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Electrochemical aldehyde hydrogenation: probing the inner-sphere strategy with nickel-bipyridine complexes†

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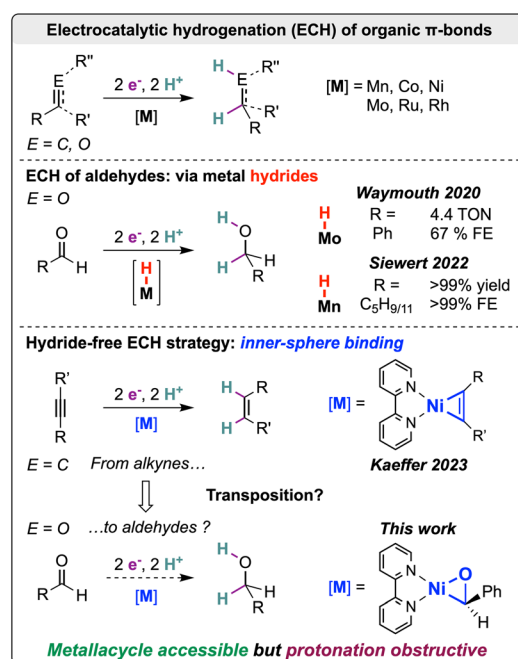
Developing electrohydrogenation routes for organics is crucial in synthesis electrification. Herein, we examine the electrocatalytic hydrogenation of aldehydes through an inner-sphere mechanism at a nickel-bipyridine complex. An (electro)reduction triggers the coordination of the aldehyde into a key nickeloxirane species, which affords hydrogenation products by stoichiometric protonations. Turn-over yet remains challenging with acids suitable for electrocatalytic conditions due to sluggish proton transfers, which we probed by combined reactivity and computational studies.

The electrification of synthetic processes is empowering the use of renewable and sustainable resources in chemistry.^{1–5} This virtuous approach is often propelled by electrocatalysis to incorporate energy efficiency and selectivity. A key to the rational development of these electrocatalytic systems is the decoding of the mechanisms involved. The well-defined nature of molecular complexes facilitates access to mechanistic information. This strategy has led to molecular electrocatalytic systems for the hydrogenation of organic multiple bonds.^{6–17} In contrast to CO₂ reduction, the electrocatalytic hydrogenation (ECH) of organic carbonyls with molecular complexes remains largely under-explored.¹⁸

Siewert and co-workers demonstrated the repurposing of {Mn(bpy)}-type hydrogenation electrocatalysts from CO₂ to organic carbonyls, including aliphatic aldehydes,^{15,16} while Waymouth and co-workers addressed the challenging ECH of benzaldehyde using a Mo Shvo-type complex¹⁴ (Scheme 1). These systems perform hydrogenation through the evolution of a metal hydride that is transferred to the electrophilic C–O carbon.

In our exploration of electrocatalyzed synthesis, we recently employed the coordination ability of nickel-bipyridine complexes to achieve alkyne ECH through successive electron and proton transfers, bypassing metal hydride intermediates.^{19,20} This approach exploits hydride-free selective pathways that are at odds with catalysis in thermal hydrogenation and reported ECHs. Herein, we investigate the challenges in transposing the hydride-free strategy from the hydrogenation of C–C multiple bonds to that of C–O bonds (Scheme 1).

Knowing that [Ni(bpy)(BzO)₂] (1) is a hydrogenation electrocatalyst for alkyne substrates,²⁰ we aimed at probing this complex for carbonyl substrates.



