Electronic Supplementary Information for

Organometallic Ni pincer complexes for the electrocatalytic production of hydrogen

Oana R. Luca[†], James D. Blakemore[†], Steven J. Konezny, [†] Jeremy M. Praetorius[†], Timothy J. Schmeier[†], Glendon B. Hunsinger, [‡*] Victor S. Batista, [†*] Gary W. Brudvig,[†*] Nilay Hazari,[†*] and Robert H. Crabtree[†*]

[†]*Department of Chemistry, Yale University 225 Prospect St., New Haven, CT, 06520-8107 USA,* [‡]*Department of Geology and Geophysics: Earth Systems Center for Stable Isotopic Studies, Yale University, 210 Whitney Ave., New Haven, CT 06511 USA.*

Fax: (+)1 203 432 6144

*E-mail: glendon.hunsinger@yale.edu,victor.batista@yale.edu, gary.brudvig@yale.edu, nilay.hazari@yale.edu, robert.crabtree@yale.edu

Table of Contents

1. Cyclic Voltammetry

Table S1. Tabulated cyclic voltammetry data of 2 mM nickel complexes (**1**and **2**)* in 0.1 M NBu_4BF_4 acetonitrile solutions at a glassy carbon working electrode.

Catalyst	1^{st} reduction $E_{1/2}$	ΔE_1 Peak 1 separation[a]	2^{nd} reduction $E_{1/2}$	ΔE_2 Peak 2 separation[a]	Oxidation $E_{1/2}$	ΔE_{ox} Oxidation peak separation[a]
Glassy carbon (Background)	n/a	n/a	n/a	n/a	n/a	n/a
1	~ -1.085 V	0.168 V	n/a	n/a	~1.660 V	~0.135 V
2	-1.189 V	0.086 V	n/a	n/a	~1.754 V	~0.173 V

[a] Expected peak separation for a perfectly $1e^-$ reversible wave: 0.059 V * extracted ΔE values are approximates.

Cyclic voltammograms were recorded using a Teflon coated BASi glassy carbon working electrode, and a Platinum wire counter electrode in an 0.1 M NBu_4BF_4 acetonitrile solution versus a pseudoreference electrode: silver wire (BASi double junction reference electrode setup) referenced externally vs. the Fc/Fc^+ couple at 690 mV vs. NHE. All CVs were recorded after rigorous Argon purge.

Scan rates are 100mV/s unless otherwise stated.

Figure S1-1. Cyclic voltammograms of a background 0.1 M NBu_4BF_4 acetonitrile solution (*black*) in the presence of 10µL (*red*), 20µL (*blue*), 30µL (*purple*) and 40 µL (*green*) 1 M HCl (100 mV/s). Smoothed 5 point adjusted averaging was used to remove electrical noise.

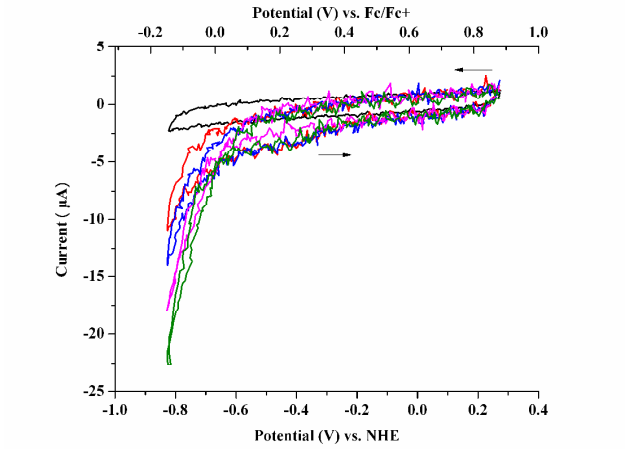


Figure S1-2. Cyclic voltammograms at 100 mV/s (*black*), 200 mV/s (*red*), 300 mV/s (*blue*) of 2 mM **2-MeCN**$^+$ in 0.1 M NBu_4BF_4 acetonitrile solution.

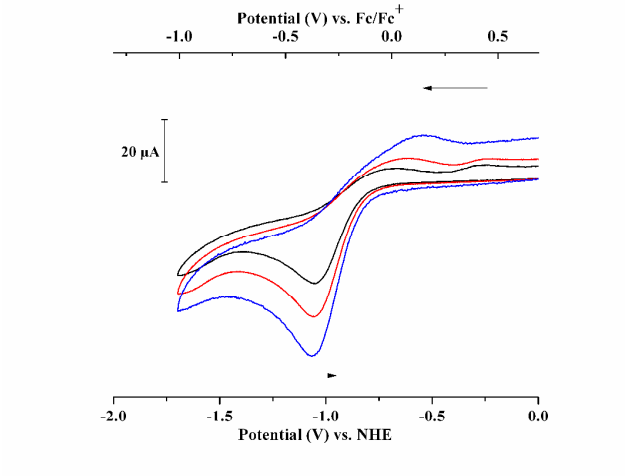


Figure S1-3. Cyclic voltammograms of 2 mM **2-H** in 0.1 M NBu_4BF_4 acetonitrile solution (*navy*) overlaid with **2-MeCN**$^+$ in the presence of 10 µL, 20 µL, 30 µL and 40 µL 1 M HCl.

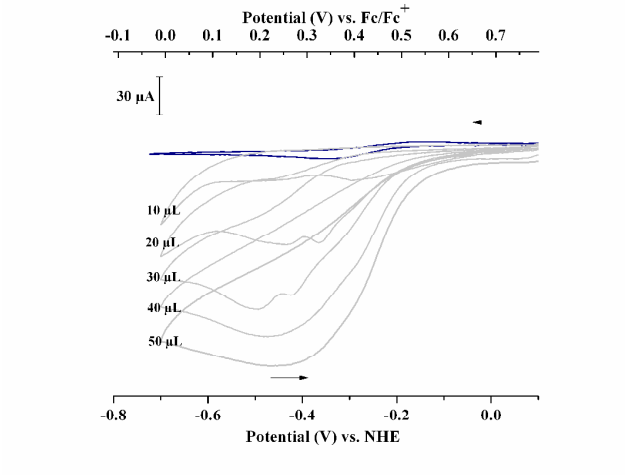


Figure S1-4. Cyclic voltammograms at 100 mV/s (*black*), 200 mV/s (*red*), 300 mV/s (*blue*) of 2 mM **1** in 0.1 M NBu_4BF_4 acetonitrile solution.

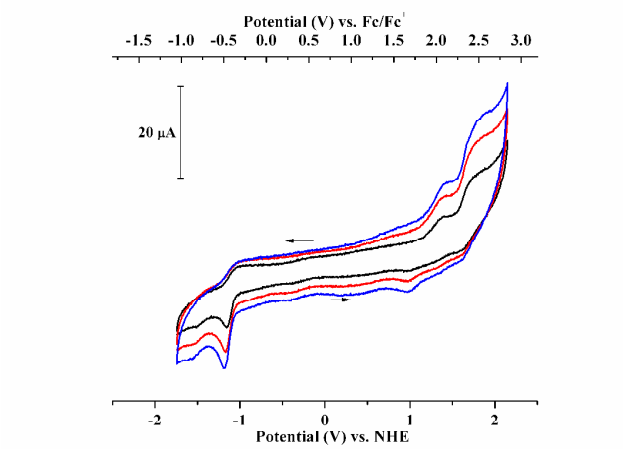


Figure S1-5. Cyclic voltammograms of 2 mM **1** in 0.1M NBu_4BF_4 acetonitrile solution (*black*) in the presence of 10 µL (*red*), 20 µL (*blue*), 30 µL (*purple*) and 40 µL (*green*) 1 M HCl. at 100 mV/s.

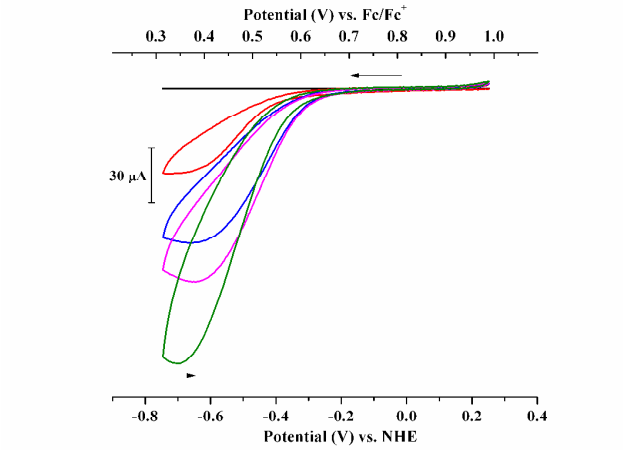


Figure S1-6. Cyclic voltammograms at 100 mV/s(*black*), 200 mV/s(*red*), 300 mV/s (*blue*) of 2 mM **2** in 0.1 M NBu_4BF_4 in acetonitrile solution.

