Electronic Supplementary Information

Electrocatalytic Reduction of Protons to Dihydrogen by the Cobalt Tetraazamacrocyclic Complex [Co(N_4H)Cl_2]^{+}: Mechanism and Benchmarking of Performances

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Experimental section

**Synthesis.** All reagents were purchased from Sigma Aldrich or Strem and used as obtained unless otherwise stated. Reagent-grade solvents were employed without further purification. Electrochemistry grade \( \text{NBu}_4\text{NBF}_4 \) and \( \text{NBu}_4\text{NPF}_6 \) were purchased from Sigma-Aldrich and used as received. Cobaltocene was purchased from Sigma Aldrich and stored at -20 °C in an argon-filled glovebox. Acetonitrile (extrady, over molecular sieves) was purchased from Fischer Scientific. 1H NMR spectra were recorded at 298 K in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probe head operating at 300.0 MHz for 1H. Chemical shift values are given in ppm with reference to solvent residual signal.

\[ \text{Co}^{\text{III}}(\text{N}_4\text{H})\text{Cl}_2\text{ClO}_4 \text{ (Cat1)} \] was synthesized according to a previously reported procedure.1-3 6-diacetylpyridine (686 mg, 4.2 mmol) was dissolved in ethanol (6.3 mL) and kept at 40°C under argon. \( \text{CoCl}_2 \cdot 6\text{H}_2\text{O} \) (1 g, 4.2 mmol) and water (4.2 mL) were added and the mixture was stirred at 55°C to dissolve the salt, giving a purple solution. The reaction mixture was warmed at 75°C and 3,3'-diaminodipropylamine (0.59 mL, 4.2 mmol) was added. The colour turned to dark blue and the solution became cloudy on addition of the amine. Glacial acetic acid (0.17 mL) was added to solubilize and clarify the solution, which was stirred at 75°C for 5 hours under argon. After cooling down, a concentrated HCl aqueous solution (37%, 0.39 mL, 4.62 mmol) was added, after which the solution turned to an orange/brown colour. The mixture was aerated for about 6 hours affording a green solution. The volume was reduced to 1 mL before slow addition of cold ethanol (7 mL) at -8°C to precipitate \[ \text{Co}^{\text{III}}(\text{N}_4\text{H})\text{Cl}_2\text{Cl} \] as green microcrystals. The green crystals were filtered off and washed with cold ethanol. The product was recrystallized from a mixture of water and cold ethanol (-8°C) and dried under vacuum (710 mg, 40 %). \[ \text{Co}^{\text{III}}(\text{N}_4\text{H})\text{Cl}_2\text{Cl} \] was dissolved in water (5 mL) and an aqueous saturated solution of LiClO\(_4\) was added dropwise to yield \[ \text{Co}^{\text{III}}(\text{N}_4\text{H})\text{Cl}_2(\text{ClO}_4) \] as a green precipitate. The product was filtered off, recrystallized in hot water, filtered off a second time and dried under vacuum, affording green crystals (690 mg, 34%). Its purity and identity was verified by cyclic voltammetry (Figure S1), 1H NMR (Figure S2) and ESI-MS.

\( p\)-cyanoanilinium tetrafluoroborate (pCNAH) was prepared according to the literature.4 Fluoroboric acid (48% aq, 1.6 mL, 0.012 mol) was added to a filtered solution of \( p\)-cyanoaniline (1.20 g, 0.010 mol) in diethyl ether (90 mL). The protonated salt precipitated from solution and was filtered, washed with diethyl ether, and dried in vacuo.
Electrochemistry. Electrochemical data were acquired with an Autolab PGSTAT 100N potentiostat. Cyclic voltammetry measurements were run in acetonitrile with $n$Bu$_4$NBF$_4$ supporting electrolyte (0.1 M) under an argon atmosphere at room temperature, using a three-electrode setup. The working electrode was glassy carbon (1.6 mm diameter, polished with 2 mm diamond paste (Mecaprex Presi)). The reference electrode was made of an Ag/AgCl wire dipped into a KCl 3 M solution, separated from the supporting electrolyte by a Vycor® frit, and denoted below as Ag/AgCl. The auxiliary electrode was a Pt wire. All potentials given in this work ($E_{pa}$, anodic peak potential; $E_{pc}$, cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$) are reported with respect to the Fc$^+$/Fc couple. The voltammograms were referenced by addition of ferrocene as an internal standard at the end of each experiment. For the electrocatalytic study, ohmic drop compensation using the positive feedback method was conducted before each measurement. Simulations of cyclic voltammogram reported in Table S2 have been performed using the DigiElch-Professional 7 software (http://www.elchsoft.com/) with an EC reaction scheme using $E^0(\text{Co}^{III}/\text{II}) = -0.45$ V vs Fc$^+$/0, $E^0(\text{Co}^{III}/\text{Co}^{II}_{LH}) = -0.28$ V vs Fc$^+$/0; protonation thermodynamic constant $K= 10^4$; protonation rate = $10^7$ mol$^{-1}$. L.s$^{-1}$.

