Supplementary Information

Optimizing Conditions for Utilization of an H₂ Oxidation Catalyst with Outer Coordination Sphere Functionalities

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Table S1. Measured equilibrium potentials in methanol in the presence of various amounts of acid and water.

<table>
<thead>
<tr>
<th>[H⁺] (mM)</th>
<th>[H₂O] (M)</th>
<th>E_{H⁺/0.5H₂} (mV vs. FeCp²⁺/0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
<td>-1010</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>-795</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>-750</td>
</tr>
<tr>
<td>12</td>
<td>1.0</td>
<td>-700</td>
</tr>
<tr>
<td>18</td>
<td>1.0</td>
<td>-680</td>
</tr>
<tr>
<td>23</td>
<td>1.0</td>
<td>-660</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>-630</td>
</tr>
</tbody>
</table>

Table S2. Computationally determined pKₐ values for the pendant amines of CyArg in either the endo or exo position relative to the metal, and for the Ni(II) or Ni(0).

<table>
<thead>
<tr>
<th>Aminium</th>
<th>Acetonitrile</th>
<th>H₂O</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single endo proton</td>
<td>5.68</td>
<td>0.64</td>
<td>1.38</td>
</tr>
<tr>
<td>Single exo proton</td>
<td>8.23</td>
<td>2.73</td>
<td>3.52</td>
</tr>
<tr>
<td>Endo/Endo</td>
<td>13.48</td>
<td>7.03</td>
<td>7.90</td>
</tr>
<tr>
<td>Ni(0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endo/Exo (endo)</td>
<td>14.51</td>
<td>7.87</td>
<td>8.76</td>
</tr>
<tr>
<td>Endo/Exo (exo)</td>
<td>13.25</td>
<td>6.85</td>
<td>7.71</td>
</tr>
<tr>
<td>Exo/Exo</td>
<td>14.20</td>
<td>7.62</td>
<td>8.50</td>
</tr>
</tbody>
</table>
Figure S1. H₂ oxidation catalytic response for CyArg under various pressures (1-100 atm) and temperatures (25-72 °C): Cyclic voltammograms recorded for 6 µM CyArg at (A) 25 °C, (B) 45 °C, (C) 55 °C, and (D) 72 °C under 1 atm (black trace), 20 atm (red trace), 40 atm (blue trace), 67 atm (violet trace), and 100 atm H₂ (green trace) in water (pH 1.0), with 0.1 M Na₂SO₄. The horizontal arrow shows the initial scanning direction. The data were recorded with a scan rate at 0.1 Vs⁻¹ using a glassy carbon disc working electrode.
Figure S2. Measurement of $i_{\text{cat}}$ and overpotential: $i_{\text{cat}}$ was calculated as the distance between the extrapolated background current (horizontal dotted grey line) and catalytic response at 0.45 V (vs. SHE). The potential where the catalytic response is half of the catalytic current ($i_{\text{cat}/2}$) is denoted as $E_{\text{cat}/2}$. The difference between $E_{\text{cat}/2}$ and the equilibrium potential for the $\text{H}^+/1/2\text{H}_2$ is the overpotential. In this figure, the overpotential measurement is shown for 345 K. Experimental conditions: [CyArg] = 6 µM, water (pH 1.0) with 0.1 M Na$_2$SO$_4$, scan rate: 0.100 V/s.

Figure S3. H$_2$ oxidation by CyArg in methanol: (B) $i_{\text{cat}}$ vs. [water] and (C) $i_{\text{cat}}$ vs. [HTFSI]. Other general experimental conditions: [CyArg] = 50 µM, solution with 0.1 M $^\circ$Bu$_4$BF$_4$, and scan rate: 0.100 V/s.
Figure S4. H₂ oxidation by CyBn in methanol: (A) cyclic voltammograms of CyBn in methanol under H₂, under H₂ with 0.28 M water, and under H₂ with 0.28 M water and 25 mM acid. (B) \( i_{\text{cat}} \) vs. [water] and (C) \( i_{\text{cat}} \) vs. [HTFSI]. Experimental conditions: [CyBn] = 0.5 mM, solution with 0.1 M nBu₄BF₄, and scan rate: 1 V/s.

Figure S5. Catalytic cyclic voltammograms of CyBn in methanol from 1-100 atm H₂ at 298 K. Experimental conditions: [CyBn] = 0.5 mM, solution contains 0.28 M H₂O and 25 mM HTFSI. The horizontal black arrow shows the initial scan direction. Data were recorded at a scan rate of 0.5 Vs⁻¹ using a glassy carbon disc working electrode.
Figure S6. Rinse test for analyzing the nature of H₂ oxidation catalysis at 100 atm of H₂ in methanol containing 0.28 M H₂O and 25 mM HTFSI for (A) 50 µM CyArg and (B) 0.5 mM CyBn. At first a full cyclic voltammogram was recorded with a glassy carbon working electrode for the samples (black trace). After polishing the electrode, a partial voltammogram was recorded up to the maxima in the positive direction (0.875 V and 0.750 V for CyArg and CyBn, respectively) for each sample (red trace). Then, a subsequent voltammogram was recorded from 0.500 V and -0.250 V for CyArg and CyBn, respectively towards positive direction with same electrode (the electrode was rinsed in acetonitrile but not polished) in a fresh blank methanol containing 0.28 M H₂O and 25 mM HTFSI. No substantial residual current in the fresh solution with the unpolished electrode was observed (blue trace) suggesting that no significant amount of Ni catalyst was deposited on the electrode during the H₂ oxidation under our experimental conditions. The black and blue arrows show the initial scanning direction for each runs. Data were recorded with a scan rate of 0.5 V/s.
Figure S7. Catalytic cycle for H₂ oxidation (clockwise) and H₂ production (counterclockwise) by Ni(PR₂NR')₂²⁺ complexes.¹

REFERENCES