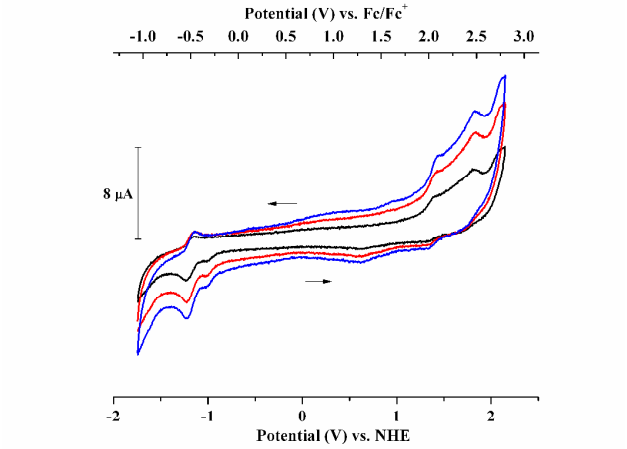


Figure S1-7. Cyclic voltammograms of 2 mM **2** in 0.1M NBu_4BF_4 acetonitrile solution (*red*) in the presence of 10 µL (*black*), 20 µL (*blue*), 30 µL (*purple*) and 40 µL (*green*) 1 M HCl at 100 mV/s.

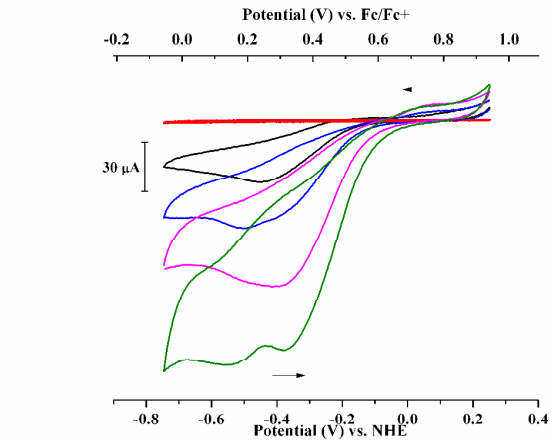


Figure S1-8. Cyclic voltammograms at 100 mV/s (*black*), 200 mV/s (*red*), 300 mV/s (*blue*) of 2 mM **2-H** solution in 0.1 M NBu_4BF_4 in acetonitrile.

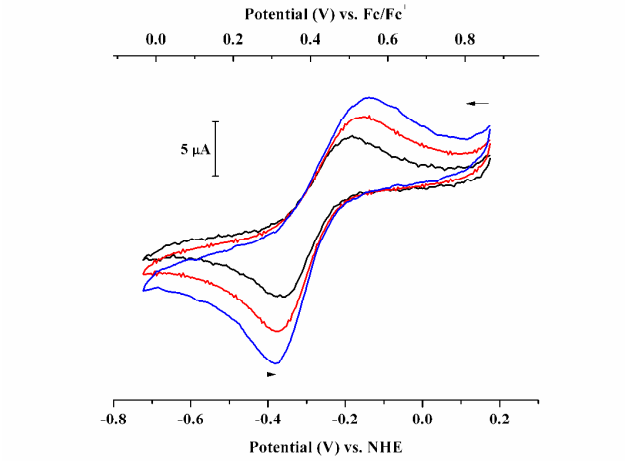


Figure S1-9. Cyclic voltammograms of 2 mM **2** (*red*) overlaid with CV of 2 mM solution **2-H** (*black*) and **2-MeCN$^+$**(*blue*) in 0.1 M NBu_4BF_4 acetonitrile solution at 100 mV/s. The reduction potential at the metal center is drastically shifted with different coordination.

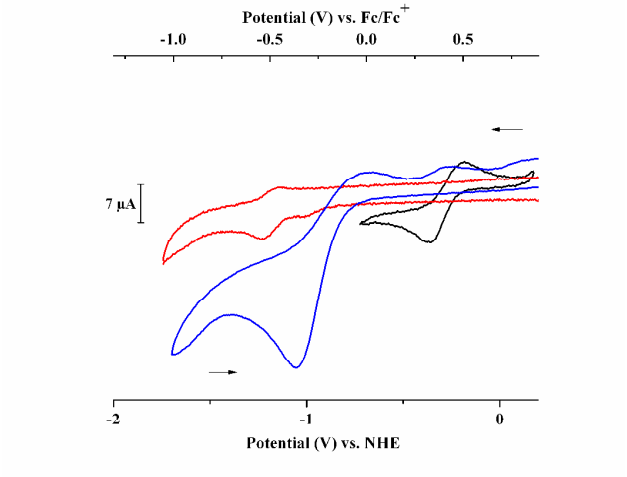
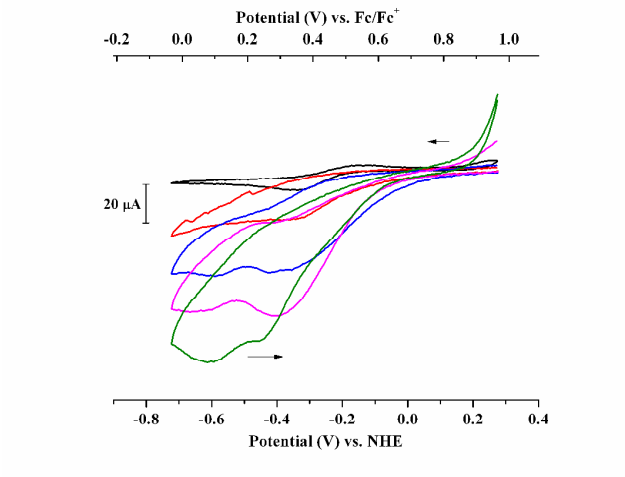
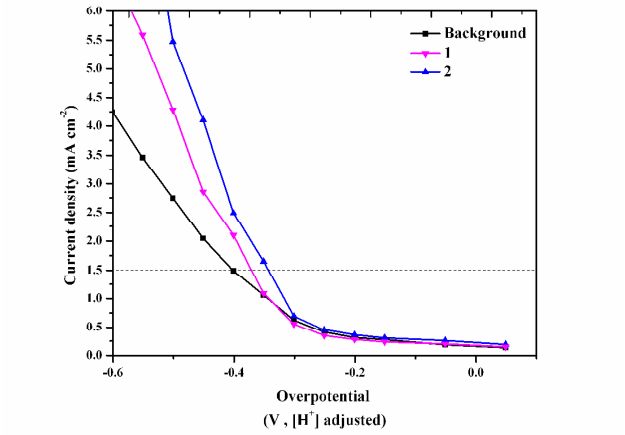


Figure S1-10. Cyclic voltammograms of 2 mM **3-H** in 0.1M NBu_4BF_4 acetonitrile solution (*black*) in the presence of 10 µL (*red*), 20 µL (*blue*), 30 µL (*purple*) and 40 µL (*green*) 1 M HCl at 100 mV/s. Bubbles on electrode formed immediately after addition of acid.



2. Current density vs. potential

Figure S2-1. Current density vs. applied potential: steady state current density at the end of chronoamperometry experiments at progressively more negative potentials - chronoamperograms (dwell time: 60 sec) at a glassy carbon electrode (in a three electrode setup- Pt counter electrode, non-aqueous Ag pseudoreference) in 5.2 mL acetonitrile NBu_4BF_4 solutions containing 200 µL 1 M aqueous HCl at catalyst concentrations of 0.2 mM with magnetic stirring.



3. Bulk electrolyses and H_2 measurement

Controlled potential experiments for headspace H_2 detection were performed at -0.6V vs. NHE (0.5 h) in a custom built two cylinder bulk electrolysis H cell: The cathode chamber had a working volume of 50 mL (0.04 mM in the respective catalyst for the catalytic runs) and 20 mL for the anode chamber. The two were separated by a coarse frit.

A stock solution was prepared from 900 mL MeCN (0.1 M NBu_4BF_4) and 100 mL 1 M HCl. In the catalytic run the cathode was charged with 50 mL stock solution and catalyst and the anode with 20 mL of the same solution. The cathode and anode chamber solutions were sparged with He for 5 min prior to starting the experiment.

Background runs were performed after the catalytic runs with the cathode containing 50 mL of the stock solution with no catalyst and the anode 20 mL of the stock solution. The working electrode was a BASi RVC electrode referenced vs. Ag/AgCl (KCl_{sat}). The counter electrode was a 2.5 cm x 2.5 cm Pt mesh.

