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## A tridentate Ni pincer for aqueous electrocatalytic hydrogen production†

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A Ni<sup>II</sup> complex with a redox-active pincer ligand reduces protons at a low overpotential in aqueous acidic conditions. A combined experimental and computational study provides mechanistic insights into a putative catalytic cycle.

H<sub>2</sub> is currently produced by steam reforming of fossil fuels<sup>1,2</sup> which is both expensive and detrimental to the environment. If H<sub>2</sub> is to be a fuel in environmentally friendly alternative energy strategies,<sup>3,4</sup> more sustainable sources of H<sub>2</sub> are required. Elemental Pt is currently the best catalyst for the reduction of protons to H<sub>2</sub><sup>5</sup> but its low abundance and high cost make it unsuitable for global use.<sup>3</sup> A range of different transition metal complexes can act either as electrocatalysts or photocatalysts, including systems involving Co,<sup>6</sup> Mo<sup>7,8</sup> and Ni.<sup>9–11</sup> In a recent report, a tetradentate Co system with a redox active ligand also operates in aqueous conditions.<sup>12</sup> Improved systems that can operate in aqueous conditions with abundant first row transition metals are of current interest.

Pincer ligands are attractive because they are easy to assemble from readily available materials and impart high stability to the resulting complexes. Furthermore, their modular nature facilitates tuning of ligand properties.<sup>13</sup> Here we report that a Ni pincer gives good activity as an operationally homogeneous electrocatalyst for proton reduction in aqueous conditions. Electrochemistry in acetonitrile was used to pinpoint redox events of the metal complex in the presence of added acid and subsequently aqueous conditions. Density functional calculations (DFT) calculations offer insight into a possible mechanism.

## Results and discussion

One electron reduction of catalyst **1** (Scheme 1) is known to give a ligand-centered reduction of the NNN pincer ligand,<sup>14</sup> as shown by EPR data. In initial voltammetry in MeCN,

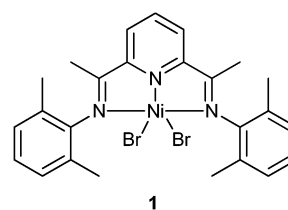
we observe a first reduction wave just above 0 V vs. NHE for complex **1** (Fig. 1) that we tentatively assign a ligand-centered process given the literature precedent. The second reduction at  $\sim -0.5$  V vs. NHE is therefore assigned as a Ni<sup>II</sup>/Ni<sup>I</sup> couple.

To the precatalyst in acetonitrile increasing amounts of acid were added and an increase in current response was observed by cyclic voltammetry (ESI: S1–2†). Assuming a rate-limiting chemical step, we applied the voltammetric kinetic treatment of DuBois *et al.*,<sup>15a,b</sup> originally developed by Nicholson *et al.*,<sup>15c</sup> (S7†) that leads to kinetic parameters for the H<sub>2</sub> evolution reaction. Like the DuBois case, our rate law follows eqn (1) and an apparent rate constant of  $1.05 (\pm 0.21) \times 10^4$  has been determined for 0.1 M H<sup>+</sup>, 5 mM **1** at  $-250$  mV vs. NHE. This corresponds to a voltammetric rate of hydrogen formation of  $105 \text{ s}^{-1}$ .<sup>16</sup>

$$\text{rate} = k[\text{H}^+]^2 [\text{cat}] \quad (1)$$

Further information was obtained at variable potential where we find sustained H<sub>2</sub> evolution in a series of chronoamperometry experiments. A plot of current density vs. overpotential (Fig. S3–1†) shows that the overpotential for **1** is a very satisfactory 140 mV at a current density of  $1 \text{ mA cm}^{-2}$ , assuming a thermodynamic potential of  $-84 \text{ mV vs. NHE}$  under our conditions (Details in S3†).

The compound can also operate in water. A high surface area reticulated vitreous carbon working electrode was used to determine quantitative H<sub>2</sub> evolution from **1** via mass spectroscopy (see ESI†). Specifically, a 50 mL 0.1 M KCl/HCl solution (pH 1) containing 0.2 mM precatalyst was held at  $-1.1 \text{ V vs. NHE}$  for one hour. The charge passed in the catalytic experiment was 212 C. After subtraction of the relevant 80 C background current, 132 C were consumed by the catalytic chemistry. This is equivalent to a predicted production of 0.68 millimoles of H<sub>2</sub>. From quantitative mass

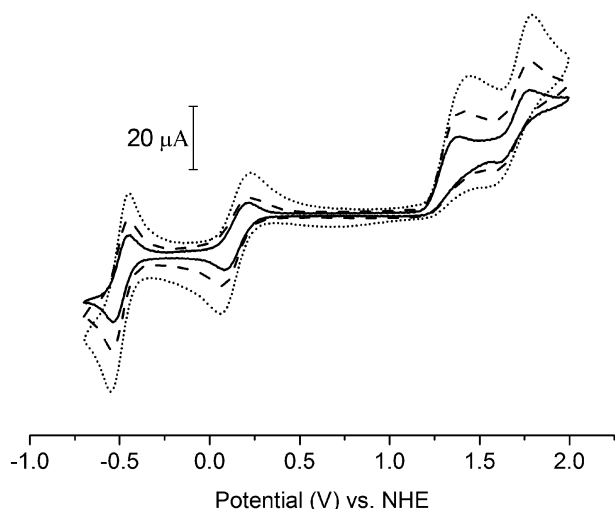
Scheme 1 Catalyst **1**.

