Bimetallic Cooperativity

Bimetallic Cooperativity in Proton Reduction with an Amido-Bridged Cobalt Catalyst

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Abstract: The bimetallic catalyst [Co1(L1)(bppy)]ClO4 (1), in which L1 is an [N3O2] fused ligand, efficiently reduced H+ to H2 in CH3CN in the presence of 100 equiv of H2O with a turnover number of 18 and a Faradaic efficiency of 94% after 3 h of bulk electrolysis at −1.6 V (vs. Ag/AgCl). This observation allowed us to propose that the bimetallic cooperativity is associated with distance, angle, and orbital alignment of the two Co centers, as promoted by the unique Co–Narylamidoco environment offered by L1. Experimental results revealed that the parent [Co3Co3] complex undergoes two successive metal-based 1 e− reductions to generate the catalytically active species [Co2Co], and DFT calculations suggested that addition of a proton to one Co1 triggers a cooperative 1 e− transfer by each of these Co centers. This 2 e− transfer is an alternative route to generate a more reactive [Co3(OC–H2) ] hydride, thus avoiding the Co3H− required in monometallic species. This [Co3(OC–H2) ] species then accepts another H+ to release H2.

Introduction

The widespread dependence of our society on fossil fuels and the impending depletion of carbon-based reserves have triggered the search for renewable and clean H2-based energy.1,2 Earth-abundant transition metals such as cobalt, nickel, and iron have attracted attention owing to their ability to generate H2.3–5 Among these metals, cobalt is particularly relevant because of its affordable redox potentials between the 3d6 Co6+, 3d7 Co7+, and 3d8 Co8+ states. The catalytically active monovalent species can be stabilized and yield the doubly-oxidized cobalt/hydride intermediate Co6−H−, which is pivotal for H+ reduction to H2 after reduction to a more reactive Co3H−.6–11 Known cobalt catalysts follow either a heterolytic or a homolytic pathway.12–15 The former mechanism relies on a single Co3H− or a Co3H− reacting with another H+ and is favored if the concentration of protons is not limiting. The latter involves the collision of two Co3H− moieties from independent molecules.16 Enhanced activity is expected from some binuclear analogues of monometallic catalysts in which close proximity between two Co centers triggers cooperativity either by facilitating homolytic pathways17 or by enabling electron transfer between the metallic centers, thus avoiding formation of a Co4H− species.

Cooperative effects have been proposed by Dinolfo and co-workers18 for a binuclear Co2 catalyst in a bicompartimental Robson/Okawa-type [N2O2] macrocycle19 with a Co–Co distance of 3.22 Å, whereas Gray and co-workers20,21 evaluated oxime-based Co2 catalysts with both flexible hydrocarbon and rigid BO2 bridges that revealed no significant catalytic enhancement. Similarly, the lack of cooperativity observed in dicobalt complexes featuring pyrazolato bridges22,23 was attributed either to the large distance of 3.95 Å between the Co centers or to the flexibility of the ligand. To date it is unclear what factors control metal cooperativity in proton reduction, and this lack of understanding prevents a more rational design of Co2 catalysts. Continuing our long-standing interest in the mechanisms of H2 generation by Co catalysts,23–26 we hypothesize that cooperativity will be dependent on 1) the distance between the Co centers, 2) the relative topology of the coordination environments, and 3) the degree of orientation and overlap between redox-active orbitals. To evaluate this hypothesis, we analyzed the catalytic potential of the bimetallic complex [Co2(L1)(bppy)]ClO4 (1),27 in which (L1)3− is the tripoly-deprotonated ligand shown in Figure 1a, by means of electrochemical, spectroscopic, and computational methods. Complex 1 is a unique bimetallic species singularly suited for this study because of the short distance between the two vicinal Co centers along with the presence of a Co–Narylamidoco unit that may foster the proper orientation of Co orbitals involved in catalysis. Our results indicate that the two Co centers of complex 1 function cooperatively in the electrocatalytic reduction of H+, thus offering a viable mechanistic alternative to homolytic and heterolytic pathways employed by mononuclear Co catalysts.

