Electronic Supporting Information (ESI) for

Solvent Influence on the Thermodynamics for Hydride Transfer from Bis(diphosphine) Complexes of Nickel

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Syntheses: General Considerations.

Air-free Techniques. Syntheses were carried out under air-free conditions in a N_2 glove box. Those syntheses employing non-ligated phosphine molecules were carried out under dry conditions in a portable N_2 glove box, but further manipulations were carried out in a glove box where water is regularly used as a solvent.

Solvents. Acetonitrile, tetrahydrofuran, dichloromethane, and diethyl ether were passed through the neutral alumina columns of an Innovative Technology, Inc., Pure Solv solvent purification system, but no further drying techniques were employed. Millipore water used in the experiments was deoxygenated by sparging with N_2. CD_3CN and *d*$_8$-THF were purchased from Cambridge Isotope Laboratories and distilled from molecular sieves prior to use. D_2O was purchased from Sigma Aldrich and used as received.

Buffers and Bases. Carbonate and phosphate buffered solutions were prepared from the potassium salts using the Henderson-Hasselbach equation and the pH was measured with a digital pH meter. KOH and Et_3N were used as received.

Starting Materials. The phosphine ligand *dmpe* (1,2-bis(dimethylphosphino)ethane, CAS # 23936-60-9) was purchased from Sigma-Aldrich and used as received. The synthesis for the aryl phosphine ligand *dmpbz* (1,2-bis(dimethylphosphino)benzene, CAS # 7237-07-2) was reported previously.[1] The metal starting material $[Ni(CH_3CN)_6][BF_4]_2$ was synthesized by the literature procedure.[2]

Gases. CO_2 (Matheson Tri-Gas, research grade) was dried prior to use by passing the gas through a VICI Metronics drying column (Part # P600-1). H_2 (Oxarc) was used as received. H_2/CO_2 (50:50, Oxarc) was used as received. Reactions pressurized to less than 2 atm were carried out in Teflon screw-top NMR tubes. Catalysis attempts at high pressures were carried out in PEEK NMR tubes connected to a custom pressure pump set up.[3] Exercise caution when working with pressurized systems.

Instrumentation. NMR spectroscopy experiments were carried out on Varian 300 and 500 MHz instruments. Residual protic resonances from deuterated solvents were used to reference ^1H NMR spectra. $^{31}P\{^1H\}$ spectra were externally referenced to H_3PO_4 (85%). For the calibration curve of chemical shift vs. pH of phosphate buffer solutions, a sealed capillary of 85% H_3PO_4 was added to the sample and used as the reference signal.

[Ni(dmpe)$_2$][BF$_4$]$_2$. Under air-free conditions, dissolution of [Ni(CH$_3$CN)$_6$][BF$_4$]$_2$ (0.202 g, 0.422 mmol) in acetonitrile (~ 5 mL) afforded a blue solution. 1,2-bis(dimethylphosphino)ethane (dmpe) (0.142 mL, 0.128 g, 0.851 mmol, 2.02 eq.) was added to the stirring solution with a microliter syringe. The solution turned yellow-orange. The stirring was continued for 35 min. Following filtration, the solution was layered with diethyl ether. The product precipitated as yellow-orange microcrystalline material, which was isolated and washed with ether (~ 2 mL) and CH$_2$Cl$_2$ (~ 1 mL) (0.132 g, ~ 55 % yield). The product was a mixture of [Ni(dmpe)$_2$][BF$_4$]$_2$ and [Ni(dmpe)$_2$(CH$_3$CN)][BF$_4$]$_2$. Variable amounts of CH$_3$CN were present in the product, but upon dissolution in H$_2$O, the CH$_3$CN signal generally integrated to approximately 1/3 eq. by NMR spectroscopy.

^{1}H NMR Spectroscopy
(500 MHz, 298 K, D$_2$O): 2.20 ppm (CH$_2$, vt, 8H), 1.74 ppm (P(CH$_3$)$_2$, vt, 24H), 2.09 ppm (CH$_3$CN, s).
(500 MHz, 298 K, CD$_3$CN): 2.07 ppm (CH$_2$, vt, 8H), 1.62 ppm (P(CH$_3$)$_2$, vt, 24H)

^{31}P{^{1}H} NMR Spectroscopy
(202 MHz, 298 K, D$_2$O): 43.3 ppm (s)
(202 MHz, 298 K, CD$_3$CN): 45.3 ppm (s)

[Ni(dmpe)$_2$H][BF$_4$]. In a glove box, [Ni(dmpe)$_2$][BF$_4$]$_2$ (0.100 g, 0.188 mmol) was dissolved in acetonitrile (~3 mL) to give a yellow-orange solution. Cesium formate (CsHCO$_2$, 0.10 g, 0.56 mmol) was added to the solution. With stirring, the solution became deep orange red, and then paled to orange. The solution was filtered through a glass-filter in a pipette to remove the excess CsHCO$_2$ and the CsBF$_4$ formed by the reaction. *In situ* yield was shown to be nearly quantitative by ^{31}P{^{1}H} NMR spectroscopy. The solvent was then removed from the homogenous orange solution under reduced pressure. An orange-brown solid remained. This material could not be recrystallized from acetonitrile/ether. Ether seemed to promote decomposition of the product.

Note that the hydride ligand is exchangeable with protic deuterated solvents. The ^{1}H signal for the hydride ligand disappears in D$_2$O, acetone-*d*$_6$, and MeOD in 30 minutes to an hour.

^{1}H NMR Spectroscopy
(500 MHz, 298 K, CD$_3$CN): 1.78 ppm (CH$_2$, vt, 8H), 1.41 ppm (P(CH$_3$)$_2$, vt, 24H), -14.0 ppm (NiH, br).
(500 MHz, 298 K, D$_2$O): 1.83 ppm (CH$_2$, vt, 8H), 1.45 ppm (P(CH$_3$)$_2$, vt, 24H), -13.6 ppm (NiH, br).

^{31}P{^{1}H} NMR Spectroscopy
(202 MHz, 298 K, CD$_3$CN): 26.4 ppm (s)
(202 MHz, 298 K, D$_2$O): 24.9 ppm (s) (NiD); 25.0 ppm (s) (NiH)

*In D$_2$O samples of [Ni(dmpe)$_2$H][BF$_4$], deuteration of the metal hydride is apparent. Signals for both species are found before deuteration is complete. The ^{31}P{^{1}H} NMR signals have a 110 ppb isotope shift between the protic and deuterated species.

The dmpbz complexes of nickel were prepared by methods modified from the procedures reported by Warren & Bennett.[4] Because the complexes were originally only characterized by elemental analysis and UV-visible optical spectroscopy, the NMR spectra are reported here.

[Ni(dmpbz)$_2$][BF$_4$]$_2$. Under air-free conditions, dissolution of [Ni(CH$_3$CN)$_6$][BF$_4$]$_2$ (0.104 g, 0.217 mmol) in acetonitrile (~ 3 mL) afforded a blue solution. 1,2-bis(dimethylphosphino)benzene (dmpbz) (0.085 g, 0.428 mmol, 1.98 eq.) was added to the stirring solution with a microliter syringe (mass was monitored during addition of the liquid). The solution turned deep red. The stirring was continued for 30 min. Following filtration, the solution was layered with diethyl ether. The product precipitated as a yellow-green microcrystalline flaky solid, which was isolated and washed with ether (~ 1 mL) (0.070 g, ~ 50 % yield).

^{1}H NMR Spectroscopy
(500 MHz, 298 K, D$_2$O): 2.05 ppm (P(CH$_3$)$_2$ vt, 24 H), 7.90 ppm (Ph, 4H), 8.08 ppm (Ph, 4H)
(500 MHz, 298 K, CD$_3$CN): 1.97 ppm (P(CH$_3$)$_2$ vt, 24 H), 7.88 ppm (Ph, 4H), 8.05 ppm (Ph, 4H)

^{31}P{^{1}H} NMR Spectroscopy
(202 MHz, 298 K, D$_2$O): 39.2 ppm (s)
(202 MHz, 298 K, CD$_3$CN): 41.8 ppm (s)

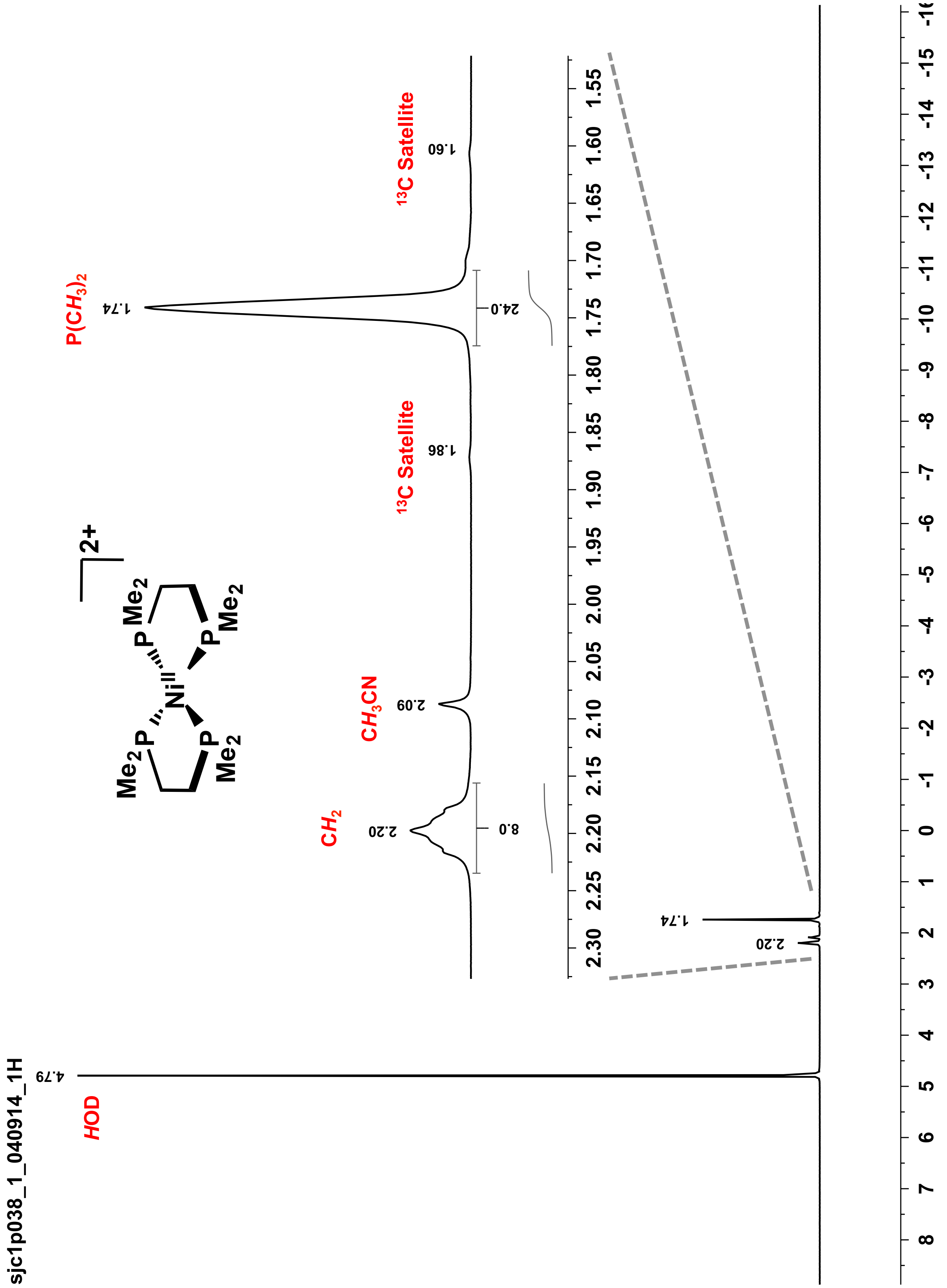
[HNi(dmpbz)$_2$][BF$_4$]. In a glove box, [Ni(dmpbz)$_2$][BF$_4$]$_2$ (0.008 g, 0.013 mmol) was dissolved in acetonitrile (~3 mL) to give a dark green solution. Cesium formate (CsHCO$_2$, 0.040 g, 0.224 mmol (vast excess)) was added to the solution. With stirring, the solution became yellow. The solution was filtered through a glass-filter in a pipette to remove the excess CsHCO$_2$ and the CsBF$_4$ formed by the reaction. The solvent was then removed from the homogenous solution under reduced pressure. A yellow-orange solid remained (0.006 g, 0.011 mmol, 85 % yield). This complex, while fully soluble in acetonitrile, was completely insoluble in water. Therefore, the product could be washed with water to remove any excess CsHCO$_2$ remaining. X-ray quality single crystals were grown by slow evaporation of acetonitrile.

