

Variable Temperature NMR Spectroscopy

Variable temperature (VT) ^{1}H and ^{31}P-{^{1}H} NMR spectra were acquired using Varian VNMRS-600 3-Channel and referenced to the residual ^{1}H resonances of the deuterated solvent and are reported as parts per million (ppm) relative to tetramethylsilane (^{1}H: CH_3CN-d_3, δ 1.94 ppm). ^{31}P resonances are reported as parts per million relative to an external sample of 85% H_3PO_5, which is set as 0 ppm. The authentic probe temperature for each set experiment was verified using an external methanol standard. Reversibility was verified by ensuring that the spectrum of the starting material could be regenerated upon returning to room temperature. The exchange rate constant (k_c) and the free energy of activation ($\Delta G^{\ddagger}$) at coalescence were determined through the following equations[2]:

$$k_c = \frac{\pi \Delta v}{\sqrt{2}} \qquad \textbf{Equation S2}$$

$$\Delta G^{\ddagger} = aT_c[10.319 + \log(T_c/k_c)] \qquad \textbf{Equation S3}$$

where Δv is the maximum peak separation of the associated resonances displaying exchange in Hz, T_c is the temperature at coalescence in K, and a is 4.575×10^{-3} kcal mol^{-1} K^{-1} s^{-1}. As these equations are only valid if the exchanging nuclei are not coupled. Only the Δv (58.4 Hz at 238.15 K) and the T_c (277.4 K) of the exchanging bound methylene linkers of the triphos ligand were considered.

X-ray Photoelectron Spectroscopy

XPS data were collected using a Kratos AXIS Ultra instrument. The monochromatic X-ray source was the Al K α line at 1486.6 eV. High-resolution detailed scans, with a resolution of ~0.1 eV, were collected on individual XPS lines of interest at a pass energy of 20. The sample chamber was maintained at $< 2 \times 10^{-8}$ Torr. The XPS data were analyzed using the CasaXPS software.

Electrochemistry

Cyclic Voltammetry (CV)

Electrochemistry experiments were carried out using a Pine potentiostat. The experiments were performed in a single compartment electrochemical cell under a nitrogen atmosphere using a 3 mm diameter glassy carbon electrode as the working electrode and a platinum wire as auxiliary electrode. The reference electrode was a Ag wire in a 0.1 M electrolyte solution in CH_3CN and was separated from the rest of the solution by a Vycor tip. Ohmic drop was compensated using the

positive feedback compensation implemented in the instrument. All experiments in this paper were referenced relative to ferrocene (Fc) with the $Fc^{0/+}$ couple at 0.0 V and all cycles were started at 0 V vs Ag/Ag^{+} of the pseudoreference Ag electrode unless otherwise stated. All electrochemical experiments were performed in acetonitrile (CH_3CN) with 0.5 mM analyte concentration and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All electrochemical experiments were performed with *iR* compensation using the current interrupt (RUCI) method in AfterMath. The diffusing nature of the **[Co(triphos)(bdt)]$^{+/0}$** is described in a previous paper.[3] Randles-Sevcik analysis was not implemented for **[Co(triphos)(bdt)]$^{0/-}$** due to the couple's irreversibility.

H/D Kinetic Isotope Effect (KIE)

Calculation of KIE values was derived from previous reports and adapted for this study (Equation S4).[4]

$$KIE = k_{H_2O}/k_{D_2O} = \left(\frac{slope_{H_2O}}{slope_{D_2O}}\right)^2 \qquad \textbf{Equation S4}$$

$$k \propto \left(\frac{i_{cat}}{i_p}\right)^2 \qquad \textbf{Equation S5}$$

As the observed reaction rate constant (k) is proportional to the square of i_{cat}/i_p (Equation S5), KIE values can be obtained by squaring the ratio of the slope of i_{cat}/i_p as a function of $[H_2O]$ or $[D_2O]$, respectively (Equation S4). In this study, i_{cat} is the peak current observed under catalytic conditions at the catalytic couple – the **[Co(triphos)(bdt)]$^{0/-}$** couple in this case, in the presence of substrate and i_p is the peak current at a reversible couple – the **[Co(triphos)(bdt)]$^{+/0}$** couple in this case.

Controlled Potential Electrolysis.

Controlled potential electrolysis (CPE) measurements to determine Faradaic efficiency were conducted in a sealed two-chambered H cell with two chambers separated by a fine porosity glass frit. The first chamber held the working and reference electrodes in 40 mL of electrolyte solution (0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN) and the second chamber held the auxiliary electrode in 21 mL of electrolyte solution. The reference electrode was a Ag wire in a 0.1 M $TBAPF_6$ electrolyte solution in CH_3CN and was separated from the rest of the solution by a Vycor tip. CPE experiments were performed in 0.1 M $TBAPF_6$ solution in CH_3CN with 0.5 mM of analyte. Glassy carbon plate electrodes (6 cm × 1 cm × 0.3 cm; Tokai Carbon USA) were used as the working and auxiliary electrodes. The working compartment was sparged with N_2 or CO_2 for 15 minutes before the experiment.

Calculation of Faradaic efficiency was performed according to Equation S6 below, which considers only the total amount of products formed and the total amount of charge passed during the electrolysis experiment. Turnover number (TON) was determined according to Equation S7 below, which considers the bulk catalyst loading in solution. This provides an underestimate of TON, as only the amount of catalyst within the electrochemical diffusion layer is active during

electrolysis studies. A total of three runs were performed for each condition studied, leading to consistent behavior. The reported FE% and TONs are an average of these values.

$$Faradaic\ Efficiency\ = \frac{total\ mols\ of\ product\ formed}{theoretical\ \ mols\ of\ product\ formed\ according\ to\ charge\ passed}\ x\ 100 \qquad \textbf{Equation S6}$$

$$Turnover\ Number = \frac{total\ mols\ of\ product}{total\ mols\ of\ catalyst} \qquad \textbf{Equation S7}$$

Calculation of the standard reduction of potential of CO_2 to HCOOH was adapted from previous reports and adapted to this study (Equation S8).[4,5]

$$E^0_{CH_3CN}\left(\frac{CO_2}{HCOOH}\right) = E^0_{aq}\left(\frac{CO_2}{HCOOH}\right) - \frac{RTln10}{F}pK_{a(CH_3CN)}(H_2CO_3) - \frac{RT}{2F}\ln\left(\frac{K_{h,CO_2,aq/g}}{K_{h,CO_2,CH_3CN/g}}\right) - \frac{2\Delta G^0_{t,H^+,CH_3CN/aq} - \Delta G^0_{t,HCOOH,CH_3CN/aq}}{2F} \qquad \textbf{Equation S8}$$

$$E^0_{aq}\left(\frac{CO_2}{HCOOH}\right) = -0.197\ V\ vs\ NHE$$
$$\Delta G^0_{t,H^+,CH_3CN/aq} = -0.48\ eV$$
$$\Delta G^0_{t,HCOOH,CH_3CN/aq} = -0.063\ eV$$
$$K_{h,CO_2,aq/g} = 29$$
$$K_{h,CO_2,CH_3CN/g} = 3.6$$

When H_2O is added to the system, carbonic acid is employed as the proton source as it is the strongest acid in solution as a result of hydration of CO_2 in the presence of H_2O (pK_a = 17.03). Potential was referenced vs $Fc^{0/+}$ couple with $E_{Ag/AgCl}$ = 0.210 V vs NHE and $E_{Fc}^{0/+}$ = 0.51 V vs Ag/AgCl and further adjusted with the inter-liquid junction potential ($E_{L/CH3CN}$ = 0.099 V). Considering this, the standard reduction potential of $CO_2/HCOO^-$ in acetonitrile is calculated to be -1.40 V vs $Fc^{0/+}$ in the aforementioned conditions.

The overpotential for the CO_2RR to formate (η) is determined by taking the difference of the standard reduction potential of CO_2/HCOOH in acetonitrile vs $Fc^{0/+}$ relative to the applied CPE potential (Equation S9).

$$\eta = \left|E^0_{CH_3CN}\left(\frac{CO_2}{HCOOH}\right) - E_{electrolysis}\right| \qquad \textbf{Equation S9}$$

Wash tests were performed by removing the post electrolysis solution of the working compartment from the H-cell via syringe under a positive pressure of CO_2 and rinsing the chamber of the electrolysis cell three times with acetonitrile. The cell was maintained under 1 atm of CO_2, and the electrode was not removed from the cell during these washings to prevent O_2-exposure. No visible material is present on the electrode following CPE, and negligible current densities are observed in the wash test relative to any of the preparative CPE studies. As such, these studies strongly suggest that the observed reactivity is due to the solubilized catalyst, as no gaseous or liquid products are observed following the wash procedure.

Gas Chromatography

Gaseous products were quantified using a Shimadzu GC-2010-Plus instrument equipped with a BID detector and a Restek ShinCarbon ST Micropacked column. In a typical experiment, 2 mL of gas were withdrawn from the headspace of the electrochemical cell with a gas-tight syringe and injected into the instrument. Calibration plots were prepared with multiple injections of syngas standards purchased from Praxair, Inc.

Formate Detection and Quantification through ^{1}H NMR Spectroscopy

Detection: Initial detection of formate was performed according to literature precedent.[6] Following CPE studies, a 5 mL aliquot of each electrolysis solution was collected and extracted with 2 mL D_2O. The aqueous portion was acidified with one drop HCl and tested for formate by ^{1}H NMR spectroscopy.

Quantification: Quantification of formate was performed according to the following procedure. A NaOH solution (0.25 mL of 0.075 mM) was added to 5 mL aliquot of the electrolysis solution, and the resulting solution was subsequently reduced under pressure and mild heating until dry. Two 1 mL aliquots of D_2O were added sequentially to the dry solid, and the resulting mixture was mixed vigorously, and sonicated for 5 minutes, before being filtered through a glass frit. One mL from the filtered solution was transferred to an NMR sample tube. A capillary containing a solution of DMF in D_2O was added to the NMR sample tube. A ^{1}H NMR spectrum (128 scans with a 10 s relaxation time) was taken for each sample in a Varian 400-MR 2-Channel instrument (See Figure S49 for example). Integration ratios were then taken of the formate proton (δ = 8.47 ppm) and the DMF formyl proton (δ = 7.96 ppm). The formate concentration of the electrolysis solution was then determined using the calibration plot described below.

Calibration: Standard formate solutions were prepared with concentrations of 0.1 M, 0.01 M, 0.001 M, and 0.0001 M. A ^{1}H NMR spectrum was taken for each solution with the aforementioned DMF/D_2O capillary, and a calibration curve was generated consisting of the integration ratios of formate to DMF against the known formate concentration.

Formate Detection and Quantification through Ion Chromatography

Ionic products were quantified using a Thermo Fisher Scientific Dionex ICS-2100-Plus equipped with a DS6 heated conductivity detector, a Dionex IonPac AS11-HC column, and a Dionex AS-AP autosampler. In a typical experiment, 0.1 mL of electrolysis solution was drawn from the working electrode of the electrochemical cell with a 1 mL syringe and diluted 1:10 with deionized

H_2O. The sample is filtered to remove any insoluble material and is again diluted 1:10 with deionized H_2O. The sample is then injected into the instrument with calibration standards of formate and oxalate via the autosampler for detection and quantification (See Figure S50 for example). Calibration plots were prepared to quantify the amount of formate and oxalate present in test samples.

Evans' Method

Evans' method was applied according to literature precedent.[7] A solution of **[Co(triphos)(bdt)]^0** (1 mM) was prepared in 50:1 deuterated solvent : protio-solvent and a sealed capillary was prepared containing 50:1 deuterated solvent : protio-solvent. The splitting between the solvent peaks was measured by a ^{1}H NMR spectroscopy study (Figure S5), and reported equations were applied to calculate μ_{eff}. A magnetic susceptibility of 1.80 μB was calculated, which corresponds to one unpaired electron for **[Co(triphos)(bdt)]^0**.

Computational Methods

Density Functional Theory (DFT)

All calculations were run using the Q-CHEM program package.[8] Geometry optimizations were run with unrestricted DFT calculations at the B3LYP level of theory using a 6-31G* basis set.[9–14] Solvation effects were considered using the SMD implicit solvent model, with acetonitrile as the modeled solvent.[15] Single point energy calculations were run on each computed structure with a larger 6-31+G* basis set for all atoms and energies from these calculations were used throughout. Vibrational frequency calculations were run from each computed structure to confirm the lack of imaginary frequencies in geometry optimized structures and one imaginary frequency in transition state structures. Hydricity values were calculated according to the following equation (S10):

$$G_{MH} - G_M - G_{H-} = \Delta G_{H-} \qquad \textbf{Equation S10}$$

where G_{MH} is the free energy of the computed metal hydride structure, G_M is the free energy of the complex by itself (without the hydride), and G_{H-} is the free energy of the free hydride. Calculations of standard reduction potentials were derived from previous reports and adapted for this study (Equation S11)[16]:

$$E^0_{X^a/X^{a+n}} = E^0_{Fc/Fc^+} - \frac{\Delta G_{X^a/X^{a+n}}}{nF} \qquad \textbf{Equation S11}$$

where $E^0{}_{X^a/X^{a+n}}$ is the standard reduction potential of X^a/X^{a+n} couple vs the ferrocene/ferrocenium couple in acetonitrile, $\Delta G_{X^a/X^{a+n}}$ is the change in the Gibbs free energy of the X^a/X^{a+n} couple, F is 23.0605 kcal mol^{-1} V^{-1}, *n* is the number electrons consumed in the conversion of X^a to X^{a+n}, and $E^0{}_{Fc}{}^{0/+}$ is the absolute standard reduction potential of ferrocene/ferrocenium couple in acetonitrile (-4.804 V).[17,18] This method was validated via comparing the experimentally obtained ΔE^0 for both **[Co(triphos)(bdt)]$^{+/0}$** and **[Co(triphos)(bdt)]$^{0/-}$** to the calculated ΔE^0 from computationally computed ΔG values for the respective redox conversion (Table S7). Both experimental and

computationally derived values show good agreement (deviation no more than 110 mV), indicating the validity of this method towards calculating the standard reduction potential of short-lived intermediates within the proposed mechanism.

Synthetic Methods

Synthesis of [Co(triphos)(bdt)][18-crown-6(K)]

In a glove box, 47 mg (0.057 mmol) of the synthesized cobalt[1,1,1-tris(diphenylphosphinomethyl)ethane][benzene-1,2-dithiolate] (complex **Co(triphos)(bdt)**, where triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, and bdt = benzene-1,2-dithiolate), was added to a 20 mL scintillation vial. The vial was then charged with 12 mL of THF and allowed to stir at room temperature until all the powder dissolved. KC_8 (23 mg, 0.17 mmol) was added to the vial, whereupon the reaction mixture slowly turned from an amber color to a dark yellow color. The reaction mixture was then stirred for 1 hr at room temperature, after which the resulting solution was filtered. 18-crown-6 (15 mg, 0.057 mmol) was added to the filtered reaction mixture and the solution was allowed to stir overnight at room temperature. The volatiles were removed under vacuum and black crystals (60% yield) were generated upon recrystallization of the resulting solid by vapor diffusion of *n*-pentane into a THF solution. ^{1}H NMR (500 MHz, CH_3CN-d_3, -30 °C): δ 8.10 (s, 2H, meta-P(C_6H_5)$_2$), δ 7.68 (s, 4H, ortho-P(C_6H_5)$_2$), 7.26 (s, 4H, para-P(C_6H_5)$_2$), 7.22 (t, 8H, ortho/meta-P(C_6H_5)$_4$), 7.18 (t, 8H, ortho/meta-P(C_6H_5)$_4$), 7.17 (t, 4H, para-P(C_6H_5)$_4$), 7.14 (m, 2H, $C_6H_4S_2$), 6.39 (m, 2H, $C_6H_4S_2$), 3.51 (s, 24H, 18-crown-6), 2.26 (d, 2H, PCH_2), 2.19 (d, 2H, PCH_2), 2.04 (s, 2H, PCH_2), 0.23 (s, 3H, CH_3). ^{31}P-{^{1}H} NMR (202 MHz, CH_3CN-d_3, -30 °C): δ 41.8 (br s, 2P), -28.2 (br s, 1P).

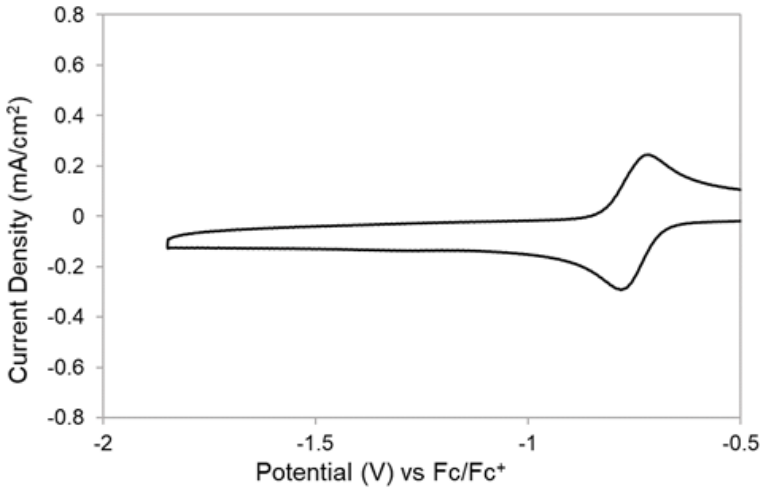


Figure S1. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2. Scan rates is 0.1 V/s.

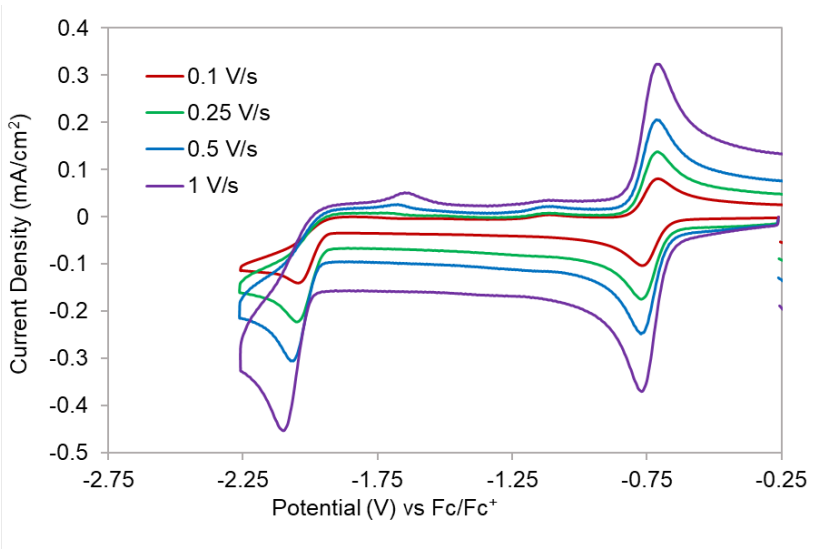


Figure S2. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2. Scan rates vary from 0.1 to 1 V/s.

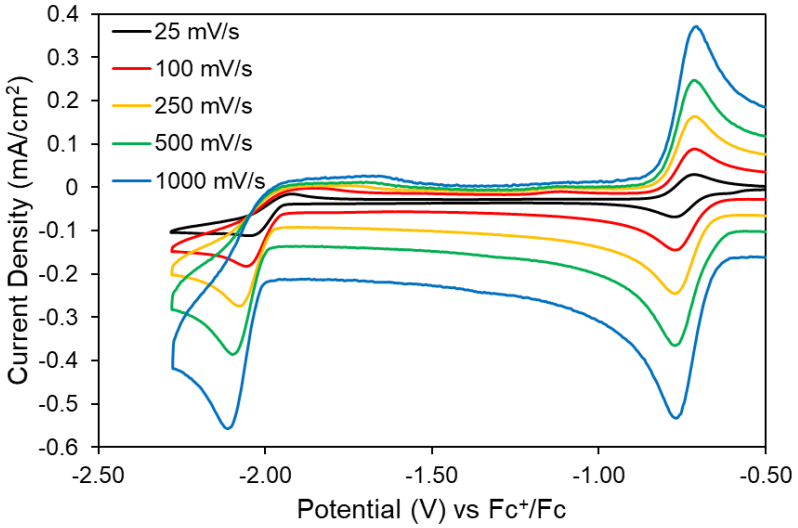


Figure S3. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2. Scan rates are 25 (black), 100 (red), 250 (yellow), 500 (green), and 1000 (blue) mV/s.

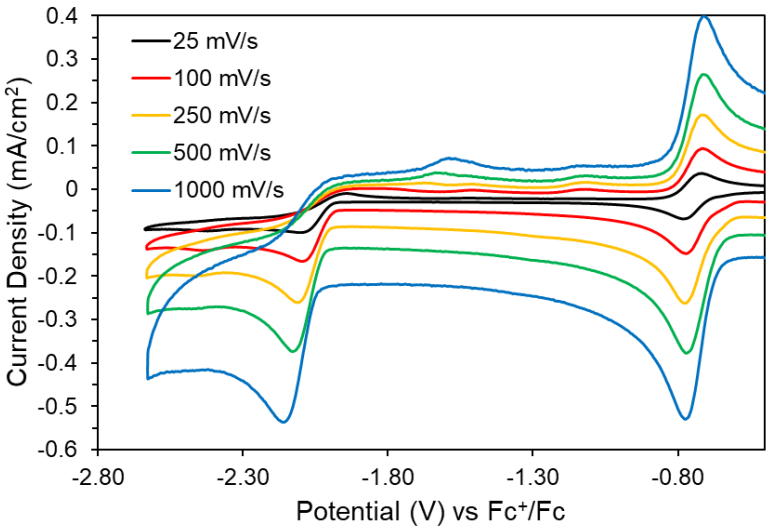


Figure S4. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^{+}$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2. Scan rates are 25 (black), 100 (red), 250 (yellow), 500 (green), and 1000 (blue) mV/s.

