Syntheses and mechanisms of two dinuclear Co-polypyridyl catalysts for the H₂ evolution reaction (HER) were reported and compared to their mononuclear analogue (R1). In both catalysts, two di-(2,2'-bipyridin-6-yl)-methane units were linked by either 2,2'-bipyridin-6,6'-yl or pyrazin-2,5-yl. Complexation with Co⁴⁺ gave dinuclear compounds bridged by pyrazine (C2) or bipyridine (C1). Photocatalytic HER gave turnover numbers (TONs) of up to 20000 (C2) and 7000 (C1) in water. Electrochemically, C1 was similar to the R1, whereas C2 showed electronic coupling between the two Co centers. The E(Co⁵⁺⁻⁴⁺) split by 360 mV into two separate waves. Proton reduction in DMF was investigated for R1 with [HNEt₃][BF₄] by simulation, foot of the wave analysis, and linear sweep voltammetry (LSV) with in-line detection of H₂. All methods agreed well with an (E)ECEC mechanism and the first protonation being rate limiting (≈10⁶ M⁻¹ s⁻¹). The second reduction was more anodic than the first one. pKₐ values of around 10 and 7.5 were found for the two protonations. LSV analysis with H₂ detection for all catalysts and acids with different pKₐ values [HBF₄, pKₐ(DMF) = 3.4], intermediate ([HNEt₃][BF₄], pKₐ(DMF) ≈ 9.2) to weak [AcOH, pKₐ (DMF) ≈ 13.5] confirmed electrochemical H₂ production, distinctly dependent on the pKₐ values. Only HBF₄ protonated Co⁺ intermediates. The two metals in the dualcore C2 cooperated with an increase in rate to a competitive 10⁷ M⁻¹ s⁻¹ with [HNEt₃][BF₄]. The overpotential decreased compared to R1 by 100 mV. Chronoamperometry established high stabilities for all catalysts with TONin of 100 for R1 and 320 for C1 and C2.

Results and Discussion

The ligands L1 and L2 were synthesized by double-lithiation of 6,6'-dibromomethylpyridine or 2,5-dibromopyrazine, respectively, and subsequent nucleophilic addition to di-(2,2'-bipyridin-6-yl)-methane (ESI).¹⁴ The final compounds C1 and C2 were obtained after addition of excess Co(BF₄)₂ to the respective ligand. Excess metal was removed by THF trituration. Crystals suitable for X-ray crystallography of both complexes were obtained by the vapor diffusion method from MeCN with CHCl₃ as anti-solvent.¹⁵ The crystal structures are shown in Figure 1, and crystallographic data are given in Tables S1 and S2. Common structural features comprise the cobalt atoms in the centers of both di-(bipyridyl)-units, each additionally coordinated by the bridging moiety, connecting both metal centers.
The sixth coordination site per cobalt is occupied by a bridging fluoride or solvent molecules, respectively, the former one being formed by fluoride abstraction from the counter ion (BF$_4^-$). Two distinct differences between both structures are notable: the “embracing” geometry of the ligand in C1 forms an envelope-shaped structure around both metal centers bringing them in close proximity (Figure 1). This strained configuration results in a twisted geometry of the bridging bipyridine unit, making electronic coupling via the ligand between the two metal centers unlikely. The distorted geometry is already anticipated in the crystal structure of the uncoordinated ligand L1, exhibiting a twisted bipyridyl-bridge connecting both di-(2,2'-bipyridin-6-yl)-methanol units (ESI). Complex C2 shows a Z-like structure, positioning the cobalt atoms in larger distances from each other on both sides of the pyrazine unit but enabling electronic coupling of the cobalt-centers via the pyrazyl moiety.

Cyclic voltammograms (CVs) of C1, C2, and R1 were recorded in DMF with 0.1 M [N(Bu)$_4$](PF$_6$) ([TBA](PF$_6$)) as electrolyte (Figure 2) and [HNET$_3$](BF$_4$) as proton source (Figure 4). Linear sweep voltammograms (LSV) with in line H$_2$ detection were recorded in the same electrolyte with either AcOH (acetic acid), [HNET$_3$](BF$_4$), or H(BF$_4$) as proton source (Figure 3; $pK_a$ values in DMF are 13.5, 9.2, and 3.4). Glacial AcOH and [HNET$_3$](BF$_4$) were added neat, H(BF$_4$) was added as [HEt$_2$O](BF$_4$). Both di-cobalt complexes are present as tetra-(BF$_4^-$) salts, with C2 being in its crystalline form.

