Supplementary Information

Optimizing Conditions for Utilization of an H_2 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.

$[H^+]$ (mM)	$[H_2O]$ (M)	$E_{H+/0.5H2}$ (mV vs. $FeCp_2^{+/0}$)
0	***1.0***	***-1010***
3	***1.0***	***-795***
6	***1.0***	***-750***
12	***1.0***	***-700***
18	***1.0***	***-680***
23	***1.0***	***-660***
30	***1.0***	***-630***

Table S2. Computationally determined pK_a 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).

	Aminium	Acetonitrile	H_2O	MeOH
Ni(II)	Single endo proton	5.68	0.64	1.38
	Single exo proton	8.23	2.73	3.52
Ni(0)	Endo/Endo	13.48	7.03	7.90
	Endo/Exo (endo)	14.51	7.87	8.76
	Endo/Exo (exo)	13.25	6.85	7.71
	Exo/Exo	14.20	7.62	8.50

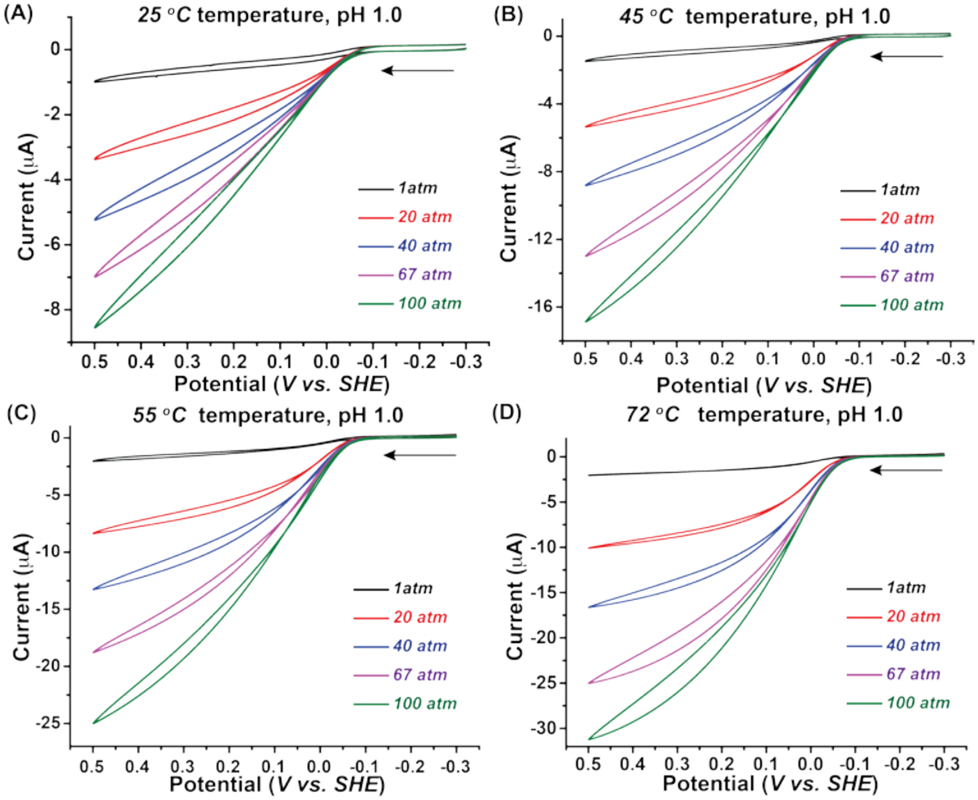

Figure S1. H_2 oxidation catalytic response for **CyArg** under various pressures (1-100 atm) and temperatures (25-72 ^{o}C): Cyclic voltammograms recorded for 6 μM **CyArg** at (A) 25 ^{o}C, (B) 45 ^{o}C, (C) 55 ^{o}C, and (D) 72 ^{o}C under 1 atm (black trace), 20 atm (red trace), 40 atm (blue trace), 67 atm (violet trace), and 100 atm H_2 (green trace) in water (pH 1.0), with 0.1 M Na_2SO_4. 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.