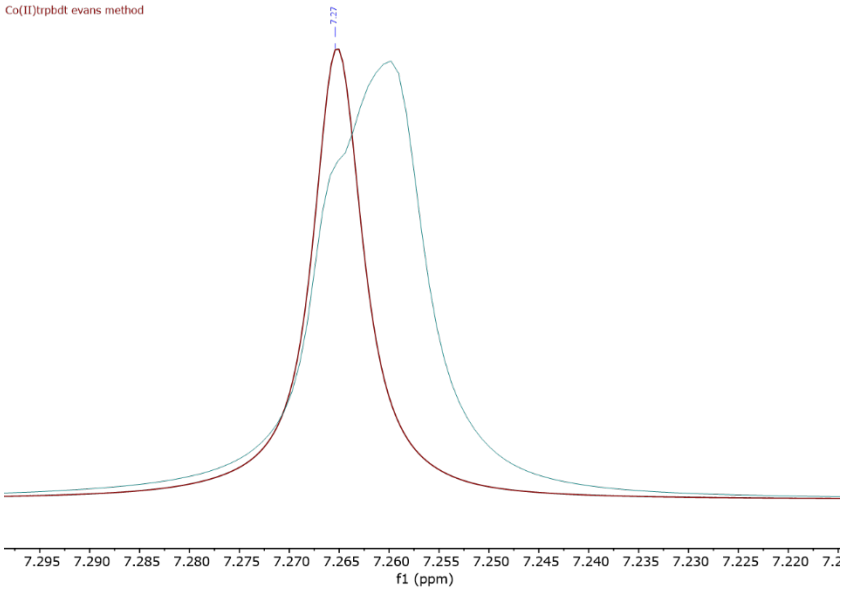


Figure S5. Overlay of 600 MHz ^{1}H NMR spectra of **[Co(triphos)(bdt)]^{0}** in $CDCl_3$. Spectrum without capillary (red) and spectrum with capillary (blue). A magnetic susceptibility of 1.80 μB was calculated, which corresponds to one unpaired electron for **[Co(triphos)(bdt)]^{0}**.

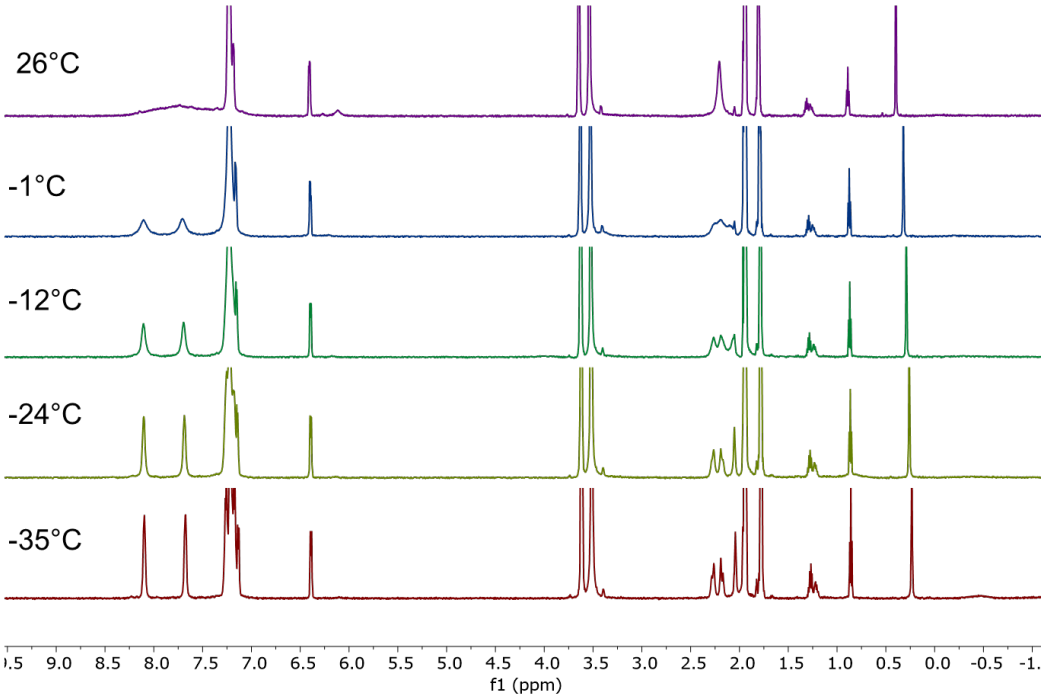


Figure S6. Overlay of 600 MHz ^{1}H NMR spectra of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3. Temperature varied between 26 and -35 °C.

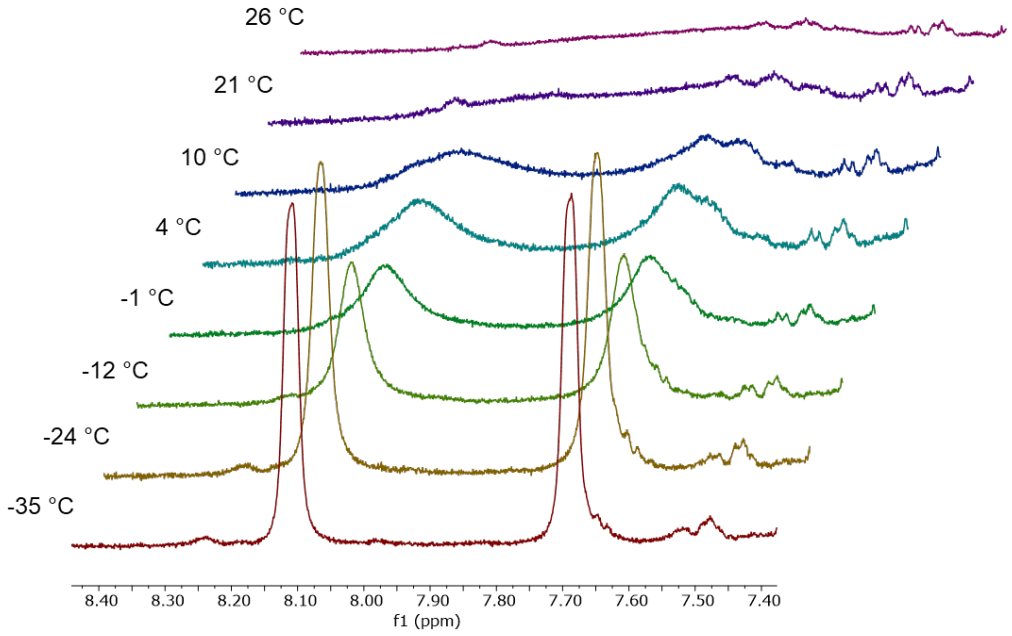


Figure S7. Overlay of 600 MHz ^{1}H NMR spectra of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3. Temperature varied between 26 and -35 °C.

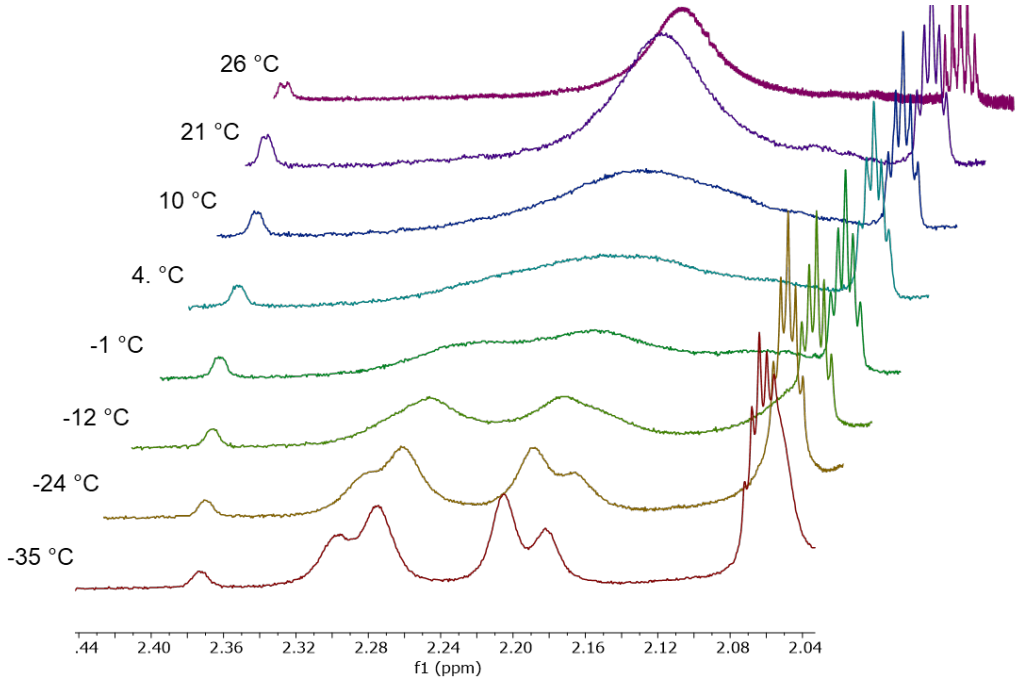


Figure S8. Overlay of 600 MHz ^{1}H NMR spectra of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3. Temperature varied between 26 and -35 °C.

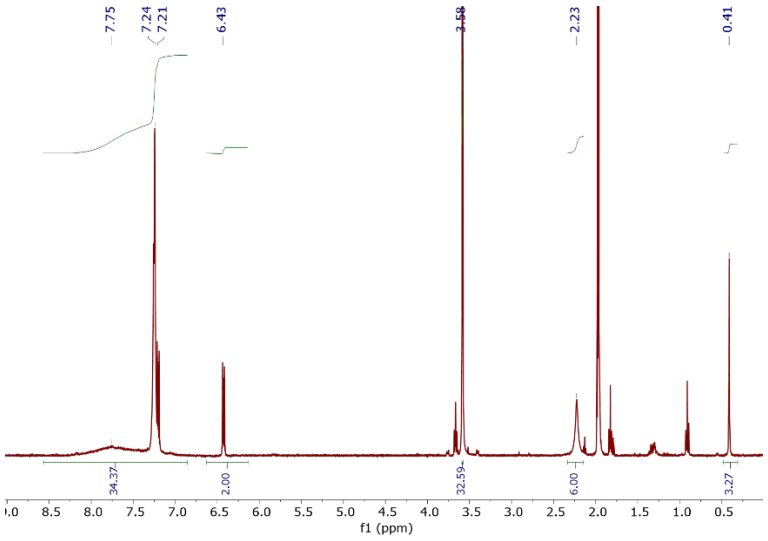


Figure S9. 600 MHz ^{1}H NMR spectrum of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3 at 26 °C.

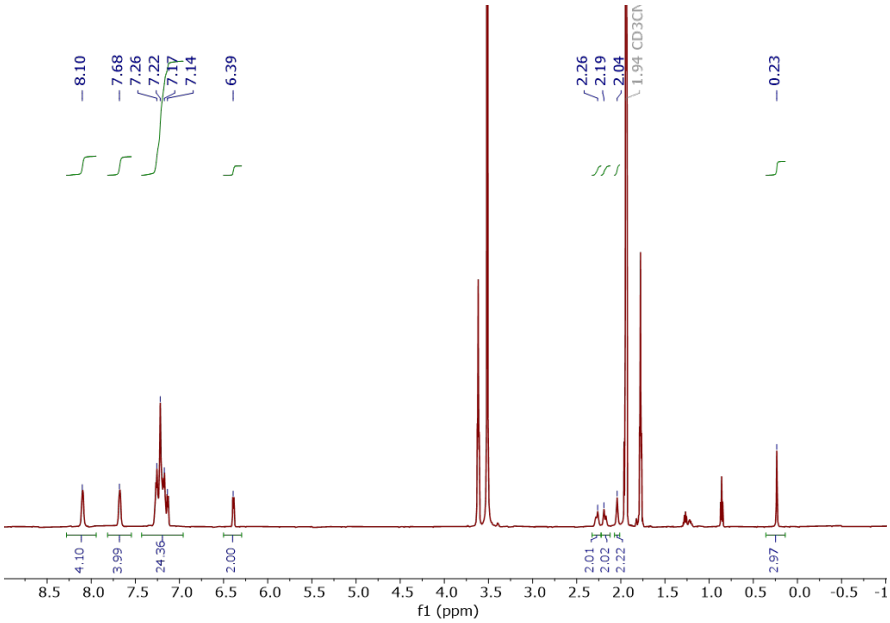


Figure S10. 600 MHz ^{1}H NMR spectrum of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3 at -35 °C.

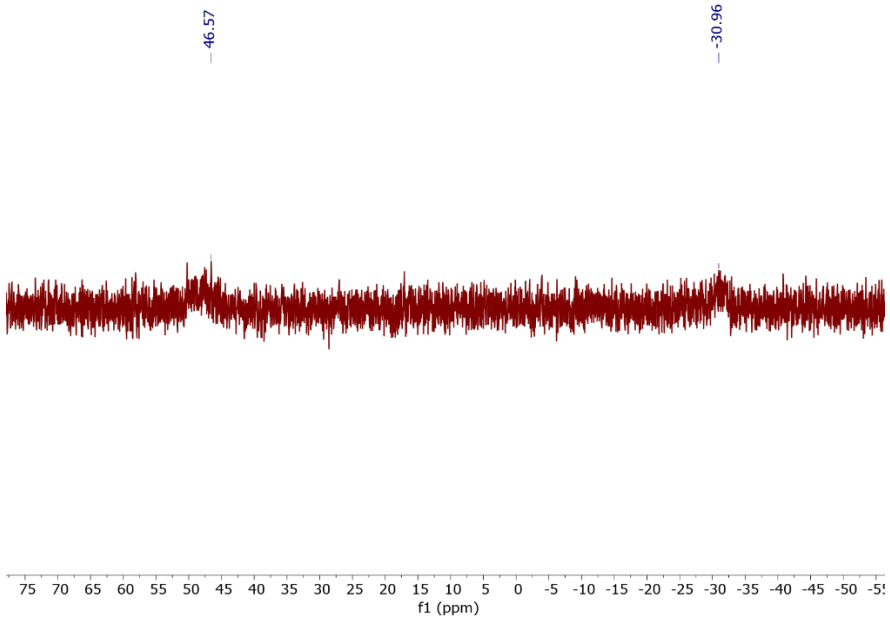


Figure S11. 600 MHz ^{31}P-{^{1}H} NMR spectrum of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3 at 26 °C.

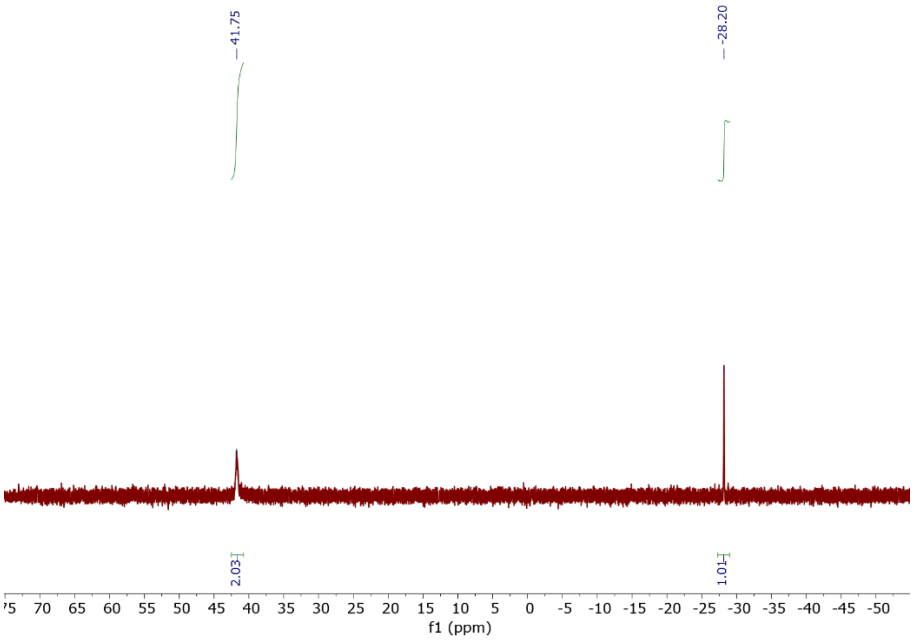


Figure S12. 600 MHz ^{31}P-{^{1}H} NMR spectrum of **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-d_3 at -35 °C.

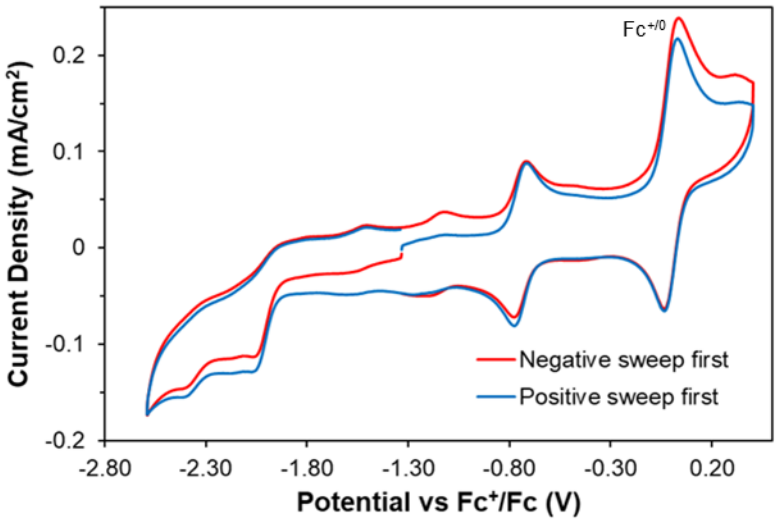


Figure S13. Cyclic voltammograms of 0.5 mM of the isolated **[Co(triphos)(bdt)][K(18-crown-6)]** in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2 and in the presence of ferrocene started at the open-circuit potential of -1.3 V. Scan rates are 100 mV/s.

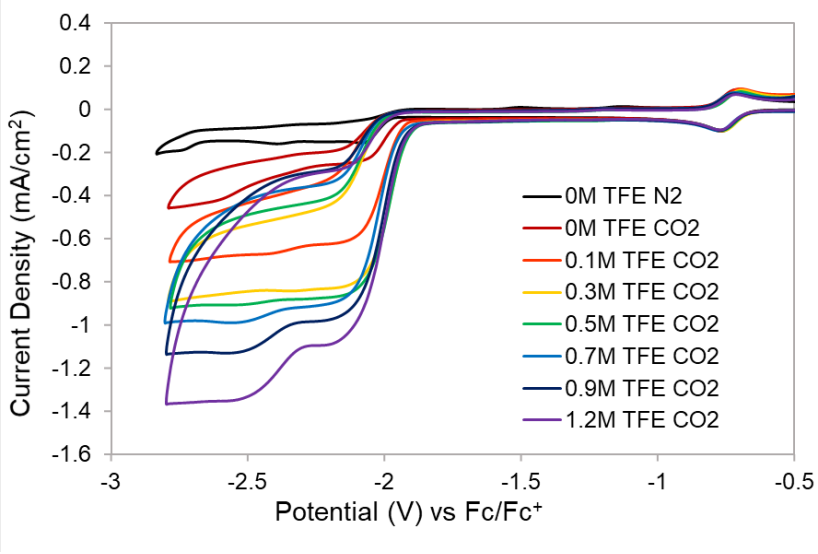


Figure S14. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^{+}$ in a CH_3CN solution containing 0.1 M [*n*Bu_4N][PF_6] under CO_2 with increasing concentrations of TFE. Scan rate is 100 mV/s.

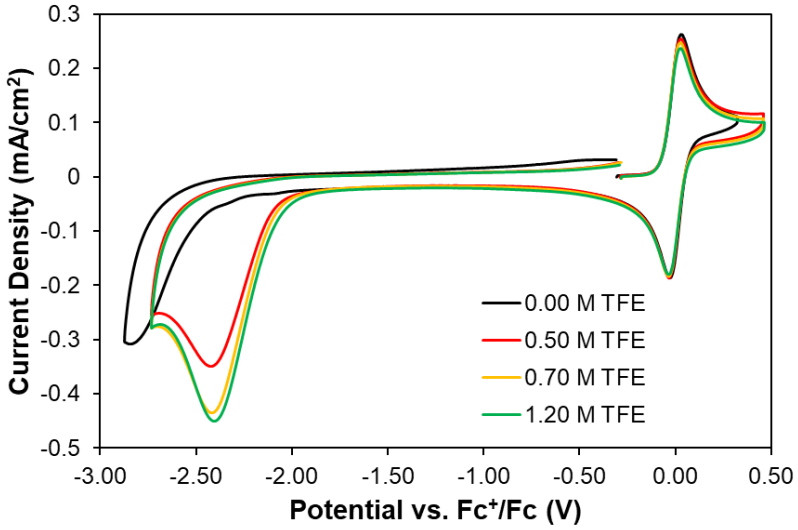


Figure S15. Cyclic voltammograms of a glassy carbon electrode in a CH_3CN solution containing 0.1 M [*n*Bu_4N][PF_6] under an atmosphere of CO_2 in the presence of ferrocene, and increasing amounts of 2,2,2-trifluoroethanol (TFE), such as 0 M (black), 0.50 M (red), 0.70 M (orange), and 1.20 M (green). Scan rates are 100 mV/s.