The region between −0.8 and −1.6 V, where the Co$_{II}^{53}$ reduction is expected for polypyridyl complexes, is magnified on the right side of Figure 2. For R1 there are three reversible reductions (grey line) at −1.37, −1.85, and −2.00 V. The first reduction is tentatively assigned to a formal reduction of Co$_{II}^{53}$ to Co$_{II}$, in line with our previous reports and density functional theory (DFT) calculations (see the Supporting Information for computational details). At lower potentials (−1.75 to −2.25 V) redox processes are often ligand-based. For fully conjugated ligand systems (such as cyanomethylene bridged bipyridyls), one single reduction was reported in this region, whereas electronically separated moieties within the ligand, as in R1, C1, and C2, lead to several subsequent reductions.
Analyses of the CVs of R1 with the software package DigiElch\textsuperscript{[10,48,49]} at varying scan rates confirm these potentials, and gives a diffusion coefficient of 2.8 $\times$ 10\textsuperscript{-6} cm\textsuperscript{2} s\textsuperscript{-1} (Figure S15 and Table S13), in line with literature reports for similar compounds.\textsuperscript{[10,48,49]}

The bipyridyl-bridged C1 (red trace) exhibits one reversible redox peak with a half wave potential of $E_{\text{1/2}} = -1.13$ V, followed by two broader peaks at $-1.84$ and $-1.98$ V. Comparison with R1 reveals an anodic shift for the first reduction by 245 mV, a significantly smaller peak separation of 48 mV (as compared to 71 mV for R1), and an approximately doubled peak current. The latter two are clear indications for a two-electron reduction in C1, as opposed to a one-electron process in R1. Simulation of the CVs indeed revealed two overlapping reversible redox processes with half wave potentials of at $-1.12$ and $-1.13$ V. At potentials more negative, C1 exhibits two reductive waves, very close to the half-wave potentials of the respective peaks of R1 but again peaking at twice the current. A simulation with four redox couples at $-1.83$, $-1.84$, $-1.95$, and $-2.01$ V reproduces the shape very well, with an increased spacing of the last two reductions leading to a broader shape of the second wave (see Figure S16 and Table S14). These events are consequently attributed to subsequent reductions of the bipyridyl subunits (bipy/bipy\textsuperscript{+}), as both R1 and C1 carry those moieties, but C1 contains twice as many. The very close spacing of all 6 reductions to three pairs in C1 suggests significant electronic separation of the two halves. Electrochemical communication would effect a dependence of the reduction potential of one cobalt on the oxidation state of its counterpart. The same is valid for the ligand-based reductions. However, in both cases, the “mirrored” units are electrochemically almost indistinguishable. We thus hypothesize that the twisted configuration of the bridging bipyridyl-unit interrupts the mesomeric structure and prevents electrochemical communication between both cobalt centers. To confirm this hypothesis, we calculated population charges and electron transfer coupling using (constrained) DFT to quantify intramolecular electronic communication of C1 and C2 (see section 6 for computational details). Quite interestingly, our calculations reveal a stable geometry of the complex in the proposed twisted form.

The CVs of the pyrazine-bridged dual-core C2 demonstrate novel features, as shown in Figure 2 (bottom). The enlarged potential window displays two clearly distinguishable reductions at $-1.0$ and $-1.36$ V. The peak separations of both events match a one-electron transfer, and the concentration-corrected peak current is equal to the reference R1. This suggests two subsequent one-electron reductions at both cobalt centers (Co$^{2+}$–Co$^{3+}$ to Co$^{3+}$–Co$^{4+}$, see also Figure 4, right bottom). Consequently, the two metal centers are electronically coupled and the reduction potential of one cobalt depends on the oxidation state of the other. In accordance with the crystal structure, electronic coupling occurs via the bridging pyrazyl moiety, coordinating to both cobalt atoms via the conjugated 6-membered ring.\textsuperscript{[10]} The next reductions, with a broad peak at around $-1.96$ V, likely consist of four overlapping, ligand based redox processes, in analogy to R1 and C1. Simulations of these processes with DigiElch gave an estimate of $-1.83$, $-1.91$, $-1.96$, and $-2.00$ V vs. Fc/Fc\textsuperscript{+} (Figure S17 and Table S15).

