Supporting Information for

Redox-Active Cyclopentadienyl Ni Complexes with Quinoid N-Heterocyclic Carbene Ligands for the Electrocatalytic Hydrogen Release from Chrmical Fuels

Oana R. Luca,[†] *Daria L. Huang,* [†]*Michael K. Takase,* [†] *Robert H. Crabtree*[†]*

[†]Department of Chemistry, Yale University 225 Prospect St., New Haven, CT, 06520-8107 USA

*E-mail: robert.crabtree@yale.edu

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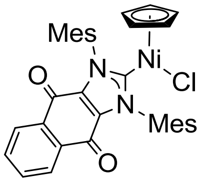
S1. Synthesis and Characterization of compound 1

To a 20 mL solution of 1.1 equivalents of nickelocene (41 mg, 0.22 mmol) in anhydrous THF, the yellow quinone-annulated dimesitylimidazolium chloride **ImQ** (0.2 mmol) was added as a solid as shown in **Eq 1**. The resulting suspension was then refluxed for 4 hours. **1** was isolated as a red solid in 69% yield by column chromatography in 4:1 hexanes/ ethylacetate as a brown-red solid. FT-ICR MS analysis was perfomed at the Yale Keck Proteomics facility on a 9.4 T Bruker Qe FT-ICR MS. Elemental Analysis was performed by Robertson Microlit.



1

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.01 (s, 2H, Ar_{CH}), 7.74 (s, 2H, Ar_{CH}), 7.20 (s, 4H, Mes_{CH}), 4.58 (s, 5H, Cp_{CH}), 2.50 (s, 6H, Mes $_{p\text{-}CH3}$), 2.08 (s, 12H, Mes $_{o,o'\text{-}CH3}$). ^{13}C{^{1}H} (126 MHz, CD_2Cl_2) δ 141.19, 135.85, 135.35, 133.00, 130.66, 128.25, 94.34, 22.46, 19.66. FT ICR MS: [M-Cl] calculated 557.1734, found 557.1721. Elemental Analysis. Expected: C: 68.77%, H: 5.26%, N: 4.72% Found: C: 68.59%, H: 5.23%; N: 4.44%.

S2. XRay Structure of 1

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn 994+ CCD detector with Cu K_α (λ = 1.54178 Å). The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97[1-2] using established refinement techniques.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). The structure crystallizes in the monoclinic space group *P*2$_1$/*c* with one molecule in the asymmetric unit.

Table S2. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{34} H_{31} Cl N_2 Ni O_2$	
Formula weight	593.77	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.7071(2) Å	a= 90°
	b = 15.6490(3) Å	b= 99.715(7)°
	c = 15.7529(11) Å	g = 90°
Volume	2844.6(2) Å^3	
Z	4	
Density (calculated)	1.386 mg/m^3	
Independent reflections	5028 [R(int) = 0.1301]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5028 / 0 / 367	
Goodness-of-fit on F^2	1.136	
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1592	
R indices (all data)	R1 = 0.0732, wR2 = 0.1732	
Largest diff. peak and hole	0.474 and -0.807 e.Å^{-3}	

S3. Additional Voltammograms

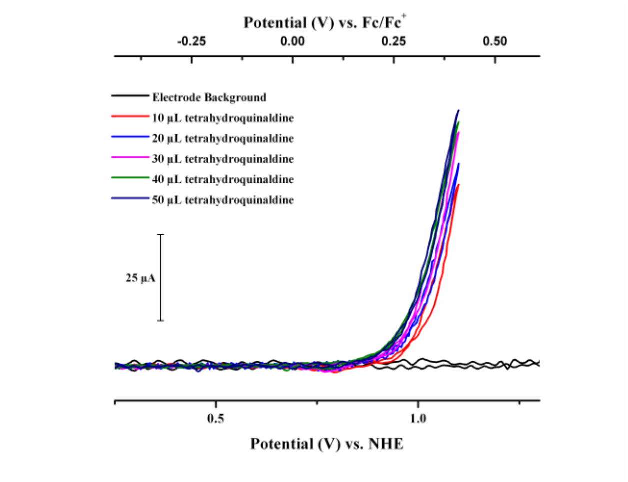


Figure S3-1. Cyclic Voltammetry of the bare Pt electrode in a 0.1 M NBu_4BF_4 acetonitrile solution at with increments of added tetrahydroquinaldine.

