Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Hydrogenation and electrocatalytic reduction of carbon dioxide to formate with a single Co catalyst

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1. General Considerations

Unless specified otherwise, all the reactions were carried out under nitrogen atmosphere in a glovebox or using Schlenk techniques. Glassware was oven-dried at 120 °C for at least 4 h prior to use except for volumetric glassware, which was dried in the anti-chamber vacuum overnight, and rinsed several times with dry solvent inside the glovebox. Elemental analysis was performed by Midwest Microlabs, and crystalline samples were sent in sealed ampules.

Materials

Chemicals were purchased from Sigma Aldrich, Oakwood Chemical, Strem Chemicals, or Alfa Aesar and were used as received without further purification unless stated otherwise. 3 Å molecular sieves were activated at 220 °C under vacuum overnight and stored under nitrogen atmosphere in the glovebox. Dry, oxygen-free solvents were used. Pentane, diethyl ether, tetrahydrofuran (THF), benzene, toluene, dichloromethane and acetonitrile were obtained from a solvent purification system by Pure Process Technology, degassed and stored over activated molecular sieves in a glovebox. Deuterated benzene and chloroform were ordered from Cambridge Isotopes, subjected to 3 freeze-pump-thaw cycles, and stored in the glovebox over activated molecular sieves. A bone-dry CO_2 (3.0 grade from Airgas, 99.9% and < 10 ppm water) tank was used in all experiments. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from Oakwood chemicals and recrystallized twice from ethanol and dried under vacuum at 80 °C overnight. Water was degassed by refluxing under N_2 overnight, followed by pumping in a Schlenk flask fitted with a Teflon screw cap, to store inside the glovebox. **P_3H** and **P_3Cl** were prepared following literature procedures.[1]

Instruments

NMR spectra of all samples were recorded on a Unity 300, Inova 400, VXR-500, or Bruker Neo 500 spectrometer. ^{31}P NMR spectra were referenced to H_3PO_4.

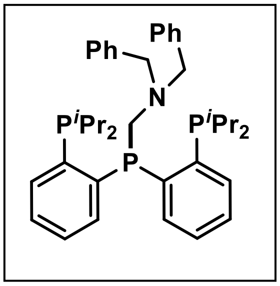
Infrared spectra were collected on an Agilent Cary 630 FTIR, and samples were prepared as KBr pellets.

All hydrogenation reactions were conducted with a Parr Model 5000 multichannel reactor with six 75 mL reactors. The system is controlled using a model 4871 process controller and SpecView version 2.5 software. A Thermo Scientific Integrion Dionex HPIC was used to quantify the concentration of formate.

Single-crystal X-ray diffraction data were collected on a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å, fine-focus sealed tube) and a BRUKER APEXII CCD detector or a Bruker D8 Venture with a Bruker Photon-III detector (Brigham Young University) utilizing Mo Kα radiation (λ = 0.71073 Å). The APEX3[2] software suite was used to manage data collection, integration, absorption correction by the Multi-scan method (SADABS),[3] structure determination via direct methods (SHLEXT)[4] and model refinement (SHELXL).[5] Crystals were cooled to 103(2) K throughout data collection. All non-hydrogen atoms were refined anisotropically with all hydrogen atoms ideally constrained to their carriers with the exception of hydrogen atoms bound to Co or N, which were allowed to refine isotropically without restraint.

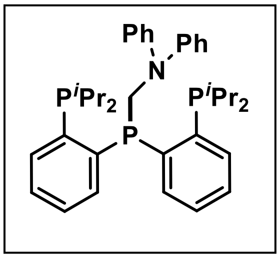
Crystal structures were deposited with the Cambridge Crystallographic Data Centre (CCDC 2010200-2010206, 2022544-5).

2. Preparation & Characterization of Compounds



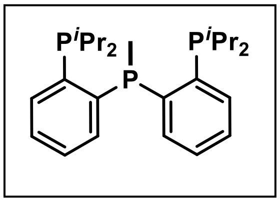
Preparation of $^{\mathrm{Bz2N}}\mathrm{P}_3$

To a flask with paraformaldehyde (0.067 g, 2.2 mmol), acetic acid (202 µL, 3.5 mmol) in 30 mL toluene, dibenzylamine (336 µL, 1.7 mmol) was added. The mixture was sparged with N_2 for 5 min and heated to 70 °C. **P_3H** (0.734 g, 1.78 mmol) in 10 mL toluene was added into the above solution dropwise. The reaction was heated at 70 °C overnight. Removal of solvents afforded a white sticky solid. Washing with pentane afforded the clean product (0.745 g, 65.2%). **^{1}H NMR (300 MHz, Benzene-d_6, δ)**: 7.01 (d, *J* = 7.2 Hz, 4H, Ar H), 6.90 – 6.61 (m, 14H, Ar H), 3.67 (s, 4H, NCH_2Ar), 3.20 (d, *J* = 5.5 Hz, 2H, PCH_2N), 2.03 – 1.64 (m, 4H, P-C*H*Me_2), 1.00 – 0.58 (m, 24H, P-CH(CH_3)CH_3). **^{31}P NMR (Benzene-d_6, δ)**: -0.6 (d, *J* = 138.29 Hz), -32.7 (t, *J* = 138.29 Hz). **^{13}C NMR (Benzene-d_6, δ)**: 139.65, 133.20, 131.56, 129.67, 128.40, 126.67, 59.59, 59.49, 54.44, 24.44, 24.22, 23.96, 20.48, 20.35, 20.27, 19.74, 19.63, 19.45, 19.30.



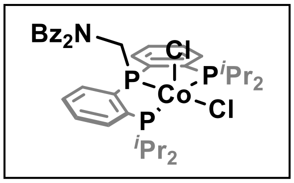
Preparation of $^{\mathrm{Ph2N}}\mathrm{P}_3$

To a flask with paraformaldehyde (0.040 g, 1.3 mmol), acetic acid (73 µL, 1.3 mmol) in 30 mL toluene, diphenylamine (0.178 g, 1.05 mmol) was added. The mixture was sparged with N_2 for 5 min and heated to 70 °C. **P_3H** (0.412 g, 0.985 mmol) in 10 mL toluene was added into the above solution dropwise. The reaction was allowed to stir overnight. Removal of solvents afforded a white solid. Clean product (0.399 g, 66.1%) can be obtained by washing with pentane and MeCN. **^{1}H NMR (300 MHz, Chloroform-d, δ)**: 7.21 – 6.92 (m, 16H, Ar H), 6.88 – 6.82 (m, 2H, Ar H), 4.39 (d, *J* = 6.7 Hz, 2H, PCH_2N), 2.15 (d, *J* = 14.5 Hz, 4H, P-C*H*Me_2), 1.09 – 0.63 (m, 24H, P-CH(CH_3)Me). **^{31}P NMR (Chloroform-d, δ)**: 1.35 (d, *J* = 136.1 Hz), -32.0 (t, *J* = 136.1 Hz). **^{13}C NMR (Benzene-d_6, δ)**: 148.51, 146.01, 145.71, 142.69, 142.53, 142.40, 142.23, 133.43, 133.34, 131.53, 128.79, 128.24, 127.52, 122.32, 121.64, 51.52, 24.02, 20.37, 20.22, 20.10, 19.92, 19.80, 19.68, 19.45, 19.29.



Preparation of $^{Me}P_3$

P_3Cl (7.67 g, 17.0 mmol) was dissolved in 150 mL THF in a Schlenk flask loaded with a stir bar. The solution was cooled down in an acetone/dry ice cooling bath. 5.7 mL 3M MeMgBr solution was diluted with 50 mL Et_2O and transferred dropwise into the $^{iPr}P_3Cl$ solution by a cannula over 15 min. The resulting solution was left in the hood warm up overnight while stirring. 50 mL benzene was cannula transferred into the reaction flask to afford a yellow solution. DI water was sparged with nitrogen at 60 °C for 45 min and cooled down under nitrogen. The reaction mixture was washed by DI water 3 times, using 100 mL DI water in total. The water layer was cannula transferred out, and the yellow organic layer was dried under vacuum at 35 °C. 30 mL pentane was used to dissolve the product. Pale yellow solids formed at -35 °C. Yield: 3.83 g, 52.1%. **^{1}H NMR (400 MHz, Benzene-d_6, δ)**: 7.35 – 7.28 (m, 2H, Ar H), 7.07 (dt, *J* = 21.0, 7.4 Hz, 4H, Ar H), 2.10 (d, *J* = 80.0 Hz, 4H, P-C*H*Me$_2$), 1.67 (dd, *J* = 5.6, 1.8 Hz, 3H, -PCH$_3$), 1.27 – 1.09 (m, 12H, P-CH(C*H$_3$*) CH$_3$), 1.05 – 0.90 (m, 12H, P-CH(C*H$_3$*) CH$_3$). **^{31}P NMR (Benzene-d_6, δ)**: -1.28 (d, *J* = 143.4 Hz), -34.83 (t, *J* = 143.4 Hz).



Preparation of $^{Bz2N}P_3CoCl_2$

$^{Bz2N}P_3$ (0.40 g, 0.63 mmol, white) and anhydrous $CoCl_2$ (86 mg, 0.62 mmol) were each dissolved in 4 mL THF. Upon mixing the solution turned orange immediately and was stirred overnight. The resulting solution was filtered through celite and washed with 5 mL THF. The filtrate was concentrated under vacuum. The product was recrystallized by vapor diffusion of THF or benzene into pentane. ***$E_{1/2}$* (Co^{II}/Co^{I}):** -1.013 V vs. Fc$^+$/Fc. **^{1}H NMR (400 MHz, Benzene-d_6)** yielded a paramagnetic spectrum. No resonances were present in the ^{31}P NMR spectrum. **Evan's method (*d_3*-MeCN):** μ_{eff} = 2.08 μ_B. **UV-visible (THF), nm ($M^{-1}cm^{-1}$):** 350 (2730 ± 30). **Anal. Calc'd (Found) for $C_{39}H_{52}Cl_2CoNP_3$:** C, 61.83 (61.94); H 6.92 (7.10); N, 1.85 (3.67). The high N was a cause of concern, so crystals from the same batch were sent again for analysis, which gave: C (50.57); H (7.02); N (1.59). There was no solvent in the crystals, and the low C on the second attempt may be due to incomplete combustion. A single crystal from this same batch was also mounted on the diffractometer, which gave the same unit cell as that of the structure.

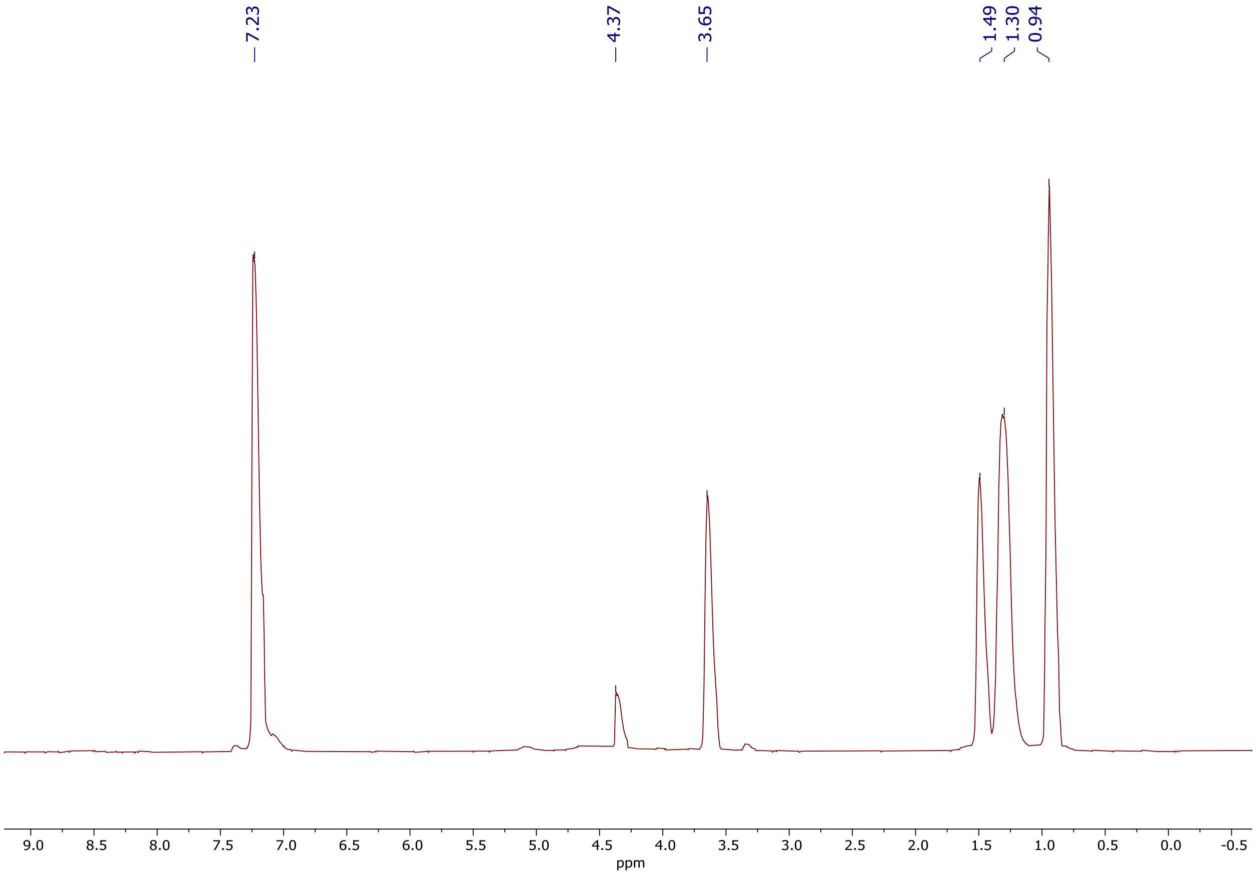
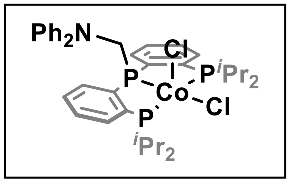


Figure S1. ^{1}H NMR spectrum of $^{\mathbf{Bz2N}}\mathbf{P_3CoCl_2}$.