The potentials of the first reductions in both C1 and C2 are anodically shifted as compared to R1. This is in line with the higher overall charge of the dual-cores C1 and C2. Moreover, this is consistent with earlier results showing less negative $E_{1/2}$.
Figure 4. Top: CVs of R1 (left), C1 (middle, both 1 mM), and C2 (right, 0.55 mM) recorded in DMF, 0.1 M [TBA][PF₆] and equivalent-wise addition of [HNEt₄][BF₄] (pink: 0 equiv. to blue: 10 equiv., in 1 equiv. steps) at a glassy carbon electrode and 0.1 V s⁻¹. Bottom: Mechanistic scheme of electron (red arrows, vertical) and proton transfers (pink, blue, and navy arrows, horizontal) of R1 (left), C1, (middle), and C2 (right). Dashed arrows indicate alternative pathways relevant at more cathodic potentials. The oxidation numbers on cobalt are formal notations, assuming a simplistic polarization of the Co state and shifting the potential in an anodic direction.

Insights to the proton reduction mechanism is gained upon incremental addition of the H⁺ source [HNEt₄][BF₄] by careful analysis of both, the CVs (Figure 4) and the LSVs with in-line H₂ detection (Figure 3). The upper part of Figure 4 shows CVs after addition of 0–10 proton-equivalents to a solution of R1, C1, and C2, respectively (left to right) in DMF. The corresponding mechanisms are illustrated in the lower part of Figure 4. Reductions are vertically arranged red arrows; protonation steps correspond to horizontally aligned pink, blue, or navy arrows (for H[BF₄]₄, [HNEt₄][BF₄], or AcOH).

Paralleling (E)EECC and (E)EECC pathways were extracted in the case of R1 upon addition of [HNEt₄][BF₄], by simulation and fitting in DigiElch (Figure S18), as depicted in the lower panel of Figure 4. Protonation thus occurs on both, [L−Co]⁺ and [L²−Co], in the former case with a pKₐ of around 10, and a rate constant of 1.3 × 10⁴ M⁻¹ s⁻¹; in the latter case, however, the pKₐ is coupled to the reduction potential E([Co⁰−H]). Assuming a realistic value of −1.8 V for the latter reduction, a pKₐ of around 13.5 is obtained for protonation of [L²−Co]⁺ (see Table S16). As for the second, final protonation step of [L−Co−H], a pKₐ of around 7.5 is obtained. A foot of the wave analysis (FOWA) of the CV data can only be used to confirm the (E)EECC pathway, operational at less negative potentials, since the (E)EECC pathway is obscured by the former.

The catalytic half wave potential is constant at −1.84 ± 0.02 V, and independent on the acid concentration (Figures S19–S117). Moreover, the first reduction remains reversible upon acid addition. This excludes a homolytic pathway, or a second, more negative reduction than the first one, indicating that the second step is faster than the first one. No further distinction between the remaining options (E)EECC, EECC and an (E)ECCE, or their analogues with one homogeneous electron transfer, (E)(E)E'C, EE'C or (E)E'C, is possible by a FOWA, since the same dependencies are expected. In any of these cases, the second protonation must be significantly faster than the first one. A rate constant for the slower first protonation of 5.3 × 10³ M⁻¹ s⁻¹ is obtained (Table S17), which is reasonably close to the 1.3 × 10⁴ M⁻¹ s⁻¹ obtained from the full simulation described before. By simulation, the seemingly simpler EECC mechanism does not reproduce the increasing irreversibility of the first catalytic wave as well as the (E)EECC mechanism. The same is true for the (E)EE'C mechanism; the simulation reveals a deviation in the shape of the reverse wave. Albeit not accessible by FOWA only, simulation thus favors the (E)EE'C or (E)E'C mechanisms.
Further confirmation of the ECEC sequence comes from the fact that the first chemical step is significantly slower than the second one. It seems unlikely that double protonation of one species (successive CC steps) becomes faster in the second step.