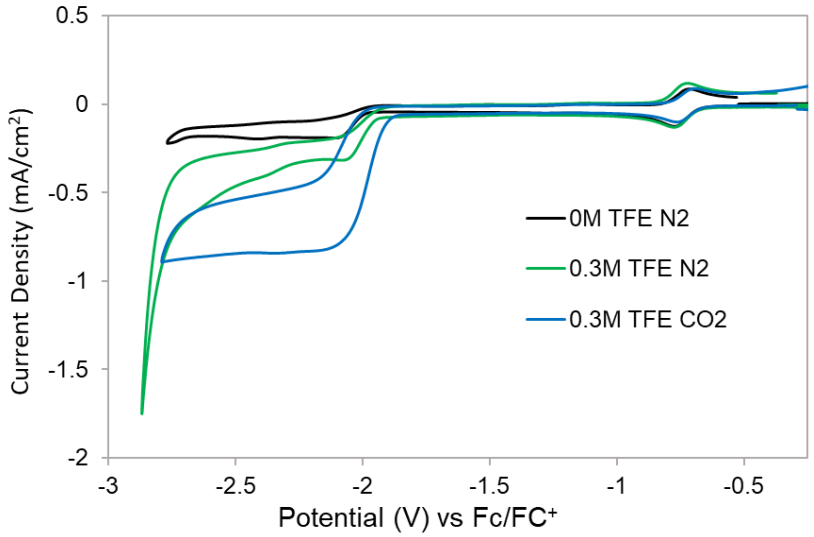


Figure S16. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu_4N][PF_6] under N_2 (black) and in the presence of 0.3 M TFE under an atmosphere of N_2 (green) and CO_2 (blue). Scan rate is 100 mV/s.

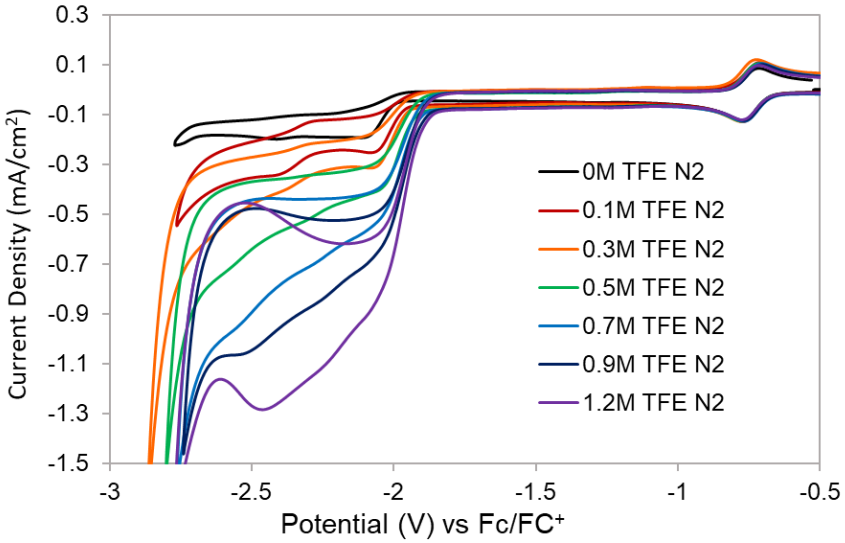


Figure S17. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under N_2 with increasing concentrations of TFE. Scan rate is 100 mV/s.

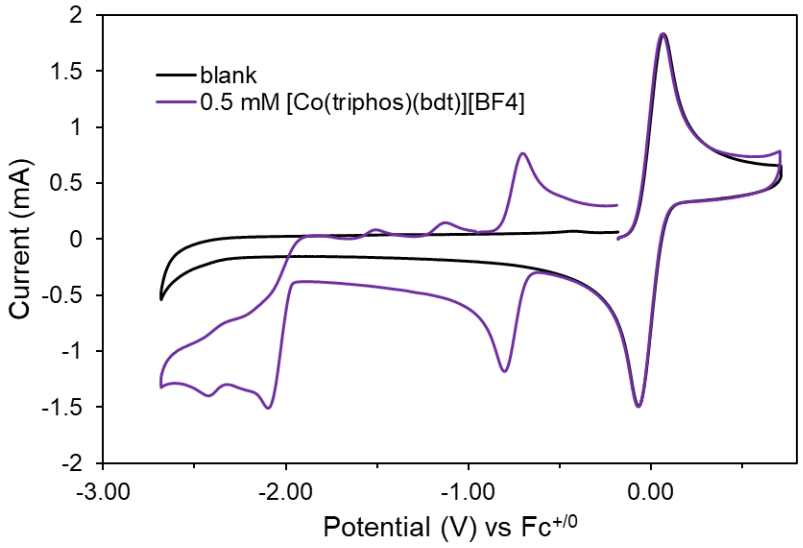


Figure S18. Cyclic voltammograms of a blank CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2 (black) and a 0.5 mM **[Co(triphos)(bdt)][BF_4]** CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2 (purple) and ferrocene. Scan rates are 100 mV/s.

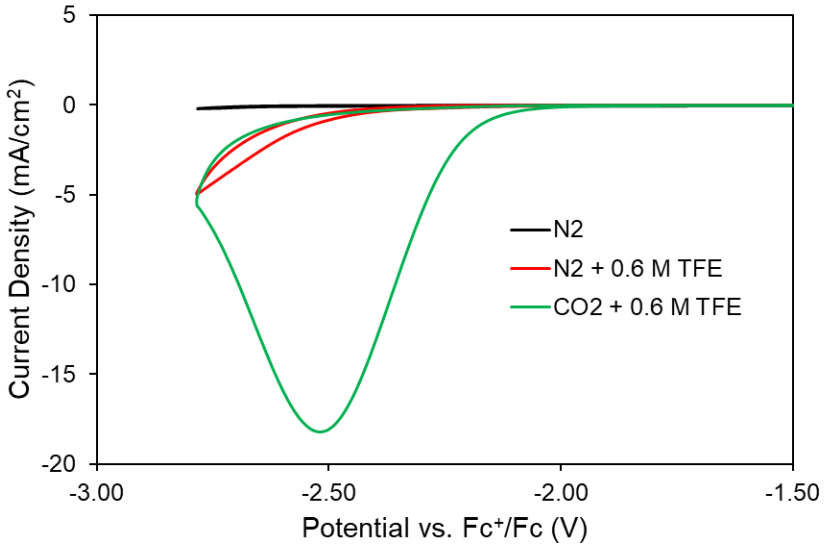


Figure S19. Cyclic voltammograms of a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2 (black), addition of 0.6 M TFE (red), and then under an atmosphere of CO_2 and 0.6 M TFE. Scan rates are 100 mV/s.

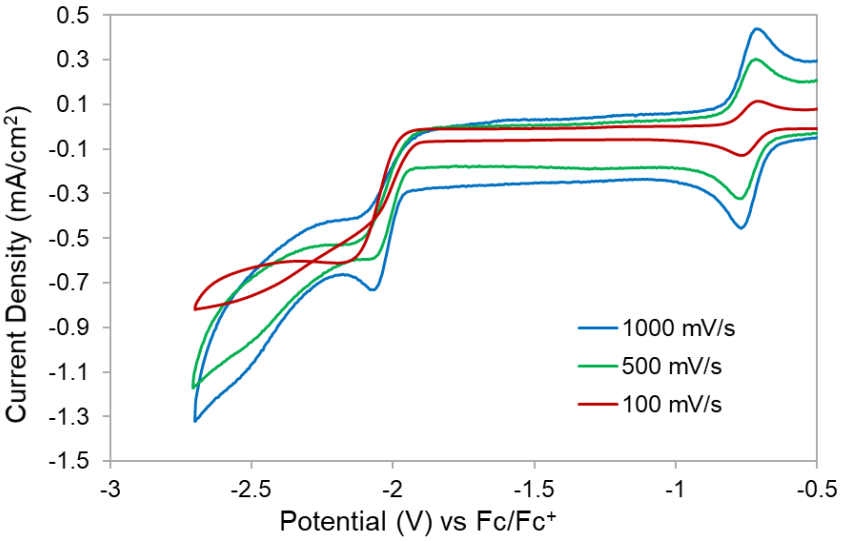


Figure S20. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] and 0.5 M H_2O under an atmosphere of CO_2. Scan rates vary from 0.1, 0.5, and 1 mV/s.

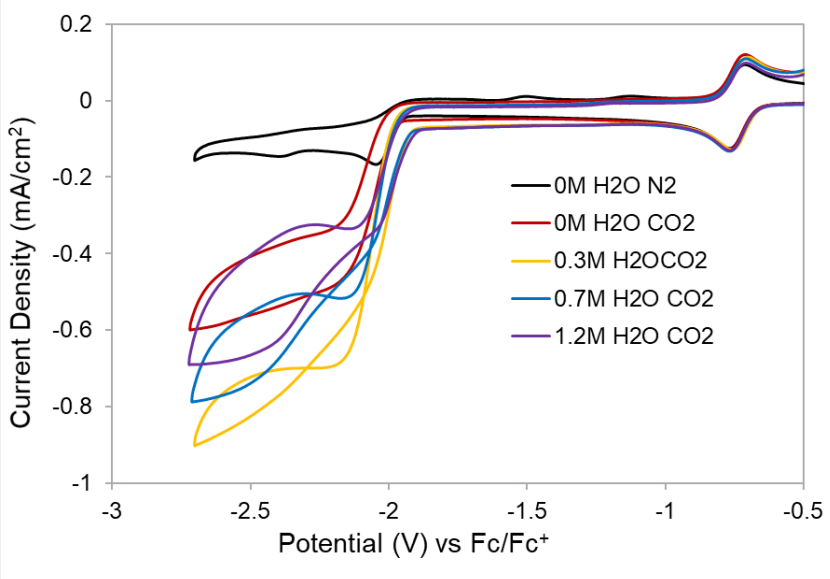


Figure S21. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under CO_2 with increasing concentrations of H_2O. Scan rate is 100 mV/s.

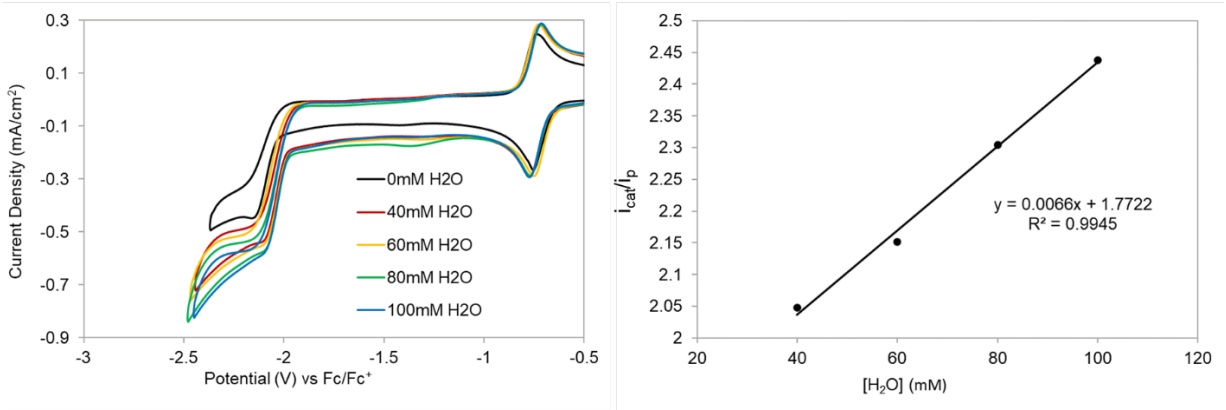


Figure S22. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under CO_2 with increasing concentrations of H_2O. Scan rate is 500 mV/s.

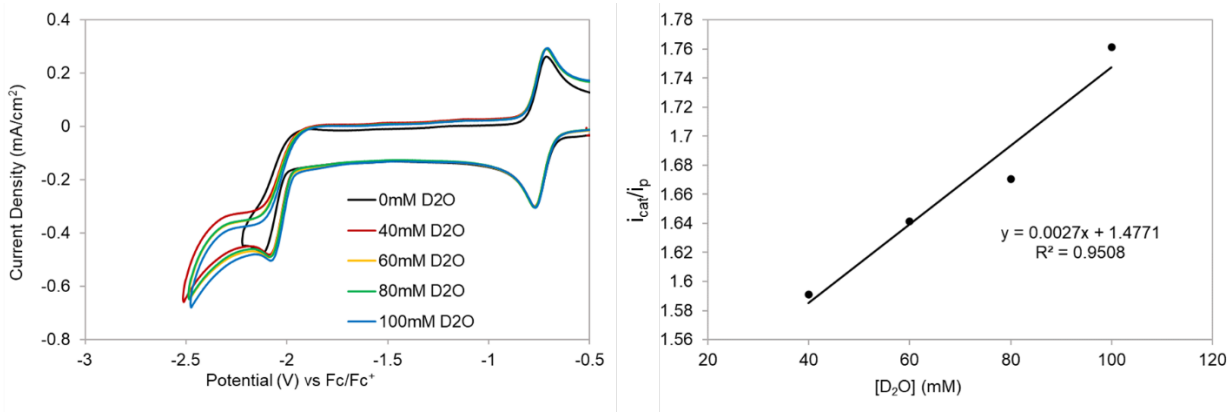


Figure S23. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under CO_2 with increasing concentrations of D_2O. Scan rate is 500 mV/s.

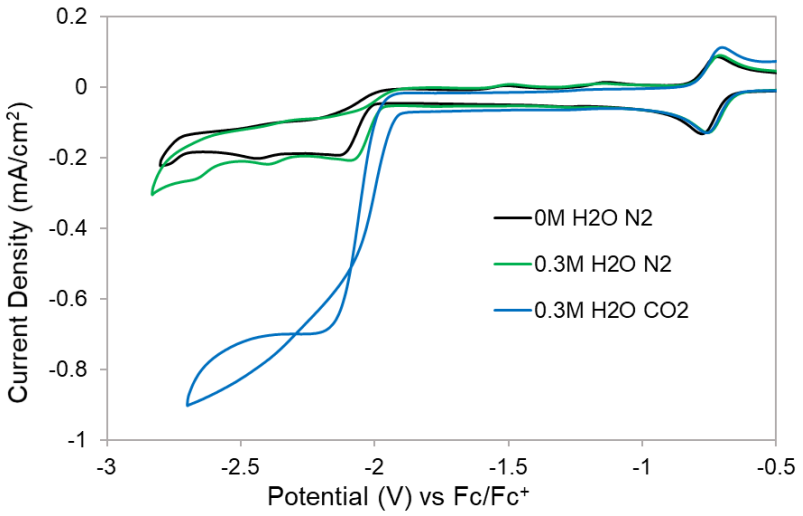


Figure S24. Cyclic voltammograms of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu_4N][PF_6] under N_2 (black) and in the presence of 0.3 M H_2O under an atmosphere of N_2 (green) and CO_2 (blue). Scan rate is 100 mV/s.

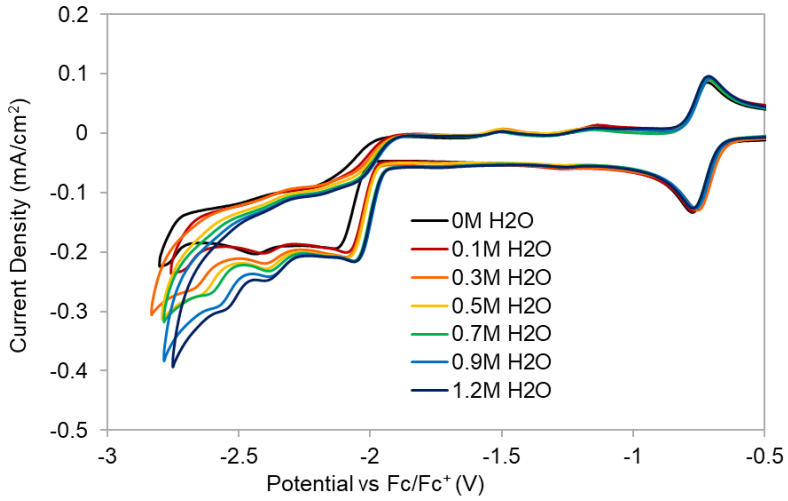


Figure S25. Cyclic voltammograms of 0.5 mM **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [$n$$Bu_4N$][$PF_6$] under N_2 with increasing concentrations of H_2O. Scan rate is 100 mV/s.

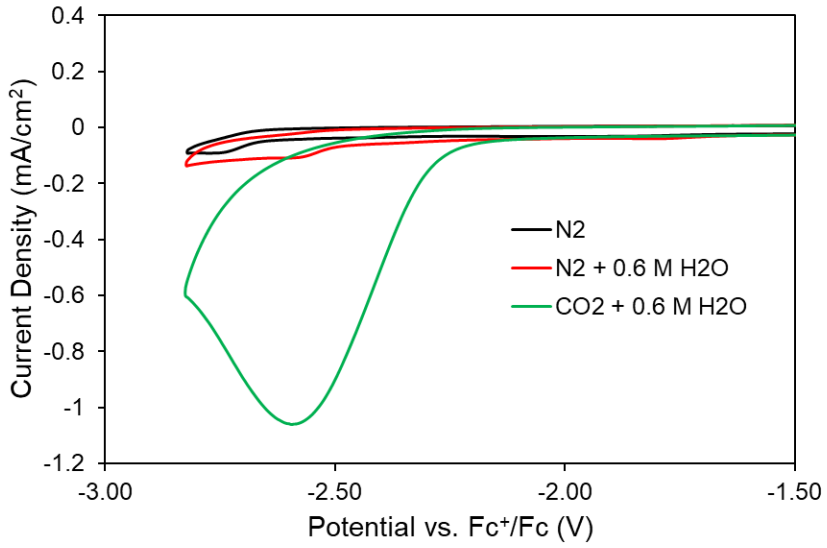


Figure S26. Cyclic voltammograms of a CH_3CN solution in the absence of the studied complex, containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of N_2 (black), addition of 0.6 M H_2O (red), and then under an atmosphere of CO_2 and 0.6 M H_2O. Scan rates are 100 mV/s.

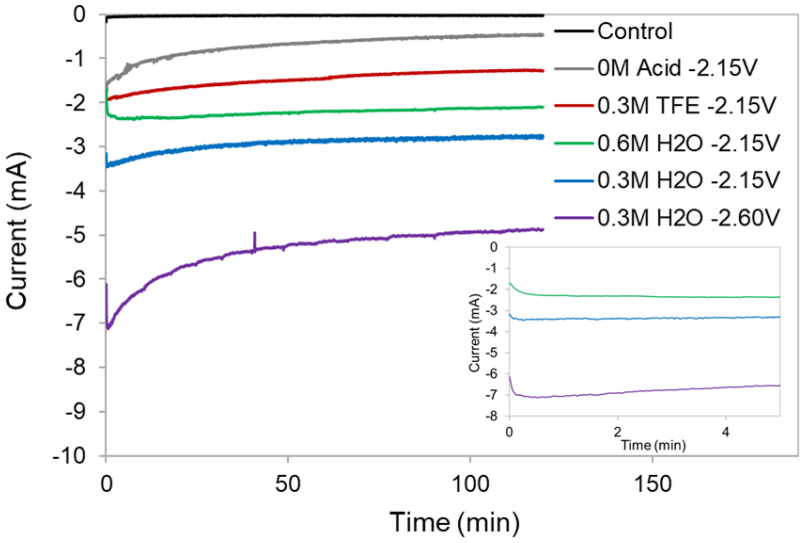


Figure S27. Controlled potential electrolysis traces measured under 1 atm of CO_2 and analyzed via gas chromatography (gas phase) and ^{1}H NMR spectroscopy (liquid phase). In all cases a solution of 0.5 mM **[Co(triphos)(bdt)]$^+$** in acetonitrile with 0.1 M [nBu$_4$N][PF_6] supporting electrolyte was held at a potential of either -2.15 V or -2.60 V vs $Fc^{0/+}$ for 2 hours in the presence of no added proton source (grey), 0.3 M TFE (red), 0.6 M H_2O (green), or 0.3 M H_2O (blue and purple). A control experiment was also conducted (black) where electrolysis was performed at -2.15 V vs $Fc^{0/+}$ for 2 hours in the presence of 0.3 M H_2O in the absence of catalyst. Inset displays current in first few minutes of the electrolysis experiments.

