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Cobalt-based molecular electrocatalysis of nitrile reduction: evolving sustainability beyond hydrogen†

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Two new cobalt bis-iminopyridines, [Co(DDP)(H₂O)₂](NO₃)₂ (**1**, DDP = *cis*-[1,3-bis(2-pyridinyl)amine]) cyclohexane) and [Co(*cis*-DDOP)(NO₃)](NO₃) (**2**, *cis*-DDOP = *cis*-3,5-bis[2-pyridinyl)eneamin]-*trans*-hydroxycyclohexane) electrocatalyse the 4-proton, 4-electron reduction of acetonitrile to ethylamine. For **1**, this reduction occurs in preference to reduction of protons to H₂. A coordinating hydroxyl proton relay in **2** reduces the yield of ethylamine and biases the catalytic system back towards H₂.

The last decade has seen an explosion of interest in molecular electrocatalysts for production of dihydrogen (HECs).^{1–5} Tremendous progress has been made in increasing speed,^{1,3} lowering overpotential,^{1,4} and understanding the mechanism of HECs.^{1,5} However, we are still some distance from molecule-based systems that can produce H₂ at industrial scale, and at a cost low enough for hydrogen to play a major role in a nascent mixed energy vector economy. Thus, it is worth considering additional applications in sustainable chemistry for the knowledge and materials developed in molecular HEC research.

Efficient, fast, electrochemically driven manipulation of protons and hydrides is intrinsic to the performance of HECs.⁵ This implies that under appropriate conditions, many HECs or derivatives thereof will be active in organic reductions, where delivery of H atoms to the correct site is essential to achieving the desired product.^{6</}

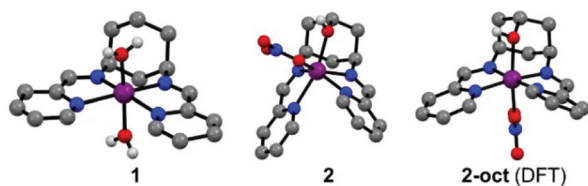


Fig. 1 Left: X-Ray crystal structures of the complex cations in **1** and **2**. Right: DFT calculated alternative structure of **2** (**2-oct**, +30 kJ mol⁻¹ vs. **2**) with pseudo-octahedral Co. C is grey; O, red; N, blue; Co, purple; H, white (CH omitted).

is replaced by a second water molecule – likely due to loss of the hydrogen bonding ligand *trans*-OH group and resulting changes to the crystal packing and hydrogen bonded network (Fig. S3†). In **2** (Fig. 1 and S2†), coordination of the –OH group pulls Co 0.9743(8) Å out of the plane of the N₄ pocket, leading to a trigonal prismatic geometry where the two pyridyl imine chelators are *ca.* 90° to one another and the shortest coordinate bond (2.075(1) Å) is to the hydroxyl O. There is no coordinated water molecule, and Co-pyridyl, imine and nitrate bond lengths are all longer than in **1** (Table S2†). Large differences in the paramagnetic ¹H-NMRs of **1** and **2** indicate that these structural differences are retained in solution (Fig. S4†). Even so, DFT calculations estimate a small (*ca.* 30 kJ mol⁻¹) Δ*E* between the observed structure of **2**, and an alternative **2-oct** (Fig. 1) where the pyridyl imines return to the equatorial plane (analogous to **1**) and the hydroxyl remains coordinated at a similar distance (*ca.* 2.078 Å). This modest energy difference, comparable to a strong hydrogen bond,⁹ suggests that **2** could change its configuration in response to protonation of –OH and/or reduction of Co, making the –OH group hemi-labile while retaining a short O-to-Co distance.

For both complexes, cyclic voltammetry (CV) reveals three quasi-reversible reductions between –0.8 and –1.8 V vs. Fc/Fc⁺, and an oxidation at *ca.* +0.5 V (Table 1, Fig. S6†). The large peak separation (Δ*E*) of the oxidation indicates Co^{II/III}, owing to the associated spin-state change (Table 1). This Δ*E* for **2** is especially large, because d⁶ Co^{III} strongly disfavours the trigonal prismatic geometry¹⁰ and forces a structural change that slows down electron transfer. The first reduction is assigned to Co^{III/I} for both **1** and **2**, in accordance with prior work,^{2b} and consistent with the large (300 mV) negative shift due to coordi-

nation of the electron-donating hydroxyl and change in geometry in **2**, and DFT calculations indicating that the HOMOs of **1**[–] and **2**[–] are predominantly metal based (Fig. 2, Fig. S5†). The two subsequent reductions can be formally assigned to the ligands for both complexes, however DFT-calculated frontier orbitals suggest participation

