SUPPORTING INFORMATION

CO₂ Reduction or HCO₂⁻ Oxidation? Solvent-Dependent Thermochemistry of a Nickel Hydride Complex

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EXPERIMENTAL SECTION

Synthetic Methods and Materials. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Manipulations involving protic solvents were performed in a separate glovebox than those with non-protic solvents. Solvents were degassed by sparging with argon gas and dried by passage through columns of activated alumina or molecular sieves. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. Reagents were purchased from commercial vendors and used without further purification unless otherwise noted. [Ni(MeCN)₆][BF₄]₂, methyl vinyl ether, and 1,2-bis[bis(methoxyethyl)phosphino]ethane (TMEPE) were synthesized according to literature procedures.¹⁻³

Physical Methods. ¹H, ¹³C{¹H}, and ³¹P{¹H} nuclear magnetic resonance (NMR) spectra were collected at room temperature, unless otherwise noted, on a Bruker AVANCE 400 MHz, 600 MHz or 500 MHz spectrometer. Chemical shifts are reported in δ notation in parts per million (ppm). ¹H and ¹³C spectra were referenced to TMS at 0 ppm via the residual proteo or natural abundance ¹³C solvent resonances. ³¹P spectra were referenced to H₃PO₄ at 0 ppm within Xwin-NMR or Bruker's Topspin software, which derives the chemical shifts from the known frequency ratios of the ³¹P standard to the lock signal of the deuterated solvent. ³¹P spectra used in determining equilibrium concentration were obtained either with only one pulse or with long delay times (10s) for 3 scans to ensure quantitative integration. Manual shimming, Fourier transformation and automatic spectrum phasing were performed using Xwin-NMR software when using the 400MHz or 500MHz spectrometers. Automatic shimming, Fourier transformation, and automatic spectrum phasing were generated using MestReNova 6.0.2 software. Peak integrations were calculated within MestReNova.

X-ray Crystallography. The X-ray diffraction study was carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data were collected at 88 K using Mo K α radiation ($\lambda = 0.71073$ Å). A full sphere of data was collected for the crystal structure. The APEX2⁴ program suite was used to determine unit-cell parameters and to collect data. The raw frame data were processed and absorption corrected using the SAINT⁵ and SADABS⁶ programs, respectively, to yield the reflection data files. Structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXTL.⁷All non-hydrogen atoms were refined anisotropically. One methoxyethyl group was found to be disordered and was refined as a two-component disorder using partial site-occupancy factors. Hydrogen atoms were placed at geometrically calculated positions and refined using a riding model, and their isotropic displacement parameters were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded.

Thermodynamic Measurements. Generation of HNi(II) from H₂ in the presence of base (for water, DMSO, and acetonitrile): Under N₂ atmosphere, $[Ni(TMEPE)_2][BF_4]_2$ was dissolved in the deuterated solvent of interest in a J. Young NMR tube containing a capillary filled with 0.5M H₃PO₄ in D₂O. One equivalent of base (Et₃N in CD₃CN or DBU in DMSO) was added to the sample to generate the corresponding [HNi(TMEPE)₂][BF₄] in equilibrium with $[Ni(TMEPE)_2][BF_4]_2$, in water the buffer participated as the base. The sample was freeze-pump-thawed to remove N₂ from both the headspace and dissolved in solution. The J. Young tube was

charged with H_2 or CO_2 for 2 minutes then allowed to equilibrate for 2 minutes. This charging process was repeated five times.

The resulting equilibrium was monitored by ${}^{1}H$, ${}^{31}P{}^{1}H$ or ${}^{13}C{}^{1}H$ NMR spectroscopy. The relative integration of complex peaks to the capillary standard was used to monitor the equilibrium of species in solution. Equilibrium was achieved when relative integrations between peaks remained constant for 3 days.

Oxidation of lithium formate. A stock solution of lithium formate was prepared in either H_2O or DMSO-d₆. In a J.Young NMR tube, a solution of **2** was prepared in solvent of interest (10 mM in H_2O , 1.5 mM in CD₃CN or DMSO-d₆). One equivalent of lithium formate solution from stock solution was added stepwise, in water and acetonitrle. Due to insolubility of lithium formate in acetonitrile, the DMSO-d₆ lithium formate stock solution was used in experiment additions for reactions in acetonitrile. The reaction of **2** and lithium formate in each solvent was monitored by ¹H, ³¹P{¹H} NMR spectroscopy and relative integrations were compared to an capillary standard containing 0.5M H₃PO₄ in D₂O.