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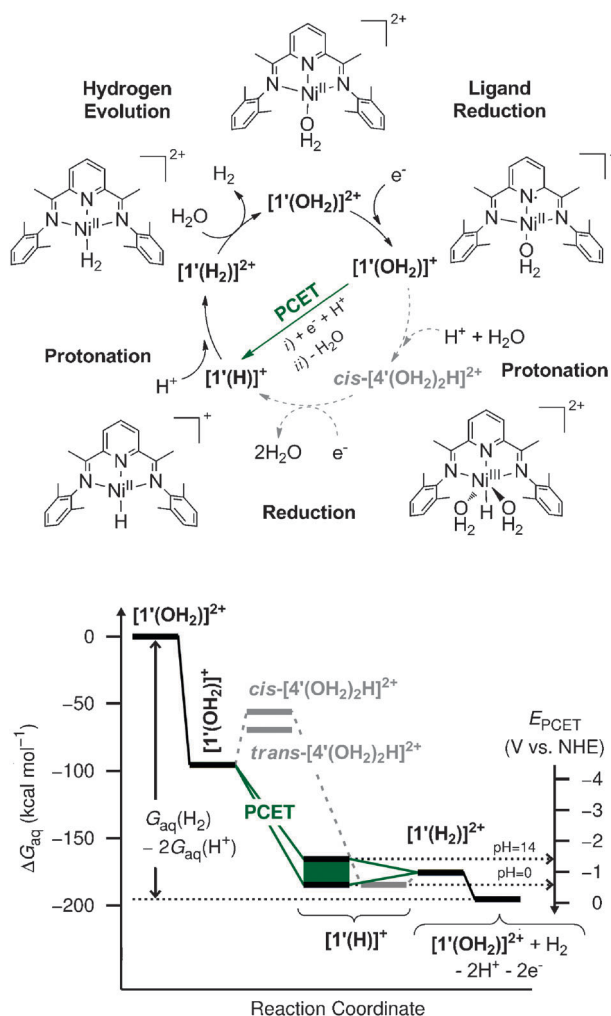
**Fig. 1** Cyclic voltammograms of 2 mM **1** in 0.1 M NBu<sub>4</sub>BF<sub>4</sub> acetonitrile solution: Solid trace: 25 mV s<sup>-1</sup>, dashed trace: 50 mV s<sup>-1</sup>, dotted trace: 100 mV s<sup>-1</sup>.

spectrometry, 0.65 millimoles of H<sub>2</sub> were detected, also after background subtraction. Thus, our Faradaic efficiency for H<sub>2</sub> production under these conditions was 95 ± 4%. These data correspond to a minimum of 65 mole H<sub>2</sub> per mole of Ni per hour (1456 L H<sub>2</sub> produced per mol of Ni catalyst per h). Only a small amount of the soluble catalyst is electroactive at any one time and thus the observed rate is a lower limit for the absolute activity.

In order to propose a mechanism of H<sub>2</sub> evolution using complex **1**, we performed *ab initio* calculations starting with the aqua complex of Fig. 2. As in previous studies,<sup>17</sup> we applied DFT/B3LYP to characterize the structural and spin/electronic properties of the reaction intermediates and performed free energy calculations.<sup>18</sup> Gas phase free-energy changes were calculated at the B3LYP/cc-pVTZ level, using minimum energy structures obtained at the DFT B3LYP/LANL2DZ level of theory, and then corrected by solvation free-energy calculations with the LANL2DZ basis set, using the Polarizable Continuum Model ( $\epsilon = 78.4$  for water) as implemented in Gaussian 09.<sup>19</sup>

Consistent with our proposal, the calculations predict that in aqueous conditions, **1** may readily lose one Br<sup>-</sup> to form a square planar complex with a *single* Br<sup>-</sup> ligand ( $\Delta G$  for ligand loss is -4.7 kcal mol<sup>-1</sup>). Subsequently, the Br<sup>-</sup> ligand can easily exchange with water ( $\Delta G$  for replacement of Br<sup>-</sup> with water is -6.3 kcal mol<sup>-1</sup>). This is consistent with experimental results indicating that dissolution of **1** in *d*<sub>6</sub>-DMSO, an even better O-donor ligand than H<sub>2</sub>O, results in the formation of a diamagnetic species, most likely a 4-coordinate square planar dication with coordinated DMSO (see the Fig. S6 in the ESI for the NMR spectrum†). Given that the catalytic experiments are performed in water, the DFT results suggest that the catalytic cycle begins with a square planar Ni<sup>II</sup> aqua complex and that **1** is only a precatalyst.

