Electronic Supporting Information

Proton reduction by molecular catalysts in water under demanding atmospheres

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Experimental Section

Reagents. All chemical reagents were obtained from commercial suppliers at the highest available purity for analytical measurements. All solvents were HPLC grade and Millipore water was used in all electrochemical analysis. $[Ni(P^{Ph}{}_2N^{PhCH2P(O)(OH)2}{}_2)_2]Br_2 \cdot HBr$ **(NiP)**[1] and $(Et_3NH)[Co^{III}Cl(dimethylglyoximato)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]$ (**CoP**)[2] were synthesised as described previously. Buffer solutions were acidified to the desired pH using dilute H_2SO_4.

General Electrochemistry. Electrochemistry was carried out with a potentiostat (Ivium/ PalmSens) in a three-electrode cell configuration. All solutions were purged for at least 10 min and measurements were taken at room temperature in buffered electrolyte solutions of triethanolamine (TEOA) and Na_2SO_4 (0.1 M each, pH 7) or trisodium citrate (0.1 M, pH 4.5). Potentials were converted to NHE according to the relationship E (*vs.* NHE) = E (*vs.* Ag/AgCl(KCl_{sat})) + 0.197 V.[3]

Cyclic Voltammetry. Cyclic voltammograms (CVs) were recorded at 100 mV s^{-1} using a 3 mm diameter glassy carbon disk working, a Pt-mesh counter and Ag/AgCl(KCl_{sat}) reference electrode (BASi) in a single compartment cell. Each voltammogram was started at 0.7 V *vs.* NHE and the second consecutive scan is presented in all figures.

Controlled Potential Electrolysis (CPE). CPE was performed in a 3-electrode cell configuration during vigorous stirring. CPE of **NiP** and **CoP** was performed with a glassy carbon rod (1.96 cm^2) working electrode, a Pt-mesh counter contained in a fritted-glass compartment and a Ag/AgCl reference electrode using 2.5 mL of solution in an air-tight cell (5.4 mL headspace) containing 0.5 mM of catalyst. CPE with a Pt working electrode (1 mm diameter) was undertaken using a single compartment cell with no catalyst in solution and a Pt-mesh counter and a Ag/AgCl reference electrode. H_2 was quantified by gas chromatography and each experiment was carried out at least three times. The standard deviation (σ) was calculated according to Eq. 1 and the Faradaic efficiency according to Eq. 2:

$$\sigma = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}} \qquad \text{(Eq. 1)}$$

$$\text{FE (\%)} = \frac{\text{H}_2\text{ (mol)}\times 2\times \text{F (C mol}^{-1}\text{)}}{\text{Charge Passed Through WE (C)}} \times 100 \qquad \text{(Eq. 2)}$$

Gas Chromatographic Analysis. Gas chromatography was carried out on an Agilent 7890A gas chromatograph with a 5 Å molecular sieve column at 45 °C and N_2 carrier gas with a flow rate of approximately 3 mL min^{-1}. Methane (2% CH_4 in N_2) was used as an external standard.

Spectroelectrochemistry. IR and UV/visible-spectroelectrochemistry was carried out using a cell designed by the authors of Ref 4. The cell contained Pt mesh working and counter electrodes with a Ag/Ag^+ reference electrode. Spectra were taken using solutions of $[CoCl(dmgH)_2(4\text{-}methoxypyridine)]$[5] (5 mM for IR; 0.25 mM for UV-visible spectra) or **NiP** (1.25 mM for IR; 0.25 mM for UV-visible spectra) with tetrabutyl ammonium bromide (0.3

M) in MeOH, which was saturated with CO. IR spectra were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer and UV-visible spectra were recorded on a Varian Cary 50 UV-visible spectrometer. In each experiment the working electrode was held at a defined potential until the current stabilised (typically 60 s) and an IR spectrum was recorded. This was repeated in 50 mV intervals over a range of potentials.[6]