Figure 1. The complex [Co1(L1)(bppy)]ClO4 (1): (a) Drawing and (b) Oak Ridge thermal ellipsoid plot (ORTEP) of the core showing a Co1–N3–Co2 angle of 86.9° expected to facilitate cooperativity.
Results and Discussion

Bimetallic [Co\[^8\]L\[^1\]ClO\[^4\]] (1)

Species 1 is prepared by treatment of 1 equiv of H\[^2\]L\[^1\] with 2 equiv of Co(CIO\[^4\])\_4 and 
pyridine in the presence of Et\[^3\]N as base. A detailed description of the synthesis of 1, 
along with its thorough characterization and molecular structure, was recently reported by 
Fiedler and co-workers.[27] Figure 1b shows that the (L\[^1\])\(^{3+}\) ligand loses two phenolic and one amido 
protons to support a dicobalt(II) core in which the metal centers lie at a short distance of 2.70 Å, 
brided by the N3 atom of a diarylamido unit with a Co1–N3–Co2 angle of 86.9°. Each 
of the five-coordinate Co\[^8\] centers is bonded to the N atom of an azomethine (N1 or N2) and the O atom of a phenolate (O1 or O2), with a bidentate 
pyridine (bpy) completing the coordination sphere. This monocationic unit is 
neutralized by a single ClO\[^4\] counterion. The low-spin (S = 1/2) nature of both 
Co\[^8\] centers is indicated by relatively short metal–ligand bond lengths, ranging between 1.89 and 2.06 Å (the average 
Co–N/O bond length is 1.95 Å). The Co\[^8\] centers are antiferromagnetically coupled as revealed by the sharpness of the 
\(^1\)H NMR features.[27] The UV/Vis spectrum of 1 was recorded in 
CH\(_2\)CN (Figure 2). The catalyst presents a yellowish brown 
color owing to the presence of intense intraligand charge 
transfers (ILCTs). The initial spectrum shows bands below 
320 nm tentatively attributed to \(\alpha^+ - \alpha\) and \(\pi^+ - \pi\) ILCT 
processes, whereas the shoulders around 343 and 452 nm are 
attributed to low-intensity \(\pi - \pi^*\) transitions typical of distorted 
environments.[27]

![Figure 2. UV/Vis spectra of 1: (a) Pre-catalytic [Co\(^8\)Co\(^8\)] at 1 x 10^{-1} M; (b) chemically reduced [CoCo], unknown concentration; (c) post-catalytic [Co\(^8\)Co\(^8\)].](image)

Electrocatalytic H\(^+\) reduction

To study the possibility of 1 as a catalyst for the reduction of 
H\(^+\) to H\(_2\), we investigated the electrochemical response of 1 in 
anhydrous CH\(_2\)CN by using a glassy carbon working electrode 
with increasing concentrations of acetic acid (HOAc, pH\(_5\) = 22.3 
in CH\(_2\)CN) as the proton source.[28] The standard reduction potential of H\(^+\) in CH\(_2\)CN, E\(^{\text{red}}\) (H\(_2\)/H\_) was determined by open-circuit 
potential measurements as \(-0.028 \pm 0.008\) V (vs. Fc\(^+/\)Fc).[26] 
Under standard conditions, E\(^{\text{red}}\) (H\(_2\)/H\_) would be \(-1.35\) V (vs. Fc\(^+/\)Fc) for HOAc; however, high concentrations can afford 
homoconjugation, leading to an incremental acidity and increasing 
the standard reduction potential.[29,30] As shown in 
Figure 3, a cyclic voltammogram of 1 shows three cathodic 
events. An irreversible wave was observed near \(-1.51\) V (vs. 
Fc\(^+/\)Fc) (\(-0.99\) V vs. Ag/AgCl) and assigned to the reduction of the 
dicobalt(II) core [Co\(^8\)Co\(^8\)] to the formal [Co\(^8\)Co\(^8\)] state.

This [Co\(^8\)Co\(^8\)] state does not seem able to afford catalysis, 
which is observed at a potential of \(-1.86\) V (vs. Fc\(^+/\)Fc) 
(\(-1.34\) V vs. Ag/AgCl), thus requiring a [Co\(^8\)Co\(^8\)] state. Upon 
increase of the HOAc concentration, this electrocatalytic current 
enhancement becomes evident and reaches its maximum at 
\(-2.08\) V (vs. Fc\(^+/\)Fc) (\(-1.56\) V vs. Ag/AgCl) with the addition of 
20 equiv of acid. Control experiments, in which HOAc is added 
to CH\(_2\)CN in absence of 1, show negligible increase in current, 
even if significantly more negative potentials are applied. 
These results validate the catalytic role of 1 and support our 
hypothsis of homogeneous H\(^+\) reduction with 1 as electroca-
talyt.