Quantitative Mass Spectrometry calibration of voltage response against H_2 detection was performed using 2.05%, 15%, 25% and 50% H_2/He custom prepared mixed gases from Tech Air and AirProducts Inc. The average of duplicate catalytic run analyses are shown.

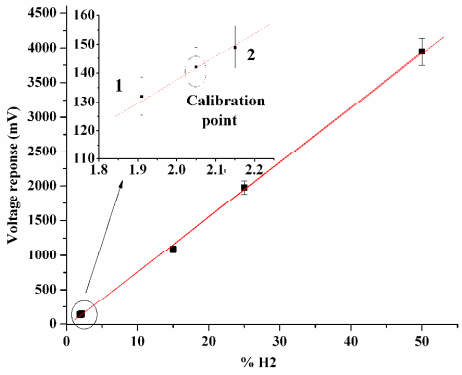


Figure S3-1. Quantitative Mass Spectrometry calibration and catalytic runs.

4. Crystal Structure Data for $[2\text{-MeCN}]^+$

The diffraction experiments were carried out on a Bruker AXS SMART CCD three-circle diffractometer with a sealed tube at 23 °C using graphite-monochromated Mo KR radiation (λ) 0.71073 Å). The software used were SMART for collecting frames of data, indexing reflections, and determination of lattice parameters; SAINT for integration of intensity of reflections and scaling; SADABS for empirical absorption correction; and SHELXTL for space group determination, structure solution, and least-squares refinements on $|F|2$. The crystals were mounted at the end of glass fibers and used for the diffraction experiments. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions.

Table S4-1. Crystal data and structure refinement for $[(PCP)Ni(NCCH_3)]^+ [BF_4]^-$

Empirical Formula	$P_2N_2C_{28}H_{49}NiBF_4$
Formula Weight	621.16
Crystal Color, Habit	yellow, chunk
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
Detector Position	49.90 mm
Pixel Size	0.146 mm
Lattice Parameters	a = 10.4927(18) Å

	b = 15.606(3) Å
	c = 10.6505(18) Å
	β = 111.242(4) °
	V = 1625.5(5) Å^3
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.269 g/cm^3
F_{000}	660.00
μ(MoKα)	7.376 cm^{-1}
Data Images	462 exposures
ω oscillation Range (χ=54.0, φ=120.0)	-120.0 - 60.0^o
Exposure Rate	60.0 sec./^{o}
Detector Swing Angle	-28.40^o
$2\theta_{max}$	52.0^o
No. of Reflections Measured	Total: 12989
	Unique: 6348 (R_{int} = 0.0485)
	Friedel pairs: 3023
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.697 - 0.863)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 – Fc^2)^2
Least Squares Weights	w = 1/ [σ^2(Fo^2) + (0.0616 · P)^2
	+ 0.0000 · P]
	where P = (Max(Fo^2,0) + 2Fc^2)/3
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6348
No. Variables	343
Reflection/Parameter Ratio	18.51
Residuals: R1 (I>2.00σI))	0.0581
Residuals: R (All reflections)	0.0768
Residuals: wR2 (All reflections)	0.1264
Goodness of Fit Indicator	1.047
Flack Parameter	-0.003(18)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.48 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.34 e$^-$/Å^3

Table S4-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Ni(1)	0.71359(5)	0.89352(4)	0.28474(5)	2.195(12)
P(1)	0.51687(12)	0.82594(8)	0.19220(11)	2.32(2)
P(2)	0.89869(12)	0.96336(8)	0.41141(12)	2.28(2)
F(1)	0.8801(6)	0.6468(3)	-0.0275(5)	9.92(16)
F(2)	1.0539(8)	0.5636(5)	0.0823(6)	15.1(3)
F(3)	1.0429(9)	0.6890(5)	0.1539(9)	19.0(4)
F(4)	0.9145(8)	0.5935(9)	0.1655(9)	21.5(5)
N(1)	0.7772(4)	0.8710(3)	0.1421(4)	2.96(8)
N(2)	0.6183(7)	1.2028(5)	0.3541(7)	7.03(15)
C(1)	0.6466(5)	0.9221(3)	0.4244(5)	2.60(9)
C(2)	0.7124(5)	0.9841(3)	0.5239(5)	2.66(9)

C(3)	0.6631(6)	1.0033(4)	0.6264(5)	3.85(11)	
C(4)	0.5478(6)	0.9641(4)	0.6308(6)	4.19(11)	
C(5)	0.4817(5)	0.9029(4)	0.5361(5)	3.44(10)	
C(6)	0.5293(4)	0.8822(4)	0.4334(4)	2.75(9)	
C(7)	0.8113(5)	0.8633(3)	0.0543(5)	3.31(10)	
C(8)	0.8577(7)	0.8559(5)	-0.0606(6)	5.12(15)	
C(9)	0.4557(5)	0.8152(3)	0.3318(5)	3.01(9)	
C(10)	0.8350(5)	1.0285(3)	0.5187(5)	3.21(10)	
C(11)	0.3869(4)	0.8935(4)	0.0641(4)	2.96(8)	
C(12)	0.3685(6)	0.9747(4)	0.1368(6)	4.83(13)	
C(13)	0.4403(6)	0.9223(4)	-0.0449(6)	4.46(13)	
C(14)	0.2473(5)	0.8498(4)	-0.0017(6)	5.20(15)	
C(15)	0.5239(6)	0.7125(3)	0.1363(5)	3.32(10)	
C(16)	0.3963(6)	0.6606(4)	0.1282(7)	4.64(13)	
C(17)	0.5380(7)	0.7091(4)	-0.0019(6)	4.72(13)	
C(18)	0.6508(6)	0.6736(4)	0.2418(6)	4.59(13)	
C(19)	1.0265(4)	0.8890(4)	0.5252(4)	2.99(8)	
C(20)	0.9626(6)	0.8482(4)	0.6198(5)	3.92(11)	
C(21)	1.0606(5)	0.8176(3)	0.4414(5)	3.73(11)	
C(22)	1.1603(5)	0.9331(4)	0.6154(5)	3.83(11)	
C(23)	0.9778(5)	1.0425(3)	0.3276(5)	3.27(10)	
C(24)	1.0710(5)	0.9993(4)	0.2641(6)	3.57(11)	
C(25)	1.0622(6)	1.1102(4)	0.4264(7)	4.57(13)	
C(26)	0.8567(6)	1.0852(4)	0.2171(6)	4.31(12)	
C(27)	0.5153(7)	1.1846(5)	0.3509(6)	4.68(13)	
C(28)	0.3800(8)	1.1604(6)	0.3473(8)	7.4(2)	
B(1)	0.9733(9)	0.6262(6)	0.0886(8)	4.84(16)	

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S4-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	0.0236(3)	0.0343(3)	0.0253(3)	-0.0015(3)	0.0086(2)	-0.0035(3)
P(1)	0.0255(6)	0.0327(7)	0.0271(6)	-0.0024(5)	0.0062(5)	0.0002(5)
P(2)	0.0245(6)	0.0305(7)	0.0305(6)	-0.0011(5)	0.0087(5)	-0.0036(5)
F(1)	0.153(5)	0.081(3)	0.086(3)	0.030(3)	-0.025(3)	0.007(3)
F(2)	0.211(8)	0.204(7)	0.115(5)	0.132(7)	0.004(5)	-0.020(5)
F(3)	0.245(9)	0.158(7)	0.200(8)	-0.014(7)	-0.061(7)	-0.056(6)
F(4)	0.150(7)	0.488(20)	0.197(8)	0.017(9)	0.083(7)	0.168(11)
N(1)	0.035(2)	0.046(3)	0.029(2)	-0.0041(20)	0.0091(18)	-0.0078(18)
N(2)	0.071(4)	0.094(5)	0.100(5)	-0.010(4)	0.028(4)	-0.020(4)
C(1)	0.029(2)	0.042(3)	0.031(2)	0.008(2)	0.013(2)	-0.0041(20)
C(2)	0.032(2)	0.035(3)	0.036(3)	0.001(2)	0.015(2)	-0.005(2)
C(3)	0.051(3)	0.055(3)	0.043(3)	0.003(3)	0.021(3)	-0.014(3)
C(4)	0.059(3)	0.062(4)	0.052(3)	-0.006(3)	0.035(3)	-0.011(3)
C(5)	0.045(3)	0.050(3)	0.045(3)	0.004(3)	0.027(2)	-0.003(3)
C(6)	0.034(2)	0.041(3)	0.030(2)	0.006(3)	0.0128(19)	0.000(2)
C(7)	0.038(3)	0.051(3)	0.041(3)	-0.003(2)	0.019(2)	-0.004(2)
C(8)	0.082(5)	0.082(5)	0.045(3)	-0.002(4)	0.039(3)	-0.006(3)
C(9)	0.035(3)	0.045(3)	0.035(3)	-0.004(3)	0.014(2)	0.005(2)
C(10)	0.041(3)	0.037(3)	0.041(3)	-0.001(2)	0.011(2)	-0.012(2)
C(11)	0.027(2)	0.038(2)	0.041(2)	0.004(3)	0.0058(19)	0.004(3)
C(12)	0.048(3)	0.056(4)	0.075(4)	0.019(3)	0.015(3)	0.016(3)
C(13)	0.045(3)	0.068(4)	0.047(3)	-0.002(3)	0.005(3)	0.020(3)