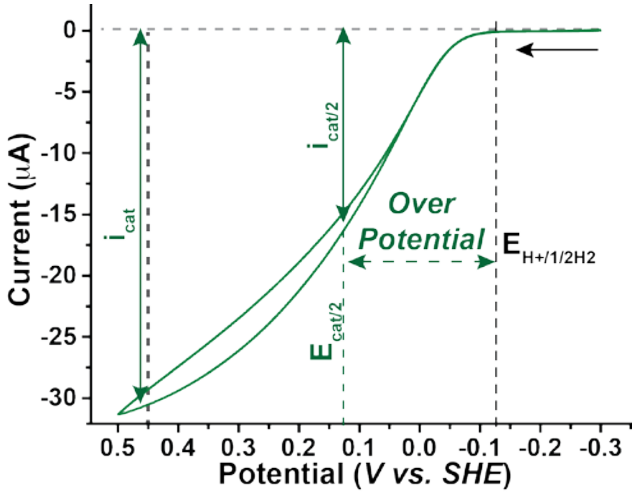

Figure S2. Measurement of i_{cat} and overpotential: i_{cat} was calculated as the distance between the extrapolated background current (horizontal dotted grey line) and catalytic response at 0.45 V (vs. SHE). The potential where the catalytic response is half of the catalytic current ($i_{cat/2}$) is denoted as $E_{cat/2}$. The difference between $E_{cat/2}$ and the equilibrium potential for the $H^+/1/2H_2$ 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_2SO_4, scan rate: 0.100 V/s.

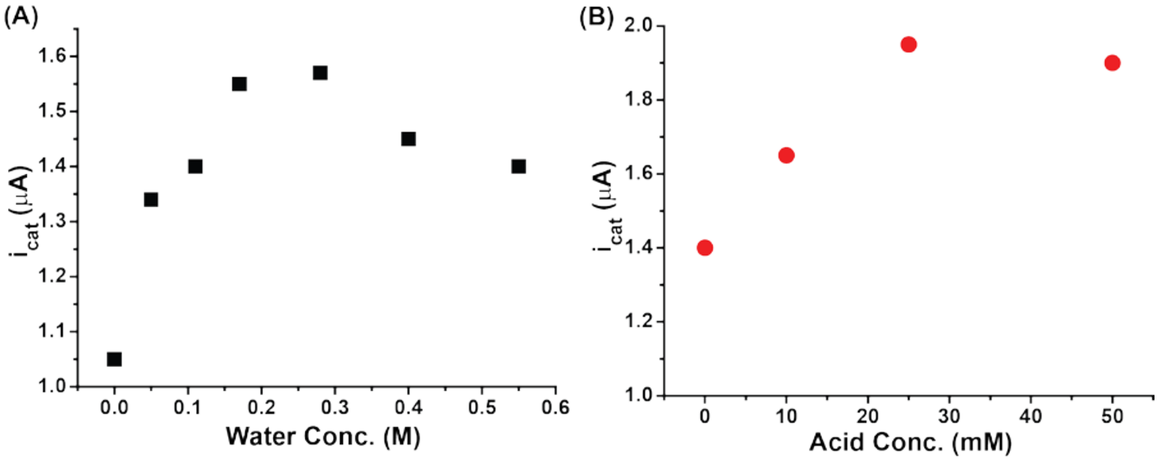

Figure S3. H_2 oxidation by **CyArg** in methanol: (B) i_{cat} vs. [water] and (C) i_{cat} vs. [HTFSI]. Other general experimental conditions: [**CyArg**]= 50 μM, solution with 0.1 M $^nBu_4BF_4$, and scan rate: 0.100 V/s.