Preparation of $^{Ph2N}P_3CoCl_2$

^{Ph2N}**P$_3$** (0.25 g, 0.42 mmol, white) and anhydrous $CoCl_2$ (58 mg, 0.45 mmol, baby blue) were each dissolved in 2 mL THF. The solutions were mixed and it turned orange immediately. It was stirred overnight and then filtered through celite and washed with10 mL. The filtrate was concentrated under vacuum. The product was recrystallized by vaper diffusion of THF or benzene into pentane (0.027 g, 9%). ***E$_{1/2}$*** **(Co^{II}/Co^{I}):** -1.050 V vs. Fc^+/Fc. **^{1}H NMR (400 MHz, Benzene-*d$_6$*)** yielded a paramagnetic spectrum: δ 9.79 (br s), 5.28 (s), 4.63 (br s), 3.98 (s), -0.32 (s). **Evan's method (*d$_3$*-MeCN):** μ_{eff} = 2.25 μ_B. **UV-visible (THF), nm ($M^{-1}cm^{-1}$):** 470 (1460 ± 53). **Anal. Calc'd (Found) for $C_{37}H_{48}Cl_2CoNP_3$:** C, 60.92 (53.69); H 6.63 (6.79); N, 1.92 (1.81). The low C may be due to incomplete combustion.

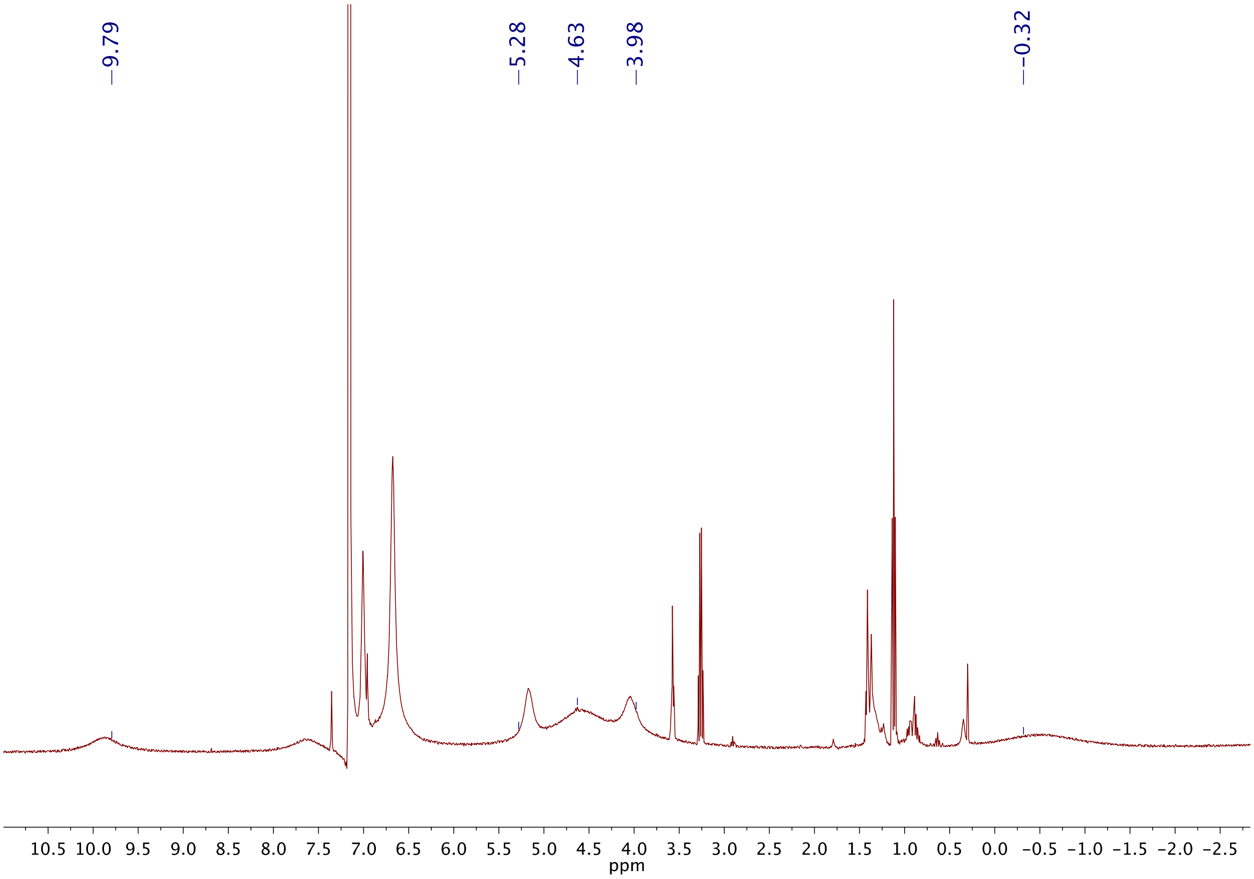
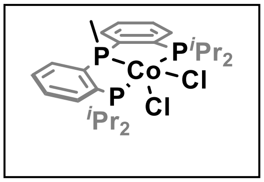


Figure S2. ^{1}H NMR spectrum of **$^{Ph2N}P_3CoCl_2$**.



Preparation of $^{Me}P_3CoCl_2$

One equivalence of ^{Me}**P$_3$** ligand (0.4024 g, 0.93 mmol) was weighed into a 20mL scintillation vial and dissolved in about 5mL of THF (light yellow). To another scintillation vial, one equivalence of $CoCl_2$ (0.1209 g, 0.93 mmol) was added and dissolved in about 5mL of THF (light blue). The $CoCl_2$ solution was added to the ligand solution and an immediate color change was observed, from a light-yellow solution to a dark red-brown. The solution mixture was stirred at room temperature overnight. The solvent was removed under vacuum. About 10mL of pentanes was added to the dried product. The product was scrapped off the vial walls and left to stir over night, then filtered with a glass frit and Celite. The solids were washed with an additional 20-30mL of pentanes before being dissolved in THF. The product was crystallized by evaporation of THF into toluene. This afforded small crystals that were collected and washed with pentanes before being dried under vacuum. **^{1}H NMR (400 MHz, CD_3CN)** yielded a paramagnetic spectrum: δ 20.3 (bs), 8.8 (bs), 5.2 (bs), 4.8 (bs), 1.4 (bs), 0.7 (bs). **(Co^{II}/Co^{I}):** -1.089 V vs. Fc/Fc^+. **Evan's method (*d_3*-MeCN): μ_{eff}** = 2.20 μ_B. **UV-visible (THF), nm ($M^{-1}cm^{-1}$):** 350 (2350 ± 20). **Anal. Calc'd (Found) for $C_{25}H_{39}Cl_2CoP_3$:** C, 53.40 (46.00); H 6.99 (6.74). N, 1.84 (4.39). The low C may be incomplete combustion.

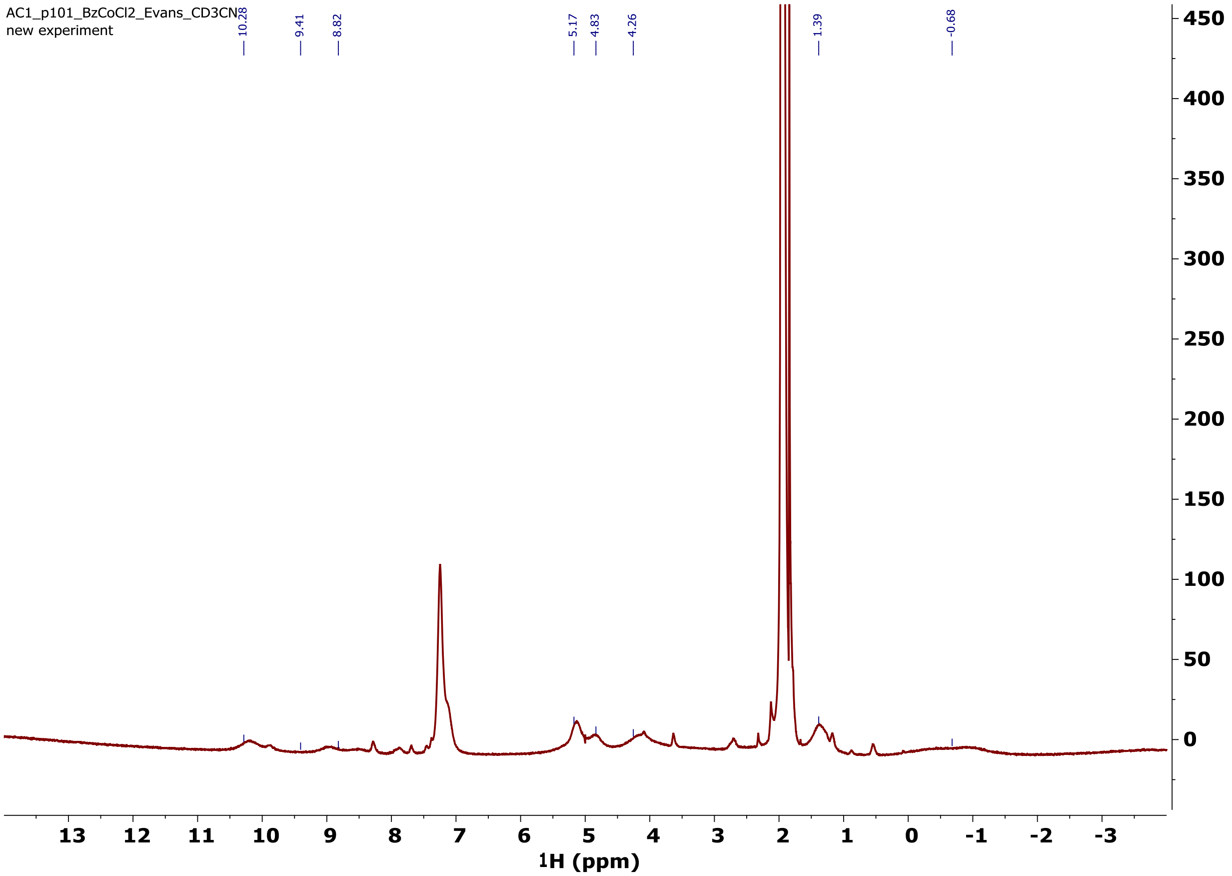
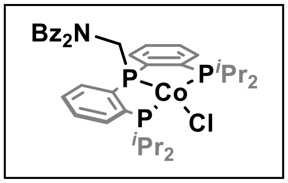


Figure S3. ^{1}H NMR spectrum of ^{Me}**P$_3$CoCl.**

Preparation of $^{Bz2N}P_3CoCl$



$^{Bz2N}P_3$ (4.47 g, 7.12 mmol) was dissolved in 40 mL THF and added to 60 mL THF solution of $(PPh_3)_3CoCl$ (6.21 g, 7.07 mmol) while stirring. The mixture turned chocolate brown at once and was kept stirring for 4 h. Removal of solvent gave a sticky brown solid. Approximately 150 mL pentane was added, and the solution was stirred overnight. The brown mixture was filtered through a fritted funnel, and washed with 6X10 mL pentane. The brown powder was collected and dried under vacuum (4.84 g, 94.2%). The powder was recrystallized via vapor diffusion of a concentrated benzene solution into heptane at room temperature. **^{1}H NMR (400 MHz, Benzene-*d*$_6$)** yielded a paramagnetic spectrum: δ 8.30 (s), 6.46 (s), 2.31 (s), 1.37 (s), 1.25 (s), -0.55 (s). **Evan's method (*d*$_3$-MeCN):** μ_{eff} = 1.38 μ_B. **UV-visible (THF), nm ($M^{-1}cm^{-1}$):** 372 (2730 ± 10). **Anal. Calc'd (Found) for $C_{39}H_{52}ClCoNP_3$:** C, 64.87 (64.78); H 7.26 (7.26); N, 1.94 (4.89). The high N was a cause of concern, so crystals from the same batch were sent again for analysis, which gave: C (58.17); H (7.30); N (1.93). There was no solvent in the crystals, and the low C on the second attempt may be due to incomplete combustion. A single crystal from this same batch was also mounted on the diffractometer, which gave a different unit cell than anticipated. A full dataset was collected to confirm that the crystals were comprised of the desired complex.