triples the current observed with no acid for the reduction wave, which from 5 eq. onwards shifts to more positive potential by *ca.* 60 mV per $-\log[\text{AcOH}]$ (Fig. S7†), without further significant increase in current at 100 mV s⁻¹. At 10 mV s⁻¹, however, current continues increasing up to 30 eq. AcOH (Fig. S9†). These observations are consistent with slow catalysis on the second wave, which we assign as 2-proton, 2-electron proton coupled electron transfer (PCET) followed by slow H₂ evolution – as confirmed by detection of traces of H₂ upon bulk electrolysis at -1.5 V vs. Fc/Fc⁺. The slow nature of this process (TOF *ca.* 0.3 s⁻¹), occurring near the potential for imine reduction, implies that H₂ evolution is occurring from a 2-electron, 2-proton reduced imine ligand. Ligand-based H₂ evolution is documented for more electron rich bis-iminopyridines, at TOFs up to 19.4 s⁻¹.¹¹ Finally, a third, catalytic wave develops at more negative potential (Fig. S7†). Its potential shifts positive and current increases in proportion to the concentration of acid, indicating PCET, and is likely initiated through formation of a Co^{II} hydride. Prior work on Co-bis-iminopyridines found that in weakly acidic conditions metal protonation only occurred upon transfer of a second electron to Co, and postulated involvement of the imino-pyridines in the reaction pathway.^{2b}

The behaviour of **2** is more complex (Fig. S10–12†). With AcOH present, three waves occur before the main catalytic process, corresponding to a similar series of electron transfers to those of **1**: Co^{II} to Co^I, followed by two PCETs that reduce the imino-pyridines and result in slow H₂ evolution. The reason for the split in the imino-pyridine PCETs is not clear, but may relate to lower symmetry inequivalencing the two “arms” on the CV timescale, and/or a difference in the strength of communication between them. Notably, as more acid is added the PCETs begin to merge (Fig. S12†) and the catalytic half-wave potential for **2**, initially *ca.* 230 mV more negative than that of **1**, shifts such that by 30 eq. AcOH the difference is only 130 mV. This is consistent with acid encouraging decoordination of $-\text{OH}$, producing behaviour more similar to **1**, and potentially enabling it to act as a proton relay that lowers the potentials associated with the metal centre.¹²

The observed response to a weak proton source encouraged investigation of the main catalytic wave by bulk electrolysis (BE) of solutions of acetic acid in acetonitrile (Table 2). Both catalysts have a lower faradaic efficiency (η_F) for H₂ evolution than the blank glassy carbon (GC) electrode, and for **1** the chemical yield of H₂ was also lower than for GC alone. This indicates that H₂ evolution cannot be a major pathway for **1**, and is not the only one for **2**. A ninhydrin test indicated the presence of amines in the catholyte, treatment with 2,4-dinitrofluorobenzene (DNFB) enabled quantification of ethylamine (as *N*-ethyl-2,4-dinitroaniline) by ¹H-NMR (Table 2, Fig. S18–20†), and also revealed small quantities of 2,4-dinitroaniline – confirmed by MS (Fig. S23–25†). The faradaic yield (η_F) of Et

saturation was reached for **1**, and until the concentration used for BE was reached for **2** (Fig. S16†). Adjusting for η_F , this gives estimates of TOF(EtNH₂) of 2.3 s⁻¹ for **1** and 1.5 s⁻¹ for **2**, under the BE conditions. While **2** appears capable of accessing faster rates, direct AcOH reduction current from the GC electrode becomes problematic as more acid is added. TOF(H₂) is not estimated for either catalyst as it cannot be delineated from the electrode contribution. Use of H-terminated boron doped diamond (BDD) electrodes (Fig. S17†),¹⁸ which have less activity for AcOH reduction, indicates that **2** can indeed access maximum current densities close to an order of magnitude higher than those of **1**, and thus much faster reaction rates (for both H₂ and EtNH₂).

Overall, current evidence supports a mechanism where **1** and **2** are first reduced from Co^{II} to Co^I, and then undergo a ligand (imine) based 2-electron, 2-proton reduction that results in slow H₂ evolution. Additional PCET before H₂ evolution occurs results in reduction of acetonitrile solvent to ethylamine, further reduction of the ligands, and for **2** likely also initiates a faster hydrogen evolution process. This, and the reaction by-products observed, indicates the likely involvement of hydrides, implying that fast catalysis is initiated by formation of [H₂LCo^{II}-H]. Tentatively, we suggest that **1** favours EtNH₂ production more than **2** because it requires simultaneous coordination of both MeCN and hydride – in **2**, the hydroxyl makes this more difficult to achieve. However, this additional hydroxyl donor may help **2** access higher reaction rates by stabilising against degradation as the acid concentration increases. It may also act as a proton relay in the de-coordinated geometries indicated by DFT (2⁻/2³⁻, Fig. 1), notably rate enhancements (up to 10³×) have been seen for inclusion of pendant amine groups in Fe and Ni based HECs.^{3a} Moreover, subsequent re-coordination of -OH would increase the reactivity of resulting Co hydride species. However, current data do not exclude direct PCET to coordinated MeCN, or PCET from the reduced ligand to MeCN. Thus, work to eliminate the electrode contribution and elucidate mechanism is ongoing.

In conclusion, we have shown that two complexes designed as molecular HECs perform a challenging electrocatalytic hydrogenation with high selectivity for the organic product. Although this behaviour is previously unreported, it is likely not unique and thus presents an interesting perspective for investigation of HECs as electrocatalysts for more environmentally benign organic reactions.

Conflicts of interest

There are no conflicts to declare.

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