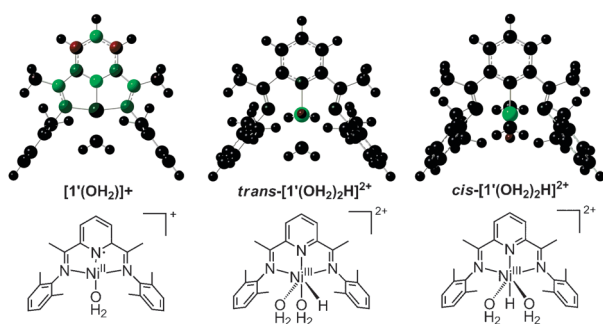
The first step in the catalytic cycle (Fig. 2) could involve either protonation of the Ni<sup>II</sup> starting material to give a formally Ni<sup>IV</sup> hydride or reduction of [I'(OH<sub>2</sub>)]<sup>2+</sup>. Both experimental and theoretical data suggest that reduction can be thermodynamically favored over protonation to the unfavorable Ni<sup>IV</sup> oxidation



**Fig. 2** Upper panel: Catalytic cycle based on formation of a Ni<sup>II</sup>-hydride intermediate by PCET proposed based on calculations at the DFT B3LYP/cc-pVTZ level of theory. Lower panel: Reaction free energy profile showing that PCET enables transformation of [I'(OH<sub>2</sub>)]<sup>2+</sup> into [I'(H)]<sup>+</sup> at low voltage. Transformation of [I'(OH<sub>2</sub>)]<sup>+</sup> into [I'(H)]<sup>+</sup> via an alternative pathway (shown in grey, lower panel) with sequential protonation and reduction without invoking PCET is thermodynamically unfavorable.

state. The lowest energy reduction product is the square planar, water-ligated, complex [I'(OH<sub>2</sub>)]<sup>+</sup>,<sup>20</sup> with high-spin density on the pincer ligand (as shown by the spin-distribution in Fig. 3). However, our DFT calculations indicate that an isomer of [I'(OH<sub>2</sub>)]<sup>+</sup> with the unpaired electron on the Ni is close in energy to the isomer with the ligand centered radical and within the errors of DFT we cannot differentiate between the two. EPR measurements of the one electron reduced species<sup>13</sup> provide supporting evidence that the first reduction process is ligand centered.

Once [I'(OH<sub>2</sub>)]<sup>+</sup> has been formed, three main pathways are available: (a) further reduction to give a Ni<sup>I</sup> species with a ligand-centered radical, (b) protonation of [I'(OH<sub>2</sub>)]<sup>+</sup> to give either a Ni<sup>IV</sup> hydride with a ligand-centered radical or a Ni<sup>III</sup> hydride with a neutral ligand, or (c) proton-coupled electron transfer (PCET) to give a Ni<sup>II</sup> hydride with a neutral ligand. Our DFT and experimental results suggest that the second



**Fig. 3** Ligand-centered reduction illustrated by Mulliken spin population analysis of intermediates  $[1'(\text{OH}_2)]^+$  (left),  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  (center) and  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$  (right) showing spin delocalization (in green) in the reduced ligand for  $[1'(\text{OH}_2)]^+$ , and localization of the excess spin density mostly on the Ni center of the Ni-hydride complexes  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$  and  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$ . No excess spin is observable in the analyses of  $[1'(\text{OH}_2)]^{2+}$ ,  $[1'(\text{H})]^+$ , and  $[1'(\text{H}_2)]^{2+}$ . Color key population: dark red (−0.08)—bright green (+0.27),  $[1'(\text{OH}_2)]^+$ ; dark red (−0.20)—bright green (+0.99),  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$ ; dark red (−0.20)—bright green (+1.04),  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$ .