LSV data with inline probing for H₂ can be used to shed some more light on these findings. First, H₂ production is confirmed at the respective potentials, and balancing the spent electrons with detected hydrogen by coulometric analysis reveals one “excess” electron (Figures S19–S21), corresponding to a one-electron reduced Co²⁺ as the resting state during catalysis. Moreover, also LSV data can be subjected to FOWA analysis, adding the asset that product formation rate can be analyzed with respect to the transformed potential (1 + exp(F/RT(É–E₉₀₀)))⁻¹ instead of the current, which is often obscured by pre-catalytic reductions. In line with simulations in DigiElch and FOWA of catalytic CVs, the rate of the first protonation in a (E)ECEC mechanism is determined to be 6.8 ± 2.5 × 10⁷ M⁻¹ s⁻¹ this way (see Figure 5 and Table S18).

The catalytic CVs of the bipyridyl-bridged dual-core C1 and the reference R1 are highly compatible (see Figure 4 and discussion of redox events above). For identical conditions, DMF, [HNEt₃][BF₄] (the (E)ECEC mechanisms found for R1) would translate to an (EE)ECEC mechanism for C1. The simultaneous reduction of both Co³⁺-cores to [L–Co²⁺–Co²⁺–L] at –1.13 V is confirmed by LSV data. One subsequent ligand-based reduction initiates the catalytic wave, and two excess electrons are found on the resting state of the C1 catalyst during catalysis with [HNEt₃][BF₄] (see Figure 3 and Figures S19–S21). A catalytic half wave potential E₁/₂ of –1.82 ± 0.01 V, independent of acid concentration, is found by CV (Figure S19), matching the potential of the first ligand-based reduction at –1.83 V. This indicates a second protonation faster than the first one. A second order rate constant of 2.1 ± 0.1 × 10⁸ M⁻¹ s⁻¹ is extracted for the first, rate-limiting protonation (Table S17, Figures S19 and S110). The similarity of the CV at all potentials in the presence of acid (Figure 4) suggest furthermore an equally fast catalytic turnover as for R1, also after the second set of ligand reductions at –1.95 to –2.01 V [(EE)ECEC pathway]. C1 eludes itself from a full simulation with for example DigiElch, due to the high number of free parameters required in the simulation of catalysis on top of a 6-electron reduction. As compared to R1, a slightly lower rate constant for the first step in the ECEC pathway, an equal current magnitude in the EECC domain, and the absence of a shift of E₁/₂ to more anodic potentials all indicate a lack of cooperativity between the two cobalt centers in C1. This coincides with the electronic isolation of the two centers mentioned before; the two cores operate independently of one another, which in sum reduces the overall turnover frequency (TOF) per cobalt.

The electrochemical response of C2 upon [HNEt₃][BF₄] addition is distinctly different. The two first reductions remain unchanged (Figure 4, top right) and their characters as two one-electron transfers is further supported by two distinct events in the LSVs at those potentials (see Figure 3, top right). The shape of the next four reductions present in the absence of protons (–1.83, –1.91, –1.96, and –2.00 V), changes significantly upon addition of [HNEt₃][BF₄]: a process with a E₁/₂ of –1.76 V becomes apparent (Figure top right, Figure S19; most pronounced at lower acid equivalents). Comparison with LSV scans (500 equiv. of protons) confirms this new peak, suggesting, however, that H₂ evolution starts at slightly more cathodic potentials (Figure 3). Integration gives three excess electrons on C2 during electrocatalysis (Figure S19–21). The peak shift indicates a faster first (k₁), and a slower second (k₂) chemical step, according to Equation (1):

\[
E_{1/2} - E_{1/2} = \frac{RT}{2F} \log \frac{k_1}{k_2}
\]

Rates of 1.5 ± 0.1 × 10⁷ M⁻¹ s⁻¹ for the first and 8.2 ± 0.4 × 10⁶ M⁻¹ s⁻¹ for the second protonation are obtained from FOWA analysis of CV data (Figures S14–S17, Table S17). An (EE)ECEC mechanism with a fast first protonation and a slower second protonation leading to release of H₂ is compatible with these observations. Due to the fast first protonation, Co³⁺–Co²⁺–H is the resting state of the catalyst during catalysis, in line with the coulometric analysis (Figures S19–S21). As subsequent reductions of the complex take place, alternative mechanisms, for example (EE)ECEC, and later, as noted for R1 and C1, (EE)ECEC, come into play, obscuring the former pathway with increasing potential. Thus, C2 reacts remarkably different from R1 and C1 in the lowest energy pathway. Upon reduction to the Co⁰ intermediate, one ligand-based reduction initiates catalysis by double protonation. Likely the basicity of the [H–Co²⁺–Co²⁺] is increased by electronic coupling to the neighboring Co¹ and thus allows for its protonation.