The experimentally determined redox events were further 
studied by using DFT calculations in model compounds. 
Complex 1 was modeled with two low-spin Co\(^8\) centers in agree-
ment with NMR data. Each center contains one unpaired elec-
tron, and the [CoCo\(^8\)] core is antiferromagnetically coupled to 
provide a singlet (S = 0) ground state.[23] For simplicity, the \(\text{Bu}\) groups on the phenolates are replaced by methyl groups.[31] 
The results for relevant species are shown in Figure 4 as calcu-
lated spin-density plots with Mulliken spin-density values. 
The initial singlet [CoCo\(^8\)] \(^{5}\)d\(^{3}\)d\(^{-}\)\(^{5}\)d\(^{1}\)d\(^{-}\) core in 1 is reduced to the 
doublet [CoCo\(^8\)] \(^{10}\)d\(^{3}\)d\(^{-}\)\(^{8}\)d\(^{1}\)d\(^{-}\) core in A. Species A, therefore, 
contains a high-spin 3d\(^{1}\) Co with two unpaired electrons and 
can be further reduced to the singlet [CoCo\(^8\)] B with a \(^{10}\)d\(^{3}\)d\(^{-}\) \(^{10}\)d\(^{3}\) core at a calculated potential of \(-1.64\) V (vs. Fc\(^+/\)Fc). The
the monovalent species B was confirmed experimentally by UV/Vis spectroscopy by chemically reducing an ample of [Co\text{II}Co\text{II}] (1) with 2 equiv of KC8 under inert atmosphere. The resulting spectrum is shown in Figure 2b and displays bands typical of previously reported Co\text{I} species; based on similarities to the spectrum of the Co\text{II}-containing species, the band at 285 nm is attributed to ILCT processes. Bands at 344, 409, and 700–900 nm are comparable to those observed for a Co\text{I} tetraaza-macrocyclic catalyst[32] and associated with d–d bands. In an octahedral Co\text{I} bis(pyridine-2,6-diimine) complex these broad bands are attributed to d–π* charge-transfer processes,[33] whereas several shoulders at 500–600 nm are characteristic for the presence of radical species. Similar shoulders were observed for B between 450 and 650 nm, thus suggesting that ligand reduction may have occurred to some extent. To ascertain experimentally the overpotential at which 1 shows electrocatalytic activity, a series of 2 min bulk electrolyses (BE) were performed at applied potentials ranging between −0.7 and −1.6 V (vs. Ag/AgCl). The experiment was performed in an airtight H-type cell by using a Hg-pool working electrode, Ag/AgCl as reference, and a Pt-coil auxiliary electrode placed in an adjacent compartment separated by a frit. The main chamber was filled with catalyst 1, TBAPF6 (TBA = tetrabutylammonium) electrolyte solution, and HOAc in 20 mL CH3CN. The auxiliary chamber was filled with the electrolyte solution only. Figure 5a illustrates the total charge consumed by 1 in the presence of acid during BE; charge consumption remained constant up to −1.4 V (vs. Ag/AgCl), after which it increased significantly until −1.6 V (vs. Ag/AgCl), concomitant with evolution of H2 gas, as confirmed by GC. Figure 5b shows a plot of charge consumed versus applied potential. The graph indicates that the onset potential for catalysis is −1.4 V (vs. Ag/AgCl).

This onset potential is comparable to that of the mononuclear cobalt polypyridyl catalyst recently published by Verani and co-workers[24] and investigated under similar conditions that enable comparison. The plot of current versus concentration of HOAc at a potential of −2.08 V (vs. Fc+/Fc) is provided in Figure 6. The measured current increases linearly with the concentration of HOAc, whereas negligible current increase is observed in absence of 1. An apparent overpotential of 0.63 V was calculated assuming homoconjugation (E\text{Fc+/Fc} = 1.23 V), and a rate of H2 generation[30] (kobs) of 6.33 s−1 resulted. A charge consumption plot over 3 h is shown in Figure 7. The slight curvature observed within the first 10 min is typical for proton reduction and tentatively associated with solvent dissociation.[25] The amount of H2 produced over the same period of time was determined by BE as already

![Figure 4](image1.png)

![Figure 5](image2.png)

![Figure 6](image3.png)

![Figure 7](image4.png)
discussed, by using 100 equiv of acid at an applied potential of −1.6 V (vs. Ag/AgCl).