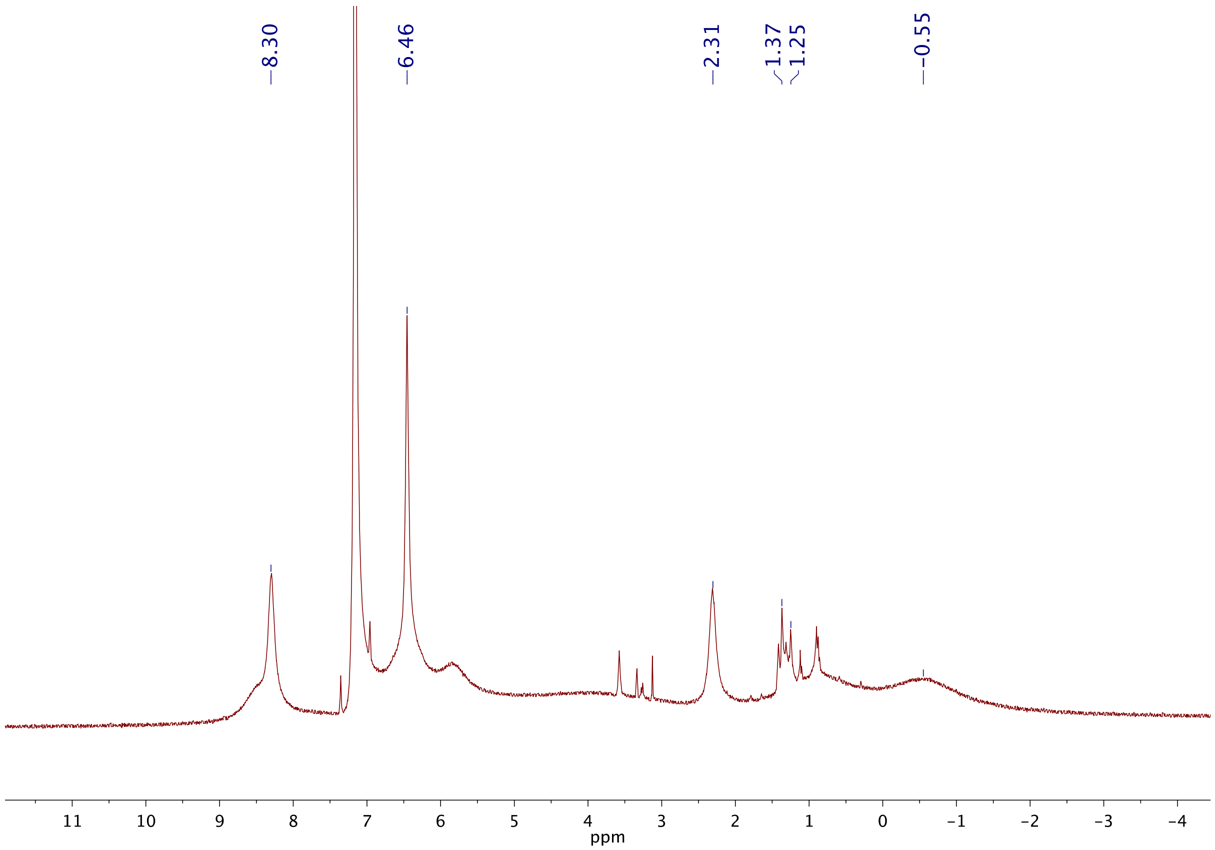
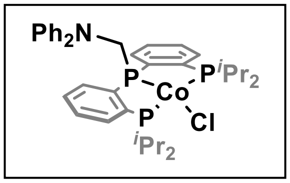


Figure S4. ^{1}H NMR spectrum of ^{Bz2N}**P$_3$CoCl**.

Preparation of ^{Ph2N}P$_3$CoCl



^{Ph2N}P$_3$ (0.86 g, 1.43 mmol) was dissolved in 10 mL THF (colorless) and added to 10 mL THF solution of (PPh$_3$)$_3$CoCl (1.30 g, 1.43 mmol, green) while stirring. The mixture turned brown at once and was stirred overnight. Removal of solvents gave a sticky brown solid. Approximately 10 mL pentane was added, and the solution was stirred overnight. The brown mixture was filtered through a fritted funnel, and the solid left on the funnel was washed with 2 mL more pentane. The brown powder was collected and dried under vacuum. Crystals were obtained by vapor diffusion of benzene into heptane at room temperature. **^{1}H NMR (400 MHz, Benzene-*d*$_6$)** yielded a paramagnetic spectrum: δ 7.40 (d), 6.23 (s), 1.31 (s), -0.41 (s), -1.06 (s). **Evan's method (*d*$_3$-MeCN): μ_{eff}** = 2.76 μ_B. **UV-visible (THF), nm (M^{-1}cm^{-1}):** 370 (2950 ± 60). **Anal. Calc'd (Found) for C$_{37}$H$_{48}$ClCoNP$_3$:** C, 64.03 (64.01); H 6.97 (7.16); N, 1.84 (4.39). The low C may be due to incomplete combustion. The high N was a cause of concern, so crystals from the same batch were sent again for analysis, which gave: C (59.04); H (5.97); N (1.84). There was no solvent in the crystals, and the low C on the second attempt may be due to incomplete combustion. A single crystal from this same batch was also mounted on the diffractometer, which gave the expected unit cell.

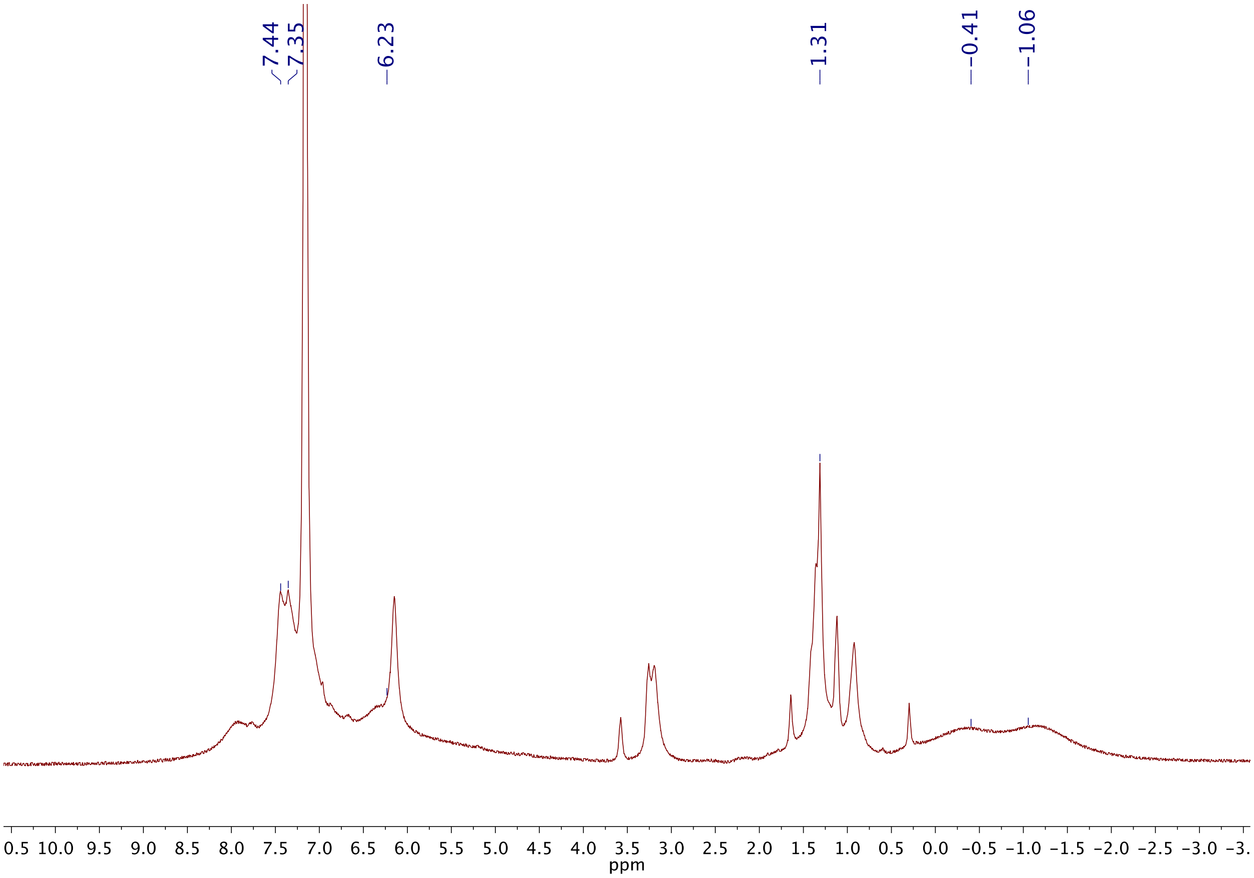
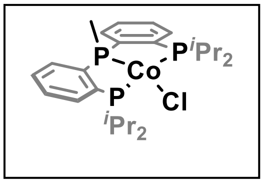
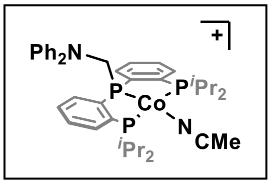


Figure S5. ^{1}H NMR spectrum of $^{\mathbf{Ph2N}}\mathbf{P_3CoCl}$.



Preparation of ^{Me}P$_3$CoCl

^{Me}P$_3$ (2.05 g, 4.86 mmol) was dissolved in 10 mL THF (light yellow solution). $(PPh_3)_3CoCl$ (4.05 g, 4.60 mmol) was dissolved in 40 mL THF (olive green solution). The two solutions were mixed and turned brown immediately. The solution was stirred overnight. Removal of solvents gave a sticky brown goo. Approximately 50 mL pentane was added, and the solution was stirred overnight to give a brown solution with brown powders in it. The mixture was filtered through a fritted funnel, and the brown solid left on the funnel was washed with 20 mL pentane. Yield: 2.25 g, 90.0 %. Big crystals were obtained by vapor diffusion of benzene into heptane at room temperature. **(Co^{II}/Co^{I}):** -1.089 V vs. Fc/Fc^+. **^{1}H NMR (400 MHz, Benzene-*d*$_6$)** yielded a paramagnetic spectrum. **Evan's method (*d*$_3$-MeCN):** μ_{eff} = 2.19 μ_B. **UV-visible (THF), nm ($M^{-1}cm^{-1}$):** 375 (2970 ± 60). **Anal. Calc'd (Found) for $C_{25}H_{39}ClCoP_3$:** C, 56.99 (54.11); H 7.46 (7.50). N, 1.84 (4.39). The low C may be due to partial oxidation or incomplete combustion. Crystals from the same batch were sent again for analysis which showed low C that cannot be due to oxidation, suggesting incomplete combustion: C (50.66); H (7.04). A single crystal from this same batch was mounted on the diffractometer, and a full dataset was collected, confirming the structure.



Preparation of [^{Ph2N}P$_3$Co(MeCN)][BArF]

NaBArF (0.095 g, 0.11mmol) was dissolved in 5 mL THF to give a clear colorless solution. ^{iPr}P$_3$N^{Ph}CoCl (0.074 g, 0.11 mmol) was dissolved in 4 mL THF to give a brown clear solution and was added into NarBArF solution. No immediate color change was observed. The mixture was stirred overnight and then dried under vacuum. 5 mL benzene was added to give a dark green solution. This solution was filtered with Celite and the dark green filtrate was collected. Drying the filtrate under vacuum gave a green powder. Crystals were grown from slow evaporation of MeCN. **(Co^{II}/Co^{I}):** - 0.863 V vs. Fc/Fc^+. Cyclic voltammetry was used to assess purity. **^{1}H NMR (400 MHz, Benzene-*d*$_6$)** yielded a paramagnetic spectrum: δ 8.41 (s, BArF H), 7.68 (s, BArF H), 7.00 – 6.94 (m), 3.52 (br s), 1.45 – 1.17 (m), 1.01 - 0.62 (m).

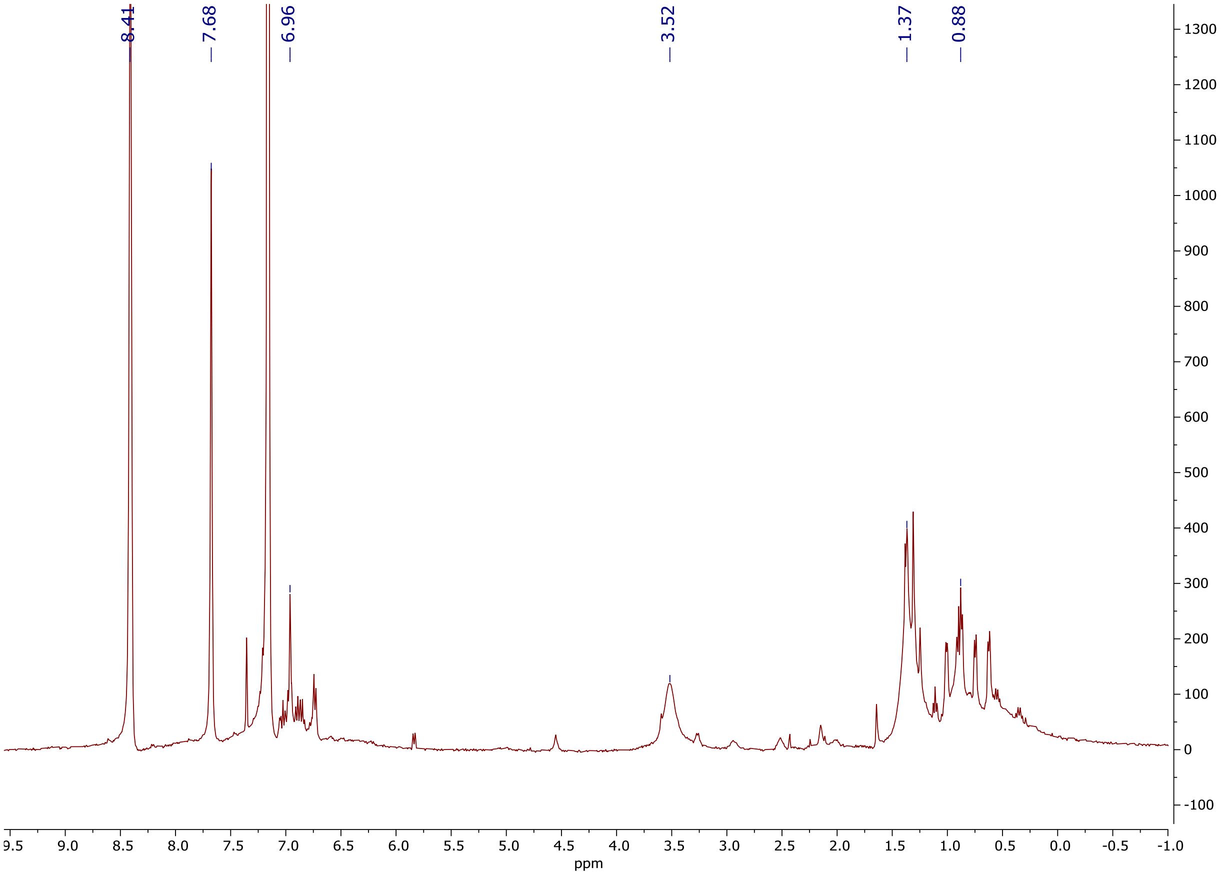
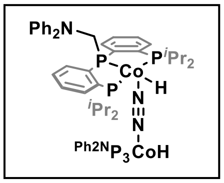


Figure S6. ^{1}H NMR spectrum of **[$^{\mathrm{Ph2N}}$P$_3$Co(MeCN)][BArF]**.