C(14)	0.039(3)	0.081(5)	0.057(4)	-0.010(3)	-0.008(3)	0.018(3)
C(15)	0.054(3)	0.035(3)	0.033(3)	-0.005(3)	0.010(2)	-0.007(2)
C(16)	0.062(4)	0.043(3)	0.068(4)	-0.013(3)	0.020(3)	0.001(3)
C(17)	0.080(5)	0.045(3)	0.062(4)	-0.013(3)	0.035(4)	-0.009(3)
C(18)	0.054(3)	0.041(3)	0.071(4)	0.008(3)	0.013(3)	-0.002(3)
C(19)	0.031(2)	0.041(3)	0.032(2)	0.002(3)	0.0001(18)	0.008(3)
C(20)	0.048(3)	0.050(3)	0.044(3)	0.002(3)	0.009(3)	0.009(3)
C(21)	0.041(3)	0.042(3)	0.054(3)	0.013(3)	0.010(3)	0.000(3)
C(22)	0.030(3)	0.059(3)	0.051(3)	-0.001(3)	0.008(2)	-0.008(3)
C(23)	0.036(3)	0.035(3)	0.054(3)	-0.003(2)	0.017(3)	0.005(2)
C(24)	0.036(3)	0.056(4)	0.053(3)	-0.008(3)	0.026(3)	0.002(3)
C(25)	0.051(3)	0.036(3)	0.093(5)	-0.012(3)	0.034(4)	-0.007(3)
C(26)	0.057(4)	0.045(3)	0.066(4)	0.007(3)	0.028(3)	0.024(3)
C(27)	0.048(4)	0.071(4)	0.058(4)	0.007(3)	0.017(3)	-0.009(3)
C(28)	0.078(5)	0.120(7)	0.084(6)	-0.019(5)	0.030(5)	-0.033(5)
B(1)	0.061(4)	0.070(5)	0.043(4)	0.006(4)	0.007(4)	-0.012(4)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Ni(1)	P(1)	2.2068(13)	Ni(1)	P(2)	2.2094(12)
Ni(1)	N(1)	1.901(5)	Ni(1)	C(1)	1.914(6)
P(1)	C(9)	1.828(6)	P(1)	C(11)	1.867(5)
P(1)	C(15)	1.879(5)	P(2)	C(10)	1.828(6)
P(2)	C(19)	1.853(5)	P(2)	C(23)	1.884(6)
F(1)	B(1)	1.309(8)	F(2)	B(1)	1.309(12)
F(3)	B(1)	1.269(11)	F(4)	B(1)	1.295(15)
N(1)	C(7)	1.122(8)	N(2)	C(27)	1.106(11)
C(1)	C(2)	1.417(6)	C(1)	C(6)	1.413(7)
C(2)	C(3)	1.399(9)	C(2)	C(10)	1.480(8)
C(3)	C(4)	1.370(9)	C(4)	C(5)	1.380(8)
C(5)	C(6)	1.395(8)	C(6)	C(9)	1.502(7)
C(7)	C(8)	1.476(9)	C(11)	C(12)	1.533(9)
C(11)	C(13)	1.528(9)	C(11)	C(14)	1.536(7)
C(15)	C(16)	1.540(9)	C(15)	C(17)	1.532(9)
C(15)	C(18)	1.522(7)	C(19)	C(20)	1.536(8)
C(19)	C(21)	1.549(8)	C(19)	C(22)	1.546(6)
C(23)	C(24)	1.532(9)	C(23)	C(25)	1.527(7)
C(23)	C(26)	1.536(7)	C(27)	C(28)	1.456(11)

Table S4-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	Ni(1)	P(2)	168.96(6)	P(1)	Ni(1)	N(1)	95.57(12)
P(1)	Ni(1)	C(1)	84.88(14)	P(2)	Ni(1)	N(1)	95.39(12)
P(2)	Ni(1)	C(1)	84.25(14)	N(1)	Ni(1)	C(1)	176.97(18)
Ni(1)	P(1)	C(9)	103.17(15)	Ni(1)	P(1)	C(11)	111.94(18)
Ni(1)	P(1)	C(15)	117.02(18)	C(9)	P(1)	C(11)	105.5(2)
C(9)	P(1)	C(15)	103.7(3)	C(11)	P(1)	C(15)	113.8(2)
Ni(1)	P(2)	C(10)	102.50(16)	Ni(1)	P(2)	C(19)	110.98(18)
Ni(1)	P(2)	C(23)	118.36(15)	C(10)	P(2)	C(19)	106.3(2)
C(10)	P(2)	C(23)	104.8(3)	C(19)	P(2)	C(23)	112.4(2)
Ni(1)	N(1)	C(7)	175.0(4)	Ni(1)	C(1)	C(2)	121.6(4)
Ni(1)	C(1)	C(6)	121.6(3)	C(2)	C(1)	C(6)	116.8(5)

C(1)	C(2)	C(3)	120.8(5)	C(1)	C(2)	C(10)	119.1(5)
C(3)	C(2)	C(10)	120.1(4)	C(2)	C(3)	C(4)	120.7(5)
C(3)	C(4)	C(5)	120.1(6)	C(4)	C(5)	C(6)	120.3(5)
C(1)	C(6)	C(5)	121.3(4)	C(1)	C(6)	C(9)	119.4(5)
C(5)	C(6)	C(9)	119.2(5)	N(1)	C(7)	C(8)	178.3(6)
P(1)	C(9)	C(6)	106.3(4)	P(2)	C(10)	C(2)	106.4(4)
P(1)	C(11)	C(12)	106.9(3)	P(1)	C(11)	C(13)	110.5(3)
P(1)	C(11)	C(14)	113.9(4)	C(12)	C(11)	C(13)	106.8(5)
C(12)	C(11)	C(14)	108.9(5)	C(13)	C(11)	C(14)	109.6(4)
P(1)	C(15)	C(16)	112.3(4)	P(1)	C(15)	C(17)	111.4(4)
P(1)	C(15)	C(18)	105.4(3)	C(16)	C(15)	C(17)	108.2(4)
C(16)	C(15)	C(18)	110.0(5)	C(17)	C(15)	C(18)	109.4(5)
P(2)	C(19)	C(20)	107.7(3)	P(2)	C(19)	C(21)	109.7(3)
P(2)	C(19)	C(22)	114.0(4)	C(20)	C(19)	C(21)	109.0(5)
C(20)	C(19)	C(22)	106.9(4)	C(21)	C(19)	C(22)	109.3(4)
P(2)	C(23)	C(24)	112.4(4)	P(2)	C(23)	C(25)	111.9(4)
P(2)	C(23)	C(26)	105.2(4)	C(24)	C(23)	C(25)	107.7(5)
C(24)	C(23)	C(26)	109.6(5)	C(25)	C(23)	C(26)	109.9(4)
N(2)	C(27)	C(28)	179.7(8)	F(1)	B(1)	F(2)	114.2(7)
F(1)	B(1)	F(3)	114.3(8)	F(1)	B(1)	F(4)	109.3(8)
F(2)	B(1)	F(3)	110.5(8)	F(2)	B(1)	F(4)	101.8(9)
F(3)	B(1)	F(4)	105.6(9)				

5. Kinetics for proton reduction

Method for EC_{cat} rate determination obtained from DuBois *et al.*

a. Pool, D. H.; DuBois, D. L. *J. Organomet. Chem.,* **2009**, *694*, 2858-2865.

b. Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J. T.; Rakowski DuBois, M.; DuBois, D. L. *J. Am. Chem. Soc.*, 2006, 128, 358-366.