A sample of the headspace gas (100 µL) was injected into a GC to quantify the amount of H₂ produced and repeated in triplicate. A calibration curve (Figure S1 in the Supporting Information) was used to standardize the calculations. An average amount of 0.072 mmol H₂ was calculated after background correction, which is associated with a turnover number (TON) of 18, equivalent to approximately 40% conversion rate. The Faradaic efficiency (FE) was calculated at 94% from the maximum charge consumed. BE experiments were performed under similar conditions as described above by using an incremental concentration of acid, leading to an increase in the calculated TONs. Accordingly, the use of 200 equiv of acid led to a TON of 75, whereas 300 equiv led to a TON of 97. In both cases the Faradaic efficiency remained consistent at >90%. As expected, because the concentration of acid was no longer a limiting factor, high yields were observed and the use of 400 equiv of acid led to the highest TON of 120 with an associated drop in FE to approximately 85%.

The charge versus time plots for these experiments are shown in Figures S2–S4 in the Supporting Information; whereas the first two graphs show an almost linear behavior in which the initial lagging observed in Figure 6 almost disappears, the plot with 400 equiv shows slightly increased activity after the first 10 min followed by a decrease after approximately 2.5 h, which is likely related to slow degradation of the catalyst under such acidic conditions. Considering the near-linearity of the graph in Figure S3, the system seems optimized in the presence of 200 equiv of acid. Comparison of activity with other reported bimetallic species[16, 18, 20,34] is hampered by the lack of information on directly measured TONs. However, simple assessment of our system (without considering variables such as proton source and applied potential) reveals that the TON, rate of conversion, and Faradaic efficiency values compare favorably with monocobalt catalysts.[23,24]

Fate of catalyst 1

The post-catalysis spectrum shown in Figure 2c displays features similar to those observed in the [Co<sup>II</sup>Co<sup>II</sup>] state (Figure 2a), thus attesting to the catalytic nature of 1 along with a decrease of approximately 10% in the UV bands and of 2% in the 450 nm band. This small discrepancy is explained by slow percolation of the solution between the chambers and through the frit of the electrochemical cell. Alternatively, a fraction of the catalyst may be deactivated, and evaluation of a grafoil sheet electrode was performed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis to assess the possibility of nanoparticle formation (Figure S5 in the Supporting Information). Notwithstanding evidence for formation of organic nanoparticles, no Co was detected on the surface of the electrode. Thus, UV/Vis, SEM, and EDX analyses support the presence of a catalyst that is molecular in nature.

Mechanism of H<sup>+</sup> reduction

The proposed catalytic mechanism of H<sup>+</sup> reduction is shown in Figure 8. Each [Co<sup>II</sup>Co<sup>II</sup>] in [Co<sup>II</sup>Co<sup>II</sup>] (1) displays one unpaired electron in the d<sub>y</sub>z-based singly occupied molecular orbital (SOMO), yielding an antiferromagnetically coupled singlet ( S = 0). The reduction of 1 generates [Co<sup>II</sup>Co<sup>II</sup>] (A) with a Co<sup>II</sup> (d<sup>3</sup>) and a Co<sup>I</sup> (d<sup>3</sup>). The Co<sup>II</sup>-based d<sub>x</sub>y<sub>2</sub>-orbital is now occupied by an electron, leading to an overall doublet ( S = 1/2) ground state. On further reduction the second Co<sup>II</sup> center in A accepts

![Figure 8. Catalytic mechanism of H<sub>2</sub> generation by 1 in CH<sub>3</sub>CN. Protonation of the [Co<sup>II</sup>Co<sup>II</sup>] intermediate B causes each Co<sup>I</sup> center to donate 1 e− to H<sup>+</sup>, resulting in the formation of the [Co<sup>II</sup>Co<sup>II</sup>]-hydride complex C. Isodensity plots of the orbitals of 1, A, B, and C are shown in Figure S7 in the Supporting Information. Free energies [kcal mol<sup>−1</sup>]<sup>[35]</sup> and potentials [V] calculated at the BPW91/SDD/6-31G(d,p) level of theory.<sup>[36]</sup>](image)
an electron to its empty d_{x^2−y^2} orbital and is transformed into a second \( \text{d}^{10}\text{3d} \) ion in [CoCo] (B). This is the proposed catalytically active species. The two adjacent d_{x^2−y^2} SOMOs in B do not overlap spatially and, therefore, are not coupled with each other. As a consequence, each of these electrons can be transferred onto an incoming H\(^+\) to reduce it to a hydride (H\(^−\)). As a result, protonation of B is favorable by 28 kcal mol\(^{−1}\) (ΔG).