^{1}H NMR Spectroscopy
(500 MHz, 298 K, CD$_3$CN): 1.69 ppm (P(CH$_3$)$_2$, vt, 24 H), -13.15 ppm (NiH, p, 1H), 7.66 ppm (Ph, 4H), 7.90 ppm (Ph, 4H)

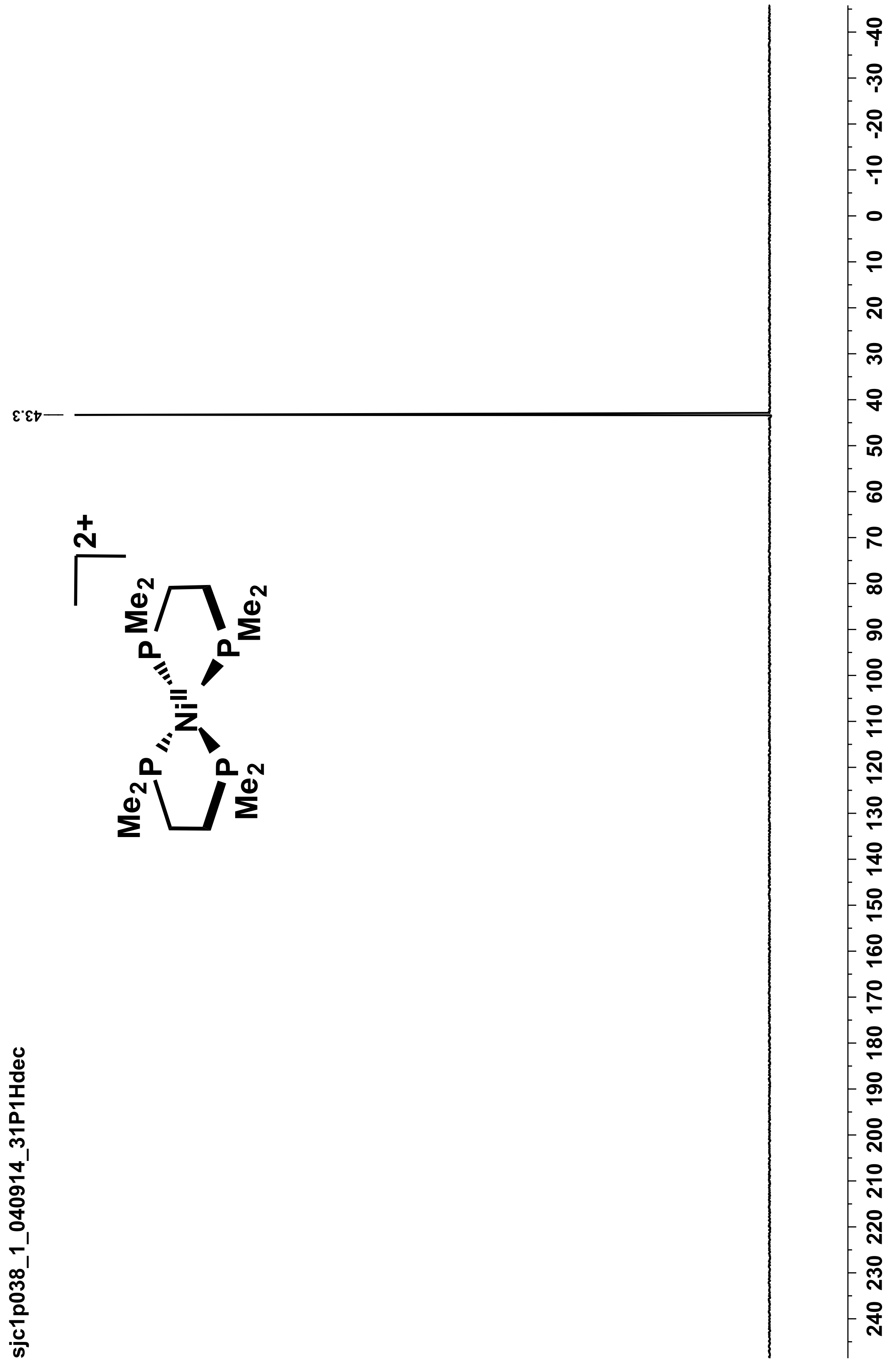
^{31}P{^{1}H} NMR Spectroscopy
(202 MHz, 298 K, CD$_3$CN): 26.7 ppm (s)

The XRD structure of [HNi(dmpbz)$_2$][BF$_4$] suggests that the phosphine ligands are nearly tetrahedral around the metal center, with no obvious coordination site for the hydride observed. Dissolution of the crystalline material in acetonitrile, however, produced NMR spectra containing the hydride resonance.

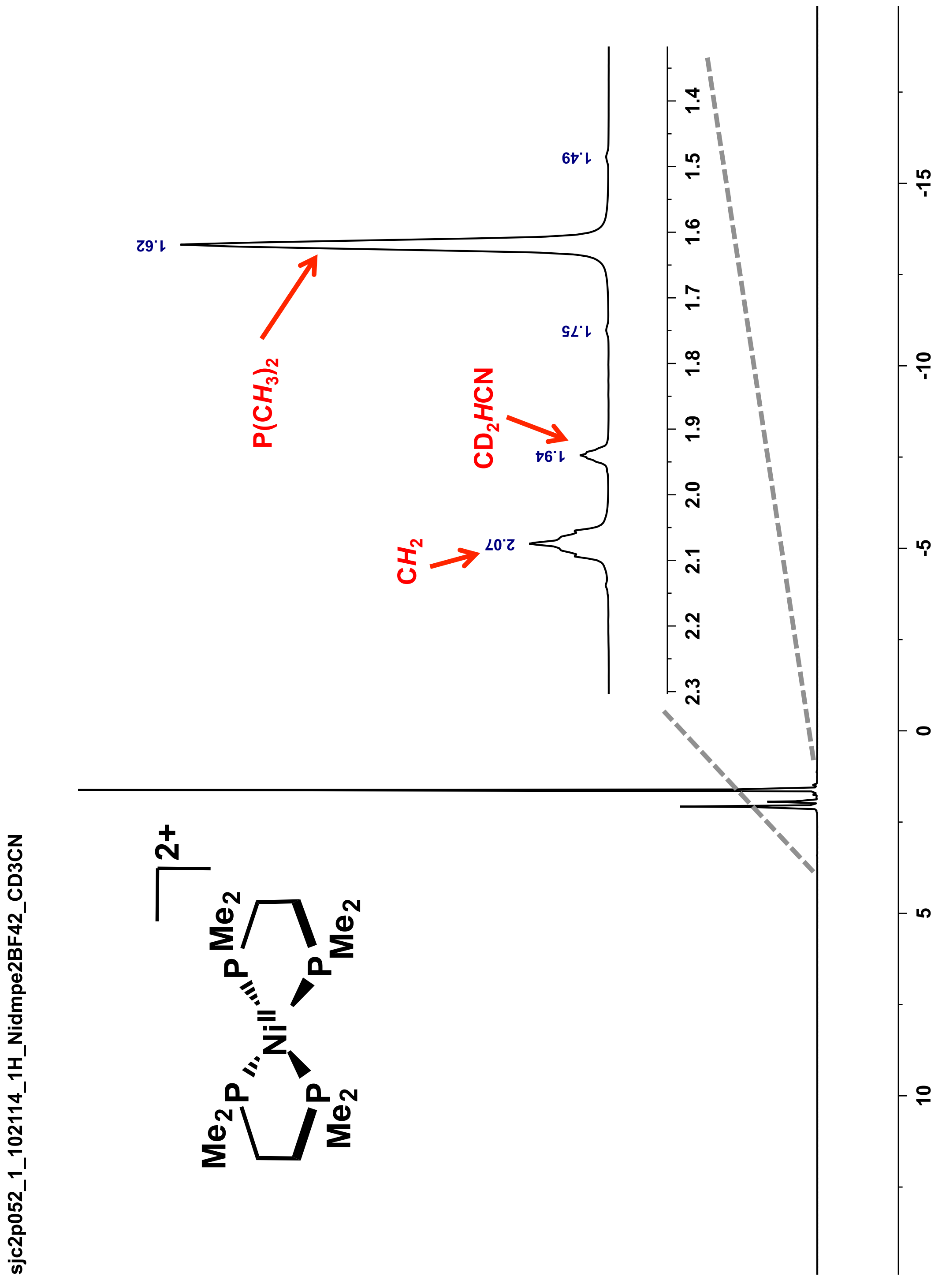
$[Ni(dmpe)_2][BF_4]_2$ in D_2O – ^1H – 500 MHz – 298 K



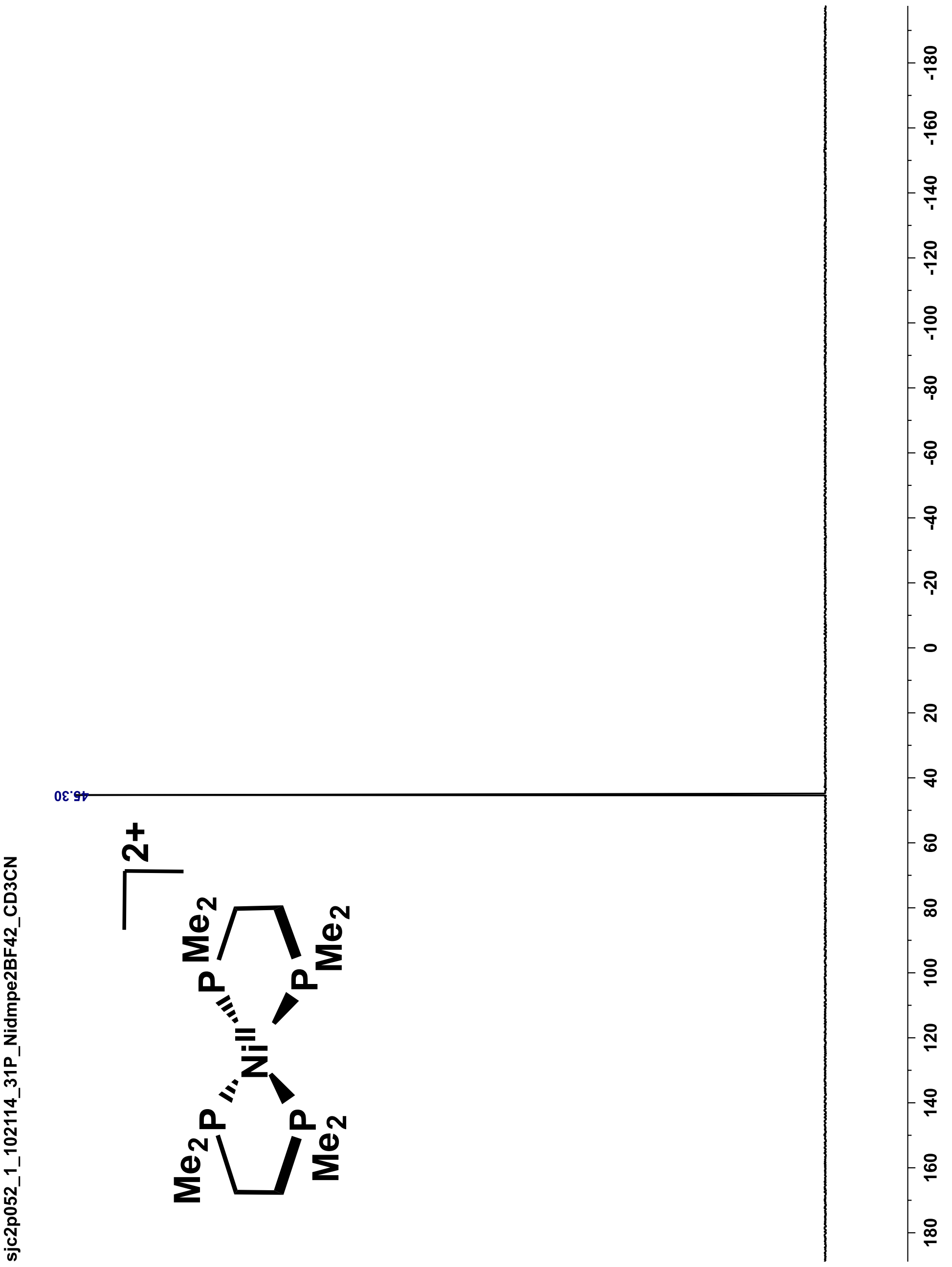
[Ni(dmpe)$_2$][BF$_4$]$_2$ in D$_2$O – ^{31}P{^{1}H} – 202 MHz – 298 K