EPR spectroscopy experiments: EPR spectra were recorded with a Bruker EMX spectrometer operating at X-band frequency with an ER-4116 dual mode cavity. Simulations were performed with the Matlab toolbox Easyspin (version 5.2.30). Sample preparations were carried out in an argon-filled glovebox using dry and degassed solvent. UV-Vis spectra of Cat1 in its unprotonated Co$^{III}$ and Co$^{II}$ states were compared to those previously reported by Collomb and coworkers to check the oxidation state of cobalt.$^3$

Electrochemical reduction of Cat1: Electrochemical reduction was performed by exhaustive bulk electrolysis of a 0.5 mM solution of Cat1 (perchlorate salt) in dry, purged acetonitrile (+0.1 M n-Bu$_4$NBF$_4$ as supporting electrolyte), applying a potential of $-0.33$ V vs. Ag/AgCl with a platinum mesh working electrode, until the current reached below 10 $\mu$A. Chronoamperometry data following bulk electrolysis of Cat1 from Co$^{III}$ to Co$^{II}$ is given in Figure S9. Reduction of Cat1 to the Co$^{II}$ state was accompanied by a visible color change from pale green to pink. UV-Vis spectra of Co$^{III}$ and Co$^{II}$ Cat1 are shown in Figure S10.

A volume of THF equal to one tenth of the solution’s total volume was added before 200 $\mu$L of the mixed solution was transferred to the EPR tube, so that the final EPR sample contained 10%
THF by volume, in order to facilitate amorphous freezing of the sample. The tube was then sealed with a lid, extracted from the glovebox and immediately frozen in liquid nitrogen.

For the experiments in the presence of acid, 200 μL of the electrolysis solution were transferred to a small flask and either 20 μL (5 eq.) of a 25 mM acetonitrile stock solution of \( p \)-cyanoanilinium tetrafluoroborate or 3.4 μL (5 eq.) of a 10% v/v solution of tetrafluoroboric acid etherate in acetonitrile were added. 200 μL of the resulting solution, plus THF (10% by final volume), was transferred to an EPR tube, which was then sealed with a lid, extracted from the glovebox and immediately frozen in liquid nitrogen.

**Chemical reduction of Cat1:** Chemical reduction was performed on a 0.63 mM solution of Cat1 ( perchlorate salt) in dry, purged acetonitrile by the gradual addition of 1 equivalent of cobaltocene with UV-visible absorption spectroscopy monitoring. UV-vis data obtained using a cobaltocene stock solution to reduce Co\(^{III}\) Cat1 to Co\(^{II}\) is shown in Figure S11.

UV-vis spectra were recorded on an Agilent Cary 60 spectrophotometer. For measurements in the glovebox, the spectrometer was equipped with an Agilent optical fiber coupler and Hellma optical fibers (600 μm, ON 0.22; total optical path 12 m). The concentration of the cobaltocene stock solution in acetonitrile was calculated beforehand from the absorbance of cobaltocene at 327 nm (\( \varepsilon = 7420 \text{ L mol}^{-1} \text{ cm}^{-1} \)), an example is shown in Figure S12. The final concentration in Cat1 (Co\(^{II}\) form) was ~0.5 mM. 200 μL of the solution were transferred to a small flask, \( \text{nBu}_4\text{NPF}_6 \) (7.7 mg, 20 μmol) was added and the flask was agitated. The solution was transferred to an EPR tube which was then sealed with a lid, extracted from the glovebox and immediately frozen in liquid nitrogen. For the experiment in the presence of acid, 20 μL (5 eq.) of a 25 mM acetonitrile stock solution of \( p \)-cyanoanilinium tetrafluoroborate were also added.