For a diffusion limited catalytic process that occurs at high enough $[H^+]$ that the concentration remains unchanged, the observed current obeys the following equation:

$$i_c = nFA\ [cat]\sqrt{Dk[H^+]^2} \qquad (\mathbf{1})$$

For a reversible one e^- wave, the current observed can be expressed as:

$$i_p = 0.443FA\ [cat]\sqrt{\frac{F\nu D}{RT}} \qquad (\mathbf{2})$$

Dividing (**1**) by (**2**) the following expression is obtained:

$$\frac{i_c}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RT}{F}}\sqrt{\frac{k[H^+]^2}{\nu}} = 0.72\sqrt{\frac{k[H^+]^2}{\nu}} \qquad (\mathbf{3})$$

A = area of the electrode, D is the diffusion coefficient of the catalyst (D for the oxidized and reduced forms are assumed equal), n = 2 for H_2 production , R = 8.314 J/(mol K), F = 96485 C/mol, υ scan rate in V/s, k is the third order rate constant.

Linearity of :

1. *plots of i_c/i_p vs acid concentration confirms the electrocatalytic process is second order in acid*
2. *plots of i_c vs [catalyst] confirms the process is first order in catalyst*

The rate law for the third order process is derived as:

$$rate = k[H^+]^2[cat]$$

Where i_p did not correspond with the onset of catalysis ,the metal centered reduction peak current at the respective scan rate was taken as i_p .

Figure S5-1. Plot of i_c currents vs. concentration of catalyst **1** at 100 mV/s, $[H^+]$=4mM.

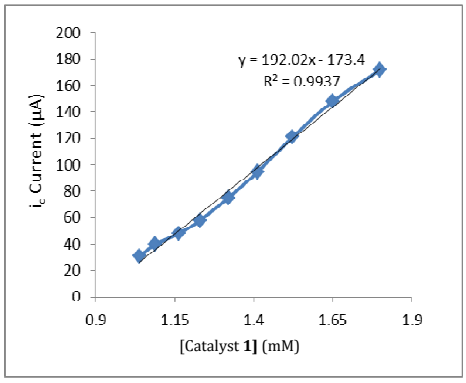


Figure S5-2. Plots of i_c / i_p ratios vs. acid concentration at 4mM catalyst **1** at 100 mV/s, 200 mV/s and 300 mV/s.

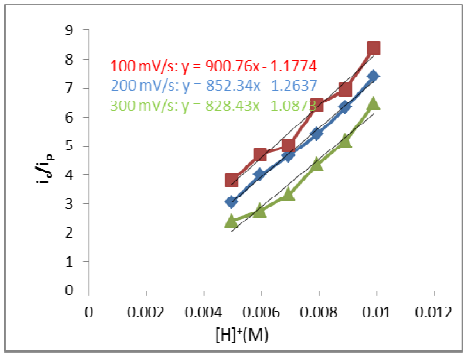


Figure S5-3. Plots of the slopes of i_c / i_p ratios vs. acid concentration in **Figure S5-2** vs. 1/(sqrt (υ)).

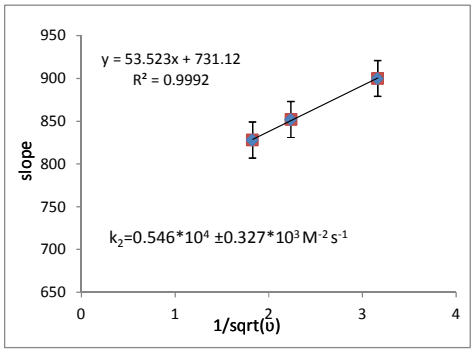


Figure S5-4. Plot of i_c currents vs. concentration of catalyst **2** at 100 mV/s, $[H^+]$=4mM.

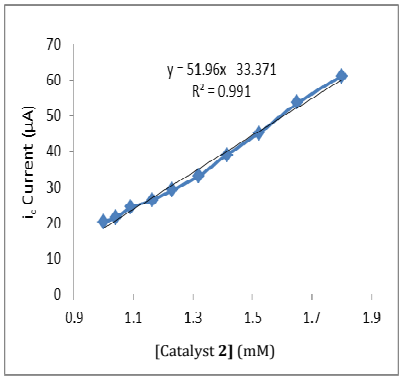


Figure S5-5. Plots of i_c / i_p ratios vs. acid concentration at 4mM catalyst **2** at 100 mV/s, 200 mV/s, 300 mV/s, 400 mV/s and 500 mV/s.

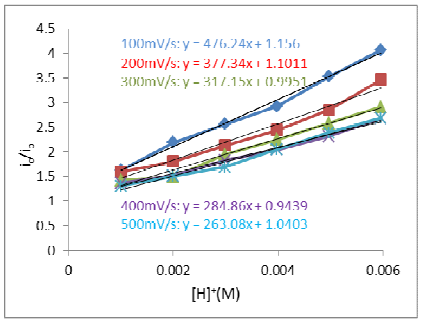


Figure S5-6. Plots of the slopes of i_c / i_p ratios vs. acid concentration in **Figure S5-5** vs. 1/(sqrt (υ)).

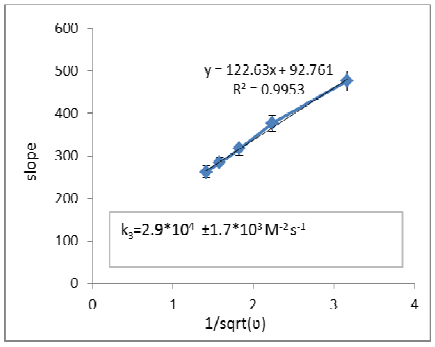


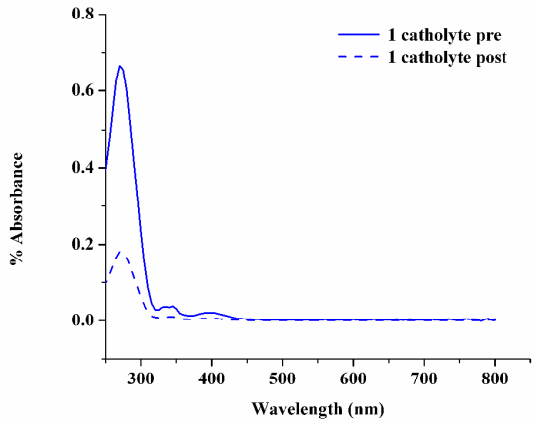
Table S5-1

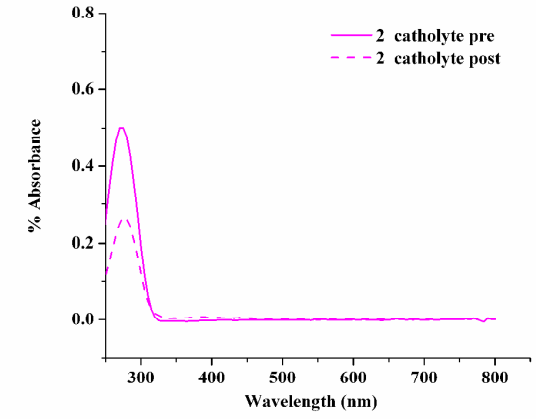
Tabulated kinetic data for catalysts **1** and **2.**

Catalyst	k ($M^{-2}s^{-1}$)	Error value	% error on k	TOF (s^{-1})	Rate ($M\ s^{-1}$)[a]	Potential at 1.5mA cm^{-2} [b]	Slope	Numeric error on slope	% error on slope
1	$0.55*10^4$	$\pm0.327*10^3$	6.05	54.6	0.275	-0.370V	53.23	1.61	3.02
2	$2.90*10^4$	$\pm1.7*10^3$	8.31	209	1.045	-0.345V	122.74	5.1	4.15

a. calculated for 0.1 M H^+, 5 mM catalyst b. as determined by plots of Current density vs. Potential constructed from a series of 60 s chronoamperometry experiments at progressively more negative potentials.

6. UV-vis of catholytes





7. Full Gaussian Reference and Computational Details

The full Gaussian reference is given below:
Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Table S7-1. Relative energies of intermediates involved in the proton reduction cycle with catalyst **2** in MeCN**.**

	ΔG(MeCN) [kcal/mol]	ΔG(MeCN) vs. NHE [eV]
[2-MeCN]$^{+}$	0	0
[2-MeCN]^{0}	-64.8	1.57
[2- MeCN]^{0} after MeCN ligand loss	-69.7	1.36
[2-H]$^{+}$	-72.0	1.26
[2-H]^{0}	-177.6	1.16
[2-H$_2$]$^{+}$	-192.7	0.51
[2-MeCN]$^{+}$ + H$_2$ - 2H^{+} - 2e^{-}	-204.4	0

[a]Assumes a normal hydrogen electrode potential of 4.48 V in MeCN [Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem., B* **2007**, *111*, 408-422.].

$$\textbf{[2-MeCN]}^{0} + H^{+} \rightarrow \textbf{[2-H]}^{+} + MeCN$$
$$\Delta G(MeCN) = -7.2 \text{ kcal/mol}$$

The 4-coordinate planar geometry of **[2-H]**$^{+}$ was compared with the octahedral six coordinate geometry with two MeCN ligands for Ni^{III}. The planar geometry is favored by 20.5 kcal/mol. The geometry must distort considerably to accommodate MeCN ligands.

$$\textbf{[2-H]}^{+} + 2MeCN \rightarrow \textbf{\textit{cis}-[2-(MeCN)}_2\textbf{H]}^{+}$$
$$\Delta G(MeCN) = 20.5 \text{ kcal/mol}$$

Table S7-2. Atomic coordinates of optimized geometries obtained at the DFT/B3LYP/LANL2DZ level of theory.