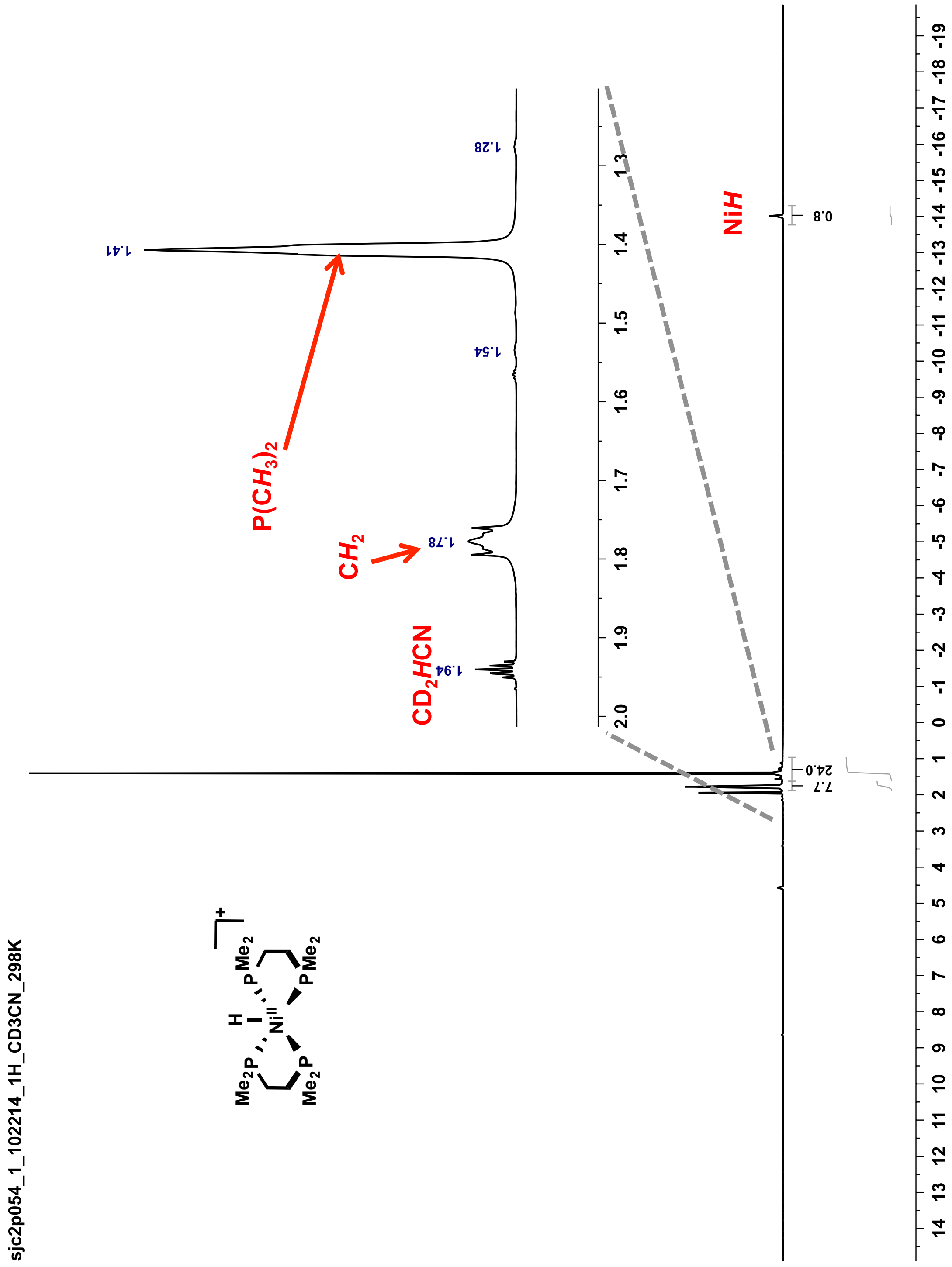
$[Ni(dmpe)_2][BF_4]_2$ in CD_3CN – ^1H – 500 MHz – 298 K



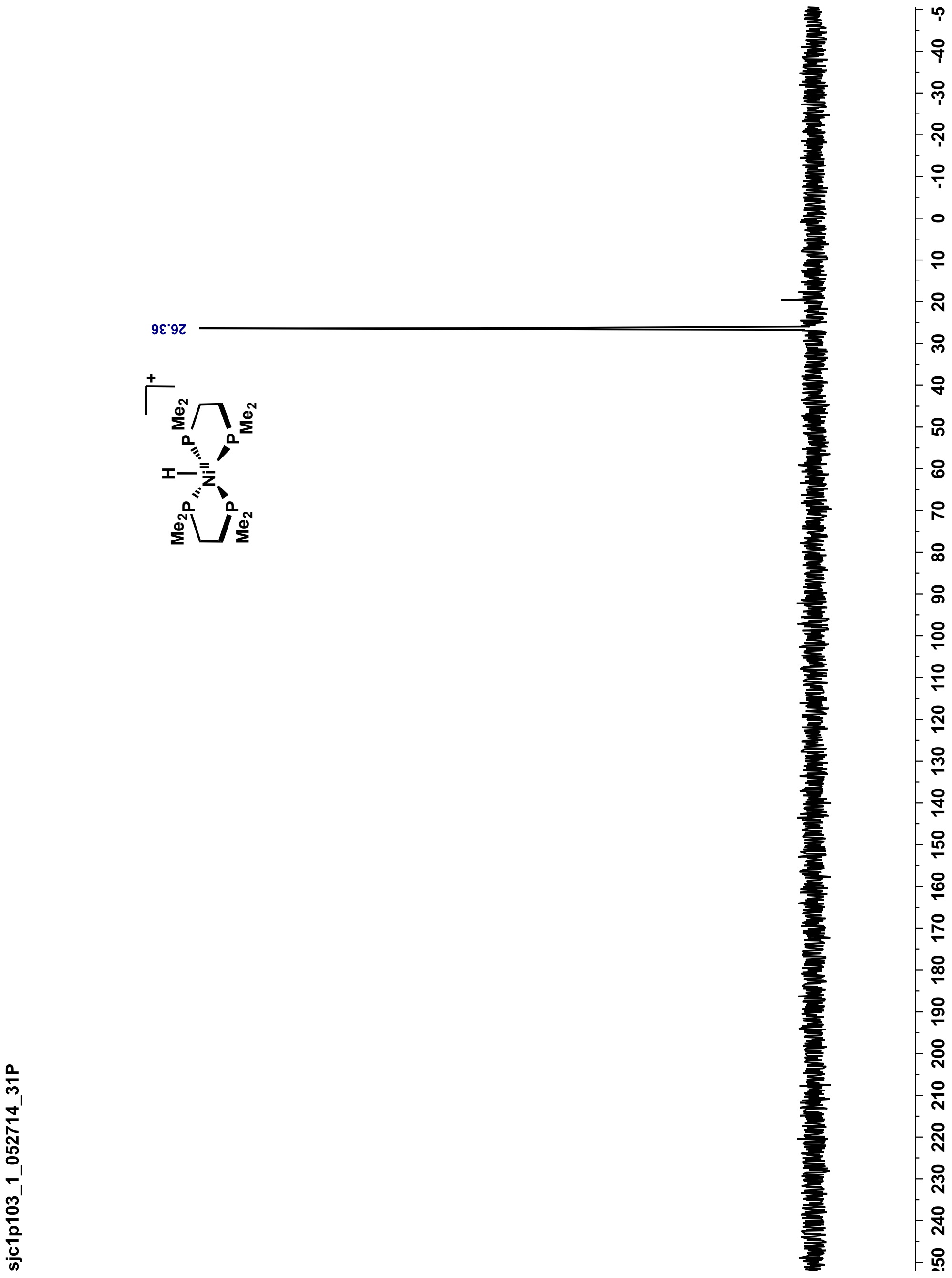
[Ni(dmpe)$_2$][BF$_4$]$_2$ in CD^{3}CN – ^{31}P{^{1}H} – 202 MHz – 298 K



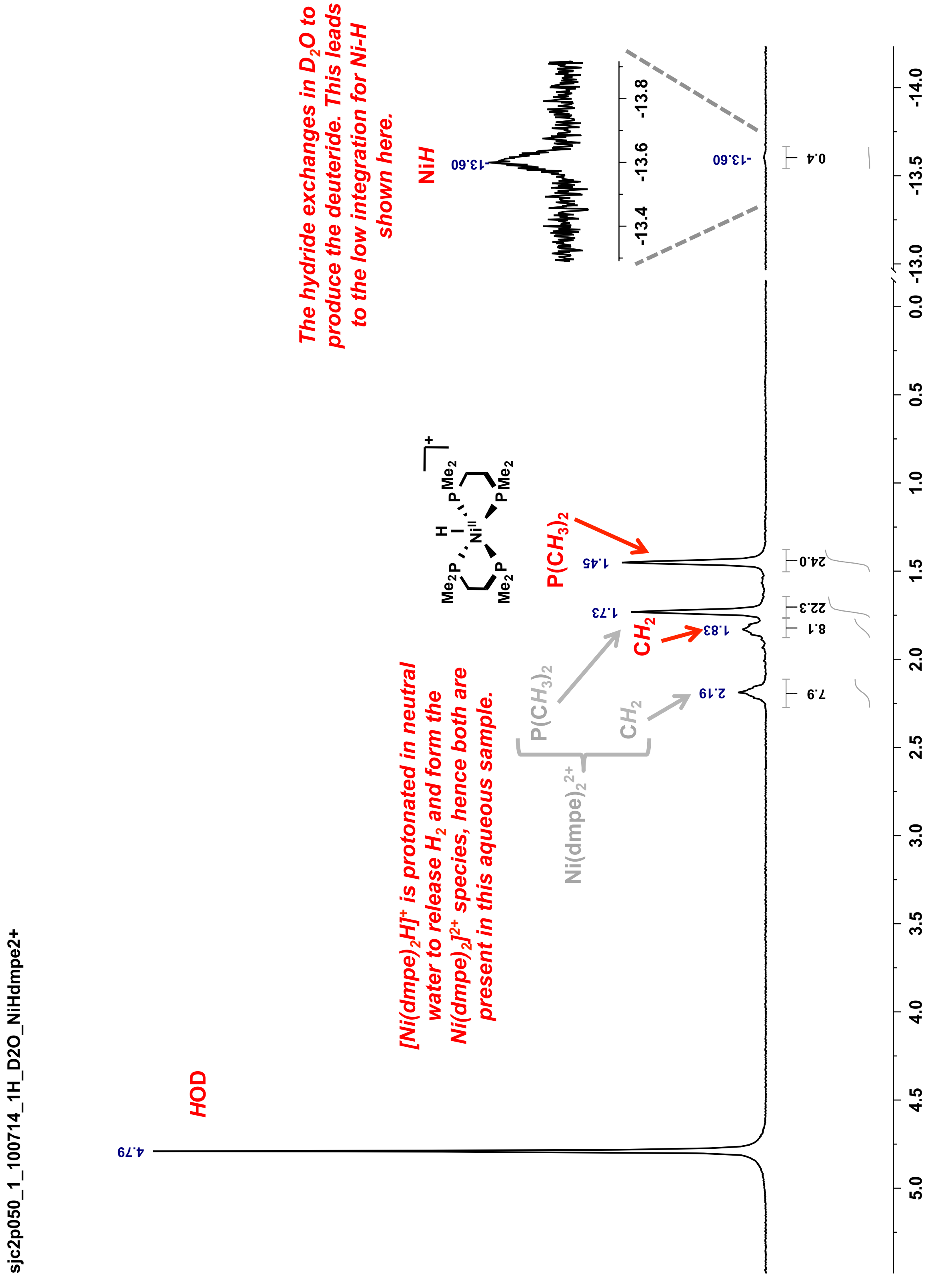
[HNi(dmpe)$_2$][BF$_4$] in CD$_3$CN – ^{1}H – 500 MHz – 298 K