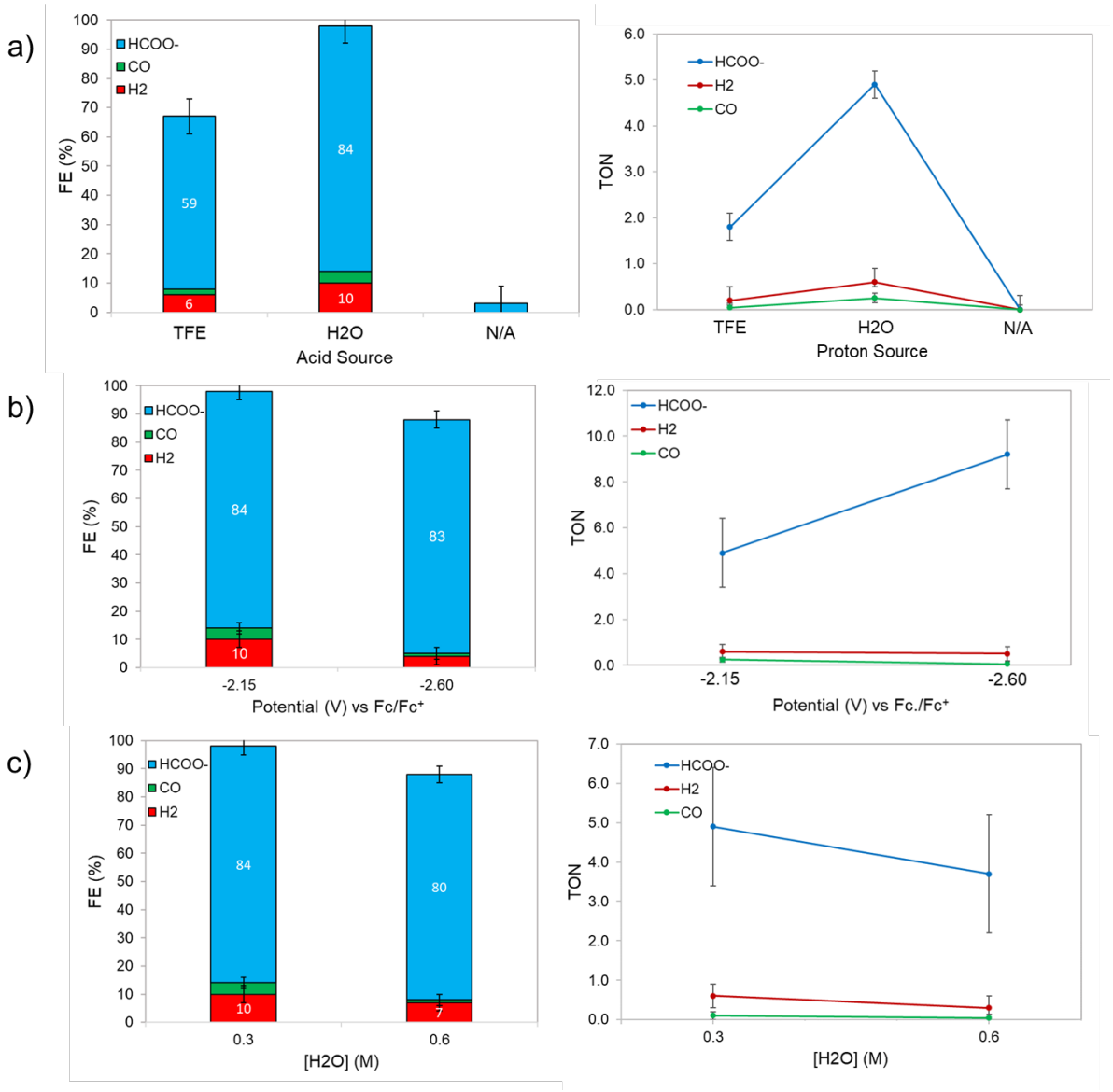


Figure S28. Comparison of the controlled potential electrolysis results from Figure S27 – Faradaic efficiencies (FE%) and Turnover numbers (TONs) quantified via gas chromatography (gas phase) and ^{1}H NMR spectroscopy (liquid phase) – in the presence of: a) 0.3 M TFE, 0.3 M H_2O, or no exogenous proton source (N/A) at -2.15 V vs $Fc^{0/+}$, b) 0.3 M H_2O at potentials of -2.15 or -2.60 V vs $Fc^{0/+}$, and c) 0.3 or 0.6 M H_2O at -2.15 V vs $Fc^{0/+}$. All electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^{+}$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of CO_2.

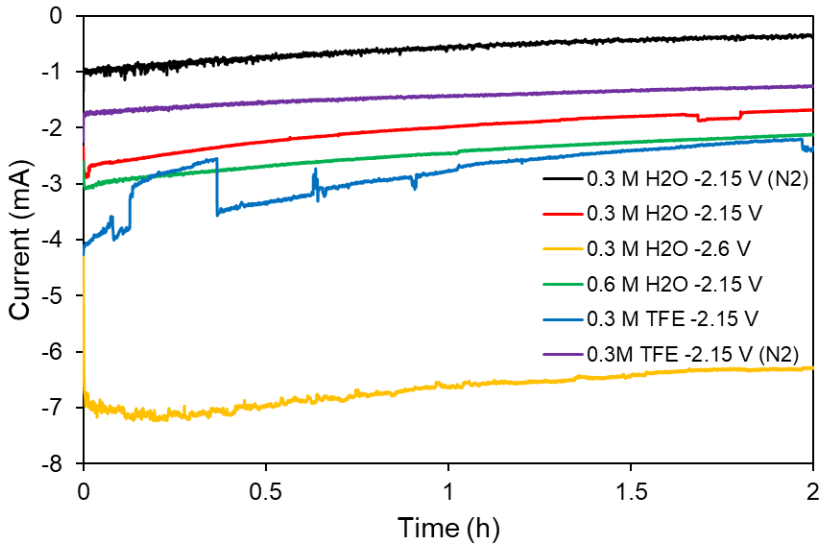


Figure S29. Summary of the controlled potential electrolysis traces used for the electrolysis of **[Co(triphos)(bdt)]**$^+$ in the presence of CO_2 and a proton source and quantified via gas and ion chromatography for the gas and liquid phase, respectively. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under an atmosphere of CO_2 or N_2.

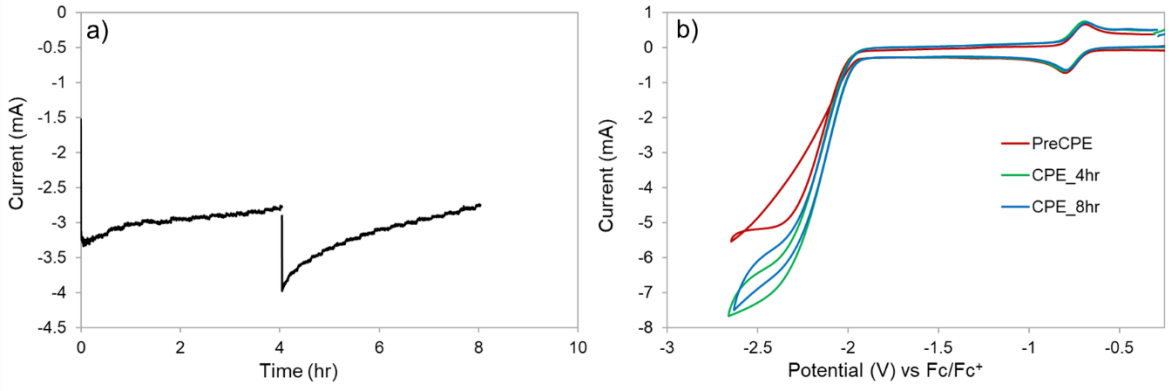


Figure S30. a) Controlled potential electrolysis trace measured under 1 atm of CO_2 in an acetonitrile solution of 0.5 mM **[Co(triphos)(bdt)]**$^+$ with 0.1 M [nBu$_4$N][PF$_6$] supporting electrolyte, which was held at a potential of -2.15 V vs $Fc^{0/+}$ for 8 hour in the presence of 0.3 M H_2O and analyzed via gas chromatography (gas phase) and ^{1}H NMR spectroscopy (liquid phase). Electrolysis was paused at the 4 hr mark to adjust for potential drift of the Ag/Ag$^+$ pseudo reference electrode. b) Cyclic voltammograms of electrolysis solution performed before electrolysis (PreCPE), at 4 hr mark of CPE (CPE_4hr), and at 8 hr mark of CPE (CPE_8hr).

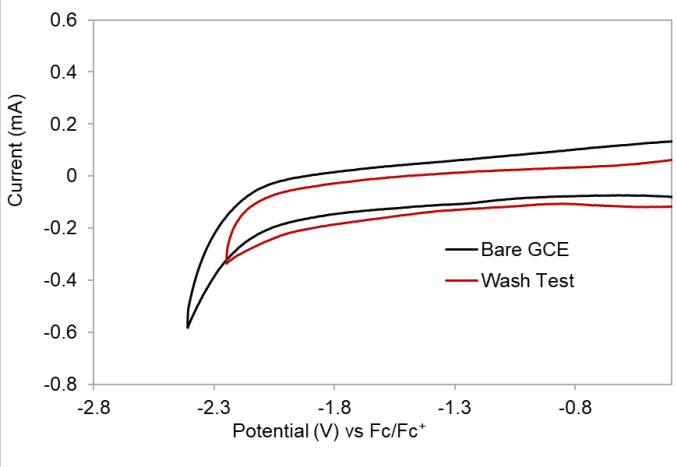


Figure S31. Cyclic voltammograms of a bare glassy carbon electrode (black – labeled "bare GCE") and a washed post-electrolysis glassy carbon electrode (red – labeled "wash test") in an acetonitrile solution containing 0.1 M [*n*Bu$_4$N][PF$_6$] and 0.3 M H_2O under an atmosphere of CO_2. The post-electrolysis glassy carbon electrode (wash test) investigated here was generated upon performing an electrolysis with a glassy carbon electrode for 8 hours at -2.15 V under CO_2 and in a CH_3CN solution with 0.5 mM of **[Co(triphos)(bdt)]**$^+$, 0.3 M H_2O, and 0.1 M [*n*Bu$_4$N][PF$_6$], analyzed via gas chromatography (gas phase) and ^{1}H NMR spectroscopy (liquid phase), and subsequently washed with clean CH_3CN under anaerobic conditions to prevent O_2 exposure of the electrode.

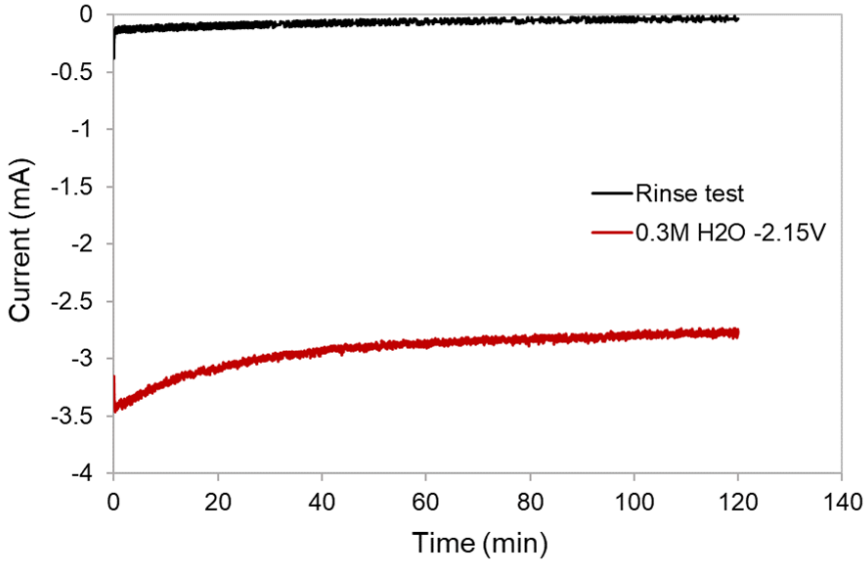


Figure S32. Comparison of the controlled potential electrolysis trace of a washed post-electrolysis glassy carbon electrode in an acetonitrile solution containing 0.1 M [*n*Bu$_4$N][PF$_6$] (black – labeled "rinse test") to that of the CPE trace of 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in CH_3CN with 0.1 M [*n*Bu$_4$N][PF$_6$] (red). Both electrolysis in this figure were performed at a potential of -2.15 V vs

$Fc^{0/+}$ for 2 hours in the presence of 0.3 M H_2O and 1 atm of CO_2 and analyzed via gas chromatography (gas phase) and ^1H NMR spectroscopy (liquid phase). The post-electrolysis glassy carbon electrode (rinse test) investigated here was generated upon performing an electrolysis with a glassy carbon electrode for 8 hours at -2.15 V under CO_2 and in a CH_3CN solution with 0.5 mM of **[Co(triphos)(bdt)]**$^+$, 0.3 M H_2O, and 0.1 M [nBu$_4$N][PF_6], and subsequently washed with clean CH_3CN under anaerobic conditions to prevent O_2 exposure of the electrode.

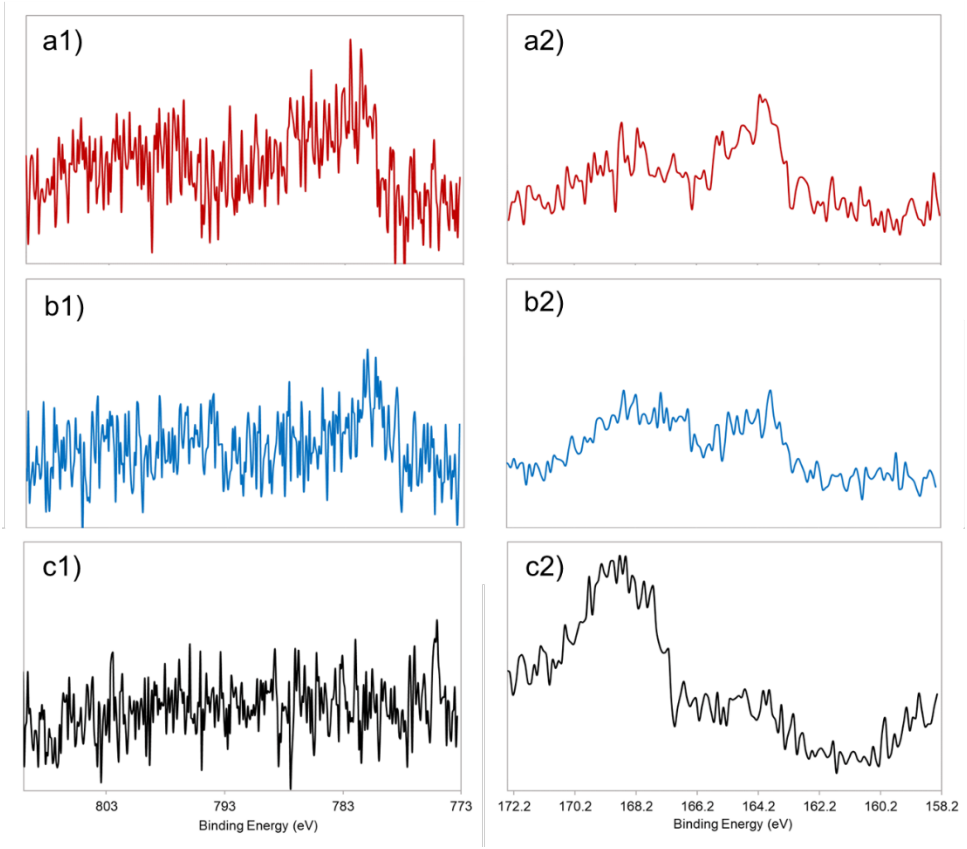


Figure S33. High-resolution X-ray photoelectron spectroscopy spectra of 1) Co 2p and 2) S 2p region of a a) washed post-electrolysis glassy carbon electrode, b) electrode immersed in 0.5 mM acetonitrile solution of **[Co(triphos)(bdt)]**$^+$ without applying any potential, and c) bare electrode. Peak at ~169 eV in the S 2p region is associated with the Si 2p plasmon loss structure from residual Si associated with Si-based polishing powder. The post-electrolysis glassy carbon electrode investigated here was generated upon performing an electrolysis with a glassy carbon electrode for 8 hours at -2.15 V under CO_2 and in a CH_3CN solution with 0.45 mM of **[Co(triphos)(bdt)]**$^+$, 0.3 M H_2O, and 0.1 M [nBu$_4$N][PF_6], and subsequently washed with clean CH_3CN.

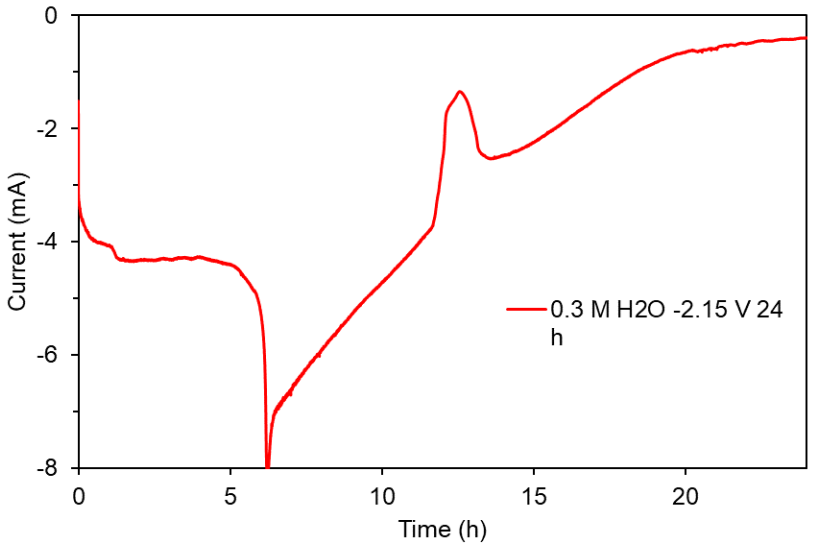


Figure S34. CPE trace used for the electrolysis of **[Co(triphos)(bdt)]**$^{+}$ in the presence of CO_2 and 0.3 M H_2O at -2.15 V. Electrolysis was performed with 0.5 mM of **[Co(triphos)(bdt)]**$^{+}$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under an atmosphere of CO_2 for 24 hours and analyzed via gas chromatography (gas phase) and ion chromatography (liquid phase). After 5 hours, a slight shift in potential is observed, resulting in an increase, followed by a decrease in current. The shift in potential is most likely caused by an increased formate concentration, which changes the potential of the Ag/Ag^{+} pseudo reference electrode.

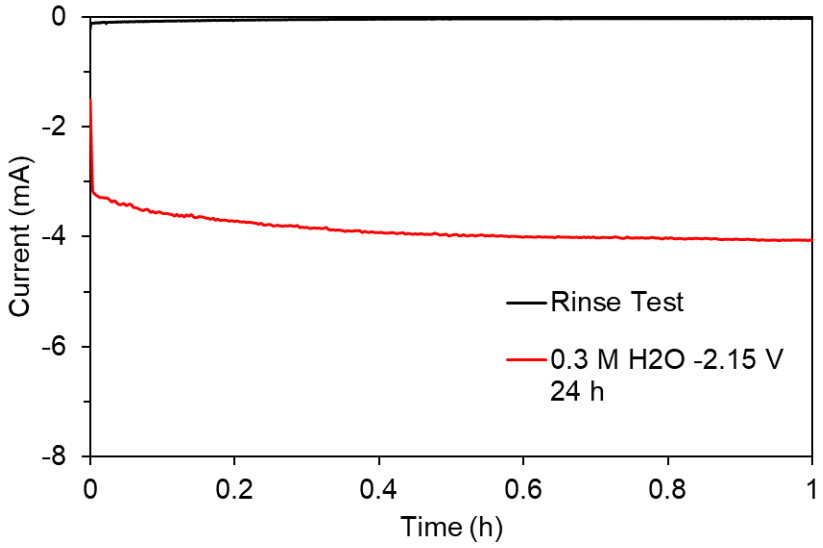


Figure S35. Comparison of the controlled potential electrolysis trace of a washed post-electrolysis glassy carbon electrode in an acetonitrile solution containing 0.1 M [nBu$_4$N][PF$_6$] (black – labeled "rinse test") to that of the CPE trace of 0.5 mM of **[Co(triphos)(bdt)]**$^{+}$ in CH_3CN with 0.1 M [nBu$_4$N][PF$_6$] (red). Rinse test electrolysis in this figure was performed at a potential of -2.15 V

vs $Fc^{0/+}$ for 1 hour in the presence of 0.3 M H_2O and 1 atm of CO_2 and analyzed via gas chromatography (gas phase) and ion chromatography (liquid phase). The post-electrolysis glassy carbon electrode (rinse test) investigated here was generated upon performing an electrolysis with a glassy carbon electrode for 24 hours at -2.15 V under CO_2 and in a CH_3CN solution with 0.5 mM of **[Co(triphos)(bdt)]**$^+$, 0.3 M H_2O, and 0.1 M [nBu$_4$N][PF_6], and subsequently washed with clean CH_3CN under anaerobic conditions to prevent O_2 exposure of the electrode.