Each of the two Co\(^{III}\) centers transfers an electron to d_{x^2−y^2} SOMO, and the resulting complex is described as the species [Co\(^{II}\)Co\(^{III}\)(H\(^−\))] (C) (Figure 8 and Figure S6 in the Supporting Information). The hydride moiety is bound more tightly to one of the Co\(^{II}\) ions, rather than symmetrically bridged between the two centers. The shortest Co\(^{II}−\text{H}−\text{Co}^{III}\) distance is calculated at 1.54 Å, whereas the other distance has a computed value of 1.85 Å. It is noteworthy that the cooperativity between both centers in species B leads to C, [Co\(^{II}\)Co\(^{III}\)(H\(^−\))]\(^{+}\), thereby precluding formation of a [Co\(^{II}\)Co\(^{III}\)(H\(^−\))] intermediate. The latter species, containing the trivalent 3d\(^{10}\) Co\(^{II}\) ion, can only be invoked if there is no cooperativity and the two metal centers function independently. Succinctly, protonation of one of the Co\(^{III}\) centers in B prompts a 2 e\(^−\) transfer in which each of the two Co\(^{II}\) centers donates an electron to the H\(^−\). As a result, the more reactive Co\(^{III}\)(H\(^−\)) unit is achieved without prior or concurrent formation of the Co\(^{II}\)(H\(^−\)) moiety.

### Conclusion

We have investigated both experimentally and theoretically the bimetallic complex [Co\(^{II}\)\(\text{L}^1\)(bpy)\(_2\)]ClO\(_4\) \(^{(1)}\). This species supports the catalytic H\(^+\) reduction to H\(_2\) in CH\(_2\)CN in the presence of a weak acid such as HOAc at an overpotential of 0.63 V. This catalytic activity relies on a 2 e\(^−\) reduction of the parent species [Co\(^{II}\)Co\(^{III}\)] \(^{(1)}\) to form a [Co\(^{II}\)Co\(^{III}\)] complex. Each of these Co\(^{II}\) centers contributes with the donation of one electron to a single incoming H\(^−\), thus forming a reactive Co\(^{II}\)-hydride. The new bimetallic cooperativity exhibited by this system arises from the close proximity of the cobalt centers and an appropriate orbital topology that avoids the formation of the Co\(^{II}−\text{H}−\text{Co}^{III}\) moiety required for proton reduction in monometallic catalysts. The second Co\(^{II}\) center plays a pivotal role in the catalytic reduction of H\(^−\), acting as an electron reservoir to donate the second electron necessary for formation of the Co\(^{II}−\text{H}−\text{Co}^{III}\) unit that favorably accepts another H\(^−\) and releases H\(_2\). Post-catalytic SEM and EDX analyses support the molecular nature of the catalyst. Therefore, the observations resulting from this work lead to considerations on how to optimize topology and orbital overlap to promote the use of a neighboring metal center as electron reservoir. These factors will become pivotal in the development of new and improved bimetallic catalysts.

### Experimental Section

#### Materials and methods

Reagents were used without further purification as purchased from commercial sources. UV/Vis spectra were obtained using a Shimadzu UV-3600 spectrophotometer. Complex 1 was obtained by dissolving the ligand H\(^+\) \((0.066\) g, 0.10 mmol), 2,2’-bipyridine \((\text{bpy}, 0.352\) g, 0.20 mmol), and Co(ClO\(_4\))\(_2\)·6H\(_2\)O \((0.073\) g, 0.2 mmol) in a 1:1 mixture of CH\(_2\)CN and CH\(_2\)Cl\(_2\) (10 mL). A detailed synthetic protocol and characterizations have been described recently.

#### Redox studies

The electrochemical behavior of 1 was investigated with a BAS 50W potentiostat/galvanostat. CVs were obtained at room temperature in CH\(_2\)CN containing 0.1 M TBAPF\(_6\), as the supporting electrolyte under argon atmosphere. The electrochemical cell employed three electrodes: glassy-carbon (working), platinum wire (auxiliary), and Ag/AgCl (reference). The Fc\(^+\)/Fc redox couple \([E^0 = 401\) mV vs. normal hydrogen electrode (NHE)] was used as internal standard. BE was performed in a custom-made air-tight H-type cell under inert conditions according to a procedure reported by Verani and co-workers.\(^{(24)}\) The cell was comprised of two compartments separated by a frit. On one side of the frit were placed the Hg-pool working and Ag/AgCl reference electrodes, whereas a coiled 30.5 cm Pt wire serving as the auxiliary electrode was placed in the other compartment. BE experiments were performed in CH\(_2\)CN (20 mL) with TBAPF\(_6\), as the supporting electrolyte until the calculated final charges were reached. All potentials were measured vs. Ag/AgCl. During BE, potentials were controlled by a BAS 50W potentiostat/galvanostat. CVs were obtained at room temperature.