[HNi(dmpe)$_2$][BF$_4$] in CD$_3$CN – ^{31}P{^{1}H} – 202 MHz – 298 K



[HNi(dmpe)$_2$][BF$_4$] in D$_2$O – ^{1}H – 300 MHz – 298 K



The hydride exchanges in D$_2$O to produce the deuteride. This leads to the low integration for Ni-H shown here.

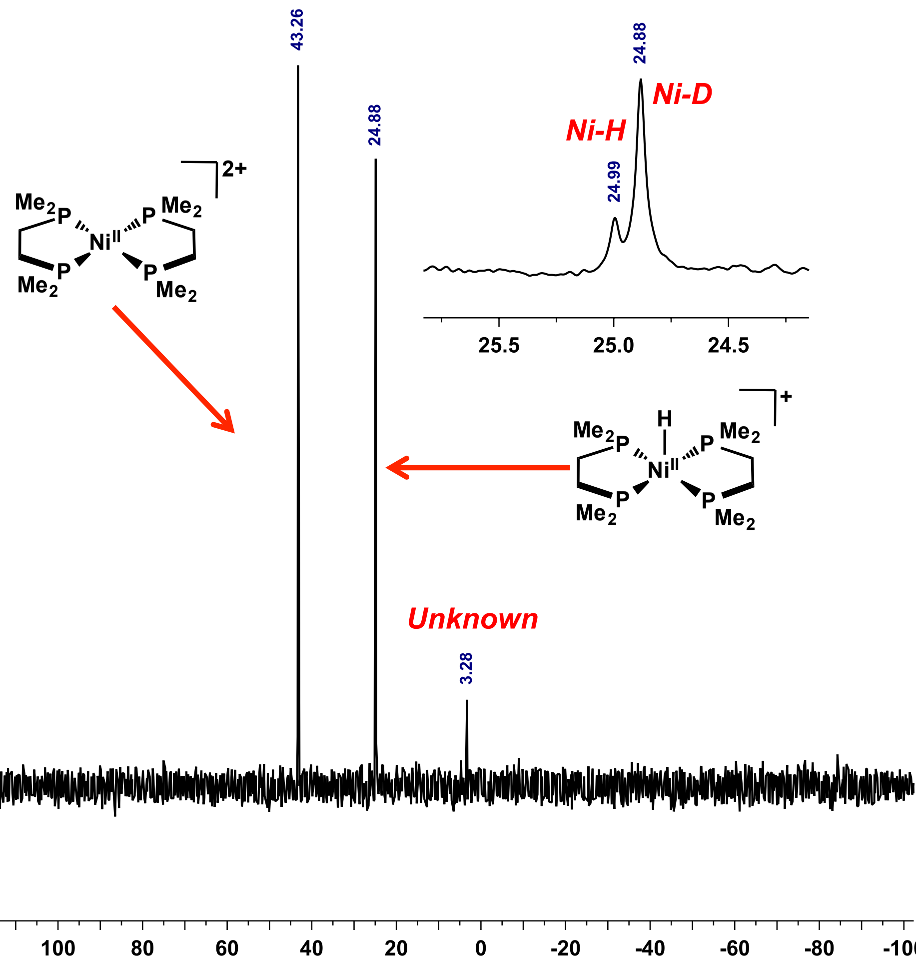
[Ni(dmpe)$_2$H]$^+$ is protonated in neutral water to release H$_2$ and form the Ni(dmpe)$_2$]$^{2+}$ species, hence both are present in this aqueous sample.

[HNi(dmpe)$_2$][BF$_4$] in D$_2$O – ^{31}P{^{1}H} – 121 MHz – 298 K

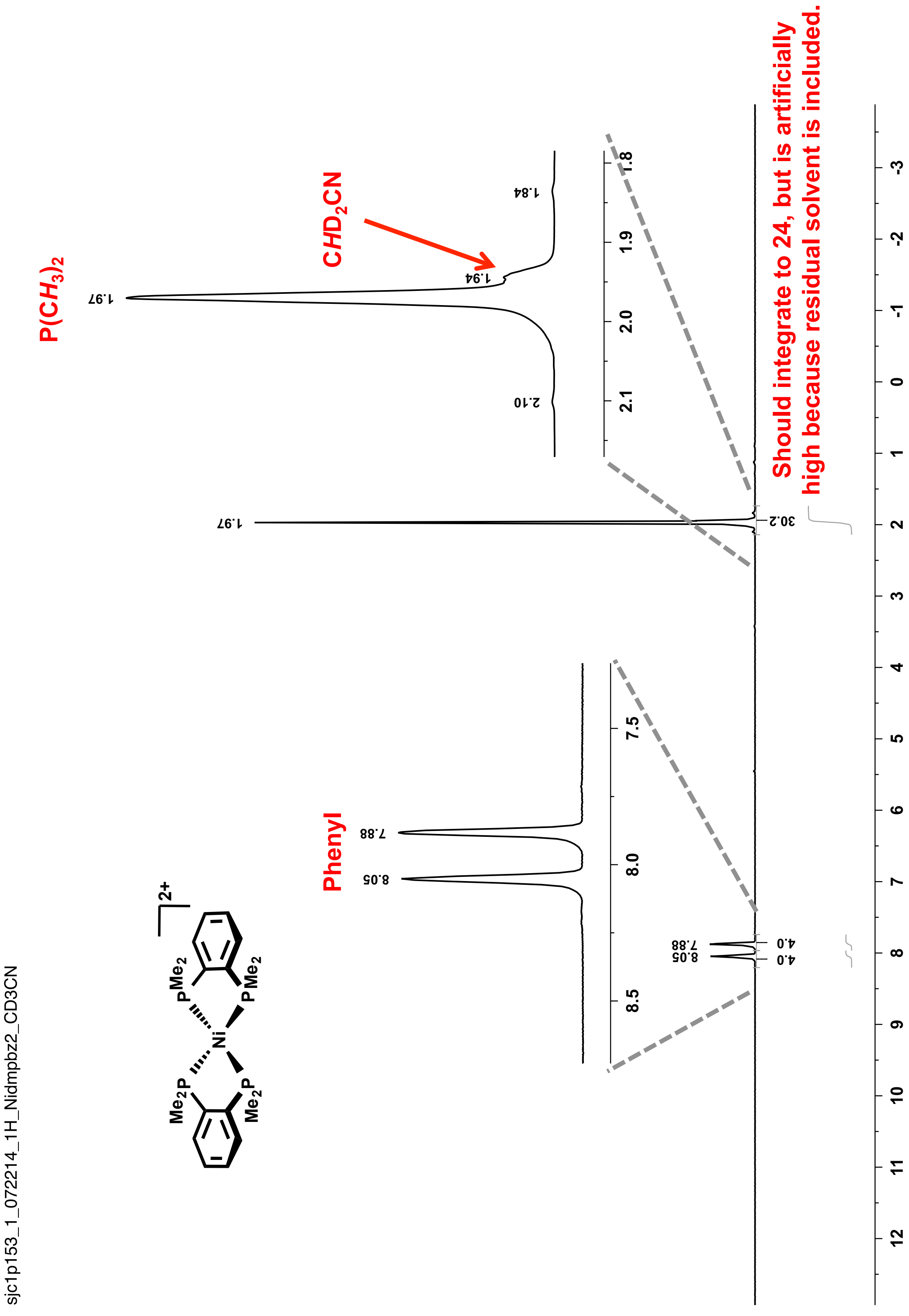
sjc2p050_1_100714_31P_D2O_NiHdmpe2+

Both [Ni(dmpe)$_2$H]$^+$ and [Ni(dmpe)$_2$D]$^+$ are apparent in this sample. Deuteration of the metal hydride occurs over the course of ~30 minutes. There is a 110 ppb isotope shift.

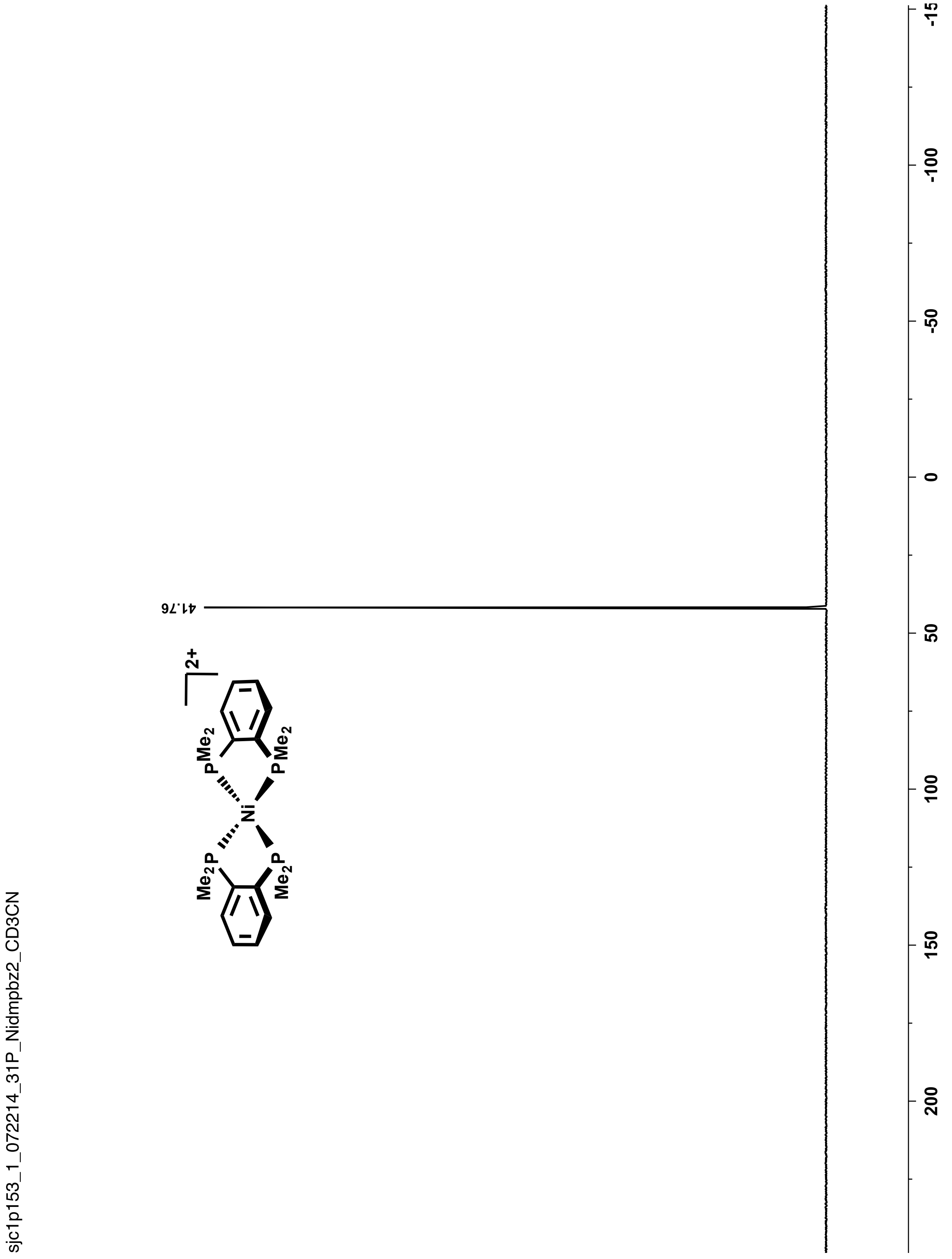
[Ni(dmpe)$_2$H]$^+$ is protonated in neutral water to release H$_2$ and form the Ni(dmpe)$_2$]$^{2+}$ species, hence both are present in this aqueous sample.