Computationally a slight increase in the atomic charge of the cobalt atom in a metal-to-metal electron transfer is found. For R1 and C1 further reduction was required to increase the basicity of the hydride. In agreement with this notion, the first protonation is two to three orders of magnitude faster than the second is. It should be noted, however, that the (EE)ECEC

![Figure 5. Catalytic Tafel plots for R1 (grey), C1 (red), and C2 (green) with H(BF₄)₃, [HNEt₃][BF₄], and AcOH. The asterisks represent the CA experiments. The solid faint green line represents the (E)ECEC mechanism for C2 and [HNEt₃][BF₄].](image-url)
mechanism as found for C1 and R1 dominates catalysis and, albeit at higher overpotential, gives rise to a beneficial catalytic Tafel plot (see Figure 5).

In all three cases, the addition of the weaker AcOH results in catalytic hydrogen production at the same potentials, but with a slower increase of hydrogen production, as is evident from the LSV scans with inline H2 detection in Figure 3. This indicates a slower hydrogen formation rate, which is confirmed by FOWA of the scans: rates of 26 ± 8, 170 ± 60, and 630 ± 240 m3 s−1 were found for R1, C1, and C2, respectively (ECCE pathway, see Figure 5 and Table S18). As in the case of [HNET2][BF4]−, protonation of reduced C2 is significantly faster than for R1 and C1, and a slow but visible sign of the (E)EECC mechanism is found for C2. The two orders of magnitude decrease in rate from [HNET2][BF4]− to AcOH is in line with the increase of pKa (9.2 to 13.5), and consistent with literature data.57 Faradaic efficiencies (FEs) between 0.80 and 0.89 were found for the respective LSV scan (Table S19), indicating alternative reductive pathways other than hydrogen formation.

Also, in the presence of the strongest acid H(BF4)−, hydrogen formation was confirmed in all three cases. In stark contrast to the weaker acids, H(BF4)− shifts the onset of H2 production anodically for all three compounds (Figure 3, bottom). In the presence of this strong proton source, H2 begins to evolve directly after the reduction to CoII (R1), resp. Co3−−CoII (C1 and C2). As opposed to the weaker acids, H(BF4)− is capable to protonate the CoII intermediates. Rate limiting constants extracted from LSV by FOWA give 110 ± 40, 0.93 ± 0.39, and 280 ± 110 m3 s−1 (see Figure 5 and Table S18). Although the catalytic half wave potential Ecat/2 shifts significantly in anodic direction, the shift in Eapp from [HNET2][BF4]− to H(BF4)− (−1.21 to −0.71 V vs. Fc/Fc+) is not compensated for R1 and C2, or at the cost of a very slow rate (C1).

The elucidation of the rate-limiting step (TOFmax) and the respective catalytic half wave potential Ecat/2 relative to the potential of proton reduction with the respective acid (Ecat/2 ± ΔE) can be used to benchmark catalysts.52,54,58,59,60 Comparison with [CoII(dmgH)2py] and [FeII(TPP)], both with [HNET2]+ in DMF, and [NiII(phen)2(NH3)2]+ using [HDMF]− in MeCN, is given in the Supporting Information (Figure S12). Clearly, [CoII(dmgH)2py] is unrivaled in terms of overpotential. Interestingly, protonation with the relatively weak acid [HNET2]+ occurs at CoII for the latter, as opposed to the cobalt polypyridyl catalysts investigated here, or elsewhere.60,61,49 This, in turn, explains the substantial difference in overpotential, and might be related to the spin state of the respective CoII intermediate: Tong and coworkers recently demonstrated a high-spin S = 1 state for a similar CoII intermediate, derived from a S = 3/2 CoIII56,57. These results coincide with a recent study on R1 and a related cobalt polypyridyl, evidencing the importance of the CoII singlet state for protonation.56,57 [CoII(dmgH)2py]−, however, is a low spin system, and might give rise to a low spin Co, and thus facilitate protonation on a full d2 orbital (e.g., oxidative addition to a d3 system). The [NiII(phen)2(NH3)2]+ catalyst of DuBois and co-workers together with the [FeII(TPP)] as described by Savéant and coworkers,59 are still one to two orders of magnitude faster than the mononuclear R1, or C1, with [HNET2]+, at comparable to slightly worse overpotentials. C2, however, in the EECEC pathway and [HNET2]+, reaches a TOFmax of 104 s−1, similar to [FeII(TPP)], but at 250 mV more anodic potentials.