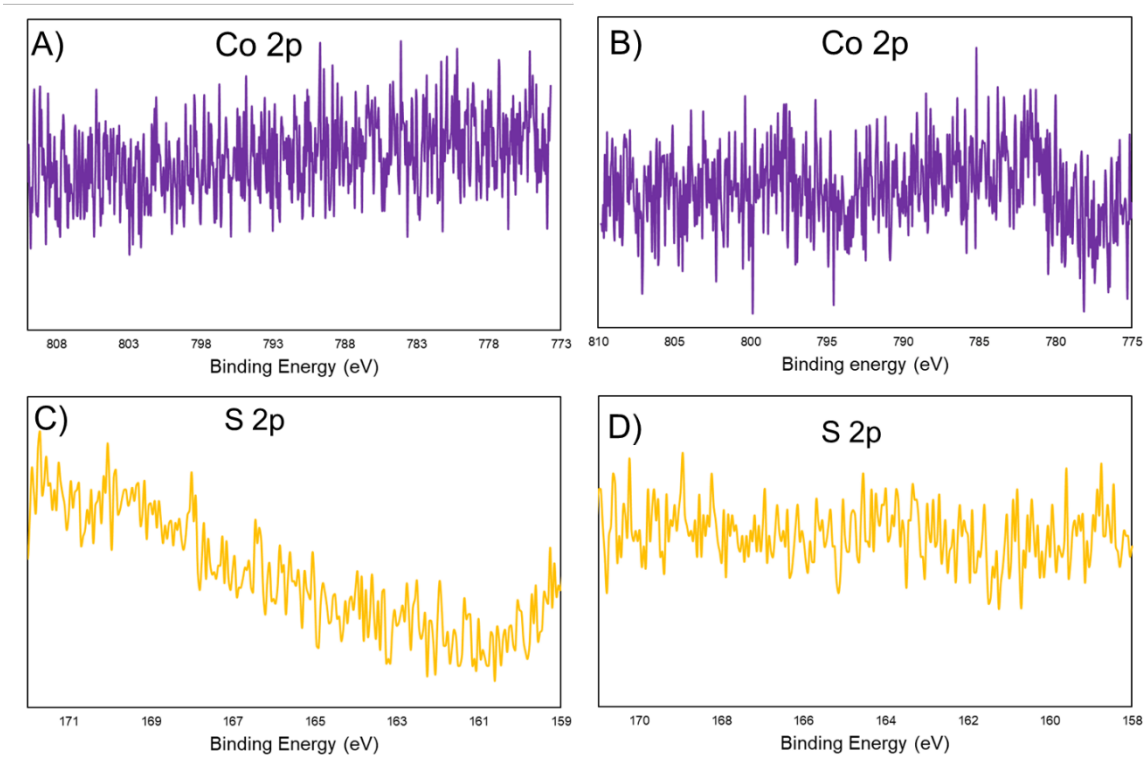


Figure S36. High-resolution X-ray photoelectron spectroscopy spectra of the Co 2p region collected from a) a bare electrode, and b) a washed post-electrolysis glassy carbon electrode, and the S 2p region collected from c) a bare electrode, and d) a washed post-electrolysis glassy carbon electrode. Peak at ~169 eV in the S 2p region is associated with the Si 2p plasmon loss structure from residual Si associated with Si-based polishing powder. The post-electrolysis glassy carbon electrode investigated here was generated upon performing an electrolysis with a glassy carbon electrode for 24 hours at -2.15 V under CO_2 and in a CH_3CN solution with 0.5 mM of **[Co(triphos)(bdt)]**$^+$, 0.3 M H_2O, and 0.1 M [nBu$_4$N][PF_6], and subsequently washed with clean CH_3CN.

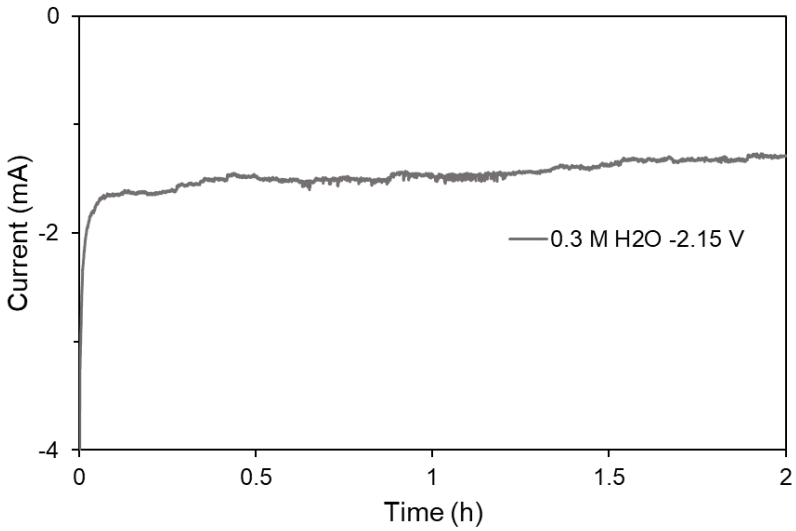


Figure S37. CPE trace of the electrolysis of 0.5 mM **[Co(triphos)(bdt)]**$^{+}$ in the presence of CO_2 and 0.3 M H_2O performed at -2.15 V using a Hg pool working electrode. Electrolysis was performed in a CH_3CN solution containing 0.1 M [*n*Bu_4N][PF_6] under an atmosphere of CO_2 for 2 hours and the products generated were analyzed via gas and ion chromatography for the gas and liquid phase, respectively.

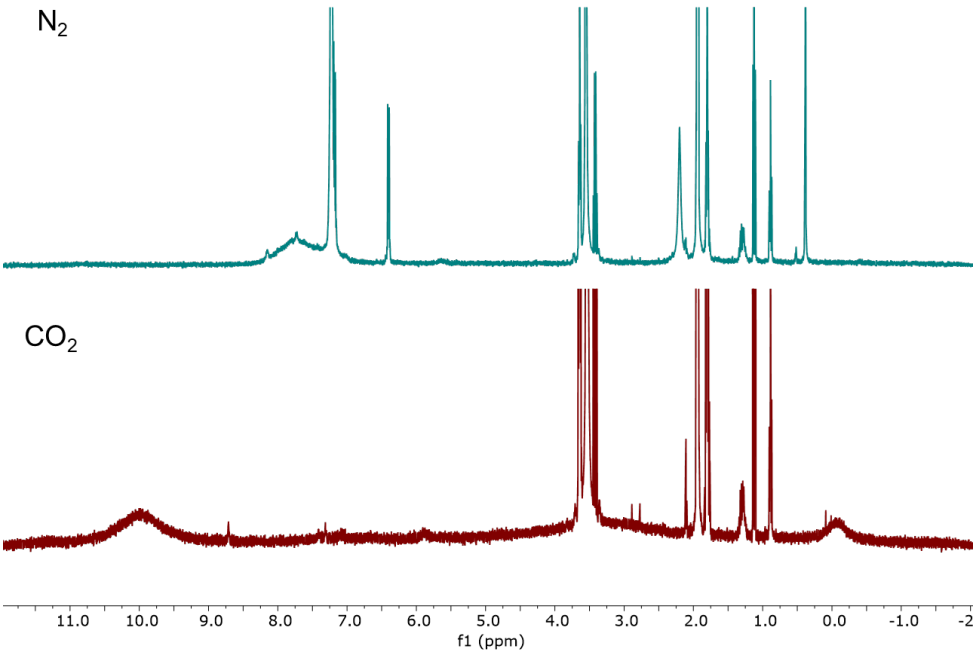


Figure S38. 600 MHz ^{1}H NMR spectra of the chemically synthesized **[Co(triphos)(bdt)][K(18-crown-6)]** in acetonitrile-*d*$_3$ exposed to 1 atm of N_2 (top) or CO_2 (bottom).

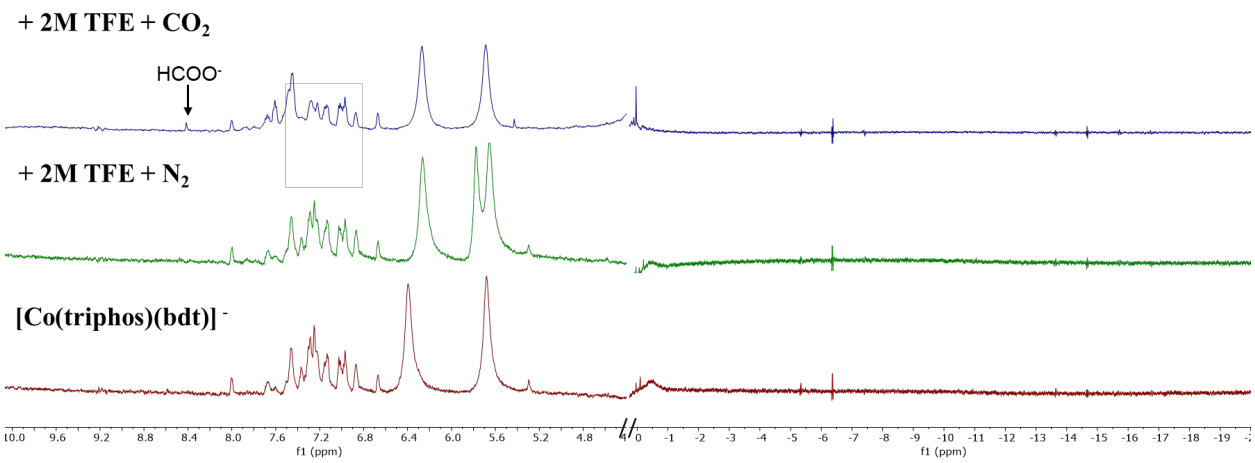


Figure S39. Overlay of 600 MHz ^{1}H NMR spectra of **[Co(triphos)(bdt)]**$^{-}$ in acetonitrile-d_3 collected at -30 °C. Red trace corresponds to the **[Co(triphos)(bdt)]**$^{-}$ from electrolysis cell, green trace corresponds to 2 M TFE addition under N_2, and blue trace corresponds to 2 M TFE addition under CO_2. The spectrum range from δ 4.7-0.1 ppm is omitted due to large proton resonances attributed to $TBAPF_6$.

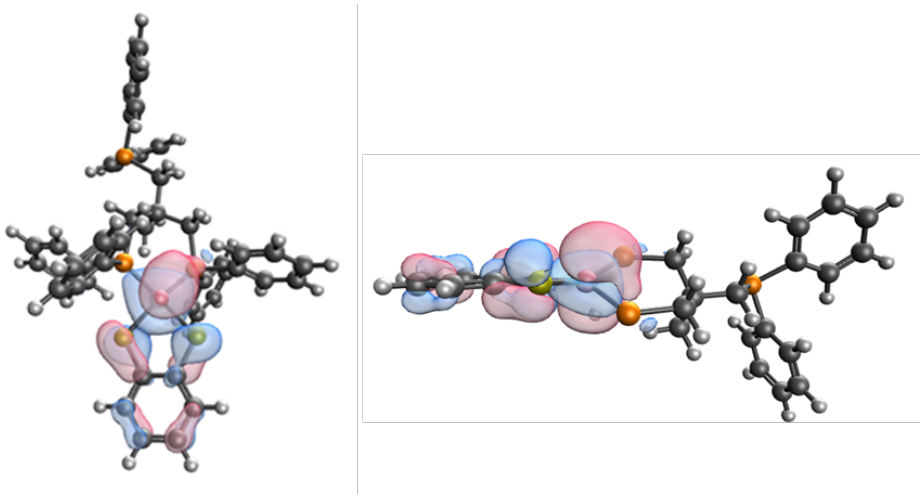


Figure S40. Calculated optimized structure of **III** at the 6-31G*/B3LYP level of theory. Structure includes calculated HOMO orbitals. Phenyl substituents removed for clarity in some images.

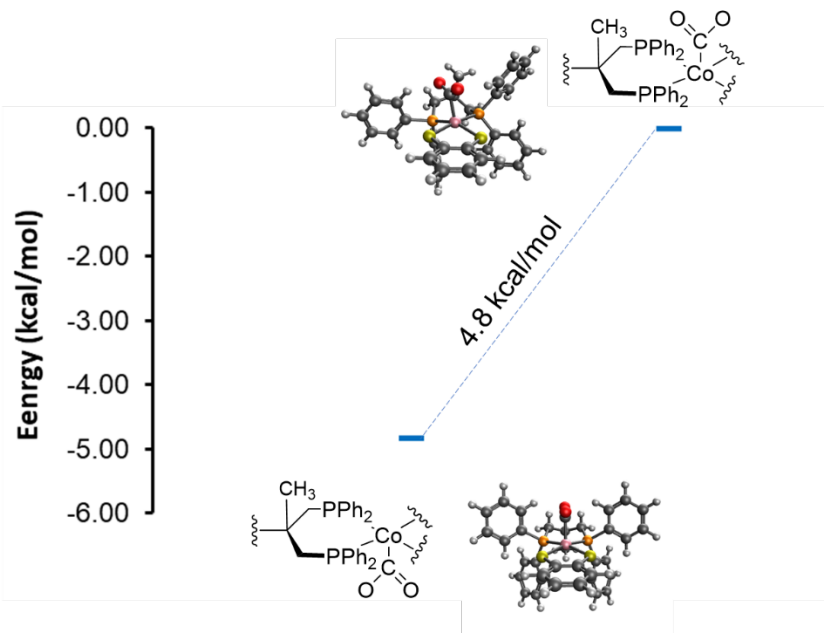


Figure S41. Calculated relative energies of potential **IV-CO_2** isomers at the 6-31+G*/B3LYP level of theory.

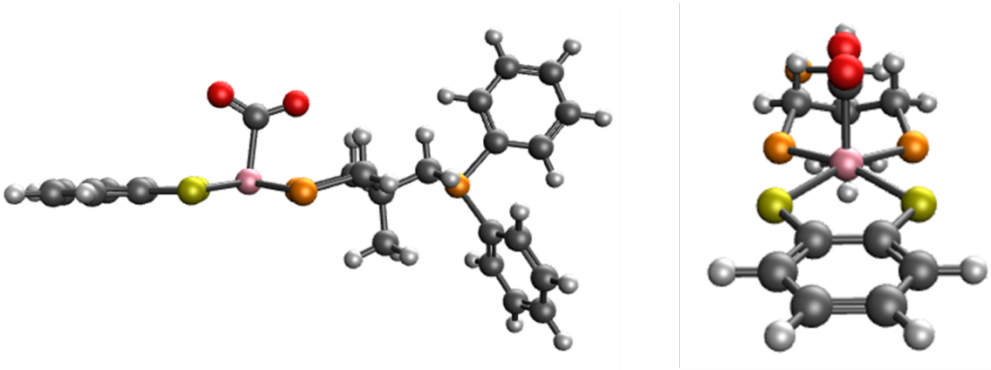


Figure S42. Calculated optimized structure of **IV-CO_2** at the 6-31G*/B3LYP level of theory. Phenyl substituents removed for clarity.

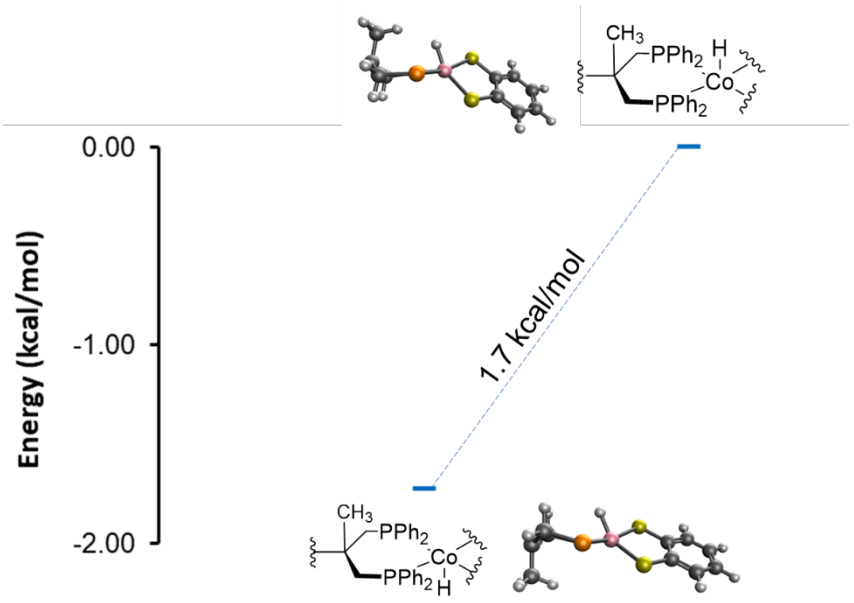


Figure S43. Calculated relative energies of potential **IV-H** isomers at the 6-31+G*/B3LYP level of theory.

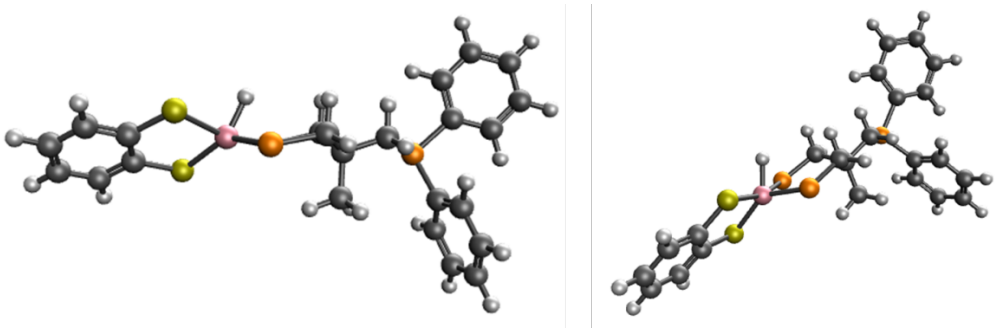


Figure S44. Calculated optimized structure of **IV-H** at the 6-31G*/B3LYP level of theory. Phenyl substituents removed for clarity.

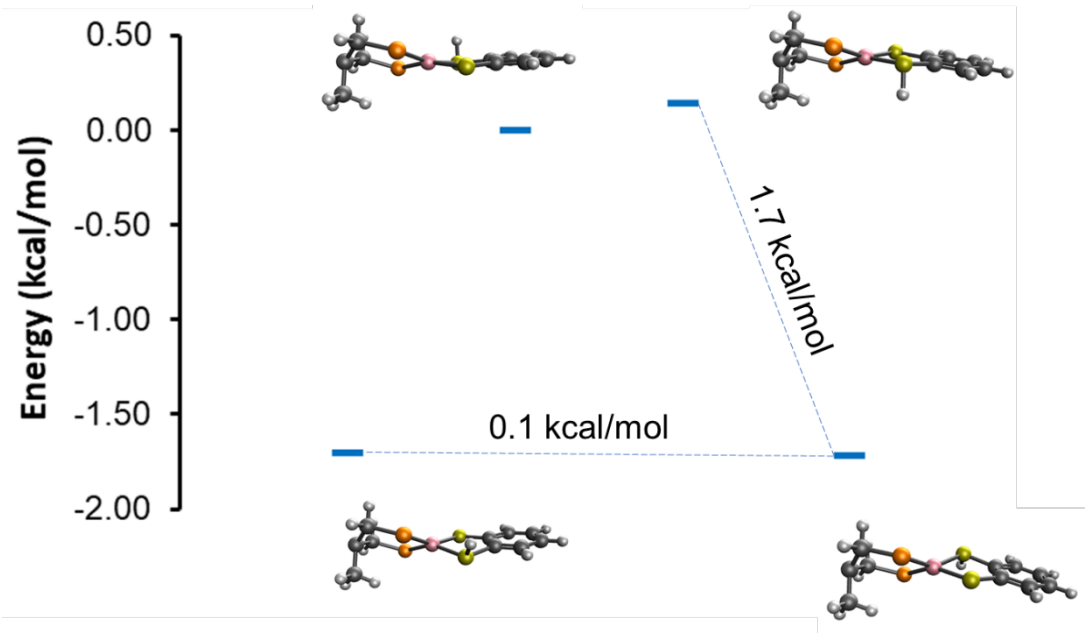


Figure S45. Calculated relative energies of potential [**Co-SH**]^{0} isomers at the 6-31+G*/B3LYP level of theory.

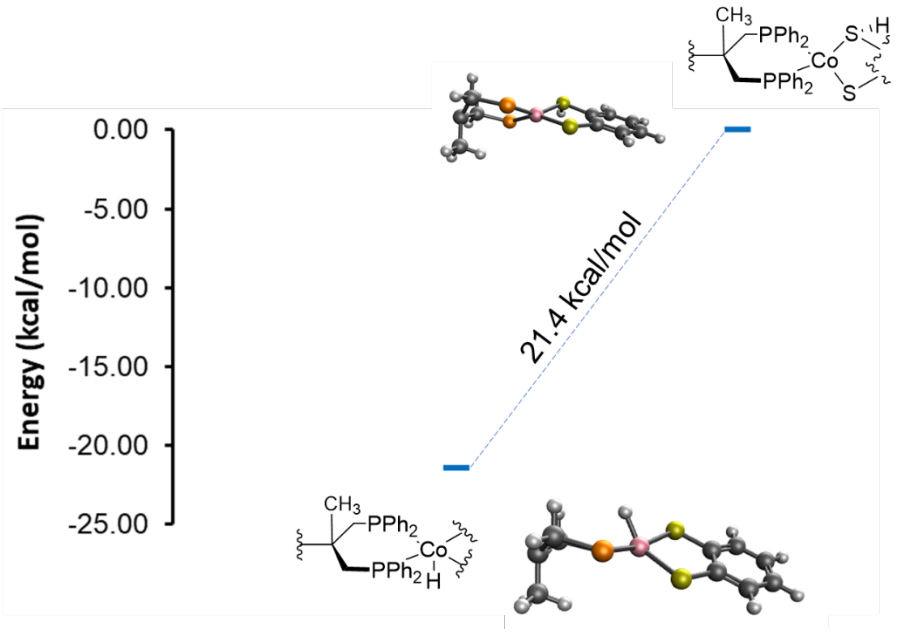


Figure S46. Calculated relative energies of **IV-H** and [**Co-SH**]^{0} at the 6-31+G*/B3LYP level of theory.