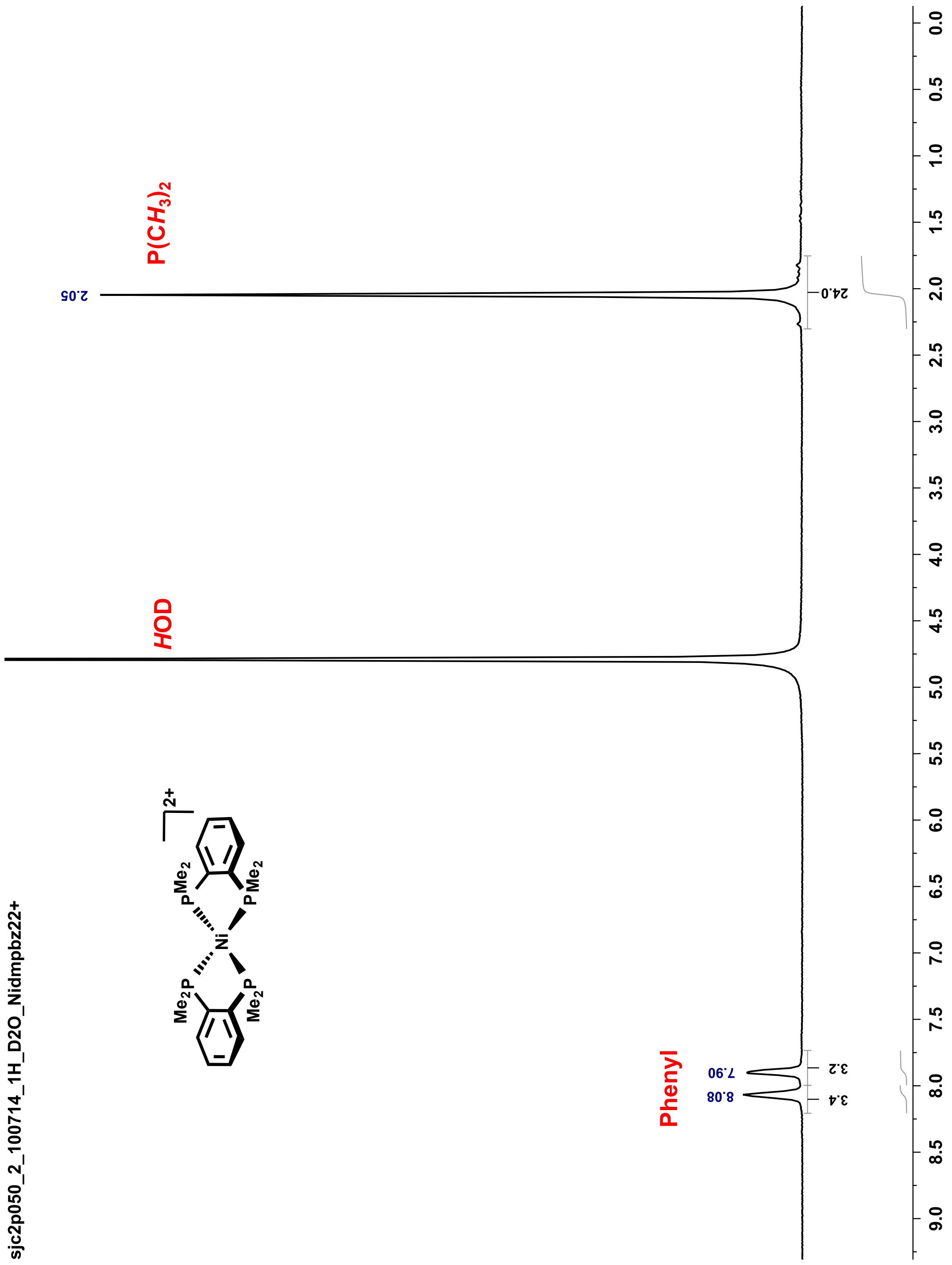
[Ni(dmpbz)$_2$][BF$_4$]$_2$ in CD$_3$CN – ^{1}H – 500 MHz – 298 K



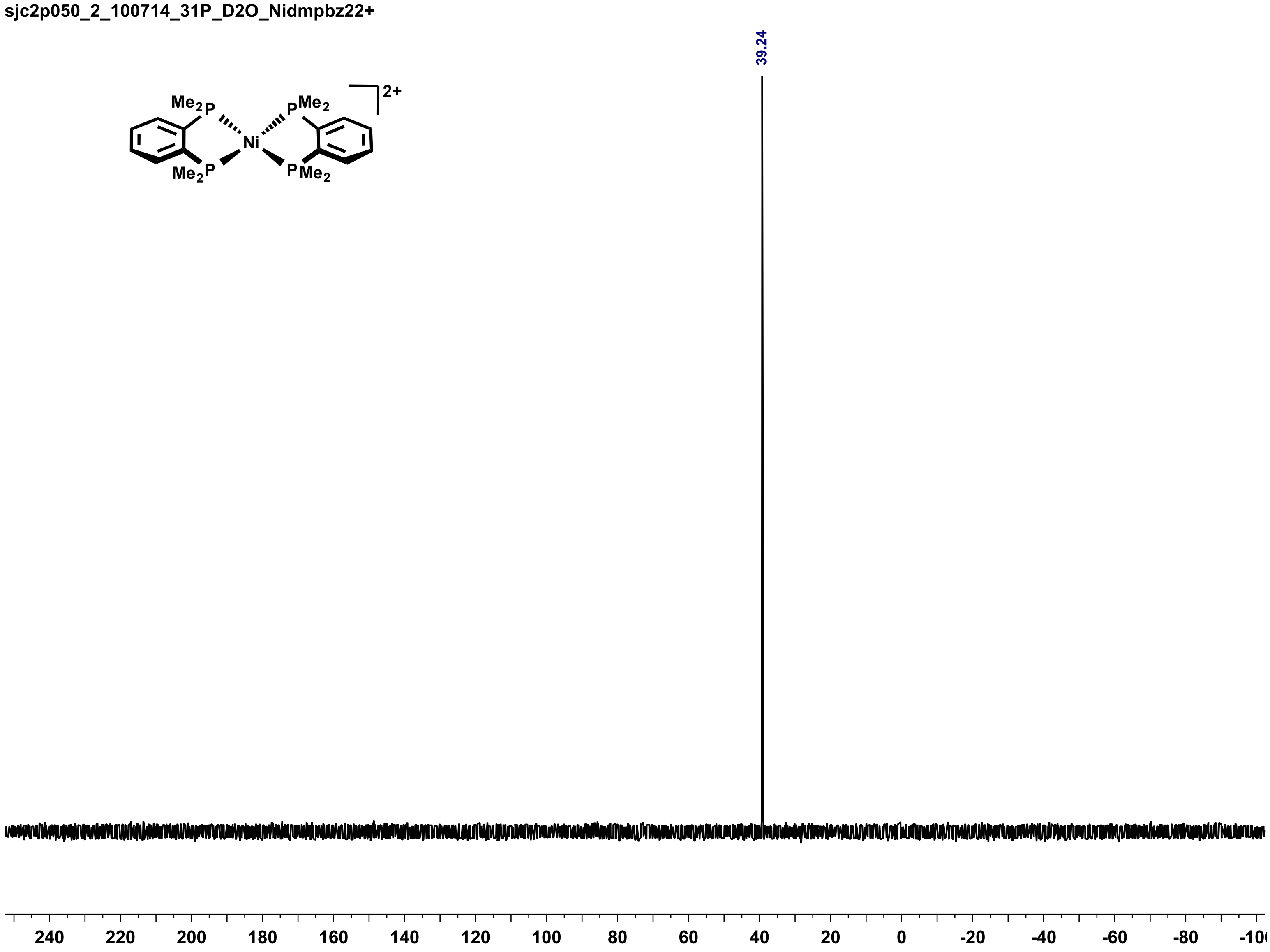
[Ni(dmpbz)$_2$][BF$_4$]$_2$ in CD$_3$CN - ^{31}P{^{1}H} – 202 MHz – 298 K



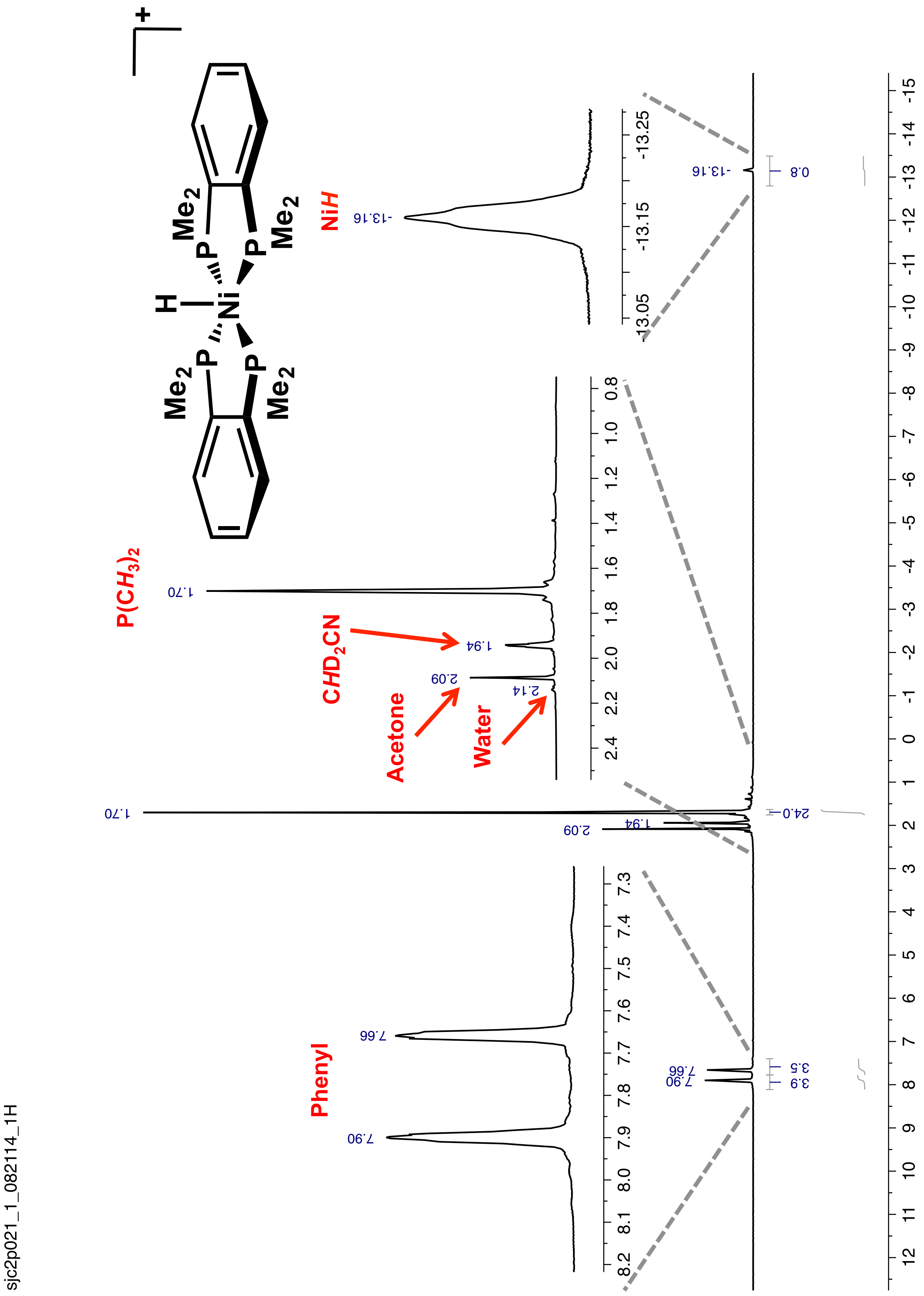
$[Ni(dmpbz)_2][BF_4]_2$ in D_2O – ^1H – 300 MHz – 298 K