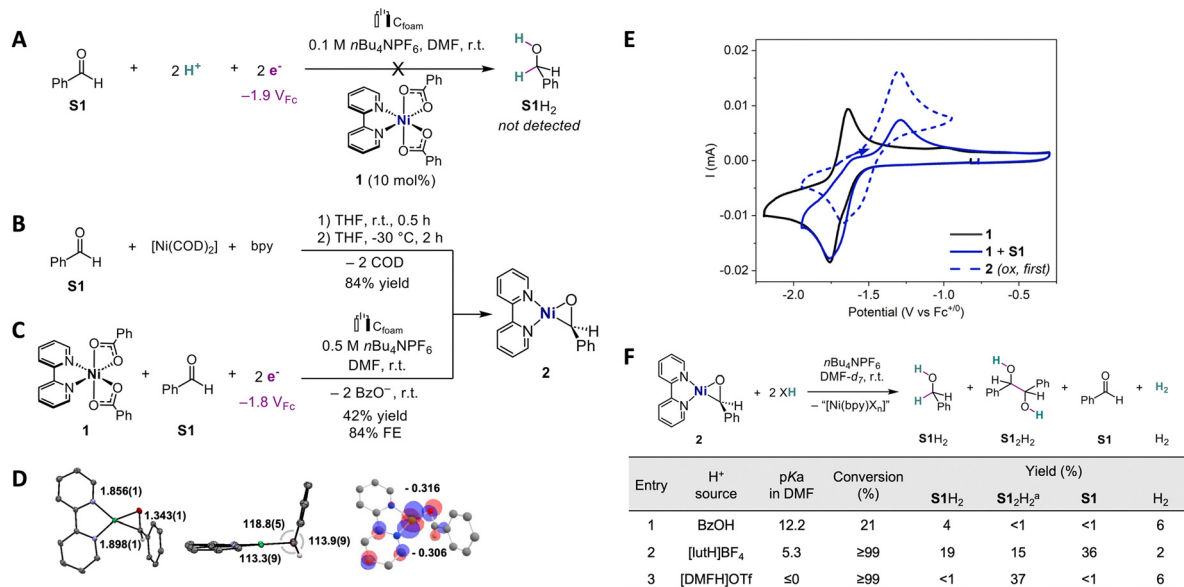
Scheme 1 Electrocatalytic hydrogenation of C–O and C–C multiple bonds by molecular complexes, including nickel-bipyridine complexes.

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Scheme 2 (A) Electrocatalytic attempt using **1** (1 mM), **S1** (10 mM), and BzOH (22 mM) after passing 8.5C (approximately 2e⁻/S1). (B) Synthesis of **2** from [Ni(COD)₂]. (C) Electrosynthesis of **2** from **1** at $E_{app} = -1.80 V_{Fc}$ (charge = 4.56C; approximately 1e⁻/1). (D) Molecular structure of **2** obtained by XRD (ORTEP; 50% probability; color code: gray: C; purple: N; green: Ni; red: O; white: H) and computed electron density of **2** with Mulliken charges at aldehydic C and O (H atoms omitted for clarity, except aldehydic ones). (E) CVs of **1**, **1** and **S1**, and **2** (1 mM each; 0.1 V s⁻¹ scan rate). (F) Protonation reactions starting from **2** (at 30 min). Unless otherwise stated, the supporting electrolyte is DMF 0.1 M *n*Bu₄NPF₆. ^a Maximum theoretical yield 50%.

However, electrolysis of benzaldehyde (**S1**) in the presence of **1** and benzoic acid (BzOH) as a proton source leads to marginal conversion and no detected hydrogenation product **S1H₂**, once approximately 2 electrons were passed per **S1** (Scheme 2A). Varying the solvent (*e.g.*, DMSO, THF) or even the substrate (*p*-MeO-PhCHO) was not productive. Moreover, greater cathodic applied potential (see ESI,† Section S3.4) or higher acidity (*e.g.*, [DMFH]OTf)²¹ trigger the direct reduction of **S1** at the electrode, and hence are not compatible with this system.

In the absence of catalysis, it is thus questionable whether a pathway involving a nickelacyclic intermediate, in analogy to the nickelacyclopentene reported for alkyne semi-hydrogenation, is viable in the case of C=O bond hydrogenation. We examined the formation of such species in the case of C–O unsaturations by reacting a 1:1 mixture of [Ni(COD)₂] (COD = 1,4-cyclooctadiene) and 2,2'-bipyridine with benzaldehyde (**S1**) in THF, inspired by previous studies and our precedents.^{20,22,23} The reaction quickly evolves a green precipitate identified after the workup as nickeloxirane [Ni(bpy)(PhCHO)]^{22–24} (**2**), obtained in 84% yield (Scheme 2B and ESI,† Section S2.1).

The molecular structure was elucidated by single crystal X-ray diffraction (XRD), and indicates a planar geometry for nickeloxirane **2** (Scheme 2D; ESI,† Section S2.4) with a C–O bond length of 1.343 Å, which was quite elongated relative to **S1** (1.210 Å).²⁵ Moreover, the ¹H NMR signature (DMSO-*d*₆) attributed to the aldehydic hydrogen of **2** is manifested by a broad singlet at 5.05 ppm, in a region typical of benzylic resonances (*vs.* 10.02 ppm in free **S1**). Additionally, the C–O stretching frequency at 1360 cm⁻¹ in **2** undergoes a substantial redshift compared to free **S1** ($\nu(C=O) = 1693 \text{ cm}^{-1}$; see ESI†, Section 2.3). This spectroscopic evidence further reinforces the C–O single-bond characteristic in **2**.