Synthesis.

Synthesis of TMEPE. The ligand TMEPE was synthesized according to a previously published method.¹ However, we followed the following purification procedure. The crude material was dissolved in acetonitrile and filtered through Celite. The filtrate was layered with pentane and chilled at -30 °C for 12 hours, during which a white solid impurity precipitated from solution and was removed by filtration. Removal of solvent under reduced pressure gave TMEPE as a viscous yellow oil (63% yield). ³¹P{¹H} NMR (CDCl₃, H₃PO₄) δ -33.1 (s). ¹H NMR (CDCl₃): δ 1.52 (m, 4H, PCH₂CH₂P); 1.67-1.72 (m, 8H, CH₃OCH₂CH₂P); 3.27 (s, 12H, CH₃OCH₂CH₂); 3.44-3.50 (m, 4H, CH₃OCH₂CH₂) ppm.

Synthesis of [Ni(TMEPE)₂][BF₄]₂ (2). A yellow solution of TMEPE (0.110g, 0.338 mmol) in 3mL of CH₃CN was added dropwise slowly to a stirring blue solution of [Ni(MeCN)₆][BF₄]₂ (0.084g, 0.169 mmol) in 3mL CH₃CN resulting in an immediate color change from blue to dark orange. The solution was stirred at room temperature for 12 hrs. The solution was then filtered through Celite and concentrated under vacuum. The concentrated sample in CH₃CN was layered with Et₂O in the freezer resulting in the precipitation of a white impurity. The solution was removed from the white impurity, concentrated in acetonitrile and layered with Et₂O in the freezer resulting in a dark orange residue. The solution was removed from residue and was triturated with pentane. The sample was dried under vacuum to yield an orange tacky residue. Yield: 0.149g (0.168 mmol, 99 % yield). Crystals suitable for X-ray diffraction analysis were grow by slow evaporation of Et₂O into a solution of THF-toluene at room temperature. ESI⁺ (DCM): 797.21 m/z {[Ni(TMEPE)₂][BF₄]⁺}. ³¹P{¹H} NMR (CD₃CN, H₃PO₄) δ 55.03 (s). ¹H NMR (CD₃CN) δ 2.09 (m, 8H, PCH₂CH₂P), δ 2.33 (m, 16H, CH₃OCH₂CH₂P), δ 3.31 (s, 24H, CH₃OCH₂CH₂P), δ 3.67 (m, 16H, CH₃OCH₂CH₂P).¹³C {¹H} NMR (CD₃CN) δ 58.5 (8C, CH₃OCH₂CH₂P), δ 67.2 (8C, CH₃OCH₂CH₂P), δ 25.9 (8C, CH₃OCH₂CH₂P), δ 22.6 (4C, PCH₂CH₂P).

Synthesis of Ni(TMEPE)₂ (3). A solution of Ni(COD)₂ (0.27 mmol,75 mg) in 3ml of THF was cooled to -35 °C for 5 minutes. Next a cooled solution (-35 °C) of TMEPE ligand (0.54 mmol, 178 mg) in 2 mL of THF was added dropwise to the cold and stirring Ni(COD)₂ solution. After

the addition the solution color changed from yellow to dark orange-brown. The solution was allowed to stir at room temperature overnight to yield complex **3**. Yield: 182.4mg (0.259 mmol, 95%yield) ³¹P{¹H}NMR (CD₃CN, H₃PO₄) δ 29.1 (s). ¹H NMR (CD₃CN) δ 1.49 (m, 8H, PC*H*₂C*H*₂P), δ 1.79 (m, 16H, CH₃OCH₂C*H*₂P), δ 3.25 (s, 24H, C*H*₃OCH₂CH₂P), δ 3.5 (m, 16H, CH₃OCH₂CH₂P). ¹³C {¹H} NMR (CD₃CN) δ 58.3 (8C, CH₃OCH₂CH₂P), δ 71.01 (8C, CH₃OCH₂CH₂P), δ 33.9 (8C, CH₃OCH₂CH₂P), δ 23.1 (4C, PCH₂CH₂P).