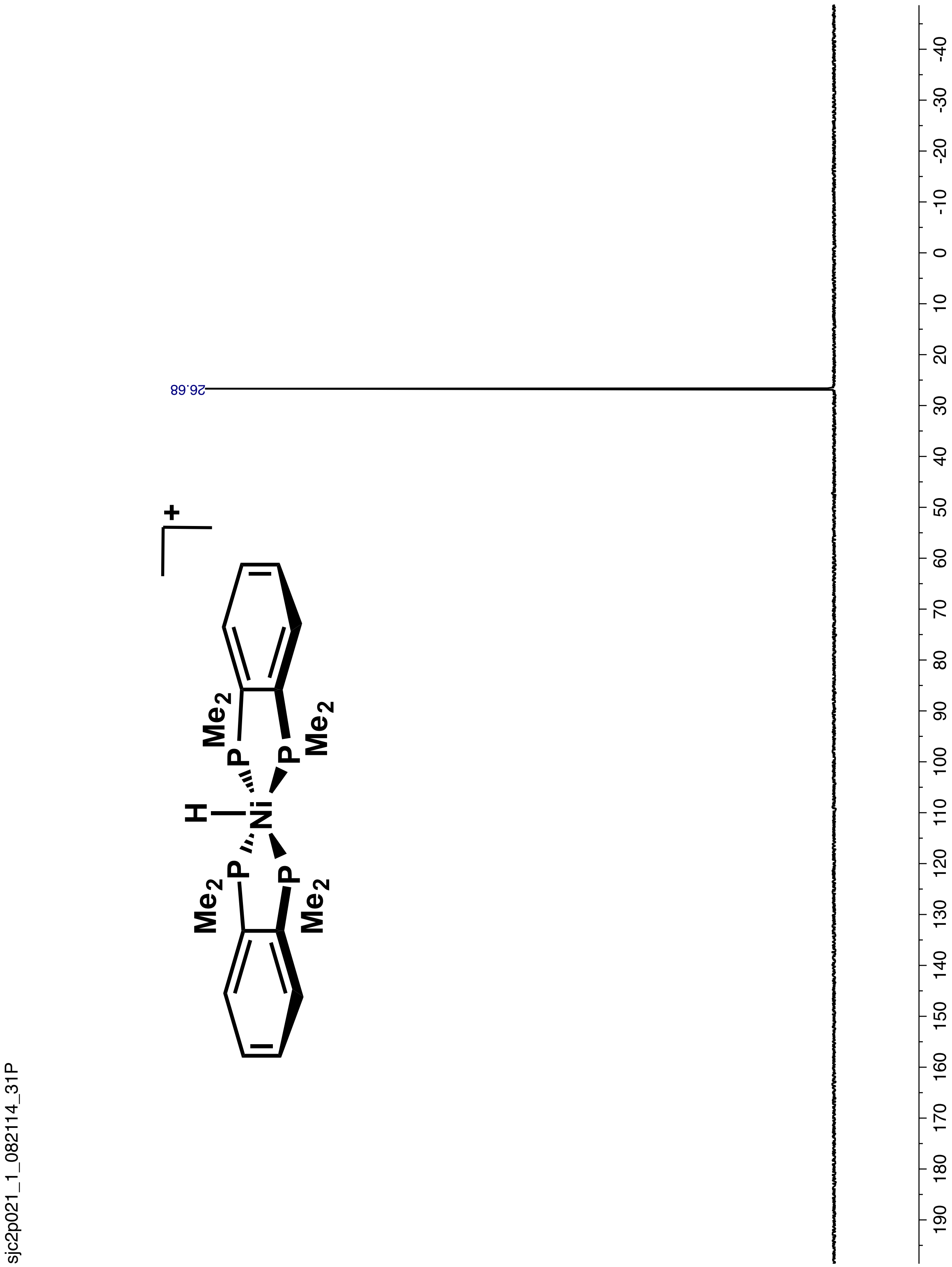
$[Ni(dmpbz)_2][BF_4]_2$ in D_2O - $^{31}P\{^1H\}$ – 121 MHz – 298 K



[HNi(dmpbz)$_2$][BF$_4$] in CD$_3$CN - ^{1}H – 500 MHz – 298 K

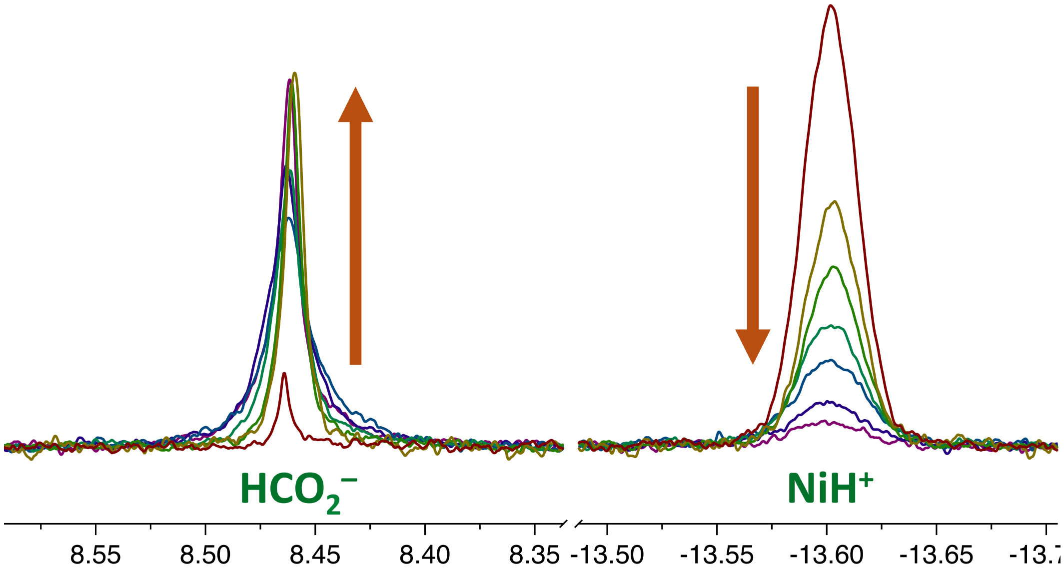


[HNi(dmpbz)$_2$][BF$_4$] in CD$_3$CN - ^{31}P{^{1}H} – 202 MHz – 298 K



^{1}H NMR Spectra for Hydride Transfer from $[HNi(dmpe)_2][BF_4]$ to CO_2

$$[Ni(dmpe)_2H]^+ + CO_2 \xrightarrow[H_2O]{} HCO_2^- + [Ni(dmpe)_2]^{2+}$$



Thermodynamic Calculations:

For a full description of the constants used for the heterolytic and homolytic cleavage of H_2 in water, please see our previous publication:

S. J. Connelly, E. S. Weidner, A. M. Appel *Dalton Trans.* **2015**, DOI: 10.1039/C4dt03841j

Gas Constant:	1.9872×10^{-3} kcal mol^{-1} K^{-1}
Faraday's Constant:	23.061 kcal V^{-1} (mol e^{-})$^{-1}$
Temperature:	298 K
Pressure:	1 atm H_2
Potentials reported[5] vs.	NHE

ΔG of a reaction can be expressed from the reduction potential or the equilibrium constant:

$$\Delta G = -n F E^{o}_{cell}$$
$$\Delta G = -RT \ln K$$

Relevant pK_a Values in Water:

Bicarbonate: $[HCO_3]^- \leftrightarrows H^+ + [CO_3]^{2-}$

$$\begin{aligned} pK_a &= 10.25 \\ K_a &= 10^{-10.25} = 5.623 \times 10^{-11} \\ \Delta G &= -RT \ln(K) \\ &= -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln(5.623 \times 10^{-11}) \quad = \mathbf{13.98\ kcal/mol} \end{aligned}$$

Triethylammonium: $[HNEt_3]^+ \leftrightarrows H^+ + NEt_3$

$$\begin{aligned} pK_a &= 10.75 \\ K_a &= 10^{-10.75} = 1.778 \times 10^{-11} \\ \Delta G &= -RT \ln(K) \\ &= -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln(1.778 \times 10^{-11}) \quad = \mathbf{14.66\ kcal/mol} \end{aligned}$$

Formic Acid: $H_2CO_2 \leftrightarrows H^+ + [HCO_2]^-$

$$\begin{aligned} pK_a &= 3.77 \\ K_a &= 10^{-3.77} = 1.70 \times 10^{-4} \\ \Delta G &= -RT \ln(K) \\ &= -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln(1.70 \times 10^{-4}) \quad = \mathbf{5.14\ kcal/mol} \end{aligned}$$

Hydricity of Formate in Water

Electrochemical Potential: $CO_2\ (g) + 2H^+ + 2e \leftrightarrows H_2CO_2\ (aq)$

Reported[6] = – 0.114 V vs. SHE (Conversion from SHE to NHE = + 0.006 V)
Potential = – 0.108 V vs. NHE

ΔG = $-nFE°$
= – (2 mol e/mol)(23.061 kcal V^{-1} mol e^{-1})(– 0.108 V)
= 4.98 kcal/mol

Hydricity Calculation:

Reactions									ΔG (kcal mol^{-1})
H^+	+	$[HCO_2]^-$	$\leftrightarrows$	H_2CO_2 (aq)					- 5.1
		H_2CO_2 (aq)	$\leftrightarrows$	CO_2	+	$2H^+$	+	2e	- 5.0
H^+	+	2e	$\leftrightarrows$	H^-					34.2
		$[HCO_2]^-$	$\leftrightarrows$	H^-	+	CO_2			24.1

The following experiments were carried out by dissolving $[Ni(dmpe)_2][BF_4]_2$ in H_2O or D_2O with the described bases. Following degassing, hydrogen was added to the headspace of the NMR tube (Teflon-screw top or PEEK) at the pressure described. The reactions were monitored by NMR spectroscopy as they reached equilibrium (generally within 4-8 hours with adequate mixing).

$$\mathbf{[Ni(dmpe)_2]^{2+} + Base + H_2 \leftrightarrows [HNi(dmpe)_2]^{+} + [HBase]^{+}}$$

$$K_{eq} = \frac{[HNi(dmpe)_2]^{+}}{[Ni(dmpe)_2]^{2+}} \times \frac{[HBase]^{+}}{Base} \times \frac{}{P_{H2}\ (atm)}$$

Experiment 1:

Base: 2 M Carbonate Buffer, pH = 11.5 (5% $[HCO_3]^-$, 95% $[CO_3]^{2-}$)
H_2 Pressure: 1.08 atm