Investigating the voltammetric behavior of **1** shows that the addition of aldehyde **S1** (1 equiv.) triggers the reduction wave at $E_{p,c} = -1.76 V_{Fc}$ ²⁰ (V_{Fc} stands for V *vs.* Fc⁺⁰) to evolve a shoulder ($E \approx -1.70 V_{Fc}$) and lose its reversibility (Scheme 2E). Most importantly, these changes are accompanied by the buildup of an anodic wave at $E_{p,a} = -1.29 V_{Fc}$, matching that observed for the oxidation of native **2**. These points suggest that **2** can also be formed by reductive electrogeneration from **1** and **S1**. Bulk reductive electrolysis of a mixture of **1** and **S1** at $E_{app} = -1.80 V_{Fc}$ (**1**/**S1** 1:1 ratio, approximately 1e⁻/1 at saturation) (Scheme 2C) further confirms the electrogeneration of **2** in 42% yield and 84% faradaic efficiency, as revealed by the characteristic voltammetric and ¹H NMR signatures (ESI,† Section S4.4).

While these results demonstrate the binding and activation of **S1** in nickelacyclic species **2**, including under electroreductive conditions, protonation is required to release the generated product and induce turnover. After 30 min, addition of 2 equivalents of BzOH (pK_a 12.2 in DMF²⁶) to **2** dissolved in DMF-*d*₇ and *n*Bu₄NPF₆ 20 mM (r.t.) affords 21% conversion of **2** and a 4% yield in **S1H₂** with H₂ as a byproduct (6% yield) (Scheme 2F; entry 1). Extending the reaction time to 24 h leads to full conversion and **S1H₂** in 17% yield (see ESI,† Section S4.1 for additional details). These results indicate the slow reactivity of BzOH with **2**, leading to hydrogenation into **S1H₂** and the hydrogen evolution reaction (HER). The latter reactivity suggests the formation of nickel hydride species, while the former can also proceed by protonations of the metallacycle as observed with alkynes.²⁰

To determine if stronger acids would accelerate the reaction or promote one reaction pattern over the other, we tested 2,6-lutidinium (lutH⁺ pK_a 5.3 in DMF;^{27,28} Scheme 2F; entry 2).



precatalyst **1** can lead to a slow HER *via* the hydride complex **IH**, as previously described.²⁰ However, **I1** is not relevant in stoichiometric experiments with **2**, yet it produces H₂. In that case, we found that the oxidative addition of BzOH at **2** leads to hydride **I4** without barriers, thus restoring the occurrence of the HER. The span of that pathway is relatively high (+25.8 kcal mol⁻¹), but it cannot be fully discarded within the uncertainty of the calculations, and hence can possibly account for H₂ produced.

For the formation of the hydrobenzoin **S1**₂H₂, a radical pathway resulting from the homolytic cleavage of the Ni–C bond of **I2** (BDE = 34.6 kcal mol⁻¹) seems reasonable. Another pathway involving ring expansion by addition of **S1** to **2** proved to be too high in energy (>29 kcal mol⁻¹; see ESI,† Section S5.2).

S1 binding into **2** and **IH** hydride generation are expected to rapidly occur from **I1**, with respective computed TSs of 2.8 and 6.2 kcal mol⁻¹, but **2** is strongly stabilized *versus* **IH** by 7.7 kcal mol⁻¹. The accumulation of the nickelaoxirane is therefore plausible in the hypothesis of slow subsequent kinetics supported by the elevated spans. In this regard, in the voltammetry of **1** recorded with excess BzOH, the addition of 1 equivalent of **S1** restores the electrochemical signature of **2** (Fig. S9, ESI†). This displacement of the electrochemical systems towards **2** even in the presence of BzOH corroborates the thermodynamic preference of the nickelaoxirane *versus* the hydride species and further shows that **S1** inhibits the HER. We note that this relative stability with respect to **IH** is lower for nickeloxirane as compared to nickelacyclopropene²⁰ ($\Delta G(\text{metallacycle} \rightarrow \text{IH}) = 7.7 \text{ vs. } 13.9 \text{ kcal mol}^{-1}$), which supports a more accessible nickel hydride in the case of aldehyde as a substrate.

In summary, in an approach to transpose a hydride-free electrocatalytic hydrogenation from C–C to C–O π -bonds, we demonstrated the successful (electro)generation of a key nickeloxirane species, leading to hydrogenation products by stoichiometric protonation. However, identifying efficient electrocatalytic conditions remains challenging. We determined that inner-sphere substrate binding is preferred over hydride formation, but subsequent protonations of the nickelacyclic species are obstructive. These findings will guide further molecular catalysis for carbonyl electrohydrogenation.

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Data availability

The data supporting this article are included as part of the ESI.† The crystallographic data for **2** have been deposited at the CCDC under number 2374778.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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