Preparation of $\{^{Ph2N}P_3CoH\}_2(\mu\text{-}N_2)$.

^{Ph2N}**P$_3$CoCl** (0.139 g, 0.20 mmol) was dissolved in 4mL THF, taken out of the glove box, and cooled down in an acetone/dry ice bath. 216 μL 1.0 M NaBHEt$_3$ was dissolved in 5 mL benzene and transferred to the ^{Ph2N}**P$_3$CoCl** solution dropwise. The brown color of the mixture turned into orangish brown. The reaction was kept cold and stirred for 20 min, followed by stirring under room temperature overnight. Solvent was removed, and the flask was taken into the glovebox. Vaper diffusion of benzene into heptane gave crystals on the wall of the vial. NMR analysis of the crystals show two isomers, the major of which is reported. **^{1}H NMR (400 MHz, Benzene-*d*$_6$)**: δ 7.88 (dd, *J* = 7.6, 4.7 Hz, 2H, Ar H), 7.33 (d, *J* = 7.5 Hz, 2H, Ar H), 7.01 (t, *J* = 7.9 Hz, 6H, Ar H), 6.95 (d, *J* = 6.8 Hz, 2H, Ar H), 6.89 (d, *J* = 8.0 Hz, 4H, Ar H), 6.77 (t, *J* = 7.2 Hz, 2H, Ar H), 4.80 (d, *J* = 3.0 Hz, 2H, PC*H*$_2$N), 2.49 – 2.17 (m, 4H, P-C*H*Me$_2$), 1.63 – 1.08 (m, 24H, P-CH(C*H$_3$*)$_2$), -11.35 (dt, *J* = 76.7, 61.1 Hz, 1H,Co-H). **^{31}P NMR (121 MHz, Benzene)**: δ 101.56 (br s), 98.92 (br s).

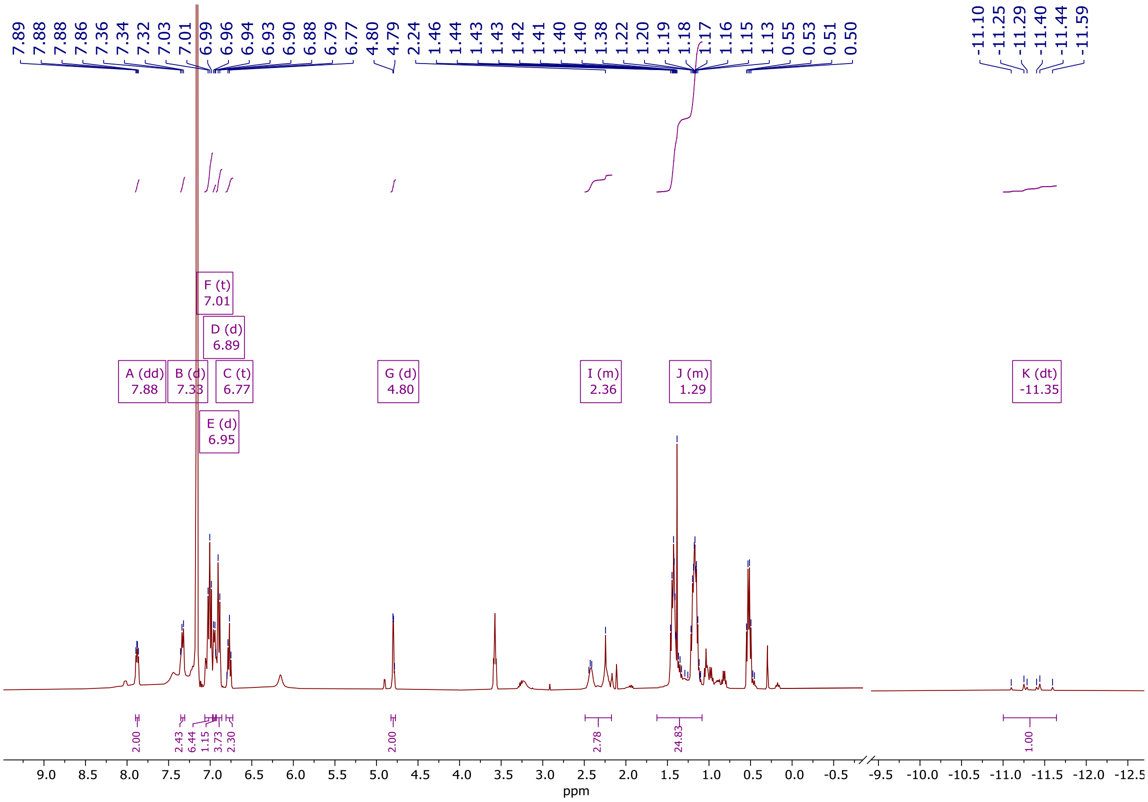


Figure S7. ^{1}H NMR spectrum of **$\{^{Ph2N}P_3CoH\}_2(\mu\text{-}N_2)$**.

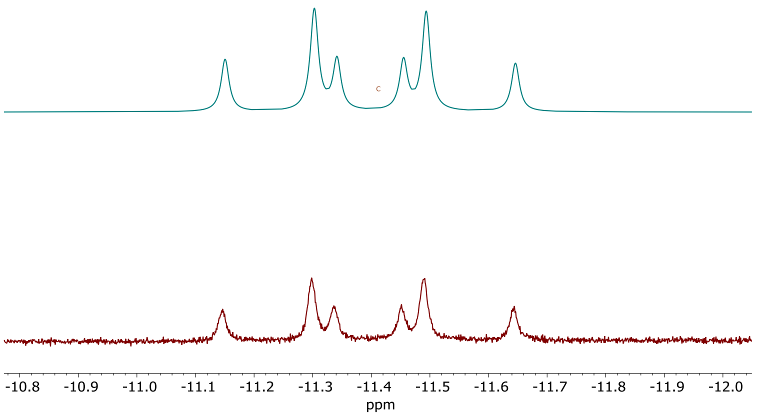


Figure S8. Hydride region of the ^{1}H NMR spectrum of **$\{^{Ph2N}P_3CoH\}_2$ (μ-N_2)**. **(top):** Simulated by MestReNova using the coupling indicated above and **(bottom):** experimental.

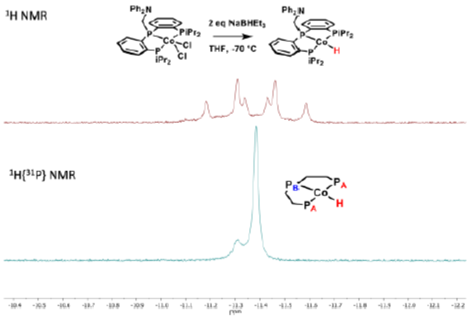


Figure S9. Hydride region of the ^{1}H (top) and ^{1}H{^{31}P} NMR spectrum of **$\{^{Ph2N}P_3CoH\}_2(\mu$-$N_2)$**, showing the presence of a second hydride species. The two hydride resonances are speculated to correspond to the monomer (as drawn) and the N_2-bridged dimer (as present in the solid-state).

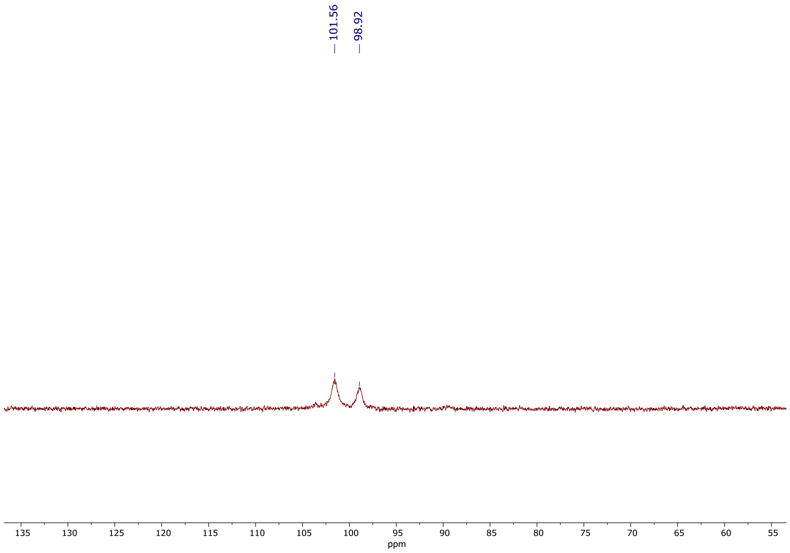
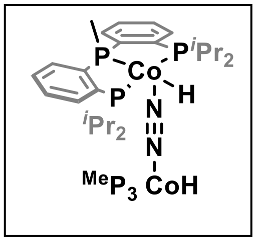


Figure S10. ^{31}P NMR spectrum of **$\{^{Ph2N}P_3CoH\}_2(\mu\text{-}N_2)$**.

Preparation of {${}^{Me}P_3CoH$}$_2$(μ-N_2).



${}^{Me}P_3CoCl$ (0.0410 g, 0.0778 mmol) was dissolved in 4mL THF, taken out of the glove box, and cooled down in an acetone/dry ice bath. 78 µL of 1.0 M $NaBHEt_3$ was dissolved in 5 mL benzene and transferred to the **${}^{Me}P_3CoCl$** solution dropwise. The brown color of the mixture turned into orangish. The reaction was slowly allowed to warm to room temperature over 3 hours. Solvent was removed, and the flask was taken into the glovebox. Product was dissolved in benzene and filtered with Celite. Slow evaporation of benzene yielded small crystals, which show two isomers (presence of small resonances in the NMR spectrum). Only the major isomer is reported (NMR data). **^{1}H NMR (400 MHz, Benzene-*d*$_6$)**: δ 7.81 (t, J = 6.5 Hz, 2H, Ar), 7.32 (d, J = 7.4 Hz, 2H, Ar), 7.14 (m, 2H, Ar), 7.08 (m, 2H, Ar), 2.38 (m, 2H, C*H*), 2.26 (m, 2H, C*H*), 1.82 (d, J_{HP} = 6.3 Hz, 3H, Me), 1.39 (m, 6H), 1.28 (m, 6H), 0.97 (m, 6H), 0.59 (m, 6H), -11.11 (dt, J_{HP} = 80.1, 61.1 Hz, 1H).**^{31}P NMR (121 MHz, Benzene**): δ 104, 93.