Besides rate and overpotential, stability, preferably in water, is a very important merit for a hydrogen production catalyst. We thus investigated the three catalysts in photochemical hydrogen production in a system with [Ru(bipy)3]2− as photosensitizer (PS), ascorbic acid (AscOH) as electron donor, and tris(2-carboxyethyl)phosphine (TCEP) to regenerate spent AscOH (Figure S12B). TOFs (mol H2 per mol of catalyst per second) between 0.1 and 1 were found, three orders of magnitude lower than what was found in electrochemistry in DMF.

This is, however, expected, as a reasonably fast catalyst is not limiting turnover in this photochemical setup. Concerning stability, turnover numbers (TONs) above 20000 have been found for R1 and C2, and about 7000 for C1. In the photochemical cycle, the catalysts are reduced by the reduced dye [Ru(bipy)3]2−, formed by reductive quenching of the excited dye by ascorbic acid. Interestingly, E([Ru(bipy)3]3+/2+) is at −1.74 V vs. Fc/Fc−, allowing reduction to the CoII state, but around 100 mV anodic of the second cobalt-based reduction. In line with this, an (EC)EC mechanism has been proposed below pH 7, with () signifying a coupled electron-proton transfer. Above pH 7, an E−(EC)C mechanism was proposed for a very closely related system.46

The high stability of the systems is further substantiated by a 7-day chronoaamperometry (CA) performed on the three catalysts in DMF with 200 mM [HNET2][BF4]−, as summarized in Table 1 (see also Figures S126 and S127). Decrease in activity in such experiments is assigned to catalyst deactivation and can be quantified by exponential fitting of charge and product build-up.59 Towards this end, τchem as described in ref. 59 of 2 to 4 days were found. This is roughly one order of magnitude higher than a related system using an amine-containing polypyridyl ligand in DMF for H2 production10 or iron.

| Table 1. Summary of CA.46 |
|--------------------------|
| **Compound** | **Eopt (V)** | **vopt (mmol s−1)** | **TOFmax (s−1)** | **TONmax** | **FE** | **τchem (h)** |
| R1 | −1.80 | 0.9 ± 0.1 | 340 ± 10 | 88 ± 1 | 0.89 ± 0.03 | 54 ± 1 |
| C1 | −1.80 | 1.6 ± 0.1 | 450 ± 150 | 319 ± 1 | 0.84 ± 0.03 | 113 ± 1 |
| C2 | −1.70 | 1.6 ± 0.1 | 2500 ± 350 | 324 ± 1 | 0.88 ± 0.03 | 114 ± 1 |

[a] 400 µM R1, C1, and C2, 200 mM [HNET2][BF4]−, 0.1 M [TBA][PF6]−, 5 mL DMF; working electrode was Hg pool, reference electrode was Ag/AgCl. V was given vs. Fc/Fc−, counter-electrode is Pt separated by a glass frit (Figures S126, S127). ΔEapp ± ΔE for 200 mM [HNET2][BF4] in DMF was calculated at −1.19 V.59,60 R2 was 60 ± 10 %.