[2- MeCN]$^+$

Ni	0.000271	-0.139984	-0.001124
C	-1.166322	3.959791	0.313195
C	-1.171597	2.548606	0.323444
C	0.001036	1.80343	-0.004332
C	1.174117	2.546443	-0.335537
C	1.169642	3.957649	-0.331917
C	0.001852	4.667829	-0.011017
H	-2.075163	4.503947	0.563712
H	2.07881	4.50011	-0.584902
H	0.00215	5.754634	-0.013519
C	-2.447785	1.826563	0.711103
C	2.449966	1.821719	-0.71945
P	2.306013	0.048161	-0.093676
P	-2.305419	0.0494	0.094754
H	-2.547879	1.788836	1.803424
H	-3.346189	2.323613	0.326863
H	3.34869	2.320232	-0.337849
H	2.549951	1.778094	-1.811593
C	3.144147	0.013956	1.674994
C	4.682699	0.169951	1.606749
H	4.985878	1.075843	1.067277
H	5.074152	0.253744	2.629896
H	5.169642	-0.692888	1.140052
C	2.54597	1.192002	2.48951
H	1.453902	1.133814	2.554165
H	2.95184	1.151107	3.509546
H	2.806753	2.168676	2.067747
C	2.768332	-1.314585	2.381145
H	3.156929	-2.195699	1.859623
H	3.196632	-1.313516	3.392627
H	1.680584	-1.41756	2.479544
C	3.281775	-1.006517	-1.427602
C	4.607413	-0.320335	-1.85189
H	5.324617	-0.246994	-1.029815
H	5.073779	-0.921726	-2.644817
H	4.447121	0.683254	-2.260338
C	3.59108	-2.431674	-0.907233
H	4.022171	-3.02274	-1.726846
H	4.322085	-2.423745	-0.09164
H	2.690336	-2.949947	-0.558535
C	2.34265	-1.098776	-2.661152
H	1.405463	-1.614979	-2.423181
H	2.092165	-0.109927	-3.065633
H	2.849359	-1.659885	-3.458012
C	-3.147372	0.006546	-1.671871
C	-2.54919	1.179695	-2.493445

H	-2.807335	2.158743	-2.075571
H	-1.457347	1.119436	-2.560319
H	-2.957453	1.134776	-3.512346
C	-2.774893	-1.326156	-2.371837
H	-3.16409	-2.203639	-1.844543
H	-3.205443	-1.329959	-3.38235
H	-1.687577	-1.431522	-2.472093
C	-4.685633	0.164675	-1.601454
H	-5.07886	0.244981	-2.624207
H	-5.172756	-0.69583	-1.13057
H	-4.986856	1.072944	-1.064914
C	-3.278371	-0.996798	1.437851
C	-2.336819	-1.078704	2.670284
H	-1.398637	-1.593717	2.433435
H	-2.088463	-0.086731	3.068326
H	-2.840353	-1.636575	3.4714
C	-4.604089	-0.308772	1.858693
H	-5.323991	-0.246371	1.038046
H	-5.066645	-0.902371	2.659671
H	-4.445038	0.699719	2.255313
C	-3.586785	-2.426564	0.92982
H	-4.023713	-3.008566	1.75282
H	-4.312824	-2.426112	0.109759
H	-2.684327	-2.950291	0.593855
N	-0.001186	-2.078309	-0.002327
C	-0.003984	-3.250749	-0.005767
C	-0.007307	-4.714622	-0.009421
H	0.881953	-5.09749	-0.522794
H	-0.897181	-5.094154	-0.524047
H	-0.008227	-5.096881	1.017759

1

2 **[2- MeCN]^{0}**

Ni	-0.000602	-0.325761	-0.000986
C	-1.166873	3.841489	0.319053
C	-1.164157	2.427353	0.328537
C	0.000226	1.668286	-0.003948
C	1.165469	2.425124	-0.338652
C	1.169686	3.839246	-0.333625
C	0.001756	4.552149	-0.008433
H	-2.074976	4.388259	0.577067
H	2.078395	4.384251	-0.593227
H	0.002322	5.640809	-0.010125
C	-2.451022	1.719425	0.754787
C	2.451595	1.714232	-0.762048
P	2.548558	-0.058349	-0.063397
P	-2.548546	-0.0569	0.065974
H	-2.464546	1.616491	1.849404
H	-3.340948	2.30378	0.4839
H	3.342073	2.299722	-0.49543
H	2.464021	1.604936	-1.856062

C	3.501964	0.168952	1.644736
C	4.983223	0.597138	1.523799
H	5.101251	1.505908	0.919725
H	5.381341	0.81493	2.527007
H	5.607124	-0.191877	1.087521
C	2.726559	1.253366	2.441056
H	1.658337	1.01864	2.509582
H	3.138251	1.31089	3.460273
H	2.814324	2.244718	1.983649
C	3.401397	-1.167211	2.42747
H	3.935928	-1.984668	1.930864
H	3.839942	-1.040049	3.4289
H	2.353669	-1.468856	2.551796
C	3.716325	-0.930994	-1.391662
C	4.918911	-0.084081	-1.878948
H	5.640087	0.113695	-1.080482
H	5.447359	-0.627648	-2.678245
H	4.599534	0.878704	-2.293842
C	4.228129	-2.28352	-0.837491
H	4.70787	-2.854465	-1.64686
H	4.971905	-2.147659	-0.043736
H	3.405849	-2.890933	-0.435971
C	2.78686	-1.219068	-2.604354
H	1.940947	-1.855733	-2.318114
H	2.377051	-0.297276	-3.036343
H	3.35866	-1.732124	-3.392469
C	-3.502389	0.161246	-1.643052
C	-2.727272	1.241619	-2.445155
H	-2.815174	2.235399	-1.993028
H	-1.659024	1.006656	-2.512458
H	-3.139034	1.293699	-3.464637
C	-3.401726	-1.178877	-2.418955
H	-3.936525	-1.99365	-1.918214
H	-3.840097	-1.056876	-3.421103
H	-2.353967	-1.48114	-2.541583
C	-4.983718	0.589759	-1.524033
H	-5.38223	0.801898	-2.528296
H	-5.607246	-0.196948	-1.083104
H	-5.10176	1.501813	-0.924945
C	-3.715646	-0.922587	1.399233
C	-2.785426	-1.204866	2.612709
H	-1.940531	-1.844106	2.329162
H	-2.374272	-0.281141	3.039273
H	-3.357049	-1.713061	3.404087
C	-4.917797	-0.073025	1.883024
H	-5.639153	0.121255	1.083857
H	-5.446105	-0.612744	2.685003
H	-4.598028	0.891582	2.293357
C	-4.228083	-2.277845	0.852319
H	-4.708424	-2.843973	1.664676

H	-4.971511	-2.1461	0.057496
H	-3.405879	-2.888169	0.45514
N	-0.000943	-2.277884	-0.00133
C	-0.001547	-3.455515	-0.002368
C	-0.002748	-4.921344	-0.002253
H	0.891183	-5.306221	-0.506884
H	-0.887489	-5.305054	-0.523723
H	-0.012349	-5.305037	1.024903