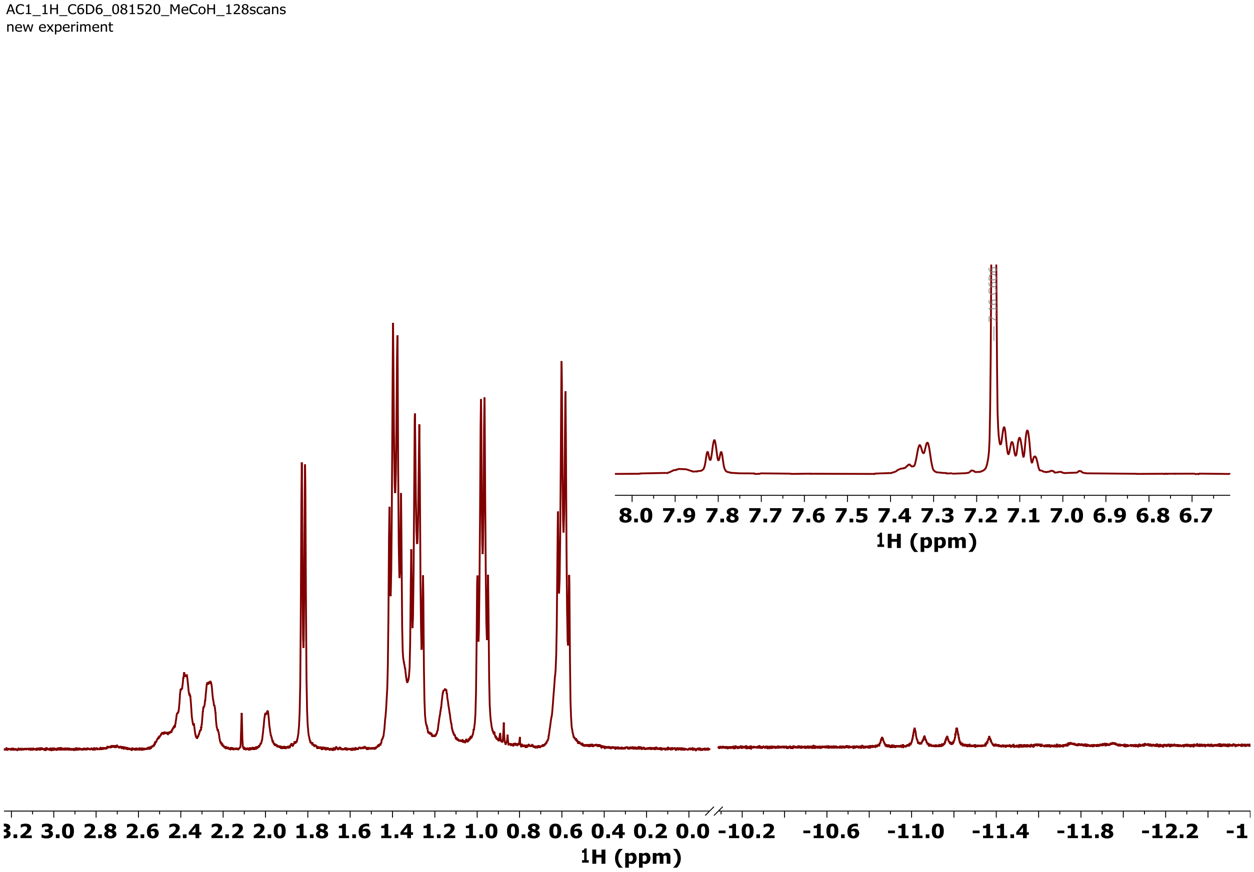


Figure S11. ^{1}H NMR spectrum of **{${}^{Me}P_3CoH$}$_2$(μ-N_2)**. Inset shows the aromatic regions.

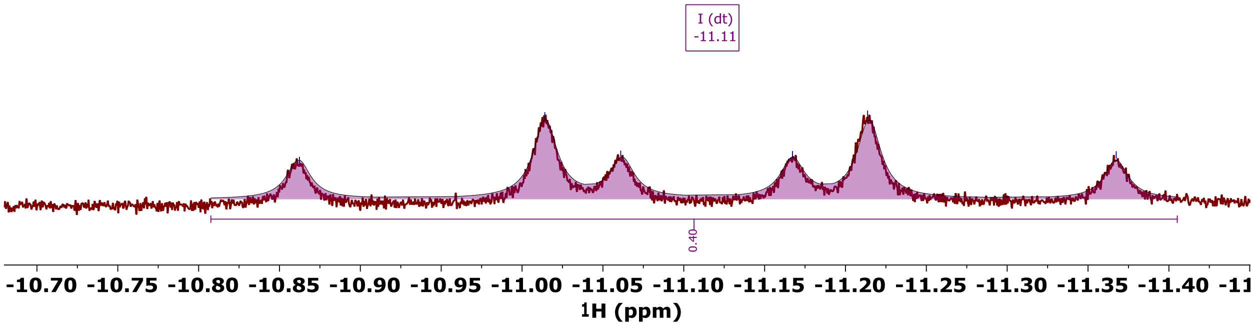


Figure S12. ^{1}H NMR spectrum of **{^{Me}P$_3$CoH}$_2$(μ-N$_2$)** at the hydride region with shading corresponding to the spin simulation.

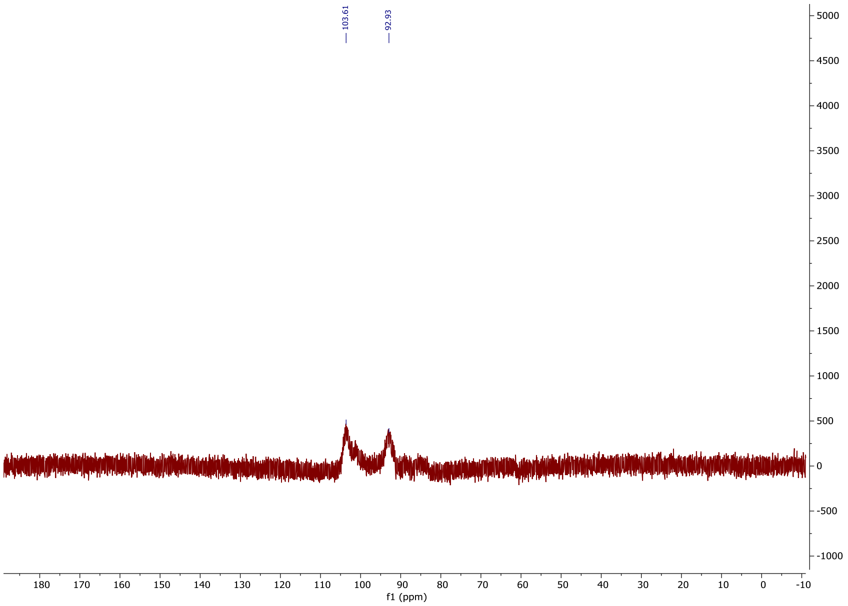


Figure S13. ^{31}P NMR spectrum of **{^{Me}P$_3$CoH}$_2$(μ-N$_2$).**

3. Reactions of $^{R}P_3CoH$ with CO_2

Reaction of $^{Ph2N}P_3CoH$ with CO_2

$^{Ph2N}P_3CoH$ (10.7 mg, 16.2 μmol) was dissolved in ~ 1 mL C_6D_6 and transferred to a J. Young NMR tube. On the Schlenk line, the tube was freeze-pump-thawed three times, and 0.85 atm CO_2 was added (this corresponds to atmospheric pressure at Salt Lake City, UT). The tube was closed, and the tube transferred to a rocker where the liquid and gas phases were allowed to mix for 3 h prior to NMR and IR analysis. We were unable to isolate the product. The ^{31}P NMR spectrum was silent, indicative of a paramagnetic species being formed.

The reaction of **$^{Me}P_3CoH$** was done analogously.

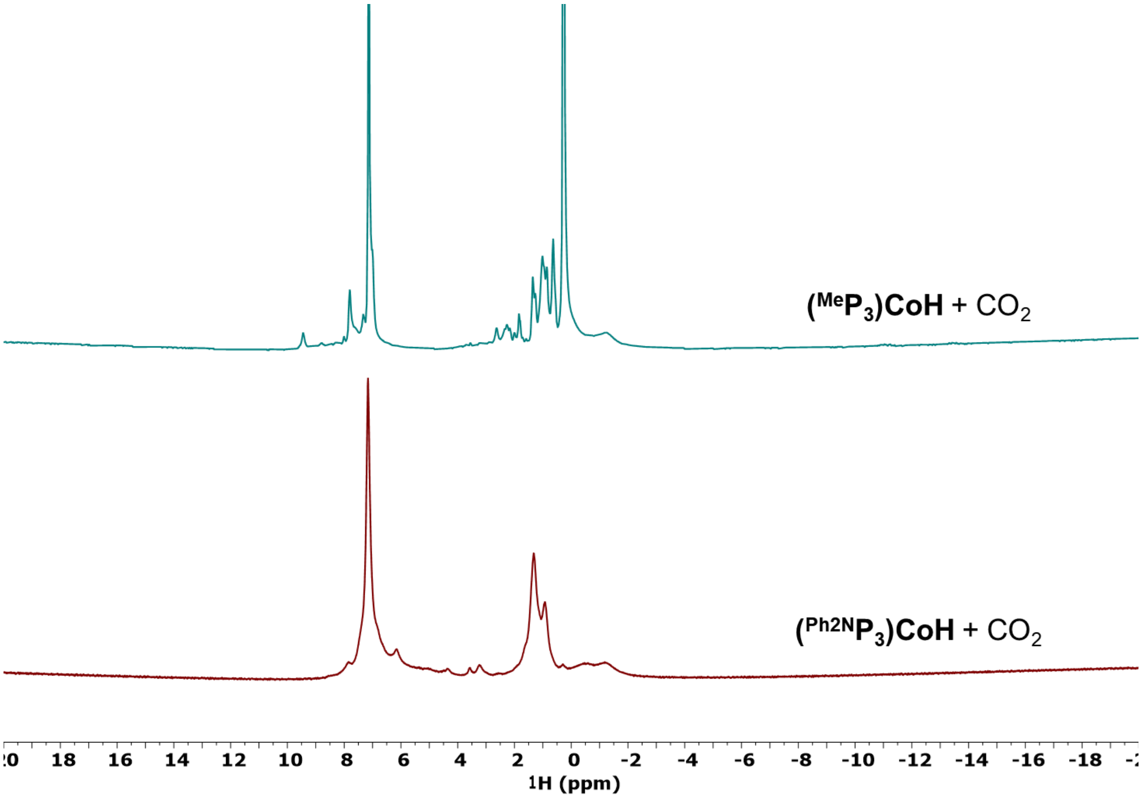


Figure S14. ^{1}H NMR spectra (C_6D_6) of the reactions of the Co-H species with CO_2, taken at *t* = 3 hours.

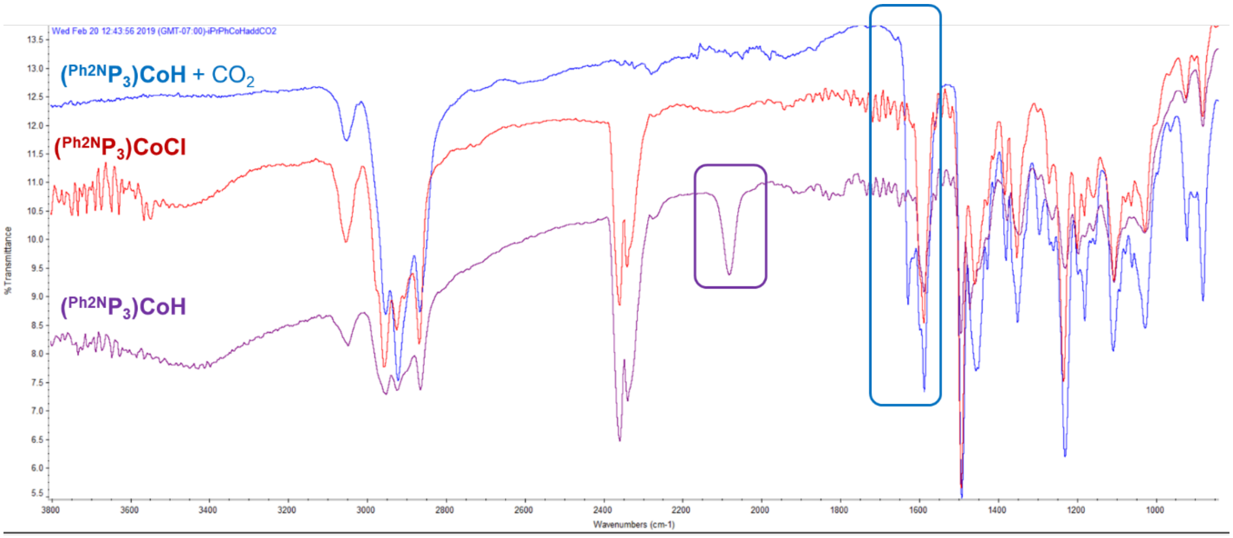


Figure S15. Stacked IR spectra for **$^{Ph2N}P_3CoX$. (purple): $^{Ph2N}P_3CoH$**, with the Co-H stretch shown in the purple box at 2082 cm^{-1}. **(red): $^{Ph2N}P_3CoCl$. (blue): $^{Ph2N}P_3CoH$** + CO_2. A new stretch at 1628 cm^{-1} is indicative of formation of a formate species such as **$^{Ph2N}P_3Co$-OCHO.**

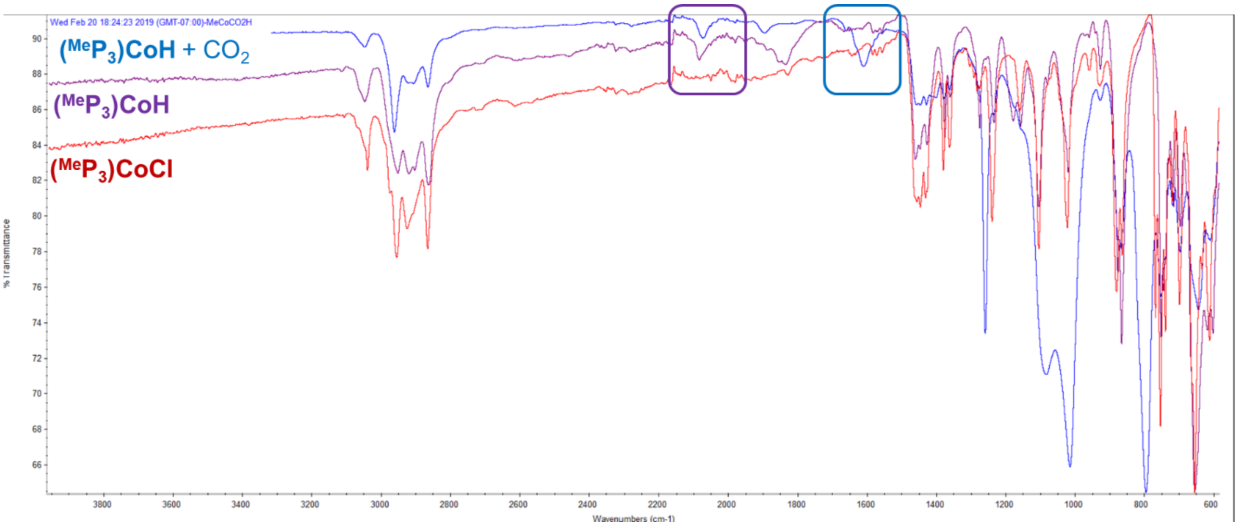


Figure S16. Stacked IR spectra for **$^{Me}P_3CoX$**. **(purple)**: **$^{Me}P_3CoH$**, with the Co-H stretch shown in the purple box at 2084 cm^{-1}. **(red)**: **$^{Me}P_3CoCl$**. **(blue)**: **$^{Me}P_3CoH$** + CO_2. A new stretch at 1610 cm^{-1} is indicative of formation of a formate species such as **$^{Me}P_3Co$-OCHO**. The presence of a hydride resonance in this spectrum is consistent with the NMR data.