Generation of [HNi(TMEPE)₂][BF₄] (1). [HNi(TMEPE)₂][BF₄] was generated *in situ* using two methods for either aprotic or protic solvents. In aprotic solvents, **1** was produced via addition of 1 equivalent of [PhNH₃][BF₄] to 1 equivalent Ni(TMEPE)₂ (**3**) in CD₃CN. **Isloation of 1 for transfer experiments:** Following in situ generation of **1** in CD₃CN, the solvent was removed under vacuum, resulting in a light brown residue. Next, the residue was dissolved in the appropriate solvent (DMSO or H₂O) for further experiments. The formation of the hydride was monitored by ¹H and ³¹P NMR spectroscopy for up to 3 days.

³¹P{¹H}NMR (CD₃CN, H₃PO₄) δ 36.6 (s). ¹H NMR (CD₃CN) δ 2.35 (m, 8H, PCH₂CH₂P), δ 2.08 (m, 16H, CH₃OCH₂CH₂P), δ 3.27 (s, 24H, CH₃OCH₂CH₂P), δ 3.56 (br m, 16H, CH₃OCH₂CH₂P), δ -14.5 (m, 1H, HNi) ¹³C {¹H} NMR (CD₃CN) δ 58.6 (8C, CH₃OCH₂CH₂P), δ 69.2 (8C, CH₃OCH₂CH₂P), δ 30.0 (8C, CH₃OCH₂CH₂P), δ 26.8 (4C, PCH₂CH₂P).

³¹P{¹H}NMR (DMSO-d₆,H₃PO₄) δ 36.8 (s). ¹H NMR (DMSO-d₆) δ 1.90 (m, 8H, PCH₂CH₂P), δ 2.02 (m, 16H, CH₃OCH₂CH₂P), δ 3.24 (s, 24H, CH₃OCH₂CH₂P), δ 3.53 (m, 16H, CH₃OCH₂CH₂P) δ -14.5 (m, 1H, HNi).

³¹P{¹H}NMR (D₂O, H₃PO₄) δ 34.2 (s). ¹H NMR (D₂O) δ 2.03 (m, 8H, PCH₂CH₂P), δ 2.14 (m, 16H, CH₃OCH₂CH₂P), δ 3.51 (s, 24H, CH₃OCH₂CH₂P), δ 3.70 (m, 16H, CH₃OCH₂CH₂P).



Figure S1. ¹H NMR spectrum of TMEPE ligand (TMEPE = 1,2bis[di(methoxyethyl)phosphino]ethane) in CDCl₃ where the black X indicate unknown impurity peaks.



Figure S2. ${}^{31}P{}^{1}H$ NMR spectrum of TMEPE ligand (TMEPE = 1,2-bis[di(methoxyethyl)phosphino]ethane) in CDCl₃ where the black X denotes impurity peaks.



Figure S3. ¹H NMR spectra of [Ni(TMEPE)₂][BF₄]₂ in CDCl₃



Figure S4. ${}^{31}P{}^{1}H$ NMR spectra of [Ni(TMEPE)₂][BF₄]₂ in CDCl₃.

rable S1. Crystal data and structure refiner	field for complex 2.	
Identification code	jyy104	
Empirical formula	C28 H64 B2 F8 Ni O8 P	4
Formula weight	885.00	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.1558(19) Å	$\alpha = 90^{\circ}$.
	b = 12.2650(12) Å	$\beta = 110.6513(11)^{\circ}.$
	c = 19.1620(19) Å	$\gamma = 90^{\circ}$.
Volume	4212.7(7) Å ³	
Z	4	
Density (calculated)	1.395 Mg/m ³	
Absorption coefficient	0.689 mm ⁻¹	
F(000)	1864	
Crystal color	yellow	
Crystal size	0.444 x 0.423 x 0.345 m	m ³
Theta range for data collection	2.012 to 29.013°	
Index ranges	-25 <= h <= 25, -16 <=	$k \le 16, -25 \le 1 \le 26$
Reflections collected	25493	
Independent reflections	5299 [R(int) = 0.0219]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equ	uvalents
Max. and min. transmission	0.7458 and 0.6939	
Refinement method	Full-matrix least-squares	s on F ²
Data / restraints / parameters	5299 / 0 / 274	
Goodness-of-fit on F ²	1.055	
Final R indices [I>2sigma(I) = 4615 data]	R1 = 0.0466, wR2 = 0.13	366
R indices (all data, ? Å)	R1 = 0.0525, wR2 = 0.14	426
Extinction coefficient	n/a	
Largest diff. peak and hole	1.189 and -0.461 e.Å ⁻³	