[2- MeCN]^{0} after MeCN ligand loss

Ni	-0.038093	-0.180131	0.241182
C	0.79512	-3.958401	-1.596731
C	0.912613	-2.739935	-0.889984
C	-0.200636	-1.868732	-0.73886
C	-1.440131	-2.261738	-1.315015
C	-1.565552	-3.48724	-2.007648
C	-0.446001	-4.332121	-2.150612
H	1.655336	-4.619678	-1.70986
H	-2.520897	-3.782732	-2.44348
H	-0.540055	-5.273359	-2.689772
C	2.24177	-2.363224	-0.229234
C	-2.635041	-1.309099	-1.217386
P	-2.346041	0.01751	0.141816
P	2.254158	-0.510258	0.276528
H	2.368956	-2.937742	0.69909
H	3.10447	-2.601951	-0.866449
H	-3.580671	-1.843095	-1.050931
H	-2.746994	-0.760851	-2.163363
C	-3.28088	-0.701764	1.710979
C	-4.821643	-0.749237	1.578936
H	-5.143009	-1.291898	0.680744
H	-5.241908	-1.274947	2.449736
H	-5.264688	0.252992	1.554281
C	-2.743413	-2.143805	1.917115
H	-1.649464	-2.158785	1.980926
H	-3.154599	-2.5481	2.854324
H	-3.034097	-2.816001	1.101983
C	-2.883724	0.144986	2.948663
H	-3.244851	1.176925	2.884743
H	-3.315873	-0.307421	3.853834
H	-1.793446	0.173617	3.068837
C	-3.266811	1.590357	-0.586999
C	-4.636927	1.283585	-1.24255
H	-5.365786	0.889175	-0.528158
H	-5.049569	2.214998	-1.659821
H	-4.547333	0.568805	-2.068636
C	-3.448032	2.658605	0.519668
H	-3.778156	3.601297	0.059331

H	-4.206431	2.365382	1.255734
H	-2.505291	2.857075	1.044629
C	-2.301191	2.157641	-1.663982
H	-1.360218	2.502688	-1.222888
H	-2.069653	1.41635	-2.44008
H	-2.77567	3.019753	-2.156461
C	3.213758	0.379813	-1.185969
C	2.493305	-0.041029	-2.495767
H	2.590157	-1.113083	-2.700105
H	1.423432	0.192352	-2.455747
H	2.938284	0.507849	-3.339129
C	3.051886	1.913345	-1.017506
H	3.567373	2.291787	-0.12786
H	3.480457	2.420689	-1.8953
H	1.995173	2.197306	-0.94478
C	4.713367	0.014474	-1.289384
H	5.127602	0.450785	-2.210988
H	5.293656	0.412852	-0.448856
H	4.873855	-1.070033	-1.338182
C	3.320717	-0.531161	1.92694
C	2.358195	-1.078809	3.016682
H	1.469324	-0.443591	3.115869
H	2.017827	-2.09812	2.793177
H	2.877565	-1.103216	3.9861
C	4.581509	-1.430473	1.872139
H	5.320796	-1.069886	1.150887
H	5.060478	-1.439714	2.863301
H	4.335726	-2.467814	1.617861
C	3.727444	0.912741	2.312032
H	4.147027	0.914211	3.329024
H	4.4922	1.317992	1.638643
H	2.863936	1.590594	2.303027
N	0.156838	4.606039	-0.67875
C	0.686995	5.653032	-0.567041
C	1.350574	6.955078	-0.428905
H	0.75032	7.740707	-0.901204
H	2.335562	6.932329	-0.908276
H	1.482498	7.204784	0.629755

1

2 **[2-H]$^+$**

Ni	-0.042732	-0.266689	0.261638
C	0.79019	-3.67941	-2.199146
C	0.914897	-2.606126	-1.28985
C	-0.207107	-1.777403	-1.009055
C	-1.450395	-2.049985	-1.645281
C	-1.561383	-3.133911	-2.543286
C	-0.443679	-3.941166	-2.820766
H	1.64693	-4.314334	-2.416758

H	-2.511146	-3.34547	-3.030795
H	-0.534324	-4.771346	-3.516551
C	2.24168	-2.373524	-0.579356
C	-2.655801	-1.153578	-1.395555
P	-2.330461	-0.059349	0.129044
P	2.222129	-0.667611	0.266403
H	2.387945	-3.127174	0.204928
H	3.099234	-2.457927	-1.25765
H	-3.582949	-1.726077	-1.271683
H	-2.814094	-0.483915	-2.250669
C	-3.229909	-0.896424	1.646547
C	-4.769332	-0.778789	1.523777
H	-5.149668	-1.1895	0.580178
H	-5.230763	-1.351331	2.339651
H	-5.110422	0.257553	1.61711
C	-2.814822	-2.391848	1.649166
H	-1.72873	-2.51753	1.737144
H	-3.279759	-2.880104	2.515853
H	-3.144939	-2.925271	0.751278
C	-2.742281	-0.233859	2.959729
H	-3.038443	0.816129	3.036174
H	-3.186419	-0.76915	3.809694
H	-1.651557	-0.285509	3.05936
C	-2.938062	1.729389	-0.343357
C	-4.344042	1.699017	-0.997007
H	-5.117176	1.33272	-0.315024
H	-4.614118	2.725046	-1.281338
H	-4.372073	1.09383	-1.910482
C	-2.948762	2.643159	0.904999
H	-3.126469	3.676433	0.579062
H	-3.74945	2.377743	1.604915
H	-1.989028	2.62242	1.433773
C	-1.891432	2.259315	-1.360149
H	-0.908132	2.402918	-0.898233
H	-1.791975	1.606521	-2.23765
H	-2.214976	3.244164	-1.721141
C	3.207936	0.559972	-0.885215
C	2.601934	0.416633	-2.307248
H	2.704791	-0.595248	-2.714369
H	1.539442	0.687875	-2.33067
H	3.133295	1.1026	-2.979941
C	3.003883	2.013666	-0.39178
H	3.448382	2.187666	0.592558
H	3.495627	2.692731	-1.101567
H	1.947929	2.299004	-0.345446
C	4.715299	0.204229	-0.918124
H	5.20821	0.845649	-1.661107
H	5.204371	0.386843	0.044929
H	4.898686	-0.836725	-1.213022
C	2.949498	-0.938648	2.05402

	C	1.844203	-1.70277	2.832545
	H	0.929713	-1.100958	2.917676
	H	1.593833	-2.667466	2.372124
	H	2.201388	-1.908313	3.850109
	C	4.250203	-1.782789	2.028113
	H	5.063853	-1.281257	1.495811
	H	4.581839	-1.94076	3.063313
	H	4.102382	-2.772808	1.58133
	C	3.210806	0.422632	2.741968
	H	3.439389	0.242973	3.801037
	H	4.069938	0.945349	2.306989
	H	2.335563	1.080922	2.693201
	N	0.58103	4.611632	-0.635118
	C	0.778305	5.774225	-0.636026
	C	1.024547	7.221373	-0.638193
	H	0.189231	7.749686	-1.11085
	H	1.940516	7.451109	-1.193579
	H	1.135783	7.590596	0.387245
	H	0.084366	0.899679	1.282527
1				
2	**[2-H]^{0}**			
	Ni	-0.316569	-0.118859	0.25289
	C	-1.784969	-3.631451	-1.733627
	C	-1.009476	-2.733828	-0.96648
	C	-1.396773	-1.367791	-0.805912
	C	-2.603633	-0.952285	-1.448388
	C	-3.382449	-1.85609	-2.20479
	C	-2.972444	-3.194724	-2.35043
	H	-1.471069	-4.669342	-1.845614
	H	-4.300577	-1.519193	-2.686389
	H	-3.570794	-3.888969	-2.937609
	C	0.251042	-3.23106	-0.264688
	C	-3.032384	0.509157	-1.340543
	P	-2.015858	1.311185	0.061381
	P	1.251464	-1.706259	0.297812
	H	-0.016044	-3.797577	0.638162
	H	0.846878	-3.905272	-0.89424
	H	-4.113725	0.623422	-1.186822
	H	-2.78787	1.045108	-2.268176
	C	-3.20994	1.344862	1.610543
	C	-4.404631	2.316306	1.457908
	H	-4.972157	2.135968	0.535702
	H	-5.094243	2.172788	2.303201
	H	-4.086477	3.365223	1.469869
	C	-3.744457	-0.103621	1.777995
	H	-2.923808	-0.824348	1.862465
	H	-4.349493	-0.155514	2.694936
	H	-4.376385	-0.415563	0.938638
	C	-2.383433	1.708448	2.871199
	H	-2.016474	2.739613	2.846801