**Determination of the diffusion constant of Cat1**

The diffusion coefficient of the catalyst \( D_{\text{cat}} \) can be determined from the scan-rate dependence of the peak current of the reversible Co\(^{III}/Co^{II}\) wave (Figure S1) and the Randles-Sevick equation (equation S1).

\[
\frac{i_0}{F^0} = 0.446FS\frac{c_0}{c_{\text{cat}}} \left( \frac{Fv}{RT} \right) D_{\text{cat}} (\text{equation S1})
\]

With \( F = 96500 \text{ C mol}^{-1} \) and \( R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \).
Using the slope of $1.7 \times 10^{-5}$ A V$^{-1/2}$ s$^{-1/2}$ measured for the first cathodic process that shows a good linearity of $i$ with $v^{1/2}$, a surface area of $2 \times 10^{-2}$ cm$^2$ and a concentration of $10^{-6}$ mol cm$^{-3}$, we determined $D_{cat}$ to be $10^{-5}$ cm$^2$ s$^{-1}$.

**Foot-of-the-Wave Analysis (FOWA) for kinetic Evaluation.**

FOWA has been demonstrated as useful to determine the $k_1$ value of an ECEC process with the second electron transfer easier than the first, following equation S2:

$$i = \frac{2 \sqrt{k_1[H^+]} [RT]}{0.4463 \sqrt{Fv}} \times \frac{1}{1 + e^{\frac{F}{RT} [E - E_{Red/Ox}^0]}}$$

(equation S2)

From data shown in Figure S13, plotting $\frac{i}{i_p}$ as a function of $1 + e^{\frac{F}{RT} [E - E_{Red/Ox}^0]}$ thus allowed a linear plot to be obtained near the foot of the catalytic wave as shown in Figure S14. The $k_1$ rate constant is calculated via equation S3 from the gradients of linear regression lines of best fit of each of the linearized FOWA plots in Figure S13, according to equation S2. The values obtained are plotted in Figure S8 and their mean value is reported in the main text.

$$k_1 = \left(\frac{\text{slope}}{4.48}\right)^2 \times \left(\frac{F}{RT} \cdot \frac{v}{C_{0[H^+]}}\right)$$

(equation S3)
Figure S1. Top: cyclic voltammograms of Cat1 (1 mM) in CH$_3$CN (+ 0.1 M $a$Bu$_4$NBF$_4$) recorded at a stationary glassy carbon electrode at different scan rates ($\nu = 0.1$, 0.2, 0.3 and 0.4 V/s); $T = 298$ K; Bottom: linear plot of $i_p$ vs. $\nu^{1/2}$ for cathodic and anodic waves. Coefficients of determination ($R^2$ values) for the linear regression lines were: 0.99814, 0.99581, 0.99954, and 0.99724 for $E_{pa1}^i$, $E_{pa2}^i$, $E_{pc1}^i$ and $E_{pc2}^i$, respectively.
Figure S2. $^1$H NMR of Cat1 (2 mM) in CD$_3$CN in the absence and presence of 1 to 16 equiv. of $p$-cyanoanilinium tetrafluoroborate (pCNAH). The bottom spectrum is for $p$-cyanoanilinium tetrafluoroborate alone.

Figure S3. Cyclic voltammograms of Cat1 (3 mM) in the presence of $p$-cyanoaniline (0 to 8 mM) at 100 mV.s$^{-1}$ in CH$_3$CN (+ 0.1 M tBu$_4$NBF$_4$).
Figure S4. CW X-band EPR spectra (9.65 GHz) of the Co$^{II}$ form of Cat1 (0.5 mM, reduction with cobaltocene) in 0.1 M $n$-Bu$_4$NBF$_4$ acetonitrile solution, alone (top), with 5 eq. of p-cyanoanilinium tetrafluoroborate (middle), or with p-cyanoaniline (bottom). Simulated spectra are shown in red. Experimental conditions: 30 K, 1 mW microwave power, 1600 G field sweep, 4 G magnetic field modulation amplitude at a frequency of 100 kHz.
Figure S5. Control cyclic voltammograms of 15 mM (black) and 60 mM (red) p-cyanoanilinium tetrafluoroborate without Cat1 are shown for comparison; scan rate: 0.1 (solid) and 10 V.s\(^{-1}\) (dashed).
Figure S6. Top: cyclic voltammograms of Cat1 (0.8 – 2.0 mM) in CH₃CN (+ 0.1 M  Bu₄NBF₄ and 1 mM ferrocene) recorded at a glassy carbon electrode in the presence of 60 mM p-cyanoanilinium tetrafluoroborate. Scan rate was adjusted to reach the pure kinetic regime (see reference 7 for a justification of this methodology). A control voltammogram of 60 mM p-cyanoanilinium tetrafluoroborate without Cat1 (gray dashed trace) is shown for comparison; middle: linear fit plot of $i_{pl}$ vs $[\text{Cat1}]$, $R^2 = 0.99851$; bottom: non-conclusive linear fit of $i_{pl}$ vs $[\text{Cat1}]^{3/2}$. 
Figure S7. Top: cyclic voltammograms of Cat1 (1 mM) in CH$_3$CN (+0.1 M $n$Bu$_4$NBF$_4$) recorded at a glassy carbon electrode in the presence of 40-60 mM $p$-cyanoanilinium tetrafluoroborate. Scan rate: 100 mV.s$^{-1}$; bottom: linear fit of $i_{pl}/i_{p0}$ vs [acid]$^{1/2}$, $R^2 = 0.99984$. 
Figure S8. Scan rate dependence of the second order rate constant $k_1$ extracted by FOWA from CVs recorded at 5 (black) and 25 (red) mM concentration of $p$-cyanoanilinium tetrafluoroborate in CH$_3$CN (+ 0.1 M $n$Bu$_4$NBF$_4$).