Supporting Figures

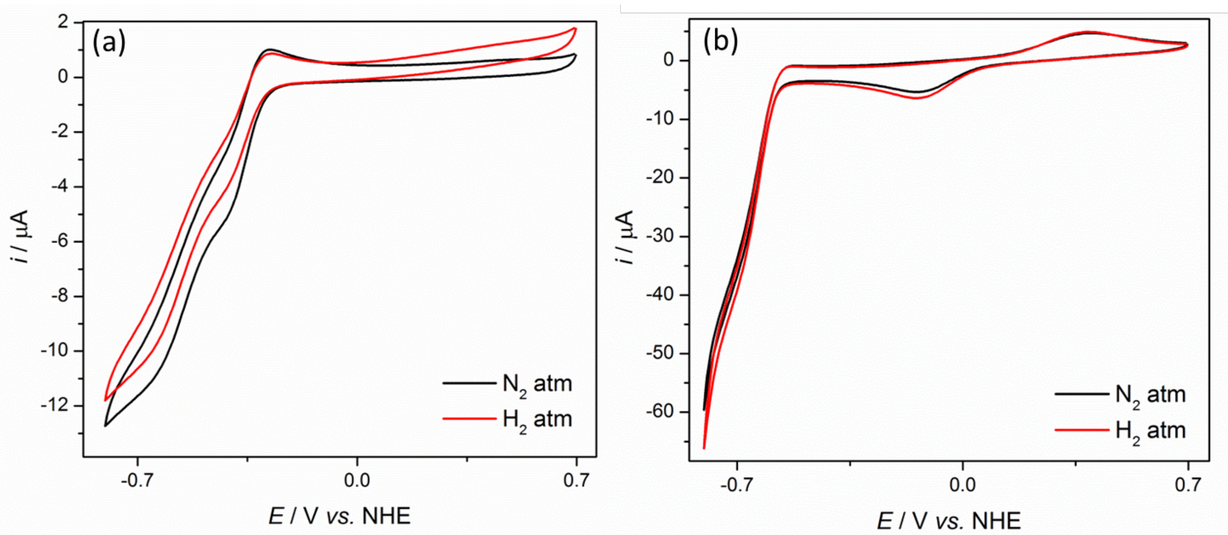

Figure S1. H_2 inhibition study (100% H_2 *vs.* 100% N_2 atmosphere) on a glassy carbon working electrode at 100 mV s^{-1} with (a) **NiP** (1 mM) in citrate buffer (0.1 M, pH 4.5) and (b) **CoP** (1 mM) in TEOA/Na_2SO_4 (0.1 M each, pH 7).

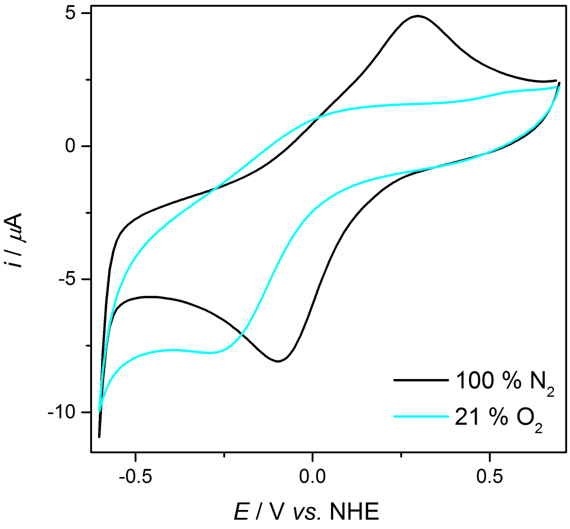

Figure S2. The effect of O_2 on the Co^{III}/Co^{II} redox wave of **CoP** (1 mM) in TEOA/Na_2SO_4 (0.1 M each, pH 7) at 100 mV s^{-1}on a glassy carbon working electrode.