Table S1. Crystal data and structure refinement for complex 2.

Ni(1)	2500	7500	5000	19(1)	
C(1)	2701(1)	9328(2)	3835(1)	31(1)	
C(2)	2306(1)	8424(2)	3296(1)	30(1)	
P(1)	3237(1)	8692(1)	4726(1)	24(1)	
C(11)	3994(1)	7922(2)	4591(1)	31(1)	
C(12)	4447(1)	8504(3)	4188(1)	38(1)	
O(11)	4028(1)	8491(2)	3412(1)	44(1)	
C(13)	4444(2)	8997(4)	3015(2)	56(1)	
C(14)	3689(1)	9847(2)	5314(1)	32(1)	
C(15)	3117(2)	10641(2)	5416(2)	40(1)	
O(12)	3463(1)	11249(2)	6082(1)	46(1)	
C(16)	2926(2)	11941(3)	6234(2)	59(1)	
P(2)	1892(1)	7454(1)	3769(1)	23(1)	
C(21)	1778(2)	6220(2)	3205(1)	38(1)	
C(22)	2469(2)	5835(3)	3075(2)	60(1)	
O(21)	3050(1)	5698(2)	3767(2)	62(1)	
C(23)	3738(3)	5367(4)	3671(4)	116(2)	
C(24A)	927(10)	7883(11)	3543(12)	34(4)	
C(25A)	839(3)	8974(4)	3986(5)	32(1)	
O(22A)	1025(2)	9906(3)	3654(2)	45(1)	
C(26A)	919(4)	10873(5)	4057(5)	69(2)	
C(24B)	906(11)	7903(17)	3482(15)	40(6)	
C(25B)	767(3)	8957(5)	3580(4)	36(1)	
O(22B)	1189(3)	9212(3)	4337(3)	35(1)	
C(26B)	1031(4)	10275(7)	4549(5)	59(2)	
B(1)	951(2)	7152(3)	1136(2)	36(1)	
F(1)	873(1)	7756(1)	1714(1)	45(1)	
F(2)	421(1)	6323(2)	969(1)	65(1)	
F(3)	1662(1)	6694(2)	1382(1)	65(1)	
F(4)	829(2)	7806(2)	522(1)	78(1)	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for complex **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S3. Bond lengths [Å] and angles [°] for complex **2**.

Ni(1)-P(1)#1	2.2199(5)	
Ni(1)-P(1)	2.2199(5)	
Ni(1)-P(2)	2.2330(6)	
Ni(1)-P(2)#1	2.2331(6)	
C(1)-C(2)	1.522(3)	
C(1)-P(1)	1.828(2)	
C(2)-P(2)	1.837(2)	
P(1)-C(11)	1.825(2)	
P(1)-C(14)	1.827(2)	
C(11)-C(12)	1.526(3)	
C(12)-O(11)	1.418(3)	
O(11)-C(13)	1.423(3)	
C(14)-C(15)	1.529(4)	
C(15)-O(12)	1.424(3)	
O(12)-C(16)	1.441(4)	
P(2)-C(24A)	1.821(18)	
P(2)-C(21)	1.828(3)	
P(2)-C(24B)	1.85(2)	
C(21)-C(22)	1.506(5)	
C(22)-O(21)	1.410(5)	
O(21)-C(23)	1.452(4)	
C(24A)-C(25A)	1.63(2)	
C(25A)-O(22A)	1.414(6)	
O(22A)-C(26A)	1.467(8)	
C(24B)-C(25B)	1.35(2)	
C(25B)-O(22B)	1.425(8)	
O(22B)-C(26B)	1.429(8)	
B(1)-F(4)	1.375(4)	
B(1)-F(1)	1.384(3)	
B(1)-F(3)	1.391(4)	
B(1)-F(2)	1.393(4)	
P(1)#1-Ni(1)-P(1)	180.0	
P(1)#1-Ni(1)-P(2)	95.429(19)	
P(1)-Ni(1)-P(2)	84.572(19)	