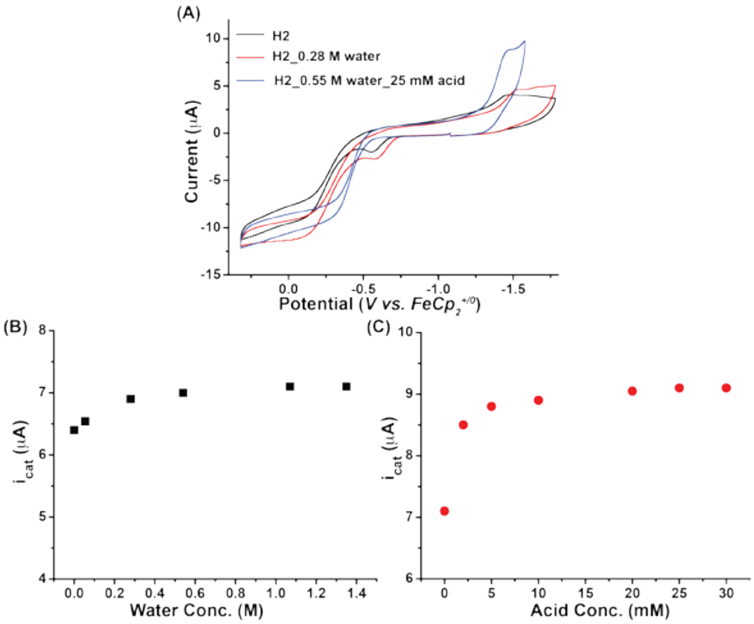

Figure S4. H_2 oxidation by **CyBn** in methanol: (A) cyclic voltammograms of **CyBn** in methanol under H_2, under H_2 with 0.28 M water, and under H_2 with 0.28 M water and 25 mM acid. (B) i_{cat} vs. [water] and (C) i_{cat} vs. [HTFSI]. Experimental conditions: [**CyBn**]= 0.5 mM, solution with 0.1 M $^{n}Bu_4BF_4$, and scan rate: 1 V/s.

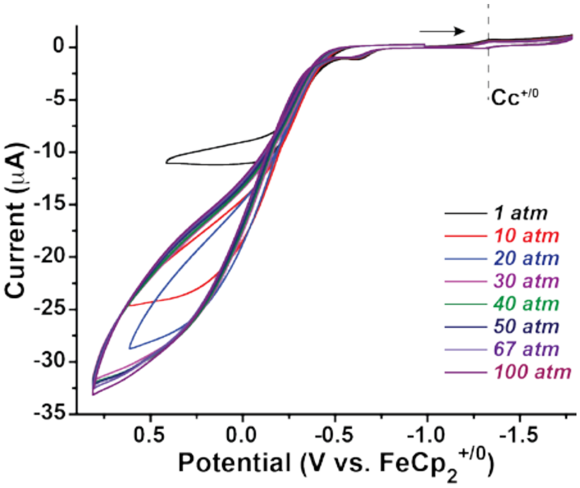

Figure S5. Catalytic cyclic voltammograms of **CyBn** in methanol from 1-100 atm H_2 at 298 K. Experimental conditions: [**CyBn**]= 0.5 mM, solution contains 0.28 M H_2O and 25 mM HTFSI. The horizontal black arrow shows the initial scan direction. Data were recorded at a scan rate of 0.5 Vs^{-1} using a glassy carbon disc working electrode.