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porphyrins for electrocatalytic CO₂ reduction. In the case of R₁, a limiting TON of around 90 was calculated, whereas 320 was found for C₁ and C₂. A [HNEt₂][BF₄] addition experiment at 6 days leads to a partial recovery of electrocatalysis, further substantiating the high stability of the latter two catalysts in DMF. As compared to the FOWA analysis, TOF substantiating the high stability of the latter two catalysts in behavior with structure and number of cores. We draw correlations of electronic and, more importantly, catalytic behavior with the equivalent mononuclear reference compound by either a bipyridyl or a pyrazyl bridge. Comparison to the new dinuclear cobalt polypyridyl water reduction catalysts the SED and the photosensitizer are 0.1 distilled water. The standard concentrations for the electron relay, R₁ extracted from the CA runs are one order of magnitude lower compared to the (E)ECEC mechanism since lower oxidation of R₁ never exceeded ∼95 °C and stired for 30 min. A solution of di-(bipyridine-6-yl)-methanone (0.6 mmol, 207 mg) in 7 mL THF was added dropwise along the glass wall of the flask, which was deeply immersed in the cooling bath by means of a syringe. The glass wall subsequently rinsed with 2 mL dry THF. The mixture was allowed to reach ∼40 °C and quenched with MeOH. The crude mixture was extracted with DCM from water (3 ×) and subjected to flash column chromatography (C₁₂-silica, flash master, H₂O/MeCN, 60 : 40, +10 % MeCN per 100 mL). The pure fractions were combined to obtain the product as white solid (95.4 mg, 37 %). 1H NMR (400 MHz, CDCl₃): δ = 8.64 (dq, J = 4.81 Hz, J = 0.81 Hz, 4H), 8.35 (dd, J = 7.6 Hz, J = 1.03 Hz, 4H), 8.20 (d, J = 7.96 Hz, 4H), 8.15 (dd, J = 7.72 Hz, J = 0.82 Hz, 2H), 7.90–7.81 (m, 10H), 7.73 (t, J = 7.84 Hz, 2H), 7.66 (td, J = 7.84 Hz, J = 1.73 Hz, 4H), 7.51 (s, J = 7.92 Hz, 2H), 7.25–7.23 ppm (m, 4H). 13C NMR (400 MHz, CDCl₃): δ = 160.8, 154.5, 152.2, 152.1, 147.6, 135.8, 135.7, 135.4, 122.2, 122.0, 121.9, 121.8, 119.6, 111.0, 115.0, 64.4 ppm.

**Conclusion**

We herein report on the synthesis and characterization of two new dinuclear cobalt polypyridyl water reduction catalysts containing equivalent pentadentate cobalt-binding sites linked by either a bipyridyl or a pyrazyl bridge. Comparison to the equivalent mononuclear reference compound R₁ allowed to draw correlations of electronic and, more importantly, catalytic behavior with structure and number of cores. This work demonstrated cooperativity of the cobalt centers in the dual-core catalyst featuring electronically coupled cobalt centers, as compared to the single-core catalyst or the electronically separated dual-core, with respect to rates and overpotentials. We hypothesize that an increase in pKₐ and thus rate, results from electronic interaction of the two cobalt centers. Additionally, an increase in stability resulted for the dual-core catalysts, which deserves further investigation.

**Experimental Section**

**Analytical methods**

**Photocatalysis:** Before use, the catalysis vials were washed by immersion in iPrOH/KOH for at least 48 h and rinsing with doubly distilled water. The standard concentrations for the electron relay, the SEM and the photosensitizer are 0.1 M NaAsc, 0.1 M TCEP, and 500 mM Ru(bpy)₃Cl₂, respectively. NaAsc, TCEP, and PS were weighted directly into the vial with appropriate accuracy and thus rate, from electronic interaction of the two cobalt centers. Additionally, an increase in stability resulted for the dual-core catalysts, which deserves further investigation.

**Synthesis**

Appropriate analytical spectra of the compounds are provided in the Supporting Information (Figures S11–S13). 6,6'-di-(2,2'-bipyridyl)-methanol)bipyridine (L1): A solution of 6,6'-dibromo-2,2'-bipyridine (0.3 mmol, 100 mg) in 8 mL dry THF was added dropwise to a solution of n-butyllithium (380 μL of a 1.6 M solution in hexane) in 4 mL dry THF at a rate so that the temperature never exceeded ∼95 °C and stirred for 30 min. A solution of di-(bipyridine-6-yl)-methanone (0.6 mmol, 207 mg) in 7 mL THF was added dropwise along the glass wall of the flask, which was deeply immersed in the cooling bath by means of a syringe. The glass wall subsequently rinsed with 2 mL dry THF. The mixture was allowed to reach ∼40 °C and quenched with MeOH. The crude mixture was extracted with DCM from water (3 ×) and subjected to flash column chromatography (C₁₂-silica, flash master, H₂O/MeCN, 60:40, +10 % MeCN per 100 mL). The pure fractions were combined to obtain the product as white solid (95.4 mg, 37 %). 1H NMR (400 MHz, CDCl₃): δ = 8.64 (dq, J = 4.81 Hz, J = 0.81 Hz, 4H), 8.35 (dd, J = 7.6 Hz, J = 1.03 Hz, 4H), 8.20 (d, J = 7.96 Hz, 4H), 8.15 (dd, J = 7.72 Hz, J = 0.82 Hz, 2H), 7.90–7.81 (m, 10H), 7.73 (t, J = 7.84 Hz, 2H), 7.66 (td, J = 7.84 Hz, J = 1.73 Hz, 4H), 7.51 (s, J = 7.92 Hz, 2H), 7.25–7.23 ppm (m, 4H). 13C NMR (400 MHz, CDCl₃): δ = 160.8, 154.5, 152.2, 152.1, 147.6, 135.8, 135.7, 135.4, 122.2, 122.0, 121.9, 121.8, 119.6, 111.0, 115.0, 64.4 ppm.