P(1)#1-Ni(1)-P(2)#1	84.572(19)
P(1)-Ni(1)-P(2)#1	95.43(2)
P(2)-Ni(1)-P(2)#1	180.00(3)
C(2)-C(1)-P(1)	107.64(16)
C(1)-C(2)-P(2)	109.62(15)
C(11)-P(1)-C(14)	105.13(11)
C(11)-P(1)-C(1)	107.53(11)
C(14)-P(1)-C(1)	103.43(11)
C(11)-P(1)-Ni(1)	107.26(8)
C(14)-P(1)-Ni(1)	124.58(8)
C(1)-P(1)-Ni(1)	107.93(7)
C(12)-C(11)-P(1)	116.83(19)
O(11)-C(12)-C(11)	108.23(19)
C(12)-O(11)-C(13)	109.8(2)
C(15)-C(14)-P(1)	111.57(16)
O(12)-C(15)-C(14)	108.7(2)
C(15)-O(12)-C(16)	110.5(2)
C(24A)-P(2)-C(21)	101.5(6)
C(24A)-P(2)-C(2)	105.9(4)
C(21)-P(2)-C(2)	103.10(12)
C(21)-P(2)-C(24B)	100.0(8)
C(2)-P(2)-C(24B)	103.5(6)
C(24A)-P(2)-Ni(1)	110.6(7)
C(21)-P(2)-Ni(1)	123.69(9)
C(2)-P(2)-Ni(1)	110.41(7)
C(24B)-P(2)-Ni(1)	113.8(9)
C(22)-C(21)-P(2)	115.4(2)
O(21)-C(22)-C(21)	109.2(2)
C(22)-O(21)-C(23)	111.4(4)
C(25A)-C(24A)-P(2)	113.4(11)
O(22A)-C(25A)-C(24A)	109.9(7)
C(25A)-O(22A)-C(26A)	108.3(5)
C(25B)-C(24B)-P(2)	118.4(14)
C(24B)-C(25B)-O(22B)	106.4(12)
C(25B)-O(22B)-C(26B)	112.9(5)
F(4)-B(1)-F(1)	109.8(3)

F(4)-B(1)-F(3)	112.1(3)
F(1)-B(1)-F(3)	108.4(2)
F(4)-B(1)-F(2)	109.8(2)
F(1)-B(1)-F(2)	107.4(2)
F(3)-B(1)-F(2)	109.3(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+3/2,-z+1

Table S4. Anisotropic displacement parameters (Å² x 10³) for complex **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2h k a^{*b*}U^{12}]$

	U11	U ²²	U33	U ²³	U13	U12	
Ni(1)	16(1)	25(1)	16(1)	0(1)	5(1)	-5(1)	
C(1)	27(1)	37(1)	26(1)	8(1)	6(1)	-7(1)	
C(2)	25(1)	42(1)	20(1)	6(1)	6(1)	-6(1)	
P(1)	19(1)	30(1)	21(1)	2(1)	6(1)	-7(1)	
C(11)	22(1)	46(1)	27(1)	1(1)	10(1)	-3(1)	
C(12)	22(1)	66(2)	25(1)	3(1)	9(1)	-7(1)	
O(11)	28(1)	83(2)	23(1)	1(1)	11(1)	-7(1)	
C(13)	36(1)	108(3)	29(1)	12(2)	17(1)	-2(2)	
C(14)	27(1)	32(1)	31(1)	1(1)	4(1)	-10(1)	
C(15)	41(1)	32(1)	36(1)	1(1)	-1(1)	3(1)	
O(12)	48(1)	38(1)	41(1)	-6(1)	3(1)	5(1)	
C(16)	67(2)	46(2)	61(2)	-1(2)	17(2)	16(2)	
P(2)	18(1)	30(1)	18(1)	2(1)	3(1)	-3(1)	
C(21)	50(2)	38(1)	21(1)	-6(1)	5(1)	-7(1)	
C(22)	89(3)	49(2)	59(2)	-16(2)	46(2)	-3(2)	
O(21)	48(1)	52(1)	93(2)	-24(1)	32(1)	1(1)	
C(23)	81(3)	76(3)	222(7)	-66(4)	91(4)	-7(2)	
C(24A)	24(7)	35(6)	38(6)	23(5)	6(4)	-4(4)	
C(25A)	24(2)	25(2)	45(4)	-5(2)	10(3)	-3(2)	
O(22A)	38(2)	26(2)	70(3)	5(2)	18(2)	1(1)	
C(26A)	58(4)	42(3)	112(7)	-7(4)	36(4)	-1(3)	
C(24B)	12(6)	68(11)	36(7)	5(7)	3(4)	8(6)	