Figure S9. Chronoamperometry trace of exhaustive bulk electrolysis of Cat1 (4.5 µmol, 0.5 mM) from Co$^{III}$ to Co$^{II}$ in 9.0 mL CH$_3$CN with $n$Bu$_4$NBF$_4$ supporting electrolyte (0.1 M). A potential of –0.33 V vs. Ag/AgCl was applied at the platinum mesh working electrode while the solution was stirred. The counter electrode was separated behind a silica frit. From integrating the current over time (shaded area), an estimated total charge of 0.40 C was passed, corresponding to 4.2 µmol of single-electron reduced Cat1, approximately 93% conversion.
Figure S10. UV-Vis spectra of Cat1 in its Co$^{III}$ state and in its Co$^{II}$ state after reduction by bulk electrolysis. Both samples are diluted to 0.17 mM in CH$_3$CN. Cuvette path length: 1 cm.

Figure S11. Example UV-Vis spectra, following the chemical reduction of Cat1 (1.0 µmol, 0.63 mM) from Co$^{III}$ to Co$^{II}$ in acetonitrile (0.16 mL) by the gradual addition of 1 equivalent of cobaltocene from stock solution in acetonitrile (here, estimated 5.7 mM, total volume added: 160 µL. The predicted cobaltocene stock volume required for 1 equivalent (i.e. 1 µmol) was estimated to be 175 µL). The end point of chemical reduction to Co$^{II}$ was realised when the isosbestic point at 373 nm destabilised (was no longer isosbestic) and the growth of peaks between 450 – 550 nm ceased. Note that beyond 1 equivalent, cobaltocene will reduce Cat1 from Co$^{II}$ to Co$^{I}$. To prepare EPR samples, aliquots of Co$^{II}$ Cat1 were then diluted to 0.5 mM by addition of either an acid stock solution or acetonitrile by itself. The electrolyte salt, $^n$Bu$_4$NBF$_4$ (0.1 M), was added to realise conditions comparable with the electrochemically reduced samples.
Figure S12. Example UV-Vis spectra, used to calculate the concentration of the cobaltocene stock solution in CH$_3$CN following a method adapted from literature, assuming that the molar extinction coefficient of cobaltocene in MeCN is approximately the same as in EtOH ($\varepsilon_{\lambda=327} = 7420$ M$^{-1}$ cm$^{-1}$). $^{5}$ 30 µL of a roughly 5 mM solution of fresh cobaltocene in acetonitrile is added each time to 3 mL of acetonitrile in a 1 cm pathlength cuvette. Here, the average increase in absorbance of 0.423 per 30 µL addition indicates a concentration of approximately 5.7 mM of the cobaltocene stock solution from the Beer-Lambert law: $100 \times 0.423 / (7420$ M$^{-1}$ cm$^{-1} \times 1$ cm) = 5.7 mM. This is used to estimate in advance what volume of cobaltocene stock solution would be precisely 1 equivalent for the Cat1 sample. This is necessary, because obtaining an accurate concentration of cobaltocene is hindered by its rapid reaction with even tiny impurities.
Figure S13. Cyclic voltammograms for FOWA calculations, from which the current-versus-potential datapoints of the foot of the reduction wave were taken for the plots in Figure S14. Note: the reversible redox couples are the internal ferrocene standard for referencing potential.
Figure S14. FOWA linearized plots (black) with linear regression lines of best fit (red, dashed). Plotted are the $i_c$ over $i_p$ ratios against the linearizing expression derived from the respective applied potential ($E$) for each $i_c$ datapoint minus the standard potential for reduction of Co$^{II}$H to Co$^0$H ($E^0$). $E^0$ was taken from the reversible redox couple seen on the left side of the high-rate CV in Figure 2 to be –0.397 V vs. Ag/AgCl (KCl, 3 M) (i.e. –0.89 vs. Fc$^{+}/0$). Currents from Figure S13 CV reduction waves were corrected to their respective baselines to give the $i_c$ values. $i_p$ values depend on scan rate and were independently measured as shown in Figure S1. They are used to avoid measuring the catalyst diffusion coefficient separately.6