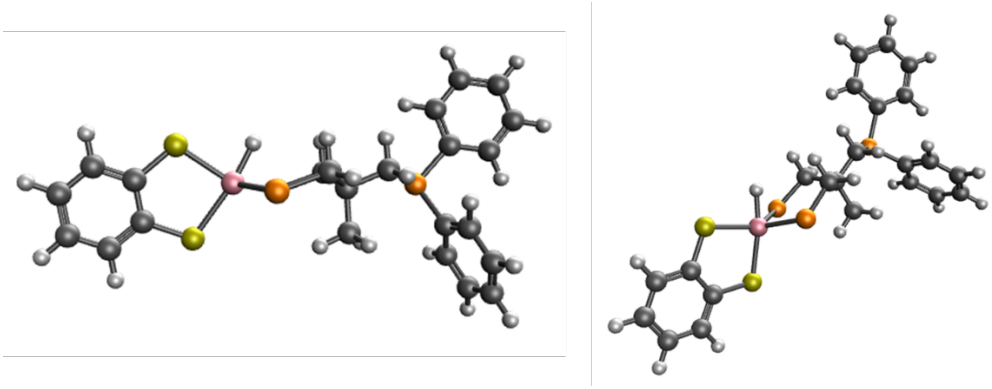


Figure S47. Calculated optimized structure of **V** at the 6-31G*/B3LYP level of theory. Phenyl substituents removed for clarity.

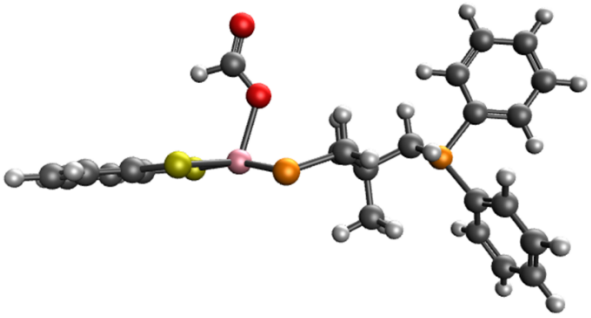


Figure S48. Calculated optimized structure of **VI** at the 6-31G*/B3LYP level of theory. Phenyl substituents removed for clarity.

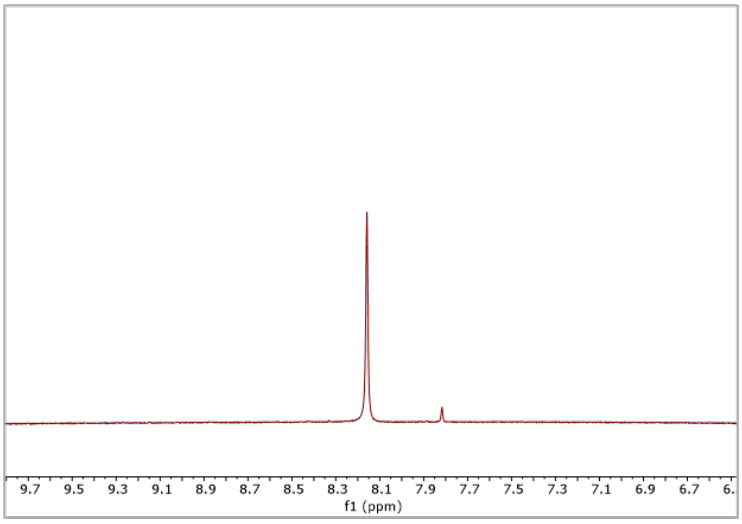


Figure S49. 400 MHz ^{1}H NMR spectrum of D_2O extracted electrolysis solution in the presence of a capillary containing DMF as an internal standard. Integration ratios were taken of the formate

proton (δ = 8.47 ppm) and the DMF formyl proton (δ = 7.96 ppm) and used to calculate the concentration of formate.

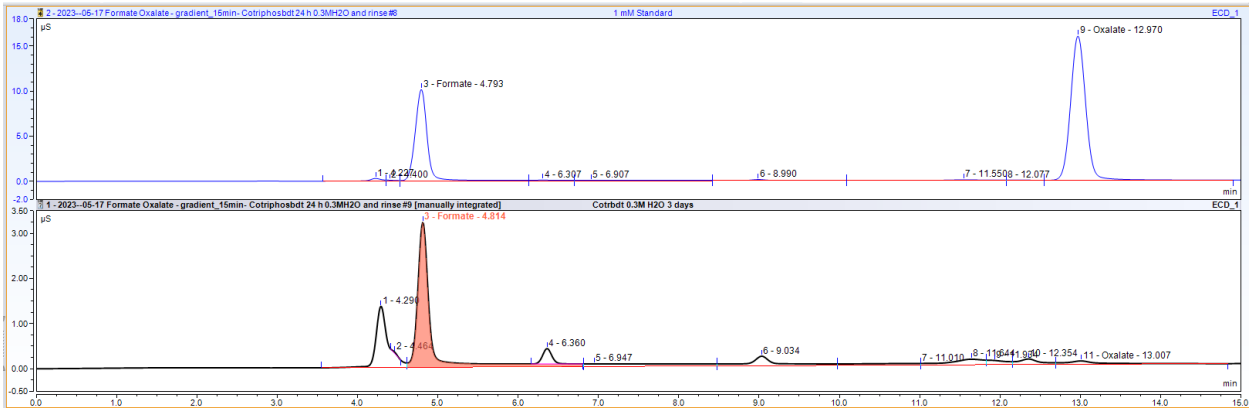


Figure S50: Ion chromatograms of a 1 mM standard of sodium formate and sodium oxalate (above) and of a 1:100 water dilution of a post CPE working electrode solution (below). Formate is identified and quantified via this method.

Table S1. Summary of the controlled potential electrolysis results and their analyses via gas chromatography (gas phase) and ^{1}H NMR spectroscopy (liquid phase), along with the conditions used for the electrolysis of **[Co(triphos)(bdt)]$^+$** in the presence of CO_2 and a proton source. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]$^+$** in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under an atmosphere of CO_2. Oxalate cannot be detected via ^{1}H NMR spectroscopy.

Entry	Acid	Time (hours)	[Acid] (M)	Potential (V) vs $Fc^{0/+}$	Charge (C) (±4)	**H_2**		**CO**		**$HCOO^-$**		**Total FE%** (±6)
						$FE\%_{H2}$ (±3)	TON_{H2} (±0.3)	$FE\%_{CO}$ (±2)	TON_{CO} (±0.10)	$FE\%_{HCOO-}$ (±3)	TON_{HCOO-} (±1.5)	
1	TFE	2	0.3	-2.15	11	6	0.2	2	0.04	59	1.8	67
2	H_2O		0.3	-2.15	20	10	0.6	4	0.25	84	4.9	98
3			0.3	-2.60	38	4	0.5	1	0.06	83	9.2	88
4			0.6	-2.15	16	7	0.3	1	0.04	80	3.7	88
5	-		-	-2.15	1	Trace	Trace	Trace	Trace	3	0.01	3
6	H_2O	8	0.3	-2.15	93	10	2.6	1	0.39	91	24.3	>99

Table S2. Summary of the controlled potential electrolysis results and their analyses via gas and ion chromatography for the gas and liquid phase, respectively, along with the conditions used for the electrolysis of **[Co(triphos)(bdt)]**$^+$ in the presence of CO_2 and a proton source. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6] under an atmosphere of CO_2.

Entry	Acid	Time (h)	Acid (M)	Potential (V) vs $Fc^{0/+}$	Charge (C)	H_2		CO		$HCOO^-$		$C_2O_4^{2-}$		**Total FE%** (±6)
						µmol (±0.5)	FE% (±3)	µmol (±0.4)	FE% (±2)	µmol (±5)	FE% (±4)	µmol (±2)	FE% (±2)	
1	TFE	2	0.3	-2.15	19.9	9.2	8	1.2	1.1	70	67	17	16	93
2	H_2O		0.3	-2.15	14.9	3.5	5	0.5	1	71	93	4	5	103
3			0.3	-2.60	47.4	18.6	8	0.9	0.3	226	92	12	5	104
4			0.6	-2.15	18.0	6.7	7	trace	trace	88	94	trace	trace	101
5		24	0.3	-2.15	262	106	8	31	2	1280	94	19	1	105

Table S3. Summary of the controlled potential electrolysis results performed at -2.15 V with Hg pool working electrode and their analyses via gas chromatography (gas phase) and liquid chromatography (liquid phase), along with the conditions used for the electrolysis of **[Co(triphos)(bdt)]**$^+$ in the presence of CO_2 and H_2O. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6].

Entry	Acid	Time (h)	Acid (M)	Potential (V) vs $Fc^{0/+}$	Charge (C)	H_2		CO		$HCOO^-$		$C_2O_4^{2-}$		**Total FE%** (±6)
						TON (±0.05)	FE% (±3)	TON (±0.03)	FE% (±2)	TON (±0.03)	FE% (±4)	TON (±0.02)	FE% (±2)	
1	H_2O	2	0.3	-2.15	11	0.155	6	0.01	0.3	2.14	79	0.30	11	96

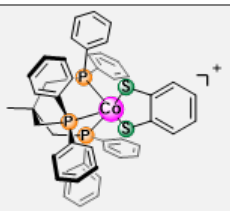
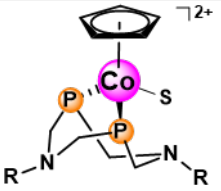
Table S4. Summary of the controlled potential electrolysis results performed at -2.15 V with Hg pool working electrode and their analyses via gas chromatography (gas phase) and liquid chromatography (liquid phase), along with the conditions used for the electrolysis of **[Co(triphos)(bdt)]**$^+$ in the presence of CO_2 and H_2O. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF_6].

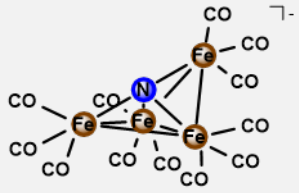
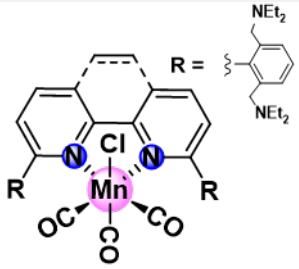
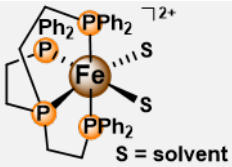
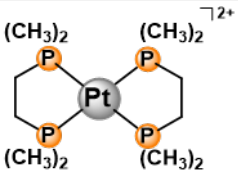
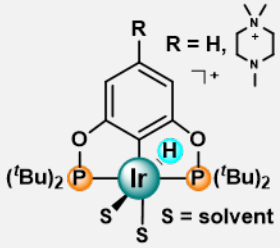
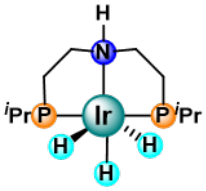
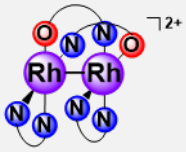
Entry	Acid	Time (h)	Acid (M)	Potential (V) vs $Fc^{0/+}$	Charge (C)	H_2		CO		$HCOO^-$		$C_2O_4^{2-}$		**Total FE%** (±6)
						µmol (±0.5)	FE% (±3)	µmol (±0.4)	FE% (±2)	µmol (±5)	FE% (±4)	µmol (±2)	FE% (±2)	
1	H_2O	2	0.3	-2.15	11	3.1	6	0.1	0.3	43	79	6	11	96

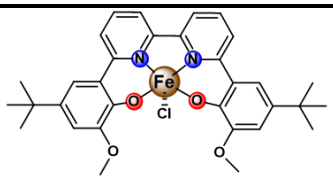
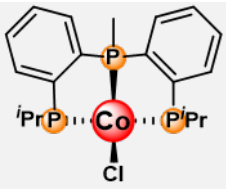
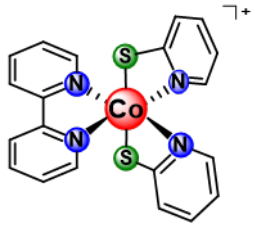
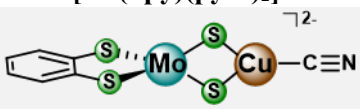
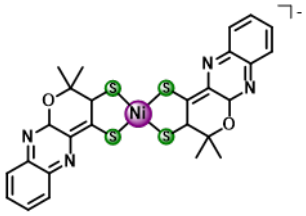
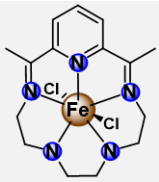
Table S5. Summary of the controlled potential electrolysis results and their analyses via gas and ion chromatography for the gas and liquid phase, respectively, along with the conditions used for the electrolysis of **[Co(triphos)(bdt)]**$^+$ in the presence of N_2 and a proton source. Electrolyses were performed with 0.5 mM of **[Co(triphos)(bdt)]**$^+$ in a CH_3CN solution containing 0.1 M [nBu$_4$N][PF$_6$] under an atmosphere of CO_2.

Entry	Acid	Time (h)	Acid (M)	Potential (V) vs $Fc^{0/+}$	Charge (C)	H_2		CO		$HCOO^-$		$C_2O_4^{2-}$		**Total FE%** (±6)
						TON (±0.05)	FE% (±3)	TON (±0.03)	FE% (±2)	TON (±0.03)	FE% (±4)	TON (±0.02)	FE% (±2)	
1	H_2O	2	0.3	-2.15	4	trace	Trace	Trace	Trace	0	0	0	0	0
2	TFE	2	0.3	-2.15	11	1.45	53	Trace	Trace	0	0	0	0	53

Table S6. Reported overpotentials and relative formate selectivity of active electrocatalysts towards CO_2RR. Table divided between formate selective (>85% FE, top section) electrocatalysts and non-selective (≤85%, bottom section) electrocatalysts.

Catalytic System	Calculated Overpotential vs $Fc^{0/+}$ (mV)[a]	Reported Overpotential vs $Fc^{0/+}$ (mV)[a]	Formate FE%	Reference
 **[Co(triphos)(bdt)]**$^+$	750	750	94	*this work*
 R = Cy, Bn S = solvent **[CpCo(P$^R_2$N$^{R'}_2$)]**$^{2+}$	700-800	500-700	95-99	[4]
	230-440	230-440	95	[19]

 $[Fe_4N(CO)_{12}]^-$				
 **fac-Mn(N∧N)(CO)$_3$Br**	370	370	89	16
 $[Fe(PP_3)](BF_4)_2$	240	N/R	97	20
 $[Pt(dmpe)_2]^{2+}$	600	90	>90	21
 $[Ir(POCOP)]^+$	650-690	N/R	85-93	22
 $(PN^HP)IrH_3$	330	N/R	97	23
 $[Rh_2L_2(Phen)_2](BF_4)_2$	640	N/R	93	24

 **Fe(^{Me}crebpy)Cl**	830	N/R	71-85	25
 **$^{Me}P_3CoCl$**	700	N/R	58	26
 **$[Co(bpy)(pynt)_2]^+$**	200	110-280	57-64	27
 **$[(bdt)Mo(O)S_2CuCN]^{2-}$**	570	800	74	28
 **$[Ni(qpdt)_2]^-$**	300	300	70	29
 **$[FeN_5Cl_2]^+$**	310	310	75-80	30

[a]Overpotential determined where electrolysis was performed and produced the highest formate selectivity. N/R – not reported.

Table S7. DFT-derived Gibbs free energy change and the calculated standard reduction potential.

	ΔG (kcal/mol)	*$ΔE^0_{DFT}$ (V)*	*$ΔE^0_{EXP}$ (V)*
[Co(triphos)(bdt)]$^{+/0}$ (I/II)	-94.67	-0.70	-0.74
[Co(triphos)(bdt)]$^{0/-}$ (II/III)	-58.24	-2.28	-2.39
[CoH(triphos)(bdt)]$^{0/-}$(IV-H/V)	-73.74	-1.61	-

Table S8. X-ray crystallography data and structure refinement for **[Co(triphos)(bdt)][K(18-crown-6)]**.

Chemical formula	$C_{67}H_{83}CoKO_8P_3S_2$	
Formula weight	1266.35 g/mol	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal size	0.58 × 0.383 × 0.209 mm	
Crystal habit	black plate	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.11250(10) Å	α = 90°
	b = 18.5920(2) Å	β = 89.7350(10)°
	c = 36.9620(5)Å	γ = 90°
Volume	6949.21(14) $Å^3$	
Z	4	
Density (calculated)	1.210 g/cm^3	
Absorption coefficient	4.080 mm^{-1}	
F(000)	2668.0	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix	
Radiation source	Cu K_α(λ=1.54184Å)	
Theta range for data collection	5.32 to 152.984°	
Index ranges	$-12 \le h \le 10$, $-20 \le k \le 23$, $-46 \le l \le 45$	
Reflections collected	63432	
Independent reflections	13663[R(int) = 0.0821]	
Coverage of independent reflections	13663	
Structure solution program	CrysAlisPro 1.171.41.123a (Rigaku OD, 2022)	
Refinement method	Full-matrix least-squares on F^2	

Refinement program	Olex2
Data / restraints / parameters	13663/6/786
Goodness-of-fit on F^2	0.867
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0618$, $wR_2 = 0.1843$
all data	$R_1 = 0.0722$, $wR_2 = 0.1954$
Largest diff. peak and hole	1.29 and – 1.05 eÅ^{-3}

Coordinates of DFT-computed structures (Charge and spin specified by first two digits respectively for each structure. Atomic coordinates listed in an order of the X, Y, then Z coordinate values, respectively.)

I

1 1

C 0.9271373 0.5690094 -3.4899568
C 0.8956738 0.5533566 -4.8981657
H -0.0320388 0.3203339 -5.4139346
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H 2.0202560 0.8224377 -6.7057662
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H -2.1112210 -1.9624655 -1.7083534
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P 0.3033836 -1.9127789 0.1956578
P -2.1027929 0.4261865 0.1492976
P 0.6896023 0.8573601 1.7422141
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S 2.1315247 0.9020261 -1.0657709

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H 0.7713914 -4.1448398 -4.2397655
C -0.4919998 -5.3458491 -2.9664999

H -0.6508094 -6.1197731 -3.7127618
C -1.0843810 -5.4537356 -1.7060214
H -1.7035286 -6.3142362 -1.4654508
C -0.8803664 -4.4611045 -0.7441584
H -1.3434587 -4.5724501 0.2313460
C 1.8506145 -2.6907077 0.8825563
C 3.0106086 -2.5033505 0.1101444
H 2.9550354 -1.9282941 -0.8098067
C 4.2340693 -3.0384579 0.5151276
H 5.1187922 -2.8812352 -0.0965248
C 4.3224962 -3.7656612 1.7050175
H 5.2752961 -4.1789113 2.0251701
C 3.1771923 -3.9585887 2.4801833
H 3.2337377 -4.5254184 3.4060500
C 1.9487531 -3.4310961 2.0701716
H 1.0759278 -3.6051795 2.6911541
C -1.0289760 -2.2334980 1.5049010
H -1.9561858 -2.4573369 0.9669307
H -0.8055037 -3.1204040 2.1052485
C -1.2958610 -1.0231750 2.4594632
C -1.9456972 -1.5978578 3.7376891
H -2.2769687 -0.7922416 4.4036640
H -1.2341002 -2.2239992 4.2890726
H -2.8170606 -2.2140510 3.4857824
C -2.3095358 -0.0052506 1.8660498
H -2.2822925 0.8928251 2.4907407
H -3.3218435 -0.4147457 1.9369470
C 0.0067757 -0.2989800 2.8976050
H 0.7776595 -1.0469651 3.0917040
H -0.1694943 0.2115118 3.8487807
C 2.4863993 1.0973108 2.2049288
C 3.2115484 0.0432905 2.7811384
H 2.7500007 -0.9198054 2.9596622
C 4.5535977 0.2083316 3.1332981
H 5.0914838 -0.6231877 3.5811325
C 5.1976685 1.4263821 2.9136226
H 6.2412357 1.5525781 3.1894400
C 4.4879577 2.4818716 2.3369624
H 4.9750149 3.4370744 2.1592143
C 3.1473794 2.3190167 1.9867010
H 2.6159662 3.1535001 1.5428943
C 0.0737643 2.5964153 2.2006415
C -0.2244299 2.9301011 3.5316608
H -0.1325255 2.1938763 4.3239345
C -0.6358080 4.2219891 3.8647215
H -0.8685192 4.4603176 4.8992049

C -0.7422261 5.2044726 2.8769572
H -1.0608186 6.2098388 3.1391823
C -0.4346649 4.8886270 1.5527194
H -0.5118776 5.6447351 0.7762096
C -0.0340412 3.5932698 1.2174538
H 0.1987086 3.3572492 0.1832807
C -2.7891157 2.1953781 -0.0329649
C -3.5752587 2.7616783 0.9828293
H -3.7527864 2.2288120 1.9105807
C -4.1458093 4.0267839 0.8188176
H -4.7476531 4.4498668 1.6187787
C -3.9464105 4.7412516 -0.3635549
H -4.3894472 5.7256335 -0.4892663
C -3.1763087 4.1807451 -1.3858984
H -3.0188368 4.7265678 -2.3126813
C -2.6029294 2.9190975 -1.2235436
H -2.0011301 2.4946968 -2.0226163
C -3.3110595 -0.5023097 -0.8021617
C -4.6754147 -0.2668003 -0.5500860
H -4.9784934 0.5242890 0.1295760
C -5.6604242 -1.0355617 -1.1690181
H -6.7080227 -0.8350454 -0.9601152
C -5.3018084 -2.0571512 -2.0536176
H -6.0690134 -2.6564813 -2.5367255
C -3.9534624 -2.2994438 -2.3120492
H -3.6588449 -3.0925358 -2.9942372
C -2.9655890 -1.5263996 -1.6927745
H -1.9265975 -1.7248159 -1.9186239
Co 0.2098242 0.3657364 -0.4595590
P 0.2741741 -1.9985770 0.1905501
P -2.0279672 0.5101957 0.0910159
P 0.7102662 0.9342099 1.6889817
S -0.3607646 0.3773685 -2.6845784
S 2.2906612 1.0577411 -1.0859867