C(25B)	27(3)	45(3)	29(3)	3(3)	2(2)	2(2)
O(22B)	30(2)	36(2)	36(2)	-4(2)	9(2)	-2(2)
C(26B)	40(3)	55(4)	76(5)	-16(4)	15(3)	7(3)
B(1)	34(1)	40(1)	30(1)	-5(1)	7(1)	-1(1)
F(1)	53(1)	47(1)	35(1)	-2(1)	14(1)	9(1)
F(2)	56(1)	57(1)	65(1)	-3(1)	2(1)	-20(1)
F(3)	49(1)	55(1)	102(2)	0(1)	38(1)	11(1)
F(4)	113(2)	80(1)	32(1)	10(1)	13(1)	-23(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å²x 10^3) for complex **2**.

	х	у	Z	U(eq)	
H(1A)	2332	9844	3901	37	
H(1B)	3038	9736	3638	37	
H(2A)	2668	8041	3119	36	
H(2B)	1911	8741	2858	36	
H(11A)	4342	7691	5087	38	
H(11B)	3780	7252	4308	38	
H(12A)	4548	9266	4366	45	
H(12B)	4930	8129	4288	45	
H(13A)	4529	9765	3162	84	
H(13B)	4164	8949	2478	84	
H(13C)	4924	8625	3132	84	
H(14A)	4015	9576	5808	38	
H(14B)	4006	10235	5083	38	
H(15A)	2937	11141	4983	48	
H(15B)	2684	10234	5450	48	
H(16A)	2730	12472	5830	89	
H(16B)	3167	12327	6706	89	
H(16C)	2516	11495	6270	89	
H(21A)	1602	5626	3452	46	
H(21B)	1384	6353	2715	46	

H(22A)	2367	5134	2800	72	
H(22B)	2617	6376	2770	72	
H(23A)	3709	4593	3538	174	
H(23B)	4158	5486	4138	174	
H(23C)	3811	5800	3272	174	
H(24A)	705	8021	3000	40	
H(24B)	643	7283	3663	40	
H(25A)	318	9035	3971	38	
H(25B)	1171	8924	4515	38	
H(26A)	398	10912	4025	104	
H(26B)	1044	11529	3833	104	
H(26C)	1245	10824	4581	104	
H(24C)	662	7730	2946	48	
H(24D)	660	7454	3757	48	
H(25C)	228	9069	3477	43	
H(25D)	920	9428	3240	43	
H(26D)	1234	10827	4304	88	
H(26E)	1260	10356	5092	88	
H(26F)	489	10370	4398	88	

Characterization of Ni(TMEPE)₂ (3).



Figure S6. ${}^{31}P{}^{1}H$ NMR spectrum of Ni(TMEPE)₂ (**3**) in CD₃CN.

Characterization of [HNi(TMEPE)₂][BF₄] (1).



Figure S7. ¹H NMR spectrum showing the protonation of one equivalent of the Ni(0) complex **3** by the addition of one equivalent of $[PhNH_3][BF_4]$ in CD₃CN to yield the nickel hydride complex **1** (o).