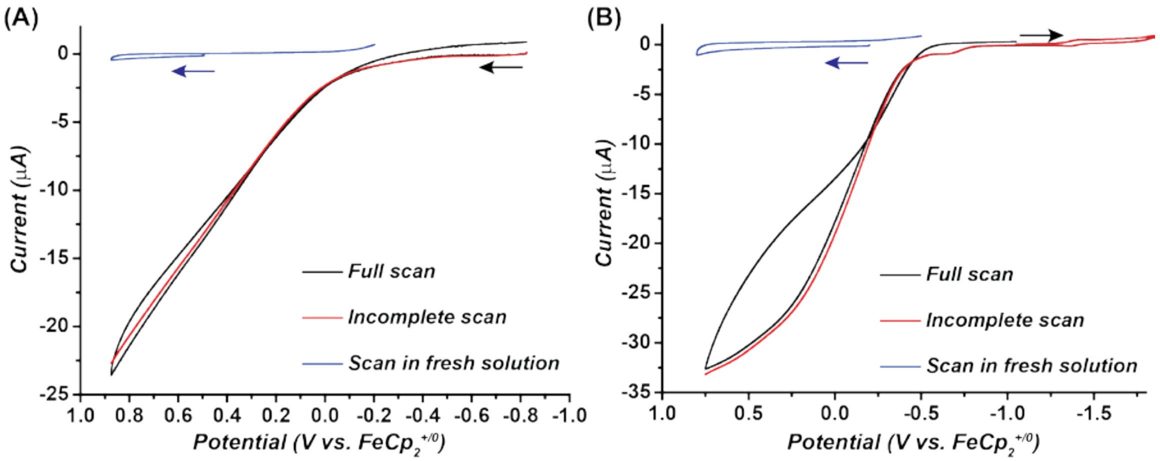

Figure S6. Rinse test for analyzing the nature of H_2 oxidation catalysis at 100 atm of H_2 in methanol containing 0.28 M H_2O and 25 mM HTFSI for (A) 50 μM **CyArg** and (B) 0.5 mM **CyBn**. At first a full cyclic voltammogram was recorded with a glassy carbon working electrode for the samples (black 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 H_2O 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 H_2 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.

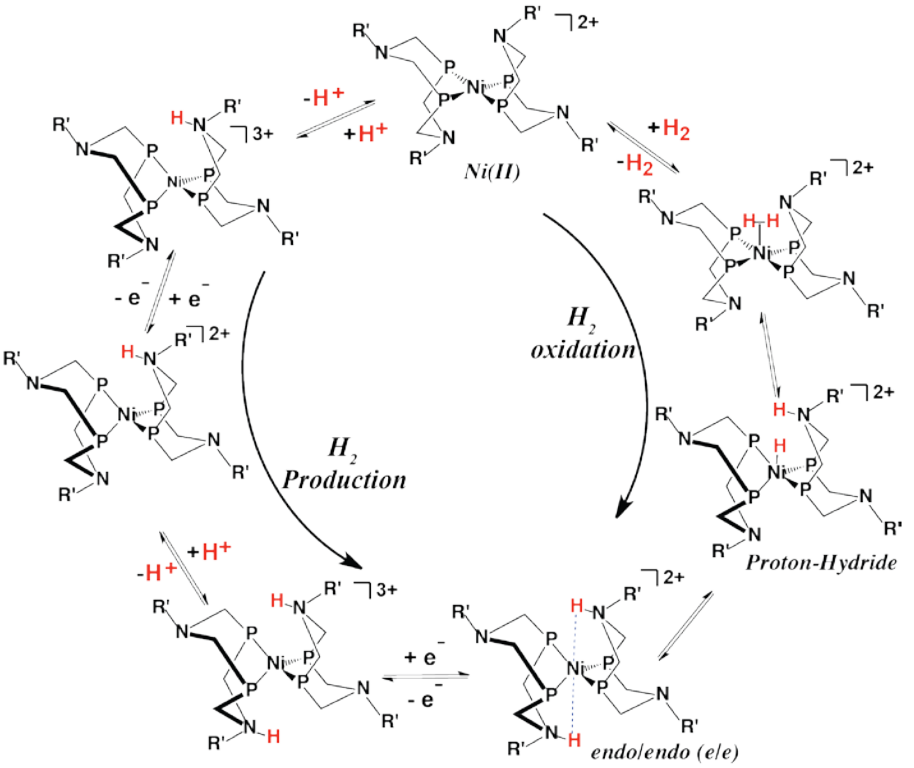

Figure S7. Catalytic cycle for H_2 oxidation (clockwise) and H_2 production (counter-clockwise) by $Ni(P^{R}{}_{2}N^{R'}{}_{2})_{2}{}^{2+}$ complexes.[1]

REFERENCES

1. DuBois, D. L. *Inorg. Chem.* **2014**, *53*, 3935-3960.