#### Computational studies

Electronic structure calculations were performed using the BPW91 density functional\(^{(43,44)}\) as implemented in a development version of Gaussian.\(^{(25)}\) The SDD basis set and effective core potential\(^{(45)}\) were used for Co atoms, and the 6-31G(d,p) basis set\(^{(46)}\) was used for the other atoms. To streamline calculations, a slightly modified model was used in which the tert-butyl substituents of complex 1 were replaced by methyl groups. Geometry optimization was performed in the gas phase, and all optimized structures were confirmed as minima by harmonic vibrational frequency calculations. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry in CH\(_2\)CN by using the implicit SMD solvation model.\(^{(25)}\) The converged wave functions in solvent were tested for self-consistent field (SCF) stability. The free energy in solution phase G(sol) was calculated as follows: \(G\(_{\text{sol}}\) = \text{E}_{\text{ECL}}\(_{\text{sol}}\) + zero-point energy(ZPE) + thermal correction−TS\(_{\text{sol}}\)\(\text{gas}\)\). \(E_{\text{ECL}}\(_{\text{sol}}\) was calculated in the solvent, whereas ZPE, thermal correction, and entropic contributions were calculated in the gas phase. The standard states of 1 m concentration were considered for all reactants and products for calculating the free energies of reactions \(\Delta G\(_{\text{sol}}\)\). The spin-density plots (iso-value = 0.004 a.u.) and corresponding orbitals\(^{(44)}\) (iso-value = 0.05 a.u.) of the calculated structures were visualized with Gauss-View.\(^{(45)}\) The literature value\(^{(46)}\) of \(-264.6\) kcal mol\(^{−1}\) was used for the free energy of a proton in CH\(_2\)CN. The calculation of the reduction potentials \((E, V\) in Volt) of the complexes included ZPE, thermal correction, and entropic contribution. The standard thermodynamic equation \(\Delta G\(_{\text{sol}}\) = −nFE\) was used. The calculated potentials were referenced to a value of \(E_{\text{red}}\(_{\text{Fc}}\) = 4.38 V for the Fc\(^+\)/Fc couple calculated under our level of theory.

#### Catalytic studies

Electrocatalytic studies to determine the amount of H produced by the catalyst, TONs, and FEs were performed as previously de-
scribed\(^{24}\) in an H-type cell (Hg-pool; Ag/AgCl | Pt-coil). The main chamber was filled with catalyst 1 (0.005 g, 4 \times 10^{-4}\,\text{mol}) and the TBAPF\(_6\) electrolyte (1.56 g) and acetic acid (0.024 g, 4 \times 10^{-4}\,\text{mol}, 100 equiv) were dissolved in CH\(_2\)CN (20 mL). The small chamber housing the auxiliary electrode was filled with TBAPF\(_6\) (0.390 g) in CH\(_2\)CN (5 mL). In a typical test, the cell was purged for 20 min followed by sampling the head space gas with a Gow-Mac 400 GC equipped with a thermal conductivity detector and a 2.4 m x 0.31 cm x 5 Å molecular-sieve column operating at a temperature of 60 °C. The amount of H\(_2\) produced was determined by GC with a calibration curve obtained with known volumes of 99.999% H\(_2\) gas and shown in Figure S1 in the Supporting Information (see the Supporting Information for sample data and relevant calculations obtained from experiments). A catalyst-free solution was electrolyzed for 3 h and analyzed by GC to provide a blank. The cell was then purged again, and the catalyst was added. Electrolysis ensued for 3 h, and the headspace with H\(_2\) gas was analyzed. The TON was then calculated after background subtraction as the ratio between mol H\(_2\) produced per mol catalyst. The FE was calculated from the GC measurements.

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### Conflict of interest

The authors declare no conflict of interest.

### Keywords

- bimetallic complexes · bimetallic cooperativity · cobalt · Co\(^{2+}\) · species · proton reduction

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