Table S1. Simulation parameters obtained by best fit. The A strain parameter refers to the cobalt hyperfine coupling. There is an anticorrelation between gStrain and AStrain.

| Species | g values | gStrain | Hyperfin coupling (MHz) | AStrain (MHz) |
|---------|----------|---------|-------------------------|---------------|
|         |          |         | 59Co | 14N |         |         |         |         |
| Coll (Fig. 3) | 2.202 | 0.04 | 5.5 | 10 |        |         |         |         |
|          | 2.190 | 0.04 | 19 | 4 |        |         |         |         |
|          | 2.003 | 0.07 | 270 | 20 |        |         |         |         |
| Coll + 5eq pCNAH (Fig. 3) | 2.240 | 0.01 | 8 | 15 | 15 | 20 |        |         |
|          | 2.130 | 0.065 | 10 | 5 | 5 | 20 |        |         |
|          | 2.004 | 0.002 | 257 | 45 | 45 | 20 |        |         |
| Coll + 5eq HBF4 (Fig. 3) | 2.240 | 0.015 | 30 | 15 | 20 |        |         |         |
|          | 2.140 | 0.062 | 30 | 5 | 5 | 20 |        |         |
|          | 2.008 | 0.0022 | 262 | 40 | 40 | 20 |        |         |
| Coll in 0.1 M Bu4NBF4 (Fig. S4) | 2.202 | 0.04 | 15.5 | 2 |        |         |         |         |
|          | 2.190 | 0.04 | 10 | 12 |        |         |         |         |
|          | 2.004 | 0.025 | 270 | 9 |        |         |         |         |
| Coll in 0.1M Bu4NBF4+ 5eq pCNAH (Fig. S4) | 2.240 | 0.0125 | 20 | 15 | 15 | 20 |        |         |
|          | 2.140 | 0.065 | 20 | 5 | 5 | 20 |        |         |
|          | 2.008 | 0.002 | 257 | 45 | 45 | 20 |        |         |
| Coll + 1eq pCNA– (Fig. S4) | 2.202 | 0.04 | 5.5 | 10 |        |         |         |         |
|          | 2.190 | 0.04 | 19 | 4 |        |         |         |         |
|          | 2.004 | 0.022 | 300 | 20 |        |         |         |         |

Table S2. Evolution of the recorded and simulated cathodic peak potential of the Co$^{III}$/Co$^{II}$ wave in the presence of various amounts of para-cyanoanilinium tetrafluoroborate at 0.1 and 10 V.s$^{-1}$.

| [acid] | log([acid]) | $E_{pc}$(Co$^{III}$/Co$^{II}$) 10 V.s$^{-1}$ | $E_{pc}$(Co$^{III}$/Co$^{II}$) 0.1 V.s$^{-1}$ |
|--------|-------------|------------------------------------------|------------------------------------------|
|        |             | Exp | Sim | Exp | Sim |
| 0      | 0           | -0.50 | -0.50 | -0.50 | -0.50 |
| 0.01   | -2.0        | -0.44 | -0.41 | -0.39 | -0.37 |
| 0.015  | -1.8        | -0.42 | -0.39 | -0.32 | -0.34 |
| 0.02   | -1.7        | -0.36 | -0.37 | -0.30 | -0.33 |

References.

1. K. M. Long and D. H. Busch, J. Coord. Chem., 1974, 4, 113-123.
2. K. M. Long and D. H. Busch, *Inorg. Chem.*, 1970, **9**, 505-512.
3. S. Varma, C. E. Castillo, T. Stoll, J. Fortage, A. G. Blackman, F. Molton, A. Deronzier and M. N. Collomb, *Phys. Chem. Chem. Phys.*, 2013, **15**, 17544-17552.
4. A. M. Appel, D. L. DuBois and M. R. DuBois, *J. Am. Chem. Soc.*, 2005, **127**, 12717-12726.
5. A. Jaworska-Augustyniak and J. Wojtczak, *Monatshefte für Chemie / Chemical Monthly*, 1979, **110**, 1113-1121.
6. C. Costentin and J.-M. Savéant, *ChemElectroChem*, 2014, **1**, 1226-1236.
7. D. Sun, A. K. Harshan, J. Pécaut, S. Hammes-Schiffer, C. Costentin and V. Artero, *ChemElectroChem*, n/a.