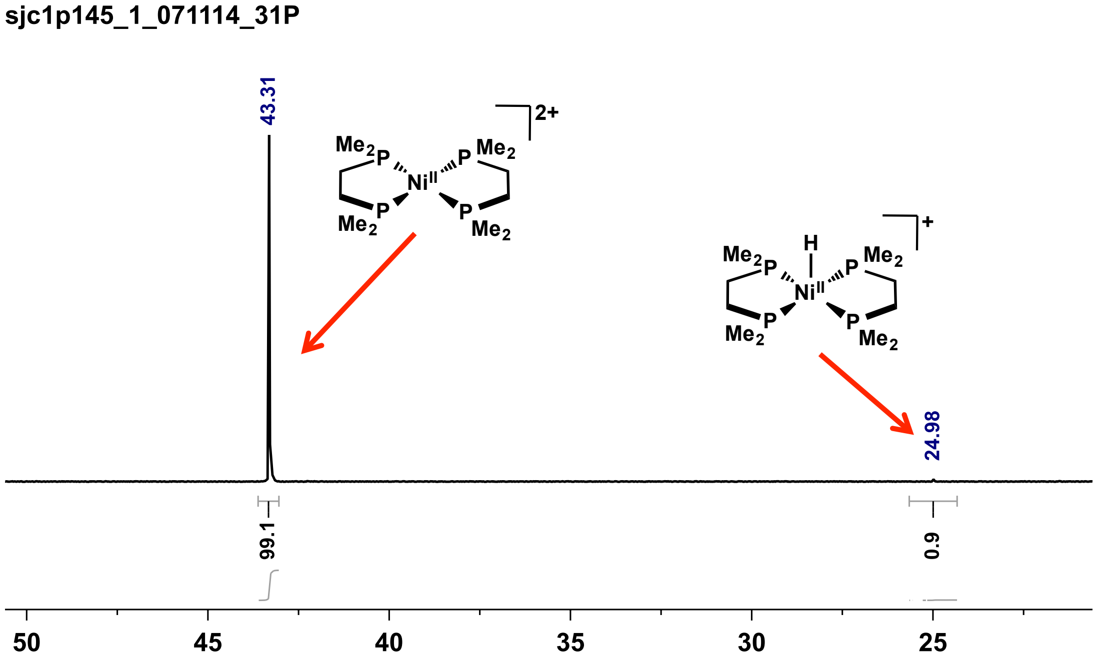
$$K_{eq} = \frac{0.9}{99.1} \times \frac{5}{95} \times \frac{}{1.1} = 4.35 \times 10^{-4}\ atm^{-1}$$

$$\Delta G = -RT \ln(K) = -(1.987 \times 10^{-3}\ kcal\ mol^{-1}\ K^{-1})(298\ K) \ln(4.35 \times 10^{-4}) = 4.58\ kcal\ mol^{-1}$$

Hydricity Calculation (Experiment 1):

Reactions									ΔG (kcal mol^{-1})
$[HNi(dmpe)_2]^{+}$	+	$[HCO_3]^{-}$	⇆	$[Ni(dmpe)_2]^{2+}$	+	$[CO_3]^{2-}$	+	H_2	- 4.6
H^{+}	+	$[CO_3]^{2-}$	⇆	$[HCO_3]^{-}$					-14.0
		H_2	⇆	H^{+}	+	H^{-}			34.2
		$[HNi(dmpe)_2]^{+}$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^{-}			15.6

$^{31}P\{^1H\}$ NMR Spectrum (202 MHz, 298 K, H_2O) at equilibrium (1.1 atm H_2)



Experiment 2:

Base: 2 M Carbonate Buffer, pH = 11.5 (5% $[HCO_3]^-$, 95% $[CO_3]^{2-}$)
H_2 Pressure: 1.7 atm

$$K_{eq} = \frac{1.7}{98.3} \times \frac{5}{95} \times \frac{}{1.7} = 5.35 \times 10^{-4}\ \text{atm}^{-1}$$

$$\Delta G = -RT\ln(K) = -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K})\ln(5.35 \times 10^{-4}) = 4.46\ \text{kcal mol}^{-1}$$

Hydricity Calculation (Experiment 2):

Reactions									ΔG (kcal mol^{-1})
$[HNi(dmpe)_2]^+$	+	$[HCO_3]^-$	⇆	$[Ni(dmpe)_2]^{2+}$	+	$[CO_3]^{2-}$	+	H_2	- 4.5
H^+	+	$[CO_3]^{2-}$	⇆	$[HCO_3]^-$					-14.0
		H_2	⇆	H^+	+	H^-			34.2
		$[HNi(dmpe)_2]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^-			15.7

$^{31}P\{^1H\}$ NMR Spectrum (202 MHz, 298 K, H_2O) at equilibrium (1.7 atm H_2)

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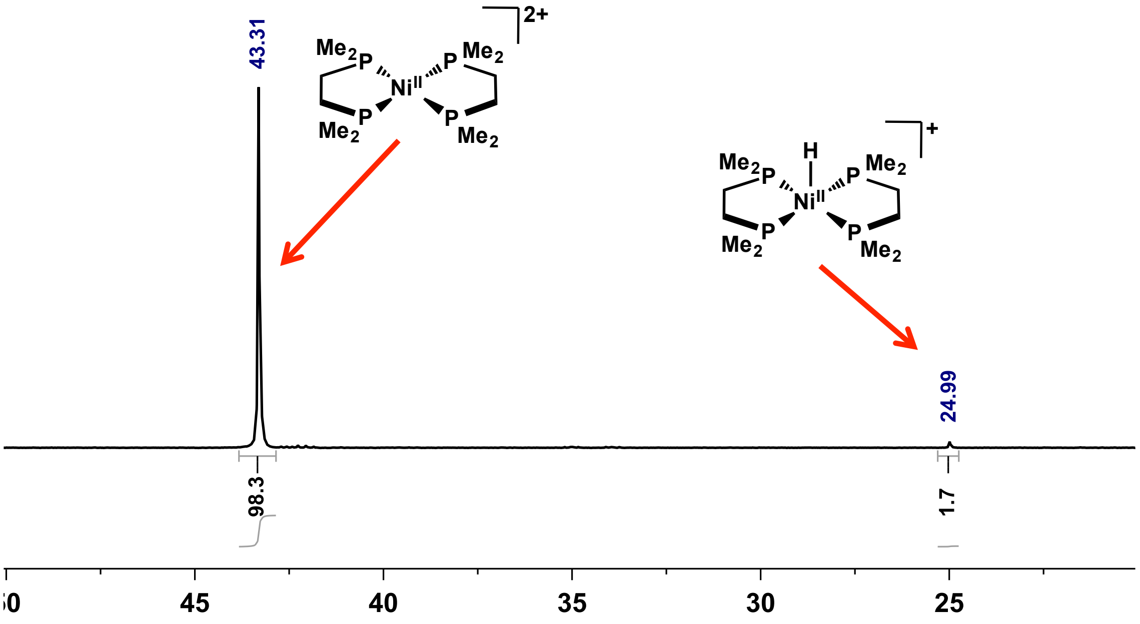


Experiment 3:

Base: 10 eq. $[CO_3]^{2-}$
H_2 Pressure: 20.4 atm

$$K_{eq} = \frac{46.7}{53.3} \times \frac{0.5}{9.5} \times \frac{}{20.4} = 2.26 \times 10^{-3}\ \text{atm}^{-1}$$

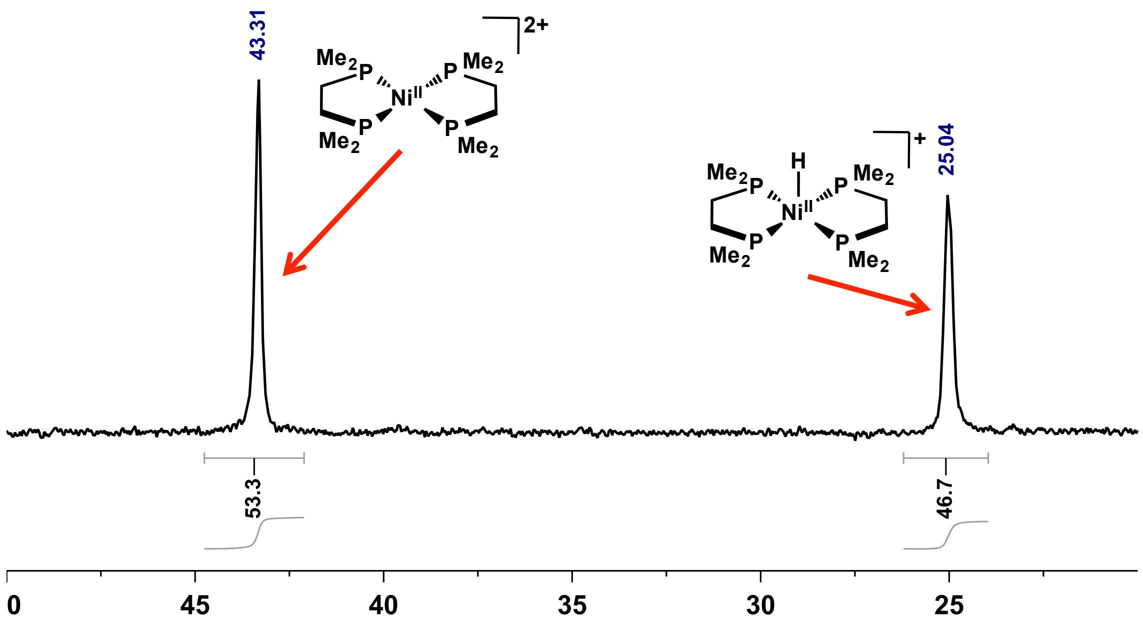
$$\Delta G = -RT \ln(K) = -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln(2.26 \times 10^{-3}) = 3.61\ \text{kcal mol}^{-1}$$

Hydricity Calculation (Experiment 3):

Reactions									ΔG (kcal mol^{-1})
$[HNi(dmpe)_2]^+$	+	$[HCO_3]^-$	⇆	$[Ni(dmpe)_2]^{2+}$	+	$[CO_3]^{2-}$	+	H_2	- 3.6
H^+	+	$[CO_3]^{2-}$	⇆	$[HCO_3]^-$					-14.0
		H_2	⇆	H^+	+	H^-			34.2
		$[HNi(dmpe)_2]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^-			16.6

$^{31}P\{^1H\}$ NMR Spectrum (202 MHz, 298 K, D_2O) at equilibrium (20.4 atm H_2, 10 eq. CO_3^{2-})

sjc1p056_1_042114_31P_186.32min



Experiment 4:

Base: 1 eq. Triethylamine
H_2 Pressure: 1.4 atm

$$K_{eq} = \frac{9.4}{90.6} \times \frac{1}{9} \times \frac{\quad}{1.4} = 8.23 \times 10^{-3}\ \text{atm}^{-1}$$