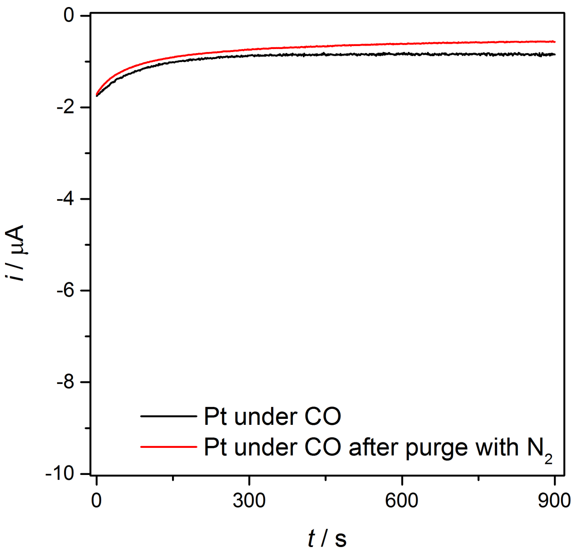

Figure S3. *I*-*t* trace from a Pt working electrode in 0.1 M citrate buffer at pH 4.5 held at –0.4 V *vs.* NHE in 100% CO and a subsequent electrolysis under 100% N_2.

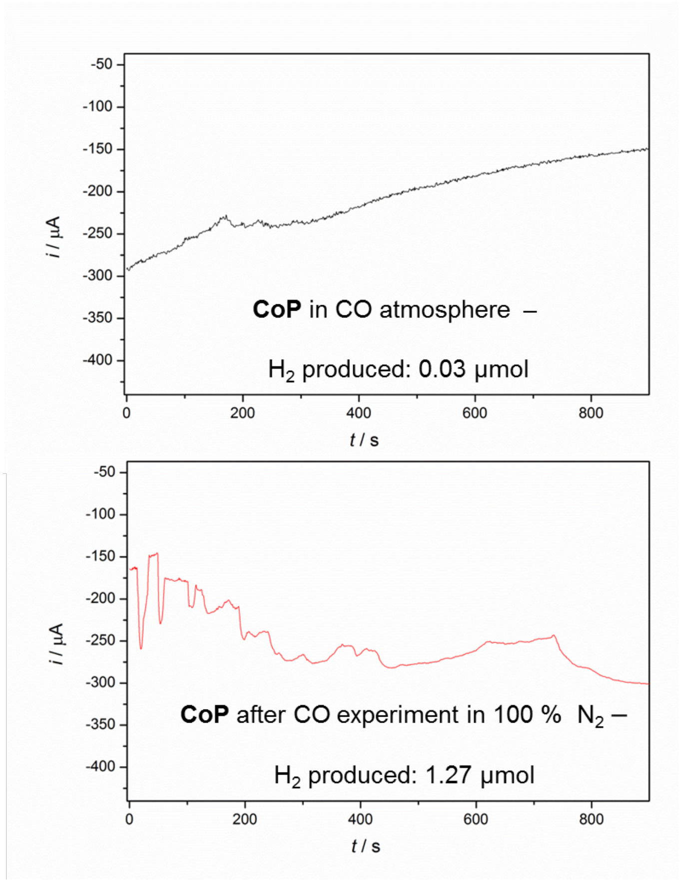

Figure S4. *I*-*t* traces and H_2 produced by **CoP** (1 mM) in 100% CO (top) and subsequently after purging with 100% N_2 (bottom). Experiments were carried out on a glassy carbon rod held at –0.7 V *vs.* NHE in TEOA/Na_2SO_4 buffer (0.1 M each, pH 7).