H	-3.018191	1.596965	3.76289
H	-1.515781	1.047458	2.974339
C	-1.600491	3.099015	-0.602154
C	-2.804781	3.817383	-1.261151
H	-3.606521	4.029175	-0.547288
H	-2.464024	4.778826	-1.673819
H	-3.228152	3.237616	-2.090092
C	-1.024316	3.969747	0.541022
H	-0.608351	4.894698	0.115041
H	-1.794887	4.258253	1.266235
H	-0.220357	3.44522	1.070925
C	-0.489271	2.880909	-1.665786
H	0.385373	2.393018	-1.221128
H	-0.836136	2.263535	-2.504851
H	-0.179786	3.855247	-2.071405
C	2.660032	-1.489698	-1.040842
C	1.940444	-1.447261	-2.416777
H	1.447766	-2.394899	-2.663762
H	1.180509	-0.658448	-2.444344
H	2.685671	-1.238191	-3.197894
C	3.374257	-0.133652	-0.819104
H	3.956982	-0.104394	0.105696
H	4.070032	0.054365	-1.647711
H	2.6606	0.695886	-0.78268
C	3.692403	-2.642776	-1.040363
H	4.358383	-2.524919	-1.908064
H	4.321685	-2.629735	-0.142999
H	3.21878	-3.630291	-1.119821
C	1.94615	-2.20933	2.052318
C	0.724812	-2.120461	3.00809
H	0.296489	-1.111572	2.995759
H	-0.066419	-2.832192	2.737947
H	1.048987	-2.352907	4.033137
C	2.533737	-3.642066	2.105416
H	3.42536	-3.74942	1.48026
H	2.824821	-3.869898	3.141894
H	1.805194	-4.401061	1.795743
C	3.009915	-1.184335	2.515943
H	3.235027	-1.355	3.579091
H	3.948507	-1.286222	1.958731
H	2.645554	-0.156689	2.402445
N	5.122732	2.662682	-0.652231
C	5.662645	3.707311	-0.577924
C	6.329738	5.010979	-0.483412
H	6.129244	5.60753	-1.380478
H	7.413266	4.87939	-0.386547
H	5.96535	5.5622	0.390714
H	0.527628	0.863361	1.089538

1

2 **[2-H_2]$^+$**

Ni	-0.089032	-0.109848	0.093404
C	0.143324	-4.324259	-0.334923
C	0.459253	-2.975467	-0.065662
C	-0.509229	-1.95114	-0.272015
C	-1.797822	-2.326901	-0.751182
C	-2.100156	-3.681361	-1.006126
C	-1.133056	-4.679383	-0.801477
H	0.893834	-5.096122	-0.175407
H	-3.089684	-3.954539	-1.367692
H	-1.371217	-5.720447	-1.002739
C	1.836465	-2.624068	0.464656
C	-2.853061	-1.266594	-1.007633
P	-2.346562	0.279367	-0.047339
P	2.107447	-0.775881	0.177024
H	1.887388	-2.796592	1.547143
H	2.628636	-3.228291	0.007841
H	-3.861325	-1.602738	-0.739894
H	-2.878231	-0.998206	-2.071636
C	-3.248481	0.212085	1.685662
C	-4.762985	0.513033	1.573873
H	-5.268277	-0.148847	0.859448
H	-5.22784	0.349081	2.555594
H	-4.962693	1.551562	1.288209
C	-3.046569	-1.217077	2.255268
H	-1.986369	-1.481521	2.333747
H	-3.48254	-1.253185	3.262694
H	-3.543778	-1.984093	1.651496
C	-2.563663	1.227127	2.637509
H	-2.651355	2.261597	2.290344
H	-3.041327	1.168099	3.624699
H	-1.49959	0.993435	2.77073
C	-2.887391	1.787157	-1.16674
C	-4.322292	1.60445	-1.725673
H	-5.08358	1.619689	-0.940898
H	-4.539208	2.43401	-2.412739
H	-4.432779	0.674808	-2.295429
C	-2.791187	3.119479	-0.383411
H	-2.988363	3.949097	-1.075786
H	-3.531883	3.183766	0.42102
H	-1.793247	3.280633	0.044281
C	-1.877189	1.82125	-2.347253
H	-0.854064	2.015704	-2.003079
H	-1.874956	0.889075	-2.926076
H	-2.159189	2.632264	-3.03195
C	3.028501	-0.587075	-1.536837
C	2.279793	-1.477785	-2.56326
H	2.347029	-2.544489	-2.322089
H	1.219235	-1.213886	-2.639628
H	2.73936	-1.33097	-3.550052
C	2.925177	0.892567	-1.987259

H	3.407516	1.584881	-1.291091
H	3.416561	1.00082	-2.963704
H	1.879443	1.202842	-2.103931
C	4.510853	-1.02798	-1.460944
H	4.936761	-1.00154	-2.473375
H	5.114374	-0.36085	-0.836156
H	4.62283	-2.053483	-1.087442
C	3.151253	-0.170133	1.7158
C	2.155162	-0.127105	2.907255
H	1.35675	0.60715	2.74397
H	1.691457	-1.102454	3.102732
H	2.697922	0.167475	3.815318
C	4.304557	-1.151698	2.048919
H	5.051118	-1.205431	1.251813
H	4.813854	-0.796339	2.955331
H	3.945231	-2.166163	2.255787
C	3.718797	1.249585	1.473867
H	4.166169	1.611928	2.409619
H	4.508412	1.251535	0.713937
H	2.948533	1.969381	1.173615
N	1.592845	3.86464	-0.031423
C	1.834338	5.005953	-0.201308
C	2.142985	6.424995	-0.411992
H	1.678491	6.783173	-1.337254
H	3.226226	6.570945	-0.486484
H	1.767035	7.025009	0.423892
H	0.633165	1.529684	0.31646
H	-0.110412	1.585588	0.539511

1

2 **[2- MeCN]$^+$ + H_2**

Ni	0.002267	-0.105823	0.03514
C	-1.153988	4.008187	0.111029
C	-1.162682	2.599871	0.202001
C	0.006914	1.834104	-0.085857
C	1.180433	2.553834	-0.464214
C	1.179388	3.962884	-0.541644
C	0.014706	4.693461	-0.257084
H	-2.060578	4.568143	0.333333
H	2.088797	4.487522	-0.829006
H	0.017794	5.778382	-0.321097
C	-2.439924	1.904953	0.632851
C	2.452574	1.804527	-0.811783
P	2.3079	0.073058	-0.078801
P	-2.303518	0.094422	0.118854
H	-2.538648	1.929674	1.725544
H	-3.33742	2.381702	0.221911
H	3.35499	2.321947	-0.465819
H	2.54536	1.695386	-1.900106
C	3.155416	0.1426	1.684517
C	4.693921	0.291129	1.599339

H	4.996048	1.16685	1.011603
H	5.091667	0.427194	2.614457
H	5.176245	-0.595846	1.175135
C	2.563113	1.367488	2.431283
H	1.470872	1.317778	2.499552
H	2.969449	1.381982	3.451873
H	2.827979	2.317709	1.955309
C	2.780745	-1.140417	2.471003
H	3.169338	-2.05192	2.004978
H	3.209359	-1.076921	3.480343
H	1.693065	-1.23718	2.575716
C	3.272478	-1.067041	-1.346874
C	4.59069	-0.407701	-1.833572
H	5.310474	-0.256981	-1.024405
H	5.059653	-1.069946	-2.57477
H	4.418966	0.555804	-2.325539
C	3.593678	-2.451592	-0.732433
H	4.010402	-3.099098	-1.515968
H	4.339457	-2.385113	0.066893
H	2.700895	-2.944078	-0.330145
C	2.321078	-1.24846	-2.56093
H	1.394822	-1.762573	-2.28007
H	2.050196	-0.290615	-3.022596
H	2.827401	-1.850654	-3.327575
C	-3.144796	-0.047564	-1.643696
C	-2.535613	1.069509	-2.532294
H	-2.776921	2.073561	-2.166989
H	-1.445125	0.990076	-2.6016
H	-2.950736	0.974469	-3.544941
C	-2.782355	-1.423832	-2.258971
H	-3.184865	-2.262859	-1.681354
H	-3.206364	-1.485199	-3.270511
H	-1.695911	-1.54758	-2.344498
C	-4.681734	0.126906	-1.585442
H	-5.07231	0.154228	-2.611997
H	-5.177249	-0.702815	-1.069917
H	-4.976602	1.065683	-1.100357
C	-3.280751	-0.867615	1.52054
C	-2.340384	-0.875859	2.75665
H	-1.403163	-1.405875	2.551683
H	-2.090201	0.137922	3.093528
H	-2.845446	-1.38321	3.589732
C	-4.606045	-0.153668	1.896464
H	-5.325485	-0.142209	1.07305
H	-5.069985	-0.695176	2.732835
H	-4.446587	0.877681	2.228656
C	-3.589924	-2.325642	1.100964
H	-4.01991	-2.857804	1.960586
H	-4.321653	-2.376055	0.287522
H	-2.688964	-2.867343	0.790556

N	-0.001445	-2.040989	0.158382
C	-0.002787	-3.211216	0.2299
C	-0.003419	-4.672269	0.318699
H	0.87278	-5.086089	-0.192813
H	-0.904747	-5.083631	-0.148852
H	0.022784	-4.988643	1.367654
H	-0.712453	-4.55346	-3.298375
H	0.029056	-4.606522	-3.339203

1