reduction of **1** to give a  $\text{Ni}^{\text{I}}$  species and a ligand-centered radical is energetically disfavored and requires a significantly greater reduction potential than that needed during catalysis (*vide supra*); pathway (a) has therefore been dismissed. Protonation of  $[1'(\text{OH}_2)]^+$  could result in the formation of two different Ni hydride isomers,  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$  or  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  that differ in the coordination geometry around Ni. In  $\text{1-[1'-(OH}_2)_2\text{H}]^{2+}$ , the hydride is coplanar with the NNN ligand with two axially-bound water ligands (which stabilize the higher oxidation state), while in  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  the hydride is perpendicular to the NNN ligand. The spin density analysis indicates that both  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$  and  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  are formally  $\text{Ni}^{\text{III}}$  hydrides (see ESI for more information<sup>†</sup>), suggesting that a  $\text{Ni}^{\text{IV}}$  species with a ligand-centered radical is not accessible. However, protonation to form  $\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}$  or  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  is significantly uphill energetically, ( $\Delta G_{\text{aq}}([1'(\text{OH}_2)]^+/\text{cis-[1'-(OH}_2)_2\text{H}]^{2+}) = 40 \text{ kcal mol}^{-1}$  (1.73 eV) and  $\Delta G_{\text{aq}}([1'(\text{OH}_2)]^+/\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}) = 26 \text{ kcal mol}^{-1}$  (1.13 eV)), and is not spontaneous. On this basis, we propose that the PCET pathway (c) is the most likely route that converts  $[1'(\text{OH}_2)]^+$  into the square planar  $\text{Ni}^{\text{II}}$  hydride  $[1'(\text{H})]^+$ . The free energy requirement for  $[1'(\text{OH}_2)]^+ \rightarrow [1'(\text{H})]^+$  conversion thus includes (1.13 + 0.059 pH) eV to protonate  $[1'(\text{OH}_2)]^+$  to give  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  minus the excess free energy (4.60 eV) due to the reduction of  $\text{trans-[1'-(OH}_2)_2\text{H}]^{2+}$  to  $[1'(\text{H})]^+$ . Therefore, by coupling protonation and reduction in PCET,  $[1'(\text{OH}_2)]^+$  is converted into  $[1'(\text{H})]^+$  at a potential (1.13 + 0.059 pH − 4.60) V. This very large driving force<sup>21</sup> of  $\Delta G_{\text{aq}}([1'(\text{OH}_2)]^+/[1'(\text{H})]^+) = -80 \text{ kcal mol}^{-1}$  (−0.97 V *vs.* NHE) at pH = 0 is consistent with our measured kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of 4.2(1).

The catalytic cycle is completed by protonation of  $[1'(\text{H})]^+$  to give the  $\text{Ni}^{\text{II}}$  dihydrogen complex  $[1'(\text{H}_2)]^{2+}$  ( $\Delta G_{\text{aq}}([1'(\text{H})]^+/[1'(\text{H}_2)]^{2+}) = 9 \text{ kcal mol}^{-1}$ ) and subsequent  $\text{H}_2$  evolution, with the  $\text{H}_2$  ligand substituted by water to regenerate  $[1'(\text{OH}_2)]^{2+}$ . Notably, the highly reactive nature of the radical intermediates proposed to intervene in the cycle

has been previously documented: a species related to the one-electron reduced catalyst precursor **1** has been shown to undergo oxidative demethylation upon exposure to air.<sup>13</sup> Our experiments were performed under rigorous Ar purge and we believe that such a degradation pathway is only accessible in the presence of adventitious oxidizing species, such as aerial dioxygen.<sup>‡</sup>

## Conclusions

Our  $\text{Ni}^{\text{II}}$  pincer complex is an excellent water reduction precatalyst in aqueous acid solutions. This seems to be the first report of such a pincer complex being an operationally homogeneous catalyst for  $\text{H}^+$  reduction. Precatalyst **1** incorporates a redox-active ligand, a factor that could be important in facilitating the catalytic process, and shows a low overpotential for  $\text{H}_2$  production with a rate of  $105 \text{ s}^{-1}$ . Bulk electrolysis followed by macroscopic determination of the  $\text{H}_2$  produced, demonstrated that complex **1** gives at least 65 mole  $\text{H}_2$  per mole of catalyst per hour (−1.1 V *vs.* NHE in 50 mL 0.1 M KCl/HCl solution pH 1 with 0.2 mmol catalyst). However, a reliable comparison of  $\text{H}_2$  evolution measurements across different systems is difficult because of the wide array of experimental conditions used in proton reduction.<sup>11</sup> Factors that change between systems include experimental setups, electrolysis potentials and choice of solvent and proton source. DFT studies suggest that the mechanism of proton reduction for **1** involves a key PCET step. Further mechanistic work is under way to investigate the proposed intermediates and to tune the properties of the pincer ligand to enhance the kinetics of proton reduction.

## Experimental

Experimental details are given in the supplementary information.<sup>†</sup>

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## Notes and references

<sup>‡</sup> We did not observe evidence of electrodeposition in background runs performed after running bulk electrolysis and voltammetry. Relevant backgrounds and controls are available in the ESI.<sup>†</sup> The  $1e^-$  reduced form of the catalyst was shown<sup>14</sup> to be  $\text{O}_2$  sensitive and our measurements were done with rigorous exclusion of air.

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