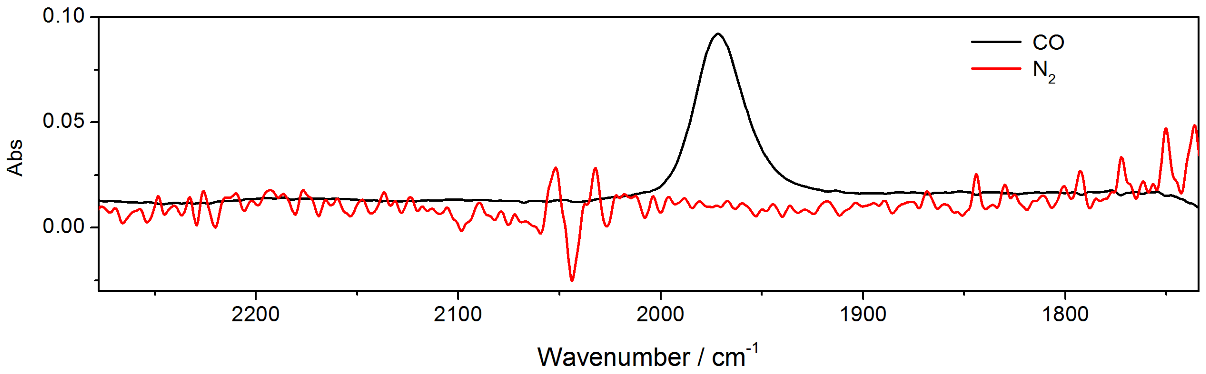

Figure S5. Infra-red spectra of [CoCl(dimethylglyoximato)$_2$(4-methoxypyridine)] (5 mM) in the presence of tetrabutylammonium bromide (0.3 M) in MeOH under an atmosphere of CO or N$_2$ at –0.8 V *vs.* Ag/Ag$^+$.

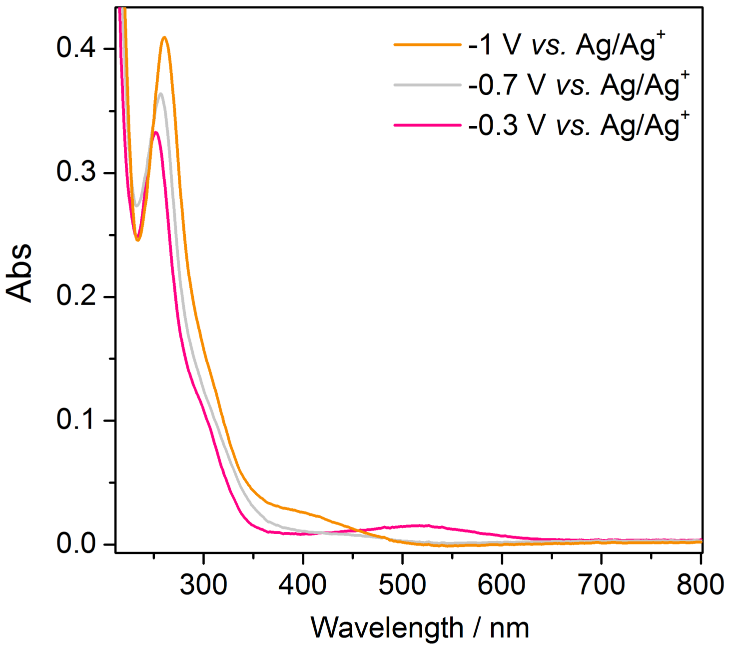

Figure S6. UV-visible spectroelectrochemical spectra of **NiP** (0.25 mM) in the presence of tetrabutylammonium bromide (0.3 M) in MeOH under an atmosphere of CO at varying potentials.

Table S1. H_2 produced and Faradaic efficiency of **NiP** (0.5 mM in 0.1 M citrate buffer at pH 4.5) and **CoP** (0.5 mM in 0.1 M TEOA/Na_2SO_4 at pH 7) from CPE at –0.4 V (**NiP** for 60 min) and –0.7 V (**CoP** for 15 min) *vs.* NHE.

	NiP				**CoP**			
Atmosphere	H_2 / µmol	σ / µmol	FE / %	σ / %	H_2 / µmol	σ / µmol	FE / %	σ / %
N_2	1.05	0.29	72.21	16.17	1.15	0.13	66.72	3.42
O_2	0.04	0.05	1.62	1.99	0.26	0.06	10.07	2.04
CO	0.76	0.06	76.09	12.00	0.03	0.00	3.56	0.53

Table S2. H_2 produced by a Pt disk (1 mm) electrode (0.1 M citrate buffer at pH 4.5) from CPE at –0.4 V *vs.* NHE for 15 min.

	Pt	
Atmosphere	H_2 / µmol	σ / µmol
N_2	0.45	0.03
CO	0.03	0.00
N_2 after CO experiment	0.00	0.00

Supporting References

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4. M. Krejčik, M. Daněk, and F. Hartl, *J. Electroanal. Chem.*, 1991, **317**, 179–187.

5. D. W. Wakerley and E. Reisner, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5739–5746.

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