4. Reactions of $^{R}P_3CoCl$ with Na/Hg

Attempts to prepare a Co(0) complex, $^{R}\mathbf{P_3CoL}$ (L = solvent or N_2) were done by treating $^{R}\mathbf{P_3CoL}$ (~ 10 mg) in 2 mL THF to 1 eq Na/Hg (0.2 wt%) and allowing to stir overnight to give a dark red solution. The samples were pumped down and dissolved in C_6D_6. There were no signals in the ^{31}P NMR spectra, and the ^{1}H NMR spectrum showed a paramagnetic species. Crystals were obtained from the NMR sample containing $^{Bz2N}\mathbf{P_3CoL}$, which gave a mixture of $^{Bz2N}\mathbf{P_3CoCl}$ (33%) and $^{Bz2N}\mathbf{P_3Co(N_2)}$ (67%). The mixture may be due to < 1 equiv reductant being added (which would be the case if the THF was a little wet), and/or the presence of NaCl in the NMR sample and re-oxidation. Nonetheless, a 4-coordinate Co(0) species is attainable.

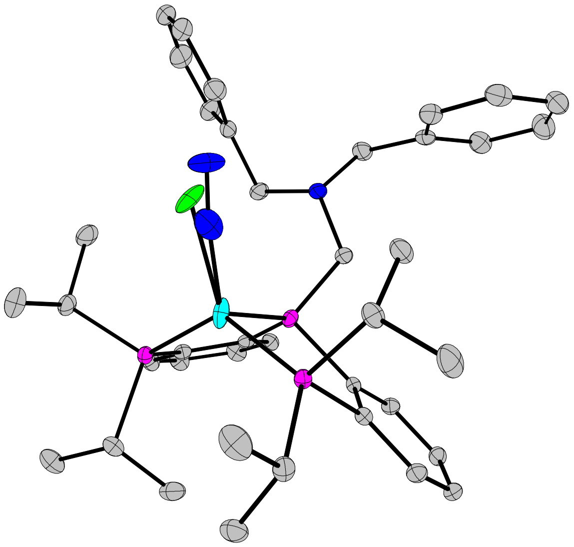


Figure S17. Thermal ellipsoid plot of $^{Bz2N}\mathbf{P_3Co(N_2)}$. The crystal contains 33% impurity of the starting Co(I)Cl. H-atoms omitted for clarity.

5. Hydrogenations

Safety: *Reactions were run at pressures well below the maximum recommended pressure, and each reactor had a pressure-release valve. The reactor was placed inside of a hood, and the sash remained lowered during the entirety of the operations. The reactors were vented in a hood as well. While reactions were running, a sign was placed on the door to alert others that high pressure reactions are ongoing, and a safety operating card was placed in front of the hood detailing the conditions in each of the reactors.*

For a standard experiment, 100 equivalents of base (*t*BuOK) was added to the reaction vessel containing a stir bar by weighing the difference. To the vessel, 200 microliters of 0.025M catalyst stock solution was added via manual pipette. To the base/catalyst solution, 10 mL of THF was added. The vessel was sealed with 6 screws and taken out of the glovebox and transferred immediately to the reactor. The thermocouple, pressure sensor, and gas inlet were attached. Before the vessel was opened to any gas, the lines were vented, evacuated, and purged with relevant gas 3 times. Each vessel was then pressurized with 30 bar CO_2 and then 30 bar H_2 at room temperature. Stirring was turned on, the vessel was heated using a temperature ramp to 120°C and kept at this temperature for 16 hours. After the reaction was complete, it was cooled to room temperature, then further cooled by placing vessel in dry ice for at least 15 minutes. The vessel was slowly depressurized by opening the venting valve. For formate detection, the entire reaction solution was dissolved in DI water and diluted to 100.0 mL. The sample solution was tested by HPIC.

Preliminary trials that used 3 mL solvent showed poor reproducibility. We found that increasing the solvent volume to 10 mL increased reproducibility, likely due to less splashing onto the walls of the reactor.

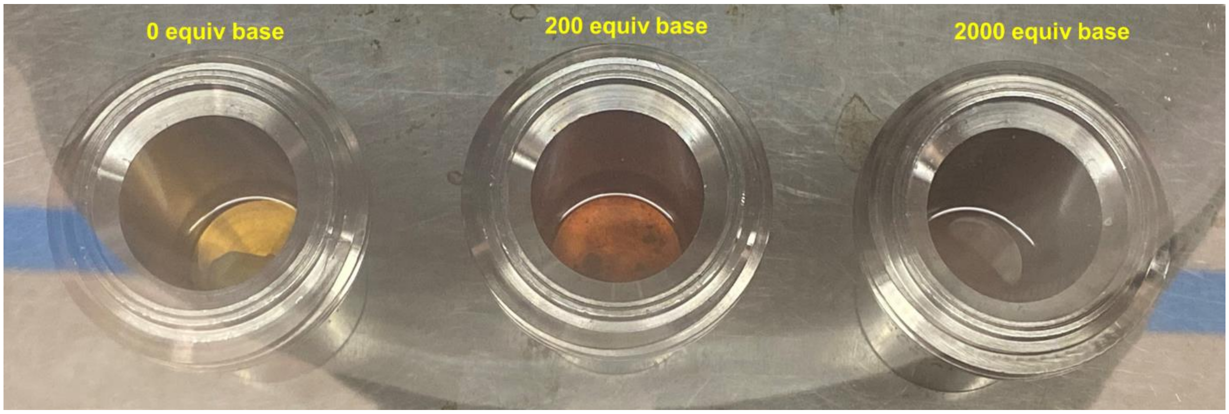


Figure S18. Photograph showing the discoloration of **$^{Bz2N}P_3CoCl$** upon addition of base.

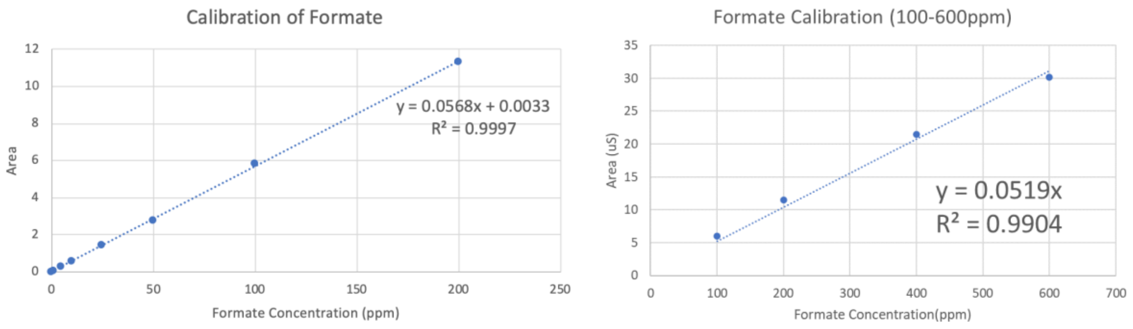


Figure S19. Calibration curves for formate detection, spanning two different ranges.

Recycling Studies:

Table S1: Recycling study of hydrogenations.

Reaction	**Complex**	**Mol of catalyst**	**Eq. of base**	**Reaction time**	**Bar CO_2**	**Bar H_2**	**TON**
1	$(^{Bz2N}P_3)CoCl$	5 μmol	100	~16 hours	30	30	19
2*	$(^{Bz2N}P_3)CoCl$	5 μmol	100 x 2	~16 x 2 hours	30	30	54

*This reaction was done simultaneously with reaction 1, which was analyzed for product following the conditions listed in the table. However, after the initial hydrogenation, the Parr reactor was depressurized on a mineral oil bubbler to prevent oxygen entering the reaction vessel. The reactor was brought into a glovebox and another 100 eq. of base was added. The vessel was then put back onto the reactor system and pressurized with CO_2 & H_2 and the hydrogenation was allowed to continue for an additional 16 hours before product analysis.

NMR analysis of the solution after a typical hydrogenation using **$(^{Bz2N}P_3)CoCl$** shows the presence of unidentifiable diamagnetic species, suggesting ligand degradation (the ^{31}P NMR spectrum showed a singlet at 46.5 ppm). Because the precatalyst is paramagnetic and do not readily show paramagnetically shifted NMR resonances, we cannot comment on how much of the pre-catalyst is viable.

6. Electrochemistry

All experiments were done using a CH instrument series 600 or 660 potentiostat. Electrochemistry was performed in a nitrogen-filled glovebox that is fitted with a CO_2 feedthrough, or on the Schlenk line under an N_2 or CO_2 atmosphere. For measurements inside the glovebox, the electrodes were connected to the potentiostat via a metal feedthrough. A custom-made 10 mL heart-shaped glass electrochemical cell with three air-tight screw ports for electrodes and a 14/20 joint for gas addition was used for the cyclic voltammetry (CV) experiments. The working electrode was a 3 mm glassy carbon (GC) from CH instruments and a platinum (Pt) wire was used as the counter electrode. A single GC electrode, freshly polished before each experiment, was used for CVs upon addition of CO_2 or water to minimize the effect of electrode fouling. The reference electrode was comprised of a Pt wire submerged in an equimolar (4 mM) solution of ferrocene (Fc) and ferrocenium hexafluorophosphate (Fc^+) solution in 0.1 M $TBAPF_6$/MeCN in a glass compartment that was sealed from the bulk solution via a Vycor frit.[6] This allowed for referencing to Fc/Fc^+ for all experiments. iR compensation was not carried out during recording CVs.

Cyclic Voltammetry

CVs were done in the glovebox. For experiments conducted under CO_2, CO_2 was introduced into the glovebox via a port, passed through our experimental setup and out of an oil bubbler that was connected to the outside of the glovebox.[7] Our experimental setup was comprised of a vial filled with pure MeCN that was connected to our electrochemical cell.[8] The CO_2-saturated vapor in the vial was used to purge the electrochemical solutions for 15 minutes.

Bulk Electrolysis

All bulk electrolysis (BE) experiments were carried out in a 75 mL H-cell fitted with a 14/20 joint fitted with a septum for gas addition and detection (Figure S20). A 7 mm diameter type 1 graphite rod (purchased from Alfa Aesar) with a 5.8 cm^2 surface area immersed in the solution was used as the working electrode (WE) and placed in the WE compartment. A Pt coil was used as the counter electrode (CE). No sacrificial oxidant was added to the 12 mL 0.1 M $TBAPF_6$/MeCN solution in the CE. The reference electrode (RE) was comprised of an Ag wire submerged in 0.1 M $TBAPF_6$/MeCN in a glass compartment that was sealed from the electrolyte solution in the WE compartment via a Vycor frit. 10 mL 1 mM solution of the catalyst in 0.1 M $TBAPF_6$ was added to the WE compartment and saturated with CO_2 for 10 min prior to the electrolysis.

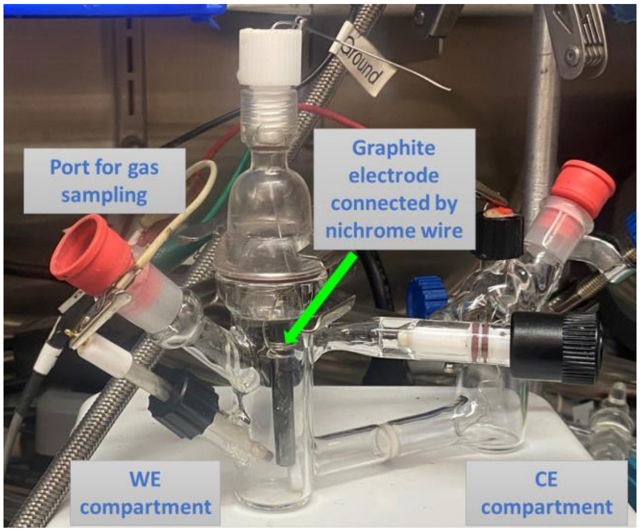


Figure S20. Typical H-cell set-up for BE in the glovebox.

Between controlled potential electrolysis experiments, the graphite rod was cleaned by rinsing with water and acetone and dried in the oven at 120 ^{o}C for at least 2 hours. The Pt counter electrode was cleaned in concentrated nitric acid and rinsed with water and dried in the oven at 120 ^{o}C for at least 2 hrs.

The pH of the electrolyte solution was measured using Fisher Scientific Accumet AE 150 pH meter. While the pH of the pure electrolyte was measured as 4.6, upon bulk electrolysis in the presence of water and CO_2 it was measured as 9.4. Despite the pH measurement is not accurate for non-aqueuos solution, such a sharp pH change is indicative of the presence of formate as the CO_2 reduction product in solution.