III

-1 1
Co 0.9175760 0.7084739 -1.9214445
P 0.0260450 -1.0879864 -1.1925298
S 0.2812027 0.2178843 -4.0349676
P 0.9874577 1.7084127 -0.0321927
S 2.4643160 2.1060792 -2.7646213
P -1.7871428 -2.1642575 3.4093357
C 1.3263757 1.1741871 -5.0972992
C 1.0528829 -2.5494602 -1.7307997
C 0.6881851 -3.3851431 -2.7975926

C 2.2832927 2.0451560 -4.5255267
C 2.9540699 2.7656570 -6.7582861
C 0.6089829 0.8177083 1.5730832
C -0.1688058 3.1756810 0.0760911
C 3.0831177 2.8359852 -5.3713926
C 4.9178227 2.0998563 1.2115575
C 3.6578674 1.6026319 0.8764942
C 2.0132946 1.8944440 -7.3252736
C 1.5371882 -4.4055595 -3.2356448
C 1.2104836 1.1086518 -6.4984637
C -1.8529462 0.2933177 1.2042023
C -1.2243259 5.0061485 1.2939891
C 2.3069732 -2.7565114 -1.1288469
C -0.0360797 -1.4344713 0.6422708
C 2.7718744 -4.6096701 -2.6168583
C -0.9281481 3.5301043 -1.0485078
C 3.1543327 -3.7780855 -1.5605680
C -0.3264916 3.9379582 1.2474208
C 2.6161680 2.4633597 0.4870850
C 5.1710900 3.4734578 1.1471098
C -1.8288637 4.5983720 -1.0069112
C -0.4767015 -0.2843974 1.5752560
C -1.9823445 5.3375045 0.1669857
C 2.8895177 3.8372260 0.4151443
C 4.1536418 4.3383968 0.7423668
C -0.5045416 -0.8297499 3.0355414
C -1.0126463 -2.9657179 4.8966001
C 0.2479335 -3.5748221 4.7464168
C 0.1804822 -4.3895868 7.0262339
C 0.8417289 -4.2698484 5.8004095
C -1.0795694 -3.8101132 7.1822291
C -1.6713914 -3.1068356 6.1286261
C -1.7036845 -1.6159552 -1.6751709
C -2.2143194 -2.8889631 -1.3627749
H -1.5784528 -3.6303991 -0.8862290
C -3.5346800 -3.2286473 -1.6622877
H -3.9061751 -4.2199306 -1.4140219
C -4.3765124 -2.2976357 -2.2782362
H -5.4056505 -2.5608272 -2.5091536
C -3.8866621 -1.0291187 -2.5913850
H -4.5325447 -0.2958532 -3.0680664
C -2.5624668 -0.6939733 -2.2906757
H -2.1891375 0.2953030 -2.5376873
C -3.1981746 -1.2066958 4.1316418
C -3.0492715 -0.1730961 5.0731918
H -2.0600549 0.0980288 5.4318541

C -4.1625534 0.5085766 5.5669932
H -4.0284690 1.3055323 6.2941169
C -5.4464578 0.1663766 5.1304136
H -6.3126486 0.6984478 5.5150912
C -5.6106022 -0.8607822 4.1998717
H -6.6051000 -1.1332387 3.8559284
C -4.4935979 -1.5405286 3.7051275
H -4.6300307 -2.3359243 2.9761115
H -0.2649311 -3.2414134 -3.2955267
H 3.5821731 3.3855958 -7.3941085
H 0.3593339 1.5693833 2.3294951
H 1.5516757 0.3612444 1.8924986
H 3.8127779 3.5112735 -4.9286009
H 5.7034192 1.4132262 1.5175510
H 3.4921487 0.5283838 0.9100211
H 1.9056183 1.8297048 -8.4057459
H 1.2300801 -5.0405018 -4.0632329
H 0.4777166 0.4345745 -6.9378200
H -1.8438659 0.7648309 0.2176466
H -2.1587337 1.0554771 1.9307524
H -2.6237764 -0.4852877 1.1874732
H -1.3310444 5.5805586 2.2109860
H 2.6365036 -2.1097108 -0.3197249
H 0.9714046 -1.7432130 0.9410292
H -0.6865556 -2.3026251 0.7918747
H 3.4318860 -5.4036948 -2.9564128
H -0.8108775 2.9566769 -1.9641415
H 4.1160106 -3.9203390 -1.0736539
H 0.2609791 3.7091779 2.1323478
H 6.1530244 3.8626081 1.4038811
H -2.4092577 4.8487181 -1.8914964
H -2.6832562 6.1675106 0.2051100
H 2.1151627 4.5286771 0.0992382
H 4.3395301 5.4079186 0.6786896
H -0.6387272 0.0051172 3.7337115
H 0.4717338 -1.2727579 3.2634965
H 0.7747778 -3.5106511 3.7968406
H 0.6411638 -4.9327952 7.8471234
H 1.8202186 -4.7228032 5.6606892
H -1.6077916 -3.8994331 8.1284537
H -2.6513134 -2.6636476 6.2777261

IV-CO_2'

-1 1
Co 0.2420993 1.0816993 -2.1582949
P -0.1769032 -0.9482689 -1.2464392

S 0.8866541 0.0314736 -4.0717435
P 0.5429382 1.9585409 -0.0792458
S 0.9652392 3.0261248 -3.0373872
P -1.6923910 -2.0939478 3.4334352
C 1.2311913 1.3407676 -5.2068955
C 1.1965530 -2.1541366 -1.5833853
C 1.0482316 -3.1947690 -2.5131369
C 1.2866291 2.6738533 -4.7420938
C 1.8867746 3.4263670 -6.9819347
C -0.5919688 1.4390240 1.3051045
C 0.4949178 3.8001038 0.1615827
C 1.6203266 3.7028840 -5.6414011
C 3.8721942 0.8105839 2.1751227
C 2.5597843 1.1187346 1.8057171
C 1.8232012 2.1057347 -7.4458355
C 2.1039440 -4.0691064 -2.7825866
C 1.4976951 1.0767428 -6.5633661
C -2.5469416 -0.1381347 0.9723393
C 1.4938115 5.9034179 0.8724208
C 2.4390512 -2.0002251 -0.9455900
C -0.1833855 -1.0267755 0.6207469
C 3.3282457 -3.9173811 -2.1295293
C -0.6793497 4.4993052 -0.1724081
C 3.4922257 -2.8765375 -1.2123530
C 1.5795708 4.5207881 0.6849985
C 2.2571548 1.5381605 0.4996717
C 4.9113859 0.9300586 1.2507401
C -0.7623459 5.8790193 0.0203044
C -1.0776097 -0.0479571 1.4196834
C 0.3230911 6.5873732 0.5428715
C 3.3165719 1.6602019 -0.4186341
C 4.6291342 1.3634325 -0.0466702
C -0.9624449 -0.4261655 2.9290347
C -0.7550120 -2.4115914 5.0055280
C 0.6503663 -2.4778847 4.9535348
C 0.7546815 -3.1167880 7.2875674
C 1.3966549 -2.8176625 6.0825170
C -0.6392474 -3.0754164 7.3482075
C -1.3868904 -2.7282442 6.2192373
C -1.6695392 -1.9334541 -1.7375730
C -1.9569897 -3.1557869 -1.1020270
H -1.3052625 -3.5392656 -0.3227409
C -3.0758453 -3.9041530 -1.4666743
H -3.2818106 -4.8443175 -0.9616038
C -3.9258150 -3.4469731 -2.4783442
H -4.7995861 -4.0283128 -2.7613016

C -3.6421156 -2.2438021 -3.1239603
H -4.2947634 -1.8820250 -3.9146486
C -2.5198186 -1.4909808 -2.7608379
H -2.3179453 -0.5513399 -3.2643404
C -3.3865580 -1.6408534 4.0368536
C -3.6512652 -0.5442752 4.8760804
H -2.8343501 0.0785293 5.2300762
C -4.9567627 -0.2449822 5.2677691
H -5.1445457 0.6079548 5.9151224
C -6.0209701 -1.0396093 4.8290492
H -7.0377629 -0.8032509 5.1320197
C -5.7727397 -2.1357155 4.0014301
H -6.5946853 -2.7581894 3.6574563
C -4.4639004 -2.4326108 3.6093136
H -4.2785128 -3.2839318 2.9586385
H 0.1056390 -3.3288996 -3.0322179
H 2.1392197 4.2362915 -7.6622783
H -1.4611547 2.0881979 1.1828823
H -0.1097478 1.7550113 2.2364190
H 1.6674475 4.7280081 -5.2798017
H 4.0785254 0.4809383 3.1901617
H 1.7793803 1.0278930 2.5533247
H 2.0244715 1.8802503 -8.4904991
H 1.9645932 -4.8702580 -3.5039792
H 1.4495323 0.0505168 -6.9215594
H -2.6662780 0.2516025 -0.0403510
H -3.1810559 0.4628140 1.6358067
H -2.9103167 -1.1710859 1.0012057
H 2.3462156 6.4418789 1.2791189
H 2.5986068 -1.1913267 -0.2405673
H 0.8560485 -0.8801133 0.9270200
H -0.4388653 -2.0541457 0.8968190
H 4.1481823 -4.6003517 -2.3353875
H -1.5168794 3.9528114 -0.5943595
H 4.4421083 -2.7429695 -0.7010383
H 2.4996832 4.0124271 0.9522413
H 5.9313202 0.6898340 1.5391464
H -1.6779148 6.4029172 -0.2435699
H 0.2570255 7.6623388 0.6900752
H 3.1139787 1.9933353 -1.4327581
H 5.4294851 1.4669401 -0.7748462
H -1.4286806 0.3620889 3.5314708
H 0.0961433 -0.4522919 3.2103324
H 1.1726628 -2.2644380 4.0236630
H 1.3349898 -3.3835003 8.1668997
H 2.4813679 -2.8526838 6.0179611

H -1.1524327 -3.3107113 8.2774906
H -2.4696447 -2.7019984 6.2924345
C -1.6021488 1.6468135 -2.3671841
O -2.0305403 1.5914116 -3.5316699
O -2.1733070 2.0248185 -1.3183820

IV-CO_2

-1 1
Co 1.3823912 0.5736889 -1.8983177
P 0.1270951 -1.1741029 -1.2041304
S 1.3093460 -0.3155025 -3.9793666
P 1.0210962 1.7392139 0.0118572
S 2.1640391 2.4970793 -2.7916567
P -1.5039190 -2.2999457 3.4877209
C 2.0956152 0.8770415 -5.0212296
C 0.6842251 -2.8374108 -1.8121055
C 0.0014326 -3.5230588 -2.8287740
C 2.4743385 2.1312293 -4.4930572
C 3.3077929 2.7972453 -6.6860836
C 0.7274929 0.7647199 1.5734065
C -0.3982259 2.9330002 -0.0476731
C 3.0788167 3.0787635 -5.3399942
C 4.6826340 2.9988931 1.4611452
C 3.6048529 2.2151624 1.0457716
C 2.9338076 1.5523153 -7.2097836
C 0.4670183 -4.7546873 -3.2975227
C 2.3346756 0.6047266 -6.3812279
C -1.7525691 0.2032460 1.3212106
C -1.9349599 4.4659019 1.0591690
C 1.8576420 -3.4086854 -1.2881448
C 0.0244289 -1.5074795 0.6252918
C 1.6214243 -5.3227973 -2.7568322
C -1.0691022 3.1738967 -1.2552393
C 2.3144244 -4.6436643 -1.7514797
C -0.8429012 3.5993913 1.1086878
C 2.4278186 2.8159236 0.5638061
C 4.6128450 4.3927691 1.3900924
C -2.1652228 4.0403119 -1.3059497
C -0.3466706 -0.3572834 1.5932767
C -2.6037323 4.6846981 -0.1489581
C 2.3733323 4.2159733 0.4836683
C 3.4570155 4.9972862 0.8941037
C -0.2828645 -0.9267608 3.0448205
C -0.6570451 -3.0048959 4.9834213
C 0.6027784 -3.6081530 4.8061766
C 0.6621392 -4.2764187 7.1330216

C 1.2592207 -4.2276512 5.8697745
C -0.5962128 -3.7017424 7.3175256
C -1.2504157 -3.0728506 6.2537828
C -1.6447767 -1.1275121 -1.7470689
C -2.5766944 -2.0808811 -1.2978742
H -2.2644101 -2.8844502 -0.6367036
C -3.9111325 -2.0199332 -1.6998252
H -4.6150486 -2.7669291 -1.3419626
C -4.3405921 -1.0043549 -2.5594773
H -5.3809832 -0.9559648 -2.8701323
C -3.4248835 -0.0575523 -3.0193243
H -3.7456893 0.7329731 -3.6928278
C -2.0871837 -0.1218606 -2.6178548
H -1.3794220 0.6080956 -2.9965856
C -2.9485924 -1.3849312 4.1999716
C -2.8422630 -0.2912716 5.0768374
H -1.8645252 0.0540359 5.4011813
C -3.9843036 0.3579049 5.5488226
H -3.8837327 1.2033669 6.2247396
C -5.2538116 -0.0774309 5.1552501
H -6.1419994 0.4305794 5.5218692
C -5.3753430 -1.1670391 4.2914226
H -6.3582526 -1.5123979 3.9812708
C -4.2301138 -1.8136746 3.8180954
H -4.3330951 -2.6566319 3.1386613
H -0.8987916 -3.1017979 -3.2631238
H 3.7782855 3.5428721 -7.3226898
H 0.5100291 1.4829755 2.3710401
H 1.7000463 0.3174589 1.7899912
H 3.3694463 4.0444947 -4.9315393
H 5.5816244 2.5169423 1.8376066
H 3.6825879 1.1328697 1.0740731
H 3.1110500 1.3207839 -8.2574280
H -0.0772853 -5.2676640 -4.0864526
H 2.0448830 -0.3628477 -6.7859617
H -1.8251039 0.6653089 0.3344563
H -2.0151260 0.9642019 2.0645951
H -2.5079984 -0.5885175 1.3660734
H -2.2636194 4.9692561 1.9646884
H 2.4279196 -2.8705413 -0.5381464
H 1.0200112 -1.8710135 0.8883456
H -0.6735774 -2.3387921 0.7650515
H 1.9815497 -6.2825101 -3.1184810
H -0.7263969 2.6910831 -2.1639724
H 3.2202598 -5.0721380 -1.3292722
H -0.3348908 3.4503208 2.0570052

H 5.4536089 5.0008580 1.7137549
H -2.6731804 4.2084820 -2.2520685
H -3.4575849 5.3561009 -0.1866819
H 1.4850956 4.7078713 0.1025340
H 3.3924541 6.0802804 0.8252513
H -0.3942717 -0.1027408 3.7595242
H 0.7134763 -1.3521853 3.2121776
H 1.0782771 -3.5976566 3.8276513
H 1.1708546 -4.7622673 7.9614859
H 2.2356355 -4.6779886 5.7090014
H -1.0745232 -3.7372413 8.2933735
H -2.2272018 -2.6306012 6.4240474
C 3.0167668 -0.2301644 -1.2234267
O 2.9350807 -0.7102338 -0.0618070
O 3.9804718 -0.1941185 -1.9978349

IV-H'

0 1
Co 0.4947163 0.9633488 -1.8973156
P -0.0847737 -0.9906234 -1.1894067
S -0.2344899 0.5706338 -3.9625256
P 0.8347022 1.9380685 0.0831886
S 2.3967325 1.7482283 -2.7098017
P -1.8122807 -2.1496023 3.3718575
C 1.1303686 0.9445718 -5.0168824
C 1.1170718 -2.2344522 -1.8372775
C 0.8636487 -2.9121079 -3.0408782
C 2.3016131 1.4985416 -4.4603238
C 3.2853748 1.6449661 -6.6777955
C 0.4782162 0.9661234 1.6355267
C -0.2062811 3.4595911 0.2284844
C 3.3708605 1.8509025 -5.3038784
C 4.8612596 2.0006281 0.9544733
C 3.5487268 1.5934631 0.7152982
C 2.1247634 1.0822113 -7.2305393
C 1.8085070 -3.7905746 -3.5728194
C 1.0582457 0.7343293 -6.4074541
C -1.9611970 0.3463574 1.2439640
C -1.1606223 5.2798027 1.5316509
C 2.3530883 -2.4292748 -1.1997535
C -0.0600796 -1.2947230 0.6443501
C 3.0268208 -3.9943981 -2.9200738
C -0.8006569 4.0040138 -0.9201701
C 3.2974311 -3.3075012 -1.7352478
C -0.3868992 4.1208547 1.4556011
C 2.5426021 2.5384612 0.4501707

C 5.1922472 3.3579885 0.9202881
C -1.5714405 5.1664286 -0.8449407
C -0.5604493 -0.1809472 1.5967411
C -1.7576093 5.8043207 0.3822339
C 2.8865001 3.8970612 0.4071824
C 4.2029158 4.3025258 0.6429043
C -0.5620729 -0.7731223 3.0398850
C -1.0199947 -2.9676067 4.8399518
C 0.2498737 -3.5518305 4.6723197
C 0.2047609 -4.4122055 6.9356455
C 0.8594279 -4.2574542 5.7101256
C -1.0640445 -3.8572402 7.1080996
C -1.6719429 -3.1433421 6.0709371
C -1.7458953 -1.6469259 -1.6646044
C -2.0267814 -3.0145150 -1.4909279
H -1.2546913 -3.6914549 -1.1361820
C -3.2934689 -3.5235530 -1.7778373
H -3.4896791 -4.5836633 -1.6413696
C -4.3037218 -2.6738083 -2.2359397
H -5.2910996 -3.0698146 -2.4578513
C -4.0390178 -1.3139166 -2.4026197
H -4.8187612 -0.6431715 -2.7533199
C -2.7698906 -0.8039308 -2.1173702
H -2.5837186 0.2577319 -2.2400962
C -3.2451398 -1.2398656 4.1111770
C -3.1190963 -0.2282165 5.0796458
H -2.1366063 0.0505778 5.4511603
C -4.2467211 0.4218240 5.5831193
H -4.1307539 1.2021869 6.3310093
C -5.5218792 0.0684971 5.1300279
H -6.3994281 0.5755807 5.5225761
C -5.6629553 -0.9376538 4.1731373
H -6.6506546 -1.2183783 3.8165913
C -4.5317153 -1.5855231 3.6680623
H -4.6501763 -2.3641173 2.9180132
H -0.0739958 -2.7574285 -3.5640785
H 4.1193705 1.9182820 -7.3190811
H 0.1926054 1.6885722 2.4059974
H 1.4389426 0.5464741 1.9488523
H 4.2693011 2.2852843 -4.8718830
H 5.6252087 1.2563747 1.1632321
H 3.3147093 0.5321037 0.7297496
H 2.0555657 0.9161759 -8.3026428
H 1.5915354 -4.3133646 -4.5005437
H 0.1570096 0.3012949 -6.8349047
H -1.9710334 0.8844114 0.2923815

H -2.3119379 1.0380309 2.0182271
H -2.6873611 -0.4697448 1.1649574
H -1.2930622 5.7740353 2.4903805
H 2.5974390 -1.8970424 -0.2855790
H 0.9720971 -1.5308856 0.9188231
H -0.6464055 -2.2064861 0.7991810
H 3.7617897 -4.6785179 -3.3354534
H -0.6661112 3.5142384 -1.8791716
H 4.2456852 -3.4501156 -1.2240129
H 0.0815499 3.7455552 2.3603271
H 6.2150007 3.6756318 1.1047928
H -2.0246186 5.5692269 -1.7467598
H -2.3608054 6.7061509 0.4438083
H 2.1313144 4.6456780 0.1905932
H 4.4515877 5.3600448 0.6093442
H -0.7191249 0.0359068 3.7622481
H 0.4269170 -1.1958151 3.2510547
H 0.7707439 -3.4593268 3.7218507
H 0.6776593 -4.9637376 7.7439072
H 1.8446319 -4.6913858 5.5581571
H -1.5866889 -3.9740807 8.0543585
H -2.6584622 -2.7199223 6.2323584
H -0.9026401 1.2345812 -1.5894986

IV-H

0 1
Co 1.2526930 0.4823001 -1.8326516
P 0.0817321 -1.2708880 -1.1442106
S 0.3624567 0.3172839 -3.8578618
P 1.0842544 1.6688897 -0.0086525
S 2.8604918 1.7836795 -2.6576656
P -1.6345077 -2.2139482 3.4866576
C 1.3752013 1.3084728 -4.9171373
C 0.9729127 -2.7604806 -1.7739987
C 0.5669000 -3.3907595 -2.9614448
C 2.4862899 1.9810551 -4.3706121
C 2.9833108 2.9150028 -6.5587312
C 0.7363013 0.7332832 1.5632207
C -0.1934941 2.9982949 -0.1148983
C 3.2828165 2.7881555 -5.2059742
C 4.9292725 2.4023111 1.2807301
C 3.7444149 1.7798618 0.8862067
C 1.8804379 2.2386706 -7.1028686
C 1.2973458 -4.4589752 -3.4851426
C 1.0836435 1.4413141 -6.2865673
C -1.7280851 0.2213424 1.2307584