**2,4-di-(2,2'-bipyridyl)-methanol)pyrazine (L2):** A solution of 2,4-dibromopyrazine (0.14 mmol, 33 mg) in 4 mL dry THF was added dropwise to a solution of n-butyllithium (175 μL of a 1.6 M solution in hexane) in 3 mL dry THF at −90 °C. After 1 h of additional stirring, a solution of di-(bipyridine-6-yl)-methanone (0.29 mmol, 100 mg) in 4 mL dry THF was added dropwise, and the cooling bath was...

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**Figure 6.** Experimental setup for LSV. Details can be found in the main text.
subsequently removed. The reaction was quenched at –50°C with MeOH and the solvent evaporated under reduced pressure. The crude mixture was subjected to FC chromatography (C_{18}-silica, flash master, H_2O/MeCN, 70:30, +20% MeCN per 150 mL). The pure fractions were combined, and the solvent was evaporated under reduced pressure to yield the pure product as white solid (17 mg, 16%).

\[ \text{H NMR (CDCl}_3, \delta): 8.06 (s, 2H), 8.55 (d, J = 4.76 Hz, 4H), 8.62 (dd, J = 6.96 Hz, J = 1.80 Hz, 4H), 7.85 (dd, J = 8.00 Hz, 4H), 7.25 (m, 8H), 7.59 (td, J = 7.68 Hz, J = 1.72 Hz, 4H), 7.22 ppm (dd, J = 7.44 Hz, J = 8.40 Hz, J = 1.00 Hz, 4H). \]

No suitable 13C NMR spectrum was recorded due to the small-scale synthesis.

\[ [\text{Co}_2(2,4-di(di-(6-bipyrindyl)-methanol(bipyridine)](BF_4)_2 (C1): A solution of [Co(BF_4)]_n·6H_2O (2.2 equiv.) in 10 mL MeOH was added to the ligand L1 (0.16 mmol, 130 mg) in 10 mL CHCl_3 and stirred for 5 min. The solvent was evaporated under reduced pressure and the solid triturated in THF, filtered, and washed with THF until the filtrate was not colored anymore. The pure product was washed through the filter with MeCN and obtained after freeze-drying as brownish solid (187 mg, 90%). HRMS (ESI-MS) m/z: [CoL-H]^+ Calcd for C_{39}H_{30}CoN_8O_5: 733.2014; Found: 733.1999. \]

\[ [\text{Co}_2(2,4-di(di-(6-bipyrindyl)-methanol)pyrazine)](BF_4)_2 (C2): A solution of Co(BF_4)_2 (2.5 equiv.) in 1.3 mL MeOH was added to the ligand L2 (0.02 mmol, 16.9 mg) in 1 mL CHCl_3 and stirred for 30 min. The solvent was evaporated under reduced pressure and the solid triturated in THF, filtered, and washed with THF until the filtrate was not colored anymore. The pure product was washed through the filter with MeCN and the solvent removed to obtain the pure product according to UHPLC-MS (see Supporting Information). The product was purified by crystallization by the vapor diffusion method in MeCN with CHCl_3 as anti-solvent. No appropriate yield could be determined due to the small-scale synthesis. HRMS (ESI-MS) m/z: [CoL-H]^+ Calcd for C_{39}H_{30}CoN_8O_5: 733.2014; Found: 733.1999. \]

\[ [\text{CoL-H}]^+ \text{calcld for C}_{39} \text{H}_{30} \text{CoN}_8 \text{O}_5: 733.2014; \text{found: 733.1999.} \]

\[ \text{R}^*_1 = 1.3/5 \text{ min. Crystals suitable for X-ray crystallography were obtained by the vapor diffusion method from MeCN with CHCl_3 as anti-solvent.} \]

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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The bridging F\(^{-}\) in the crystal structure of C2 is not observed in solution, as confirmed by UPLC-MS.