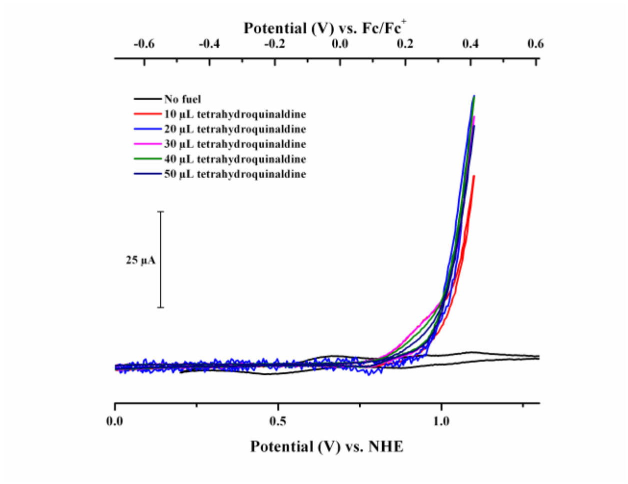


Figure S3-2. Cyclic Voltammetry of 2mM **2** Pt at electrode in a 0.1 M NBu_4BF_4 acetonitrile solution at with increments of added tetrahydroquinaldine.

S4. Electrochemistry Details

Cyclic voltammograms (CVs) in acetonitrile were collected on Pt electrodes (3 mm diameter from Bioanalytical Systems) with a platinum wire counter electrode and a silver wire reference electrode (referenced to NHE with ferrocene as external standard $E_{1/2}$=690 mV vs. NHE)[4] in a double junction BASi setup. Measurements were performed in 0.1 M NBu_4BF_4 solutions at 2 mM concentration of the respective complexes. Data workup was performed on OriginPro v8.0988 and AfterMath Data Organizer Version 1.2.3383.

Electrolyses were performed in a concentric two-cylinder cell, (an adapted Basi MF-1056 setup) using a BASi Pt gauze cylinder as the working electrode. The counter electrode was a specially-prepared high surface area RVC rod (~6 mm diameter) equipped with a pin connector (connected to the RVC by Ag conducting epoxy). The supporting electrolyte was acetonitrle with 0.2 M NBu_4BF_4. The working cell volume was 50 mL, whereas the counter chamber (E-fritted 1cm-diameter glass tube) contained 5 mL. 200 µL (1.38 mmol) tetrahydroquinaldine was added to the working chamber and the dissolved catalyst (7.5 µmol, 0.5 mol%). Controlled potential electrolysis at 1 V *vs* NHE was performed for 4 h, during which no significant change in solution volume was observed. At the end of the reaction, the solution in the working chamber was concentrated under reduced pressure and extracted with 3*75mL diethyl ether. The solvent from the yellow-orange extract was then removed under reduced pressue. Quinaldine (dehydrogenation product) was further isolated via silica gel column chromatography in 4:1 hexanes/ethyl acetate. Control experiment without catalyst yielded in no observed dehydrogenation product.

Control experiments on a 8 cm by 12 cm Stainless Steel 316 Mesh #60 (0.0075" Wire Diameter 31% Open Area Plain Weave 12" x 24") yielded no quinaldine in the absence of catalyst. Under the catalytic conditions (7.5µmol **1**, 0.5 mol%), 30% quinaldine product was observed.

Control experiments with a BASi RVC basket working electrode were performed under the previous conditions. Under catalytic conditions (7.5µmol **1**, 0.5 mol%), 55% quinaldine was isolated post-electrolysis. No product observed in the absence of the **1**, although significant charge was passed through the solution, indicating a significant amount of side-reactivity related to the electrode surface.

S5. NiO and Ni controls

Table S2 . Chemical and Faradaic yields for tetrahydroquinaldine dehydrogenation at a Pt electrode with Ni powder and NiO (0.5%).

Heterogeneous catalyst	Chemical Yield	Faradaic Efficiency
Ni	30 %	34 %
NiO	40 %	53 %

Additional References

1. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467.
2. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
3. Müller, P. *Cryst. Rev.* **2009**, *15*, 57.
4. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. Wiley: New York, **2000**.