Product Analysis

The headspace gases were analyzed by GC. Briefly, a 300 µL aliquot of the headspace was injected using a gas-tight syringe into a Thermo Scientific Trace 1310. The GC was loaded with a Supelco Carboxen 1010 PLOT capillary column. CO and H_2 were detected at a thermal conductivity detector (TCD) using Ar carrier gas using the following method: split ratio - 10:1, inlet temperature was held at 200 ^oC, oven temperature was held at 35 ^oC for 7 min and then increased to 250 ^oC at a rate of 24 ^oC/min and held for 5 min. The TCD detector was held at 250 ^oC. The FID was heated to 350 ^oC and H_2 flow was 40 mL/min, air flow was 400 mL/min and He makeup gas flow was 30 mL/min. From a calibration curve, the signal was converted to moles. Using the ideal gas law and the headspace volume of 53 mL, the number of moles of gas produced was obtained. The dissolution of H_2 and CO into the solvent at the experimental temperature was calculated to be minimal using Henry's law (5724.6 atm × mol (MeCN) × mol $(H_2)^{-1}$ at 298 K[9] and 2422.5 atm × mol (MeCN) × mol $(CO)^{-1}$ at 299 K[10]). The pressure above the headspace was assumed to be 0.85 atm, typical for Salt Lake City, UT.

Formate production was quantified using a Thermo Scientific Dionex Integrion, equipped with a Dionex Ionpac AS23 (4×250 mm) column. A combination of 4.5 mM sodium carbonate and 0.8 mM sodium bicarbonate solution in 18 mΩ water was used as the eluent. 4 mL of the post electrolysis solution was brought to a basic pH by adding 1 M NaOH (aq.) solution and then concentrated under vacuum. The solution was then extracted by 10 mL of water leaving the insoluble electrolyte behind. 0.5 mL of the solution was injected into the IC, and the signal converted to molarity from a calibration curve. Controls solutions of catalysts of same molarity as the BE solutions were prepared in MeCN and injected into the IC. A peak corresponding to some trace anionic impurity (not chloride) appeared at the same retention time as that of formate. Therefore, the FE for formate were corrected by subtracting the area under these background formate peak from ones formed from the actual catalytic runs.

The faradaic efficiency (FE) was calculated following eq 1.

$$FE = \frac{n \times F \times moles\ of\ product\ formed}{C} \times 100\%$$

Where n is the number of electrons needed to convert CO_2 to the product under consideration (n = 2 for CO, H_2 and, formate), F is Faraday's constant (96485 C.mol^{-1}), and C is the charge passed during electrolysis (C).

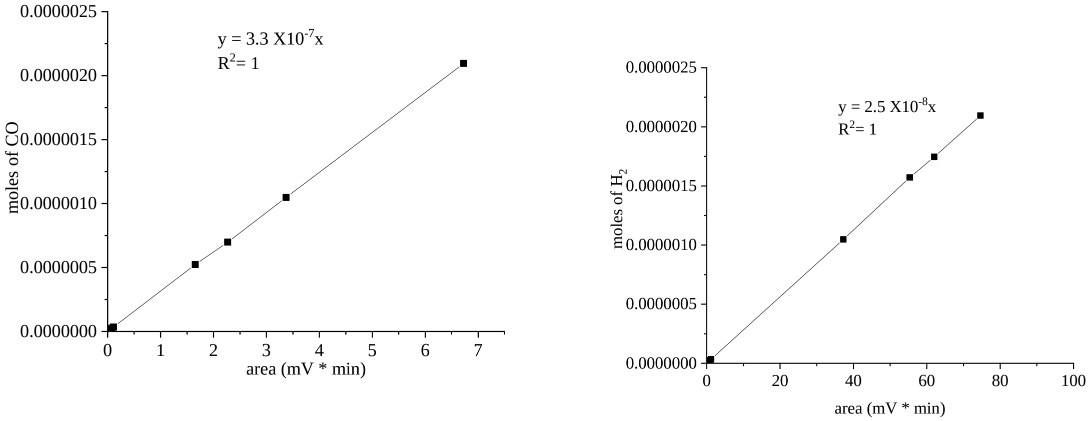


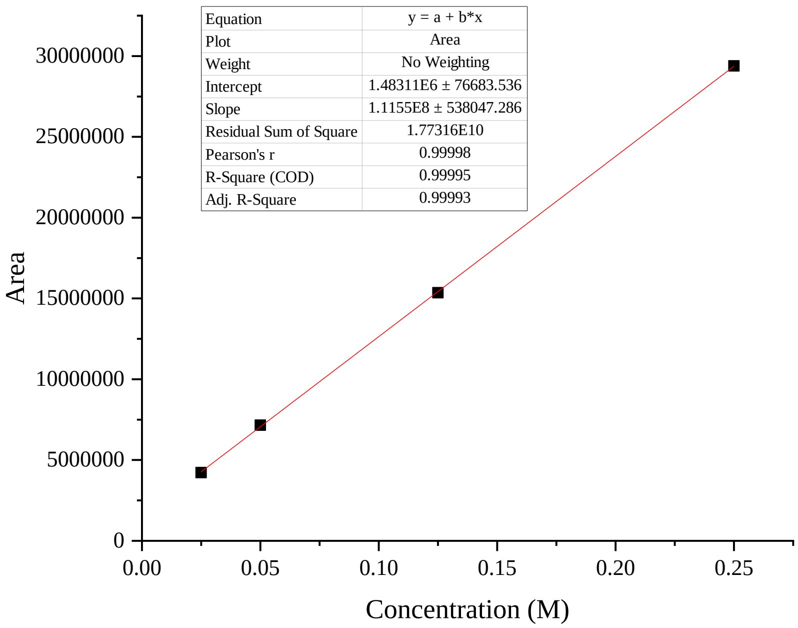
Figure S21. Calibration curve for CO (left) and H_2 (right) gas.

Methanol was detected using an Agilent 7890 B gas chromatography instrument equipped with an Agilent 5975 C insert Mass Detector. For mass detection, a 19091S-433, HP-5 MS 5% phenyl methyl Silox column was used. Helium was used as the carrier gas with a total flow of 113.39 mL/min. The inlet temperature was kept at 300 ^{o}C, with a 20:1 split ratio, 3 mL/min septum purge flow, and 105.14 mL/min split flow. The thermal auxiliary heater for the MSD transfer line was kept at 100 ^{o}C.

The quantification of MeOH was carried out by GC-FID, equipped with a 19091N-0131 HP INNOWAX column. The inlet temperature was held at 300 ^{o}C, with a 30:1 split ratio, 60 mL/min of total flow and 3 mL/min septum purge flow. The FID was held at 300 ^{o}C, with an airflow of 400 mL/min, hydrogen flow of 30 mL/min, and makeup He flow of 25 mL/min.

A calibration curve was constructed by injecting 2 µL of methanol in acetonitrile of varied concentrations.

A 2 mL aliquot of bulk electrolysis or hydrogenation solution was taken in a 10 mL round bottom flask and was subjected to 2 cycles of freeze-pump-thaw. The volatile from the flask was transferred under a static vacuum to a collecting round-bottom flask kept under liquid nitrogen. 2 µL of the liquid collected by such a method was injected into the GC using an autosampler to detect and quantify methanol.



Equation	y = a + b*x
Plot	Area
Weight	No Weighting
Intercept	1.48311E6 ± 76683.536
Slope	1.1155E8 ± 538047.286
Residual Sum of Square	1.77316E10
Pearson's r	0.99998
R-Square (COD)	0.99995
Adj. R-Square	0.99993

Figure S22. Calibration curve for MeOH detection.

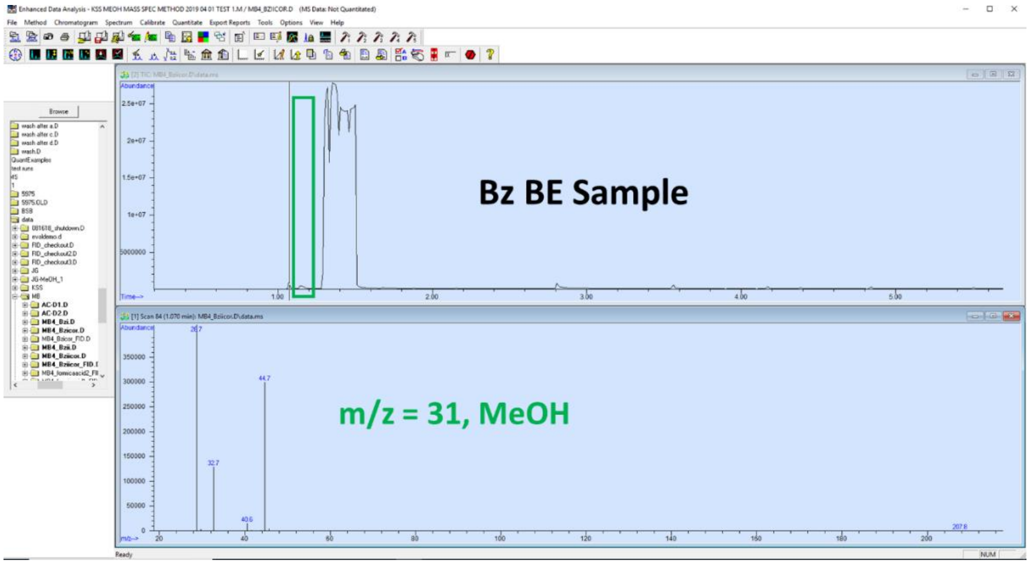


Figure S23. GC (top) and MS (bottom) of the vac-transferred liquid phase after bulk electrolysis with **(^{Bz2N}P$_3$)CoCl**. The green boxed area shows MeOH (and MeCN) by GC. Spiking the solution with MeOH showed an increase in the boxed area. The other areas correspond to MeCN.

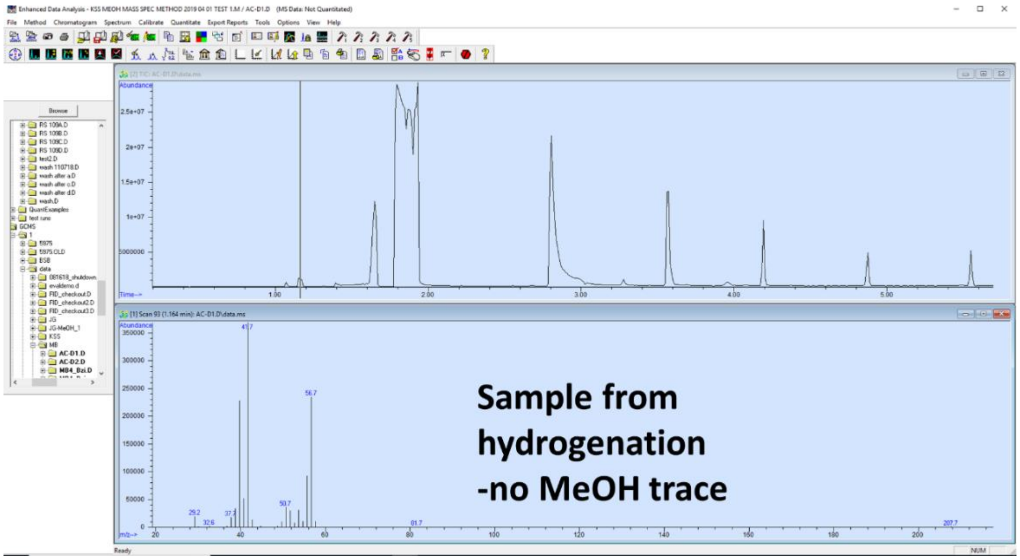


Figure S24. GC (top) and MS (bottom) of the solution after hydrogenation with **(^{Bz2N}P$_3$)CoCl**. No MeOH is present.