Figure S8. ${}^{31}P{}^{1}H$ NMR spectrum showing the protonation of Ni(0) complex **3** to nickel hydride complex **1** in CD₃CN by one equivalent of [PhNH₃][BF₄].



Figure S9. ¹H NMR spectrum showing the protonation of one equivalent of the Ni(0) complex **3** by the addition of one equivalent of $[PhNH_3][BF_4]$ in DMSO-d₆ to yield the nickel hydride complex **1**(0), where aniline peaks are denoted by A.



Figure S10. ${}^{31}P{}^{1}H$ NMR spectrum showing the protonation of complex **3** to **1** in DMSO-d₆ by one equivalent of [PhNH₃][BF₄].



Figure S11. ¹H NMR spectrum showing nickel hydride complex 1(0) in pH 10 carbonate buffered D₂O.



Figure S12. ${}^{31}P{}^{1}H$ NMR spectrum showing nickel hydride complex 1 (o) in pH 10 carbonate buffered D₂O.

Thermodynamic Determinations

Determination of Hydricity values from the heterolysis of H₂

[M-H] ⁺	∆G ⁰ H-(hydricity)	(5)
$H_2 \longrightarrow H^+ + H^-$	ΔG^0_{H2}	(4)
B ⁻ + H ⁺ = BH	-1.37 p <i>K</i> a	(3)
$[M-H]^+ + BH $ \longrightarrow $M^{2+} + B^- + H_2$	-1.37 log(K _{eq})	(2)
	$\Delta G^0 = - RTIn(K)$	

Measuring equilibria between complex 1 and 3 $M^{2+} + B^{-} + H_2 \longrightarrow [M-H]^{+} + BH$

initiai			0	v
Change	$-\Delta$	$-\Delta$	Δ	Δ
Equilibrium	x- Δ	X - Δ	Δ	Δ

$$Y = \frac{[H-NiL_2^+]}{[NiL_2^{2+}]} \qquad Z = \frac{[BH]}{[B^-]} \qquad K_{eq} = \frac{[H-NiL_2^+][BH]}{[NiL_2^{2+}][B^-]} = Y \bullet Z$$

Solvent	X (M)	n (eq)	Y	Δ	Z	K _{eq}	BH	pK _a	ΔG _{H2} (kcal/mol)	ΔG _{H-} (kcal/mol)
CH ₃ CN	0.024	1	1.15	1.3 X 10 ⁻³	1.15	1.32	Et ₃ N H ⁺	18	76	50
DMSO	0.015	1	0.09	1.2 X 10 ⁻³	0.09	8.5 X 10 ⁻³	DBU H ⁺	12	60	47
H ₂ O	0.024	1	0.5	7.9 X 10 ⁻³	0.5	0.5	0.25	8	34	22



Figure S13. ³¹P{¹H} NMR spectrum showing complete lithium formate oxidation by complex **2** in DMSO-d₆ to generate complex **1** after the addition of 1 eq of lithium formate, under N_2 .



Figure S14. ³¹P{¹H} NMR spectrum showing lithium formate oxidation by complex 2 (*) in CD₃CN to generate complex 1 (o) after the addition of 2 eq of lithium formate under N_2 .



Figure S15. ³¹P{¹H} NMR spectrum of no reaction between complex **2** (*) and one equivalent of lithium formate in D_2O under CO_2 .



Figure S16. ³¹P{¹H} NMR spectrum showing nickel hydride complex **3** (o) in pH 9 carbonate buffered D_2O with background protonation to complex **2** (*). Complex **1** generated from protonaton of Ni(0) complex **3** by [PhNH₃][BF₄] in CD₃CN.



Figure S17. ³¹P{¹H} NMR spectrum showing stability of nickel hydride complex 1 (o) in pH 10.4 carbonate buffered H₂O under N₂.



Figure S18. ³¹P{¹H} NMR spectrum showing nickel hydride complex **1** in pH 9 buffered H₂O under N₂ (top), nickel hydride complex **1** at pH 7 after addition of CO₂ (middle), nickel hydride complex **1** at pH 7 after addition of O₂. Where complex **1** is denoted by (o), complex **2** is denoted by (*), and unidentified decomposition complex is denoted by (X).

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