C -1.5855986 4.7092228 0.9101466
C 2.1426836 -3.2096900 -1.1386708
C 0.0537646 -1.5515074 0.6879906
C 2.4490332 -4.9096890 -2.8368018
C -0.7504739 3.3217330 -1.3611084
C 2.8701644 -4.2796646 -1.6637039
C -0.6214940 3.7069906 1.0220358
C 2.6296348 2.5435577 0.5002692
C 5.0213520 3.7963533 1.2901749
C -1.7155826 4.3262802 -1.4711357
C -0.3557938 -0.3655193 1.5951564
C -2.1362074 5.0205647 -0.3363910
C 2.7342822 3.9418354 0.5052067
C 3.9223733 4.5625274 0.8983717
C -0.3655742 -0.8784933 3.0674091
C -0.8788706 -2.9030161 5.0375277
C 0.3997862 -3.4868436 4.9563270
C 0.2897512 -4.1635925 7.2789492
C 0.9815738 -4.1004364 6.0659845
C -0.9881868 -3.6094108 7.3671553
C -1.5679747 -2.9863575 6.2579437
C -1.6769807 -1.5446440 -1.6395076
C -2.2815805 -2.7991756 -1.4424700
H -1.7010963 -3.6296179 -1.0502098
C -3.6282131 -2.9965956 -1.7492177
H -4.0773947 -3.9736317 -1.5927722
C -4.3936369 -1.9413390 -2.2531140
H -5.4426635 -2.0938317 -2.4924033
C -3.8061479 -0.6898858 -2.4433313
H -4.3957659 0.1374770 -2.8291615
C -2.4572818 -0.4915062 -2.1377673
H -2.0194008 0.4908330 -2.2790612
C -3.0867369 -1.2473526 4.1090026
C -2.9906863 -0.1530417 4.9861528
H -2.0199618 0.1599580 5.3606341
C -4.1342132 0.5357000 5.3936879
H -4.0424944 1.3810926 6.0709207
C -5.3945260 0.1393966 4.9344660
H -6.2837271 0.6779609 5.2516028
C -5.5058137 -0.9499229 4.0689302
H -6.4816785 -1.2651361 3.7086491
C -4.3589222 -1.6363722 3.6598319
H -4.4533958 -2.4793079 2.9791632
H -0.3226625 -3.0539791 -3.4832623
H 3.6068157 3.5404344 -7.1926730
H 0.5146273 1.4821618 2.3312206

H 1.6946490 0.2823176 1.8412719
H 4.1374450 3.3122788 -4.7849204
H 5.7804629 1.7959754 1.5788046
H 3.6979237 0.6943872 0.8725884
H 1.6457843 2.3364075 -8.1596505
H 0.9636038 -4.9369717 -4.4023151
H 0.2276832 0.9158386 -6.7033218
H -1.7203121 0.6834941 0.2408288
H -2.0158068 0.9950418 1.9512839
H -2.5062727 -0.5486628 1.2288094
H -1.9061855 5.2466293 1.7985765
H 2.5005359 -2.7258190 -0.2355578
H 1.0596726 -1.8730225 0.9755416
H -0.6142578 -2.4010274 0.8648907
H 3.0167280 -5.7416673 -3.2445840
H -0.4393442 2.7808659 -2.2496117
H 3.7688368 -4.6170058 -1.1542350
H -0.2016145 3.4900789 1.9995847
H 5.9440754 4.2810007 1.5978050
H -2.1371952 4.5608385 -2.4448038
H -2.8889753 5.7998114 -0.4202218
H 1.8930922 4.5551528 0.2013705
H 3.9850258 5.6475532 0.8968285
H -0.4956517 -0.0269995 3.7452397
H 0.6146629 -1.3123803 3.2951366
H 0.9503271 -3.4676786 4.0182137
H 0.7408031 -4.6442715 8.1430447
H 1.9744372 -4.5350144 5.9799359
H -1.5397890 -3.6562694 8.3029626
H -2.5621514 -2.5603962 6.3527740
H 2.2755773 -0.1313531 -0.9834147

IV-SH’

0 1
Co 0.8855979 0.7664301 -1.9031683
P -0.0592325 -1.0271870 -1.1743173
S 0.1943819 0.4943667 -3.9799933
P 0.9235722 1.7947373 -0.0011032
S 2.5708876 1.9981382 -2.7219508
P -1.7381710 -2.1580240 3.4402882
C 1.5019963 1.0348093 -5.0898858
C 0.9731960 -2.4327258 -1.8118409
C 0.6019634 -3.1874454 -2.9363319
C 2.5197942 1.7891448 -4.4864083
C 3.4699272 2.1254212 -6.7033243
C 0.6072518 0.8528898 1.5826410

C -0.2889887 3.2022692 0.0677668
C 3.5028414 2.3452223 -5.3285729
C 4.8624688 2.2896692 1.1145765
C 3.6208571 1.7596608 0.7638322
C 2.4483857 1.3588155 -7.2810630
C 1.4621043 -4.1524299 -3.4677545
C 1.4476523 0.8254913 -6.4699725
C -1.8637660 0.3316304 1.2660410
C -1.5086811 4.9403912 1.2611699
C 2.2406649 -2.6606127 -1.2455052
C -0.0687731 -1.3954955 0.6478258
C 2.7108555 -4.3790325 -2.8864775
C -0.9156558 3.6177735 -1.1169018
C 3.0964951 -3.6289475 -1.7722694
C -0.5947498 3.8849796 1.2579273
C 2.5248282 2.5992567 0.4979183
C 5.0367592 3.6746637 1.1918034
C -1.8295682 4.6746352 -1.1169664
C -0.4798712 -0.2499346 1.6009105
C -2.1307139 5.3370625 0.0739781
C 2.7156716 3.9862573 0.5666210
C 3.9620046 4.5192051 0.9111873
C -0.4716379 -0.8101375 3.0552471
C -0.9222601 -2.9759408 4.8955236
C 0.3323966 -3.5841959 4.7000023
C 0.3317837 -4.4255565 6.9709474
C 0.9564408 -4.2923983 5.7273547
C -0.9219641 -3.8463825 7.1718005
C -1.5443051 -3.1302037 6.1447689
C -1.7858241 -1.5126475 -1.6637493
C -2.2938634 -2.7959510 -1.3911880
H -1.6593989 -3.5479389 -0.9296720
C -3.6094646 -3.1281176 -1.7147809
H -3.9815014 -4.1264685 -1.4993436
C -4.4462999 -2.1809938 -2.3132979
H -5.4717322 -2.4400179 -2.5634233
C -3.9586709 -0.9024519 -2.5836793
H -4.6018845 -0.1564856 -3.0430170
C -2.6388168 -0.5722729 -2.2593772
H -2.2785181 0.4321798 -2.4623021
C -3.1371245 -1.2183677 4.2067245
C -2.9716301 -0.1979399 5.1598622
H -1.9759168 0.0717531 5.5012619
C -4.0766424 0.4711721 5.6880219
H -3.9301658 1.2577475 6.4239628
C -5.3683271 0.1292975 5.2747227

H -6.2281619 0.6514146 5.6863473
C -5.5486947 -0.8848495 4.3330396
H -6.5493968 -1.1569687 4.0073661
C -4.4400698 -1.5521844 3.8037813
H -4.5892755 -2.3379545 3.0668829
H -0.3671882 -3.0323317 -3.4008270
H 4.2457673 2.5550015 -7.3321144
H 0.3954847 1.5811992 2.3723328
H 1.5670892 0.3917066 1.8396147
H 4.3006967 2.9411692 -4.8927010
H 5.6945687 1.6216869 1.3221932
H 3.5072856 0.6810662 0.6868100
H 2.4273213 1.1863496 -8.3533226
H 1.1514843 -4.7266182 -4.3368681
H 0.6357141 0.2473562 -6.9044138
H -1.8778231 0.8115760 0.2831832
H -2.1513213 1.0892096 2.0040531
H -2.6345218 -0.4469449 1.2614602
H -1.7329453 5.4541012 2.1924927
H 2.5721199 -2.0798345 -0.3890221
H 0.9448999 -1.7135640 0.9127058
H -0.7215128 -2.2610308 0.8013379
H 3.3792599 -5.1303414 -3.2983291
H -0.6853016 3.1051360 -2.0463880
H 4.0680234 -3.7927982 -1.3131578
H -0.1145502 3.6066042 2.1912708
H 6.0039085 4.0901804 1.4624963
H -2.3034186 4.9768379 -2.0472732
H -2.8430084 6.1579410 0.0792638
H 1.8955418 4.6625600 0.3498463
H 4.0884758 5.5979035 0.9595269
H -0.5979604 0.0175994 3.7630509
H 0.5126720 -1.2476472 3.2581544
H 0.8300348 -3.5085074 3.7356900
H 0.8158747 -4.9791217 7.7711606
H 1.9294518 -4.7451265 5.5531955
H -1.4215948 -3.9464532 8.1323120
H -2.5188964 -2.6883672 6.3278509
H 0.0969093 -0.7764328 -4.4400414

IV-SH''

Co 0.8663018 0.7497978 -1.9349955
P -0.0289510 -1.0729499 -1.1972426
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P 0.9107850 1.7422906 -0.0185991
S 2.1801634 2.3625299 -2.7961596

P -1.7443715 -2.1890186 3.4259172
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C 0.9842947 -2.5289228 -1.7492983
C 0.5740139 -3.4153841 -2.7551839
C 2.3690901 2.0352541 -4.5541903
C 3.3044837 2.5452724 -6.7167105
C 0.6122378 0.8145937 1.5715639
C -0.2751381 3.1699909 0.0959882
C 3.2293457 2.7983668 -5.3475896
C 4.9018520 2.1669221 0.9337651
C 3.6272115 1.6588567 0.6843077
C 2.4958521 1.5475015 -7.2766205
C 1.4140540 -4.4471007 -3.1838166
C 1.6268268 0.8055863 -6.4807255
C -1.8611908 0.3057779 1.2551277
C -1.3458376 4.9851253 1.3172984
C 2.2686292 -2.6891746 -1.1996153
C -0.0689283 -1.4234707 0.6324499
C 2.6810484 -4.6055068 -2.6198415
C -1.0570410 3.4984698 -1.0219859
C 3.1071854 -3.7196646 -1.6263548
C -0.4285444 3.9343993 1.2660623
C 2.5479732 2.5177482 0.4059314
C 5.1285148 3.5462989 0.8912645
C -1.9767990 4.5494886 -0.9730483
C -0.4795668 -0.2819694 1.5881957
C -2.1253846 5.2932970 0.1984744
C 2.7920285 3.8979612 0.3510260
C 4.0719385 4.4074822 0.5944987
C -0.4745255 -0.8448527 3.0414805
C -0.9431166 -2.9840382 4.9020881
C 0.3097373 -3.6016856 4.7252038
C 0.2963369 -4.3927493 7.0140473
C 0.9267523 -4.2893573 5.7705391
C -0.9559517 -3.8044268 7.1967281
C -1.5709491 -3.1082100 6.1516519
C -1.7653622 -1.5011095 -1.6962831
C -2.3444526 -2.7442816 -1.3836641
H -1.7551977 -3.5145918 -0.8937356
C -3.6764606 -3.0136066 -1.7009384
H -4.1031146 -3.9824277 -1.4542907
C -4.4581454 -2.0409609 -2.3311639
H -5.4966384 -2.2492020 -2.5749151
C -3.8982256 -0.8013265 -2.6427639
H -4.4984444 -0.0368231 -3.1293251
C -2.5625483 -0.5347107 -2.3274421

H -2.1379185 0.4348480 -2.5706453
C -3.1572428 -1.2456803 4.1623049
C -3.0108770 -0.2014528 5.0923522
H -2.0214091 0.0876975 5.4357466
C -4.1275279 0.4682638 5.5949580
H -3.9955349 1.2737625 6.3129519
C -5.4119517 0.1031085 5.1791195
H -6.2807051 0.6259035 5.5706298
C -5.5734316 -0.9353313 4.2606964
H -6.5683021 -1.2258662 3.9330425
C -4.4532979 -1.6027579 3.7566768
H -4.5880454 -2.4069138 3.0370367
H -0.4042780 -3.3064030 -3.2108526
H 3.9803852 3.1232005 -7.3402865
H 0.3985573 1.5512711 2.3532976
H 1.5694988 0.3517705 1.8335789
H 3.8392981 3.5779223 -4.8981941
H 5.7191588 1.4855903 1.1558698
H 3.4741131 0.5826352 0.6988894
H 2.5430927 1.3483227 -8.3443667
H 1.0742834 -5.1263324 -3.9616555
H 1.0051099 0.0346000 -6.9282724
H -1.8715775 0.8032689 0.2813052
H -2.1540806 1.0491597 2.0055320
H -2.6311987 -0.4731002 1.2324934
H -1.4513509 5.5636460 2.2315229
H 2.6250722 -2.0011305 -0.4372211
H 0.9389197 -1.7515285 0.9078259
H -0.7286053 -2.2854625 0.7769575
H 3.3332645 -5.4080585 -2.9540080
H -0.9492909 2.9225654 -1.9379802
H 4.0941749 -3.8277297 -1.1838916
H 0.1753490 3.7194375 2.1432951
H 6.1221677 3.9432767 1.0812940
H -2.5758071 4.7822550 -1.8496188
H -2.8412519 6.1099811 0.2410688
H 1.9859061 4.5858490 0.1181593
H 4.2382875 5.4808205 0.5501276
H -0.5960339 -0.0174727 3.7505737
H 0.5074170 -1.2879768 3.2439364
H 0.8117178 -3.5493577 3.7614714
H 0.7748129 -4.9305129 7.8282969
H 1.8986674 -4.7496113 5.6105002
H -1.4600704 -3.8815430 8.1570212
H -2.5442674 -2.6579552 6.3209443
H 3.4474150 2.0959203 -2.4075924

IV-SH'''

0 1
Co 0.9480736 0.6683936 -1.9124598
P 0.0045968 -1.1130502 -1.1597214
S 0.4363249 0.0868629 -4.0511338
P 0.9934599 1.7049409 -0.0177668
S 2.5060683 2.0535259 -2.7470374
P -1.7769518 -2.1482834 3.4496619
C 1.4171750 1.1424154 -5.1335905
C 1.0415357 -2.5467234 -1.7293756
C 0.6926424 -3.3429000 -2.8313057
C 2.3373947 2.0002420 -4.5120121
C 3.0010689 2.7565556 -6.7315398
C 0.6237355 0.8087131 1.5803796
C -0.1783559 3.1478187 0.0247465
C 3.1315104 2.8126853 -5.3463382
C 4.9315778 2.0853823 1.1546278
C 3.6726241 1.5896225 0.8150193
C 2.0801266 1.8863897 -7.3291157
C 1.5575712 -4.3353839 -3.3006563
C 1.2898556 1.0675270 -6.5227490
C -1.8431681 0.3036943 1.2219134
C -1.2895509 4.9777449 1.1865007
C 2.2952208 -2.7568273 -1.1266203
C -0.0492151 -1.4462164 0.6697108
C 2.7909365 -4.5455346 -2.6816974
C -0.8825982 3.4959603 -1.1377582
C 3.1572552 -3.7503197 -1.5924320
C -0.3900933 3.9102764 1.1867627
C 2.6194871 2.4591272 0.4803243
C 5.1670762 3.4634284 1.1528222
C -1.7846136 4.5632613 -1.1404384
C -0.4723078 -0.2835081 1.5949687
C -1.9926384 5.3047685 0.0234340
C 2.8721524 3.8379301 0.4700322
C 4.1352710 4.3359801 0.8049094
C -0.4955952 -0.8170507 3.0591661
C -0.9893438 -2.9360089 4.9372008
C 0.2662010 -3.5529462 4.7774861
C 0.2278226 -4.3340761 7.0695098
C 0.8721403 -4.2351583 5.8328692
C -1.0274937 -3.7470684 7.2350374
C -1.6314567 -3.0563568 6.1799356
C -1.7194211 -1.5943344 -1.6671649
C -2.2357001 -2.8783484 -1.4149189
H -1.6079471 -3.6389670 -0.9584017

C -3.5521614 -3.1992528 -1.7473339
H -3.9299534 -4.1984629 -1.5463216
C -4.3823251 -2.2397035 -2.3347737
H -5.4081302 -2.4897974 -2.5922963
C -3.8880341 -0.9588575 -2.5822866
H -4.5270203 -0.2021550 -3.0298346
C -2.5678055 -0.6404144 -2.2488669
H -2.2068633 0.3696186 -2.4253121
C -3.1853855 -1.1871427 4.1711822
C -3.0340951 -0.1407798 5.0980799
H -2.0437813 0.1394058 5.4464361
C -4.1469605 0.5417345 5.5916613
H -4.0112350 1.3485102 6.3075282
C -5.4324712 0.1877191 5.1694918
H -6.2982527 0.7204484 5.5541195
C -5.5988327 -0.8522806 4.2537227
H -6.5946057 -1.1341582 3.9213052
C -4.4823788 -1.5327461 3.7588904
H -4.6206380 -2.3383627 3.0415359
H -0.2609648 -3.1966101 -3.3276576
H 3.6236187 3.3955529 -7.3529187
H 0.3905972 1.5615791 2.3406745
H 1.5690464 0.3471324 1.8846874
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References:

1 L. Yang, D. R. Powell and R. P. Houser, 2007, 955–964.

2 J. Sandstrom, *Dynamic NMR Spectrosocpy*, Academic Press Inc., New York, 1982.

3 J. A. Intrator, N. M. Orchanian, A. J. Clough, R. Haiges and S. C. Marinescu, *Dalt. Trans.*, 2022, **51**, 5660–5672.

4 S. Roy, B. Sharma, J. Pécaut, P. Simon, M. Fontecave, P. D. Tran, E. Derat and V. Artero, *J. Am. Chem. Soc.*, 2017, **139**, 3685–3696.

5 C. Costentin, S. Drouet, M. Robert and J.-M. Savéant, *Science (80-.).*, 2012, **338**, 90–94.

6 H. Fei, M. D. Sampson, Y. Lee, C. P. Kubiak and S. M. Cohen, *Inorg. Chem.*, 2015, **54**, 6821–6828.

7 G. L. Meissler, P. J. Fischer and D. A. Tarr, *Inorganic Chemistry*, Pearson, 5th edn., 2014.

8 Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr, R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Yeh Lin, T. Van Voorhis, S. Hung Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. Min Rhee, J. Ritchie, E. Rosta, C. David Sherrill, A. C. Simmonett, J. E. Subotnik, H. Lee Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3172–3191.

9 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

10 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.

11 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.

12 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724–728.

13 P. J. Stephen, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

14 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

15 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

16 M. H. Rønne, D. Cho, M. R. Madsen, J. B. Jakobsen, S. Eom, É. Escoudé, H. C. D. Hammershøj, D. U. Nielsen, S. U. Pedersen, M.-H. Baik, T. Skrydstrup and K. Daasbjerg, *J. Am. Chem. Soc.*, 2020, **142**, 4265–4275.

17 A. A. Isse and A. Gennaro, *J. Phys. Chem. B*, 2010, **114**, 7894–7899.

18 J. R. Aranzaes, M. C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288–299.

19 A. Taheri, E. J. Thompson, J. C. Fettinger and L. A. Berben, *ACS Catal.*, 2015, **5**, 7140–7151.

20 J. Bi, P. Hou, F. W. Liu and P. Kang, *ChemSusChem*, 2019, **12**, 2195–2201.

21 B. M. Ceballos and J. Y. Yang, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 12686–12691.

22 P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 5500–5503.

23 S. T. Ahn, E. A. Bielinski, E. M. Lane, Y. Chen, W. H. Bernskoetter, N. Hazari and G. T.

R. Palmore, *Chem. Commun.*, 2015, **51**, 5947–5950.

24 H. D. Manamperi, C. E. Moore and C. Turro, *Chem. Commun.*, 2021, **57**, 1635–1638.

25 A. W. Nichols, S. L. Hooe, J. S. Kuehner, D. A. Dickie and C. W. Machan, *Inorg. Chem.*, 2020, **59**, 5854–5864.

26 F. Wang, A. T. Cannon, M. Bhattacharya, R. Baumgarten, R. T. VanderLinden and C. T. Saouma, *Chem. Commun.*, 2020, **56**, 12142–12145.

27 S. Dey, T. K. Todorova, M. Fontecave and V. Mougel, *Angew. Chemie - Int. Ed.*, 2020, **59**, 15726–15733.

28 A. Mouchfiq, T. K. Todorova, S. Dey, M. Fontecave and V. Mougel, *Chem. Sci.*, 2020, **11**, 5503–5510.

29 T. Fogeron, P. Retailleau, M. Gomez-Mingot, Y. Li and M. Fontecave, *Organometallics*, 2019, **38**, 1344–1350.

30 L. Chen, Z. Guo, X.-G. Wei, C. Gallenkamp, J. Bonin, E. Anxolabéhère-Mallart, K.-C. Lau, T.-C. Lau and M. Robert, *J. Am. Chem. Soc.*, 2015, **137**, 10918–10921.