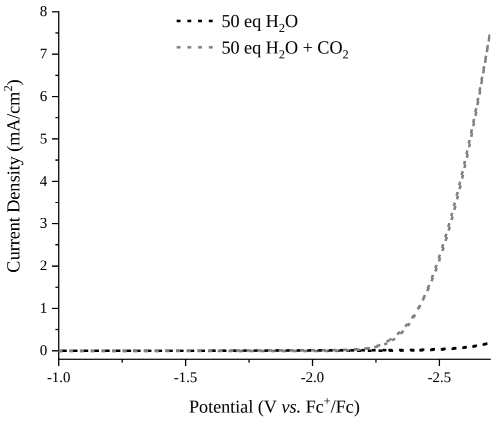


Figure S25. Cyclic voltammograms of 50 mM water in the presence (black) and absence (grey) of CO_2. Conditions: GC working electrode, 0.1 M $TBAPF_6$/ MeCN solvent, scan rate of 0.06 V/s, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

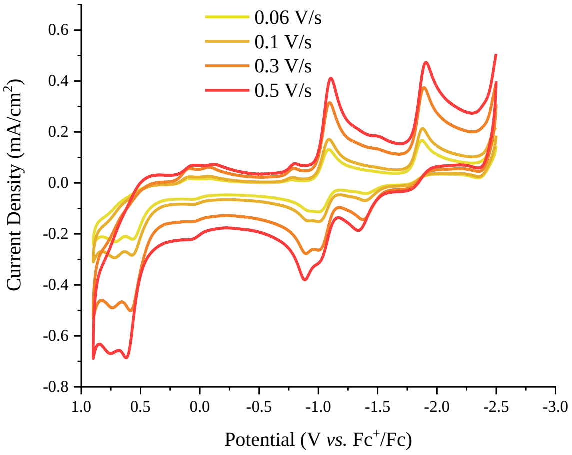


Figure S26. Scan-rate dependence of 1 mM $^{\mathbf{Ph2N}}$**P$_3$CoCl** under N$_2$. Conditions: GC working electrode, 0.1 M TBAPF$_6$/MeCN solvent, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

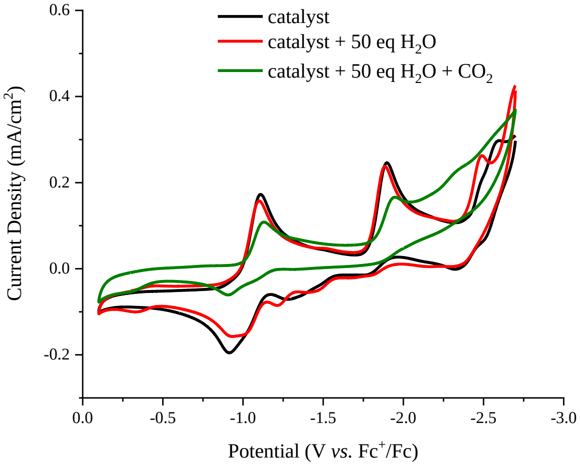


Figure S27. Cyclic voltammograms of 1 mM $^{\mathbf{Ph2N}}$**P$_3$CoCl** under various conditions; under N$_2$ (black), in the presence of 50 eq H$_2$O (red), and in the presence of 50 eq H$_2$O and CO$_2$ (green). Conditions: GC working electrode, 0.1 M TBAPF$_6$/MeCN solvent, scan rate of 0.06 V/s, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

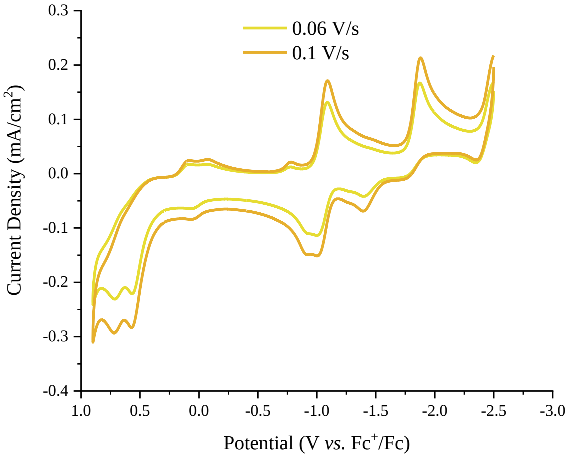


Figure S28. Scan-rate dependence of 1 mM $^{\mathbf{Ph2N}}\mathbf{P_3CoCl_2}$ under N_2. Conditions: GC working electrode, 0.1 M TBAPF$_6$/MeCN solvent, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

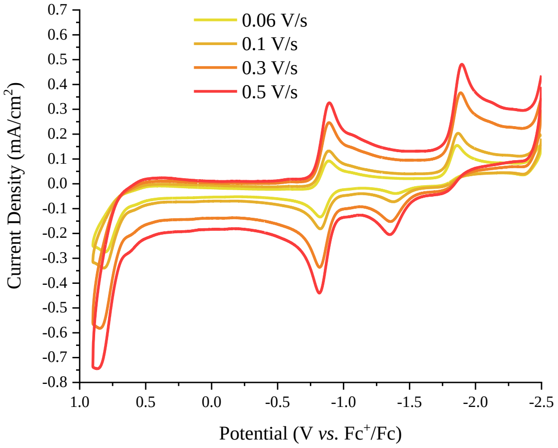


Figure S29. Scan rate dependence of 1 mM **[$^{\mathbf{Ph2N}}\mathbf{P_3Co(MeCN)}$][BArF]** under N_2. Conditions: GC working electrode, 0.1 M TBAPF$_6$/MeCN solvent, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

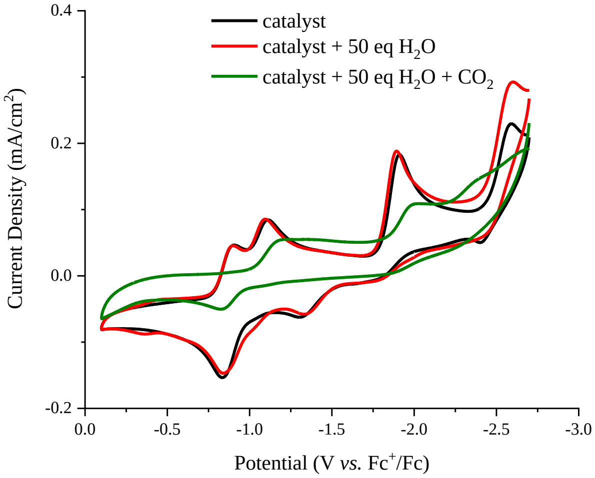


Figure S30. Cyclic voltammograms of 1 mM **[$^{Ph2N}P_3Co(MeCN)$][BArF]** under various conditions; under N_2 (black), in the presence of 50 eq H_2O (red), and in the presence of 50 eq H_2O and CO_2 (green). Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scan rate of 0.06 V/s, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

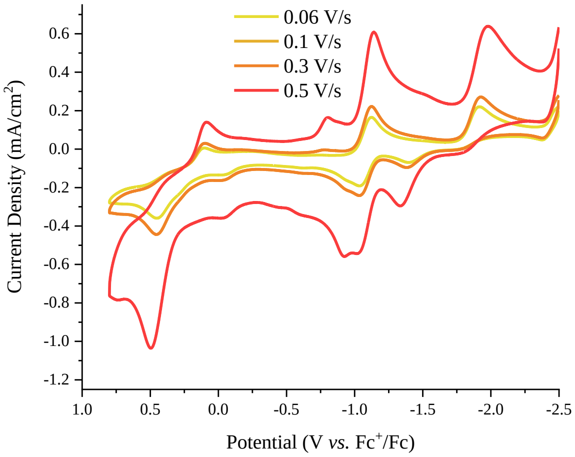


Figure S31. Scan-rate dependence of 1 mM **$^{Me}P_3CoCl$** under N_2. Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc$^+$/Fc.

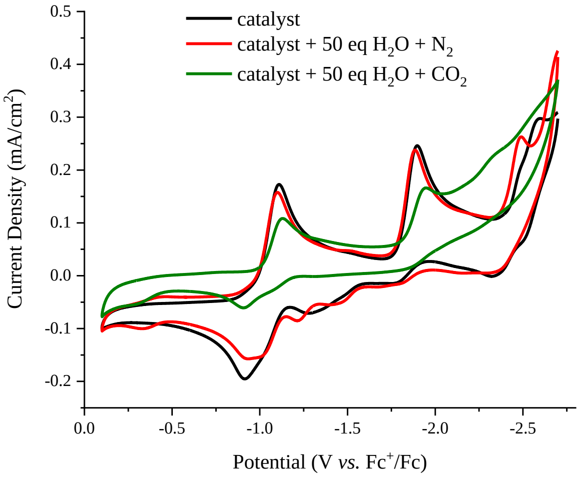


Figure S32. Cyclic voltammograms of 1 mM **^{Me}P$_3$CoCl** under various conditions; under N_2 (black), in the presence of 50 eq H_2O (red), and in the presence of 50 eq of H_2O and CO_2 (green). Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scan rate of 0.06 V/s, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc^+/Fc.

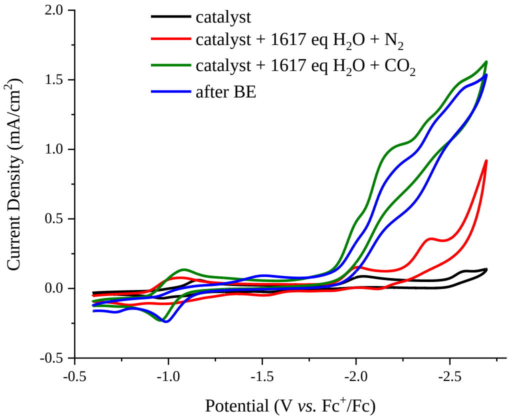


Figure S33. Cyclic voltammograms of 1 mM **^{Me}P$_3$CoCl** under various conditions during BE; under N_2 (black), in the presence of 1617 eq (3%) H_2O (red), in the presence of 1617 eq (3%) H_2O and CO_2 (green), and after 15 min of BE (blue). Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scan rate of 0.1 V/s, scanning negative, within 0 and -2.7 V *vs.* Fc^+/Fc.

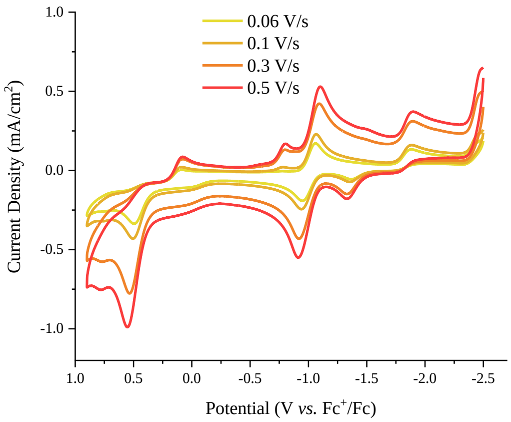


Figure S34. Scan-rate dependence of 1 mM $^{\mathbf{Bz2N}}\mathbf{P_3CoCl}$ under N_2. Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc^+/Fc.

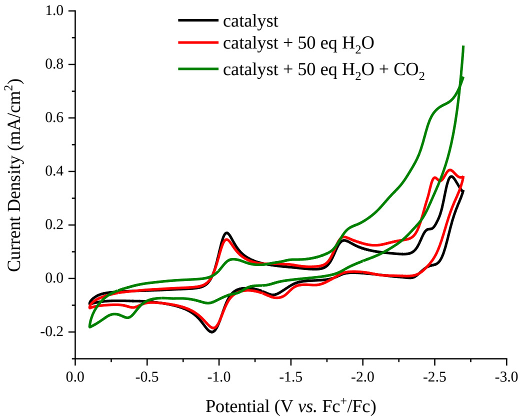


Figure S35. Cyclic voltammograms of 1 mM $^{\mathbf{Bz2N}}\mathbf{P_3CoCl}$ under various conditions; under N_2 (black), in the presence of 50 eq H_2O (red), and in the presence of 50 eq of H_2O and CO_2 (green). Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scan rate of 0.06 V/s, scanning negative, sweep 2 and 3, within -2.7 and 0 V *vs.* Fc^+/Fc.

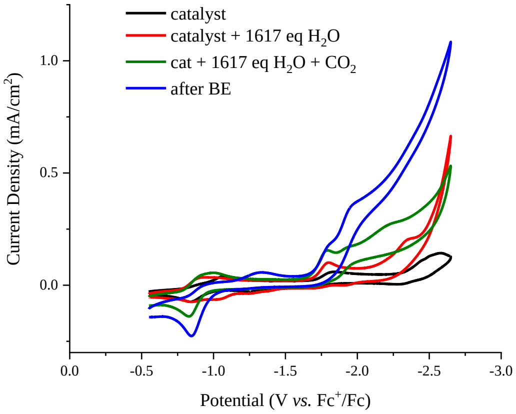


Figure S36. Cyclic voltammograms of 1 mM ^{Bz2N}**P$_3$CoCl** under various conditions during BE; under N_2 (black), in the presence of 1617 eq (3%) H_2O (red), in the presence of 1617 eq (3%) H_2O and CO_2 (green), and after 15 min of BE (blue). Conditions: GC working electrode, 0.1 M $TBAPF_6$/MeCN solvent, scan rate of 0.1 V/s, scanning negative, within 0 and -2.7 V *vs.* Fc^+/Fc.

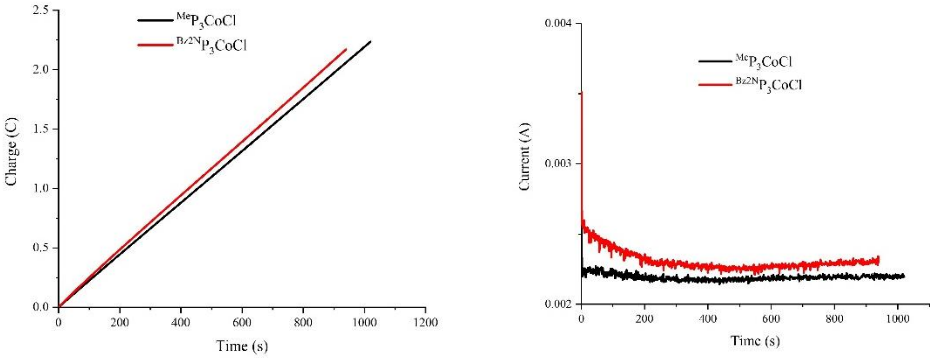


Figure S37. Charge vs. time **(left)** and current vs. time **(right)** for controlled potential electrolysis of the catalysts at -2.1 V vs. $Fc^{+/0}$.

Table S2. Product distribution of the controlled potential electrolysis (CPE) experiments.[a]

Complex	Time (s)	Charge Passed (C)	FE[b] H_2	FE[b] CO	FE[b] $HCOO^-$
$^{Me}P_3CoCl$	1062 (±127)	1.6 (±0.5)	2.5 (±2.8)	nd[c]	58 (±15)
$^{Bz2N}P_3CoCl$	1005 (±89)	1.9 (±0.3)	3.2 (±0.4)	nd[c]	36 (±18)

[a] Conditions: CPE carried out at -2.1 V *vs.* Fc^+/Fc with 1 mM catalysts using graphite rod working electrode in 0.1 M $TBAPF_6$/MeCN solvent with 380 rpm stirring; [b] Faradaic efficiency; average of four runs, standard deviation given in parenthases. [c] None detected.

7. References

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