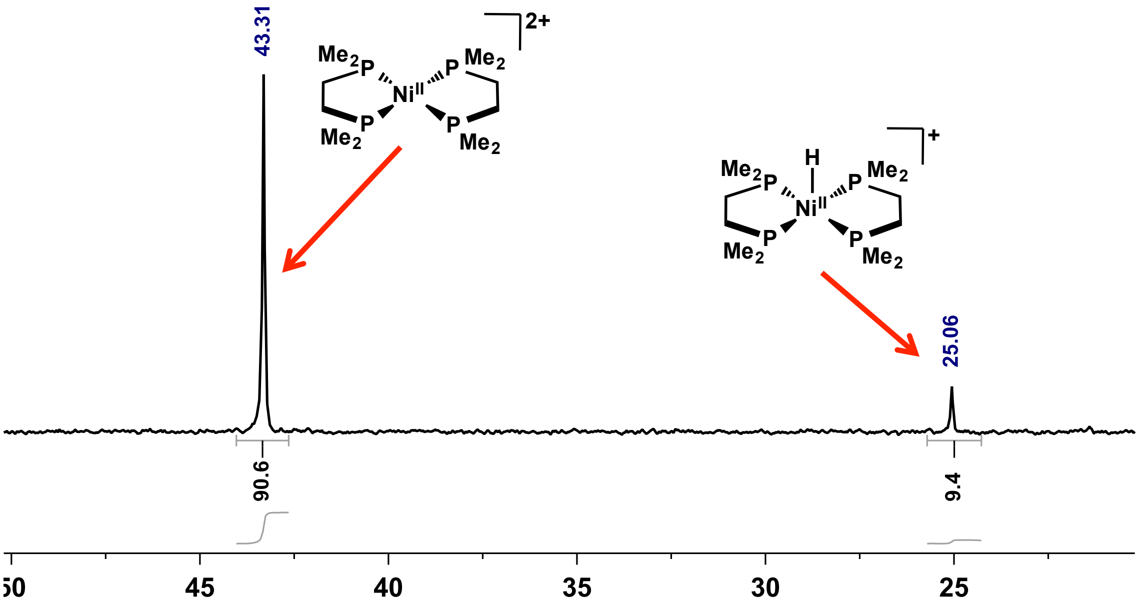
$$\Delta G = -RT \ln(K) = -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln(8.23 \times 10^{-3}) = 2.84\ \text{kcal mol}^{-1}$$

Hydricity Calculation (Experiment 4):

Reactions									ΔG (kcal mol^{-1})
$[Ni(dmpe)_2H]^+$	+	$[HNEt_3]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	NEt_3	+	H_2	- 2.8
H^+	+	NEt_3	⇆	$[HNEt_3]^+$					-14.7
		H_2	⇆	H^+	+	H^-			34.2
		$[Ni(dmpe)_2H]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^-			16.7

$^{31}P\{^1H\}$ NMR Spectrum (121 MHz, 298 K, D_2O) at equilibrium (1.42 atm H_2, 1 eq. NEt_3)

sjc2p034_1_091014_31P_Et3N_Keq



Experiment 5:

Base: 5 eq. Triethylamine
H_2 Pressure: 40.8 atm

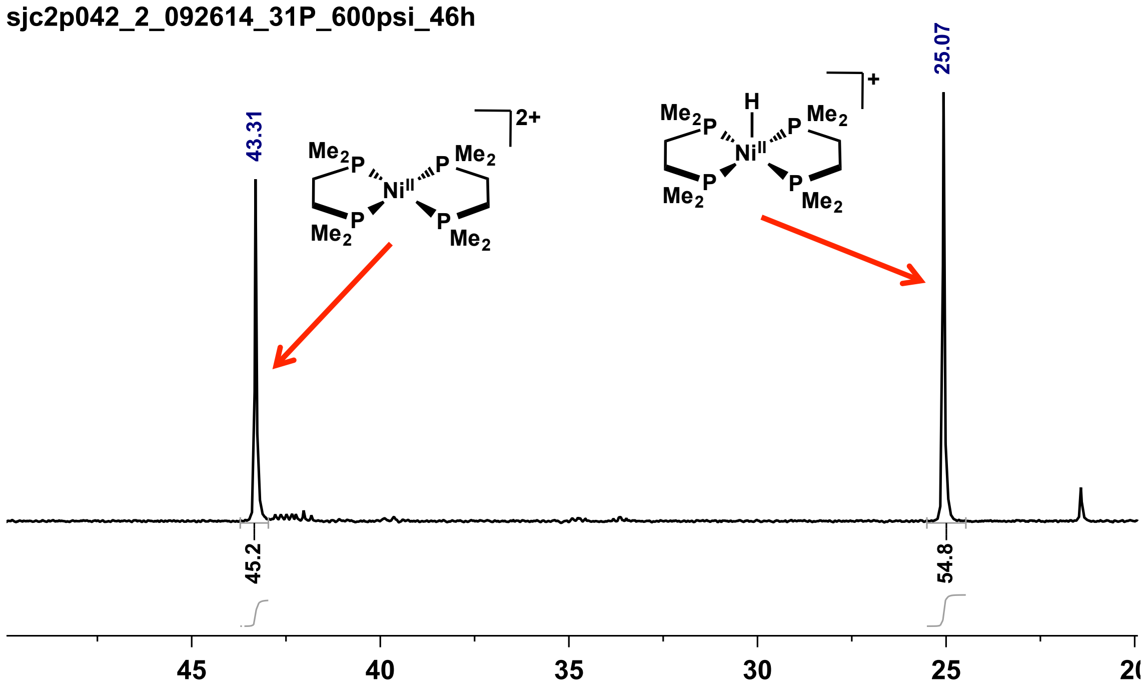
$$K_{eq} = \frac{54.8}{45.2} \times \frac{0.5}{4.5} \times \frac{\quad}{40.8} = 3.30 \times 10^{-3}\ \text{atm}^{-1}$$

$$\Delta G = -RT\ln(K) = -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K})\ln(3.30 \times 10^{-3}) = 3.38\ \text{kcal mol}^{-1}$$

Hydricity Calculation (Experiment 5):

Reactions									ΔG (kcal mol^{-1})
$[HNi(dmpe)_2]^+$	+	$[HNEt_3]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	NEt_3	+	H_2	- 3.4
H^+	+	NEt_3	⇆	$[HNEt_3]^+$					-14.7
		H_2	⇆	H^+	+	H^-			34.2
		$[HNi(dmpe)_2]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^-			16.1

$^{31}P\{^1H\}$ NMR Spectrum (202 MHz, 298 K, D_2O) at equilibrium (40.8 atm H_2, 5 eq. NEt_3)



Average Hydricity of $[HNi(dmpe)_2]^+$: = 16.2 ± 1.0 kcal/mol (std. dev. = 0.5)

Thermodynamics of Hydride Transfer from $[HNi(dmpe)_2]^+$ to CO_2 in Water

Reactions							ΔG (kcal mol^{-1})
		$[HNi(dmpe)_2]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	H^-	**16.2**
H^-	+	CO_2	⇆	$[HCO_2]^-$			**- 24.1**
CO_2	+	$[NHi(dmpe)_2]^+$	⇆	$[Ni(dmpe)_2]^{2+}$	+	$[HCO_2]^-$	**- 7.9**

Thermodynamics of Hydride Transfer from HCO_2^- to $[Ni(dmpe)_2]^{2+}$ in Acetonitrile

Reactions							ΔG (kcal mol^{-1})
		$[HCO_2]^-$	⇆	CO_2	+	H^-	**44.2**
H^-	+	$[Ni(dmpe)_2]^{2+}$	⇆	$[HNi(dmpe)_2]^+$			**- 50.9**
$[HCO_2]^-$	+	$[Ni(dmpe)_2]^{2+}$	⇆	$[HNi(dmpe)_2]^+$	+	CO_2	**- 6.7**

As reported by A. J. M. Miller, J. Labinger, J. E. Bercaw, *Organometallics,* **2011**, *30* 4308-4314.

Calculations to estimate stability of $[HNi(dmpe)_2]^+$ in aqueous solution (based on Eq. 2 of main text):

$K = e^{(-\Delta G/RT)} = e^{-\text{ 18 kcal/mol / ((1.987 × 10-3 kcal/mol K)(298 K))}} = 6.3 \text{ x } 10^{-14}$

$pK = -\log(K) = -\log(6.3 \text{ x } 10^{-14}) = 13.2$

This suggests that until the pH of the aqueous solution exceeds 13, $[HNi(dmpe)_2]^+$ is susceptible to protonation by the solution.

ΔG = 18 kcal/mol determined from Experiments 1 – 5, by combining the determined ΔG of Equation 1 (main text) with the known ΔG for protonation of the base employed.

X-ray Diffraction Studies.

[Ni(dmpbz)$_2$][BF$_4$]$_2$

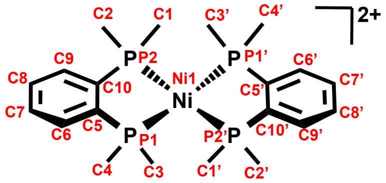
Single crystals were grown by layering an acetonitrile solution of [Ni(dmpbz)$_2$][BF$_4$]$_2$ with diethyl ether. The yellow block crystal (0.3 x 0.2 x 0.05 mm^3) was mounted on a nylon loop. Data were collected at 100(2) Kelvin on a Bruker-AXS Kappa APEX II CCD diffractometer equipped with a 0.71073 Å Mo-Kα radiation source (graphite monochromator).[7]

The data intensity was corrected for absorption and decay using SADABS.[8] Unit cell parameters were obtained from least-squares fits of all measured reflections after integration (SAINT+).[9] The structure was solved using SHELXS-97 and refined using SHELXL-97[10] in OLEX2.[11] A direct methods solution was calculated which provided most non-hydrogen atoms from the Emap. Full-matrix least squares / difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed ideally and refined as riding atoms with relative isotropic displacement parameters.

Crystallographic data are summarized here:

	[Ni(dmpbz)$_2$][BF$_4$]$_2$
Empirical Formula	$C_{20}H_{32}B_2F_8NiP_4$
Formula Weight (g/mol)	628.66
Crystal System	Orthorhombic
Space Group	Pbcn
a, Å	16.0457(14)
b, Å	9.2602(8)
c, Å	17.5605(14)
α, degrees	90
β, degrees	90
γ, degrees	90
Volume, Å^3	2609.3(4)
Z	4
Radiation (λ, Å)	Mo-Kα (0.71073)
Calc'd Density (g/cm^3)	1.600
μ, mm^{-1}	1.055
Temperature, Kelvin	100(2)
Size, mm^3	0.003
Color	yellow
Habit	block
# of Reflections	19719
# of Independent Reflections (R_{int})	2971 (0.0717)
Θ_{max}, degrees	27.518
Data/Restraints/Parameters	2971/0/250
R_1	0.0531
wR_2	0.1501
GOF (F^2)	1.020
F(000)	1288.0

Numbering Scheme for [Ni(dmpbz)$_2$]$^{2+}$



Relevant Bond Lengths

Bond Between:	Length, Å
Ni1 – P1	2.1915(14)
Ni1 – P2	2.174(5)
P1 – C3	1.814(5)
P1 – C4	1.825(5)
P1 – C5	1.832(14)
P2 – C1	1.807(10)
P2 – C2	1.796(10)
P2 – C10	1.825(11)
C5 – C6	1.445(13)
C5 – C10	1.393(10)
C6 – C7	1.358(17)
C7 – C8	1.383(13)
C8 – C9	1.400(15)
C9 – C10	1.375(17)

Relevant Bond Angles

Angle Between:	Angle (Degrees)
P1 – Ni1 – P1'	180.0
P1 – Ni1 – P2	90.22(10)
P1 – Ni1 – P2'	89.78(10)
P2 – Ni1 – P1'	89.78(10)
P2 – Ni1 – P2'	180.0
C3 – P1 – Ni1	119.67(19)
C3 – P1 – C4	105.6(3)
C3 – P1 – C5	107.1(4)
C4 – P1 – Ni1	113.7(2)
C4 – P1 – C5	105.6(4)
C5 – P1 – Ni1	104.2(3)
C1 – P2 – Ni1	113.4(4)
C1 – P2 – C10	101.6(5)
C2 – P2 – Ni1	121.7(3)
C2 – P2 – C1	105.8(5)
C2 – P2 – C10	104.1(5)
C10 – P2 – Ni1	108.1(3)
C6 – C5 – P1	121.1(6)
C10 – C5 – P1	121.4(8)
C5 – C10 – P2	114.0(9)
C9 – C10 – P2	124.9(6)
C10 – C5 – C6	117.3(11)
C7 – C6 – C5	119.9(8)
C6 – C7 – C8	122.4(9)
C7 – C8 – C9	117.9(10)
C10 – C9 – C8	121.2(8)
C9 – C10 – C5	121.1(9)

$[HNi(dmpbz)_2][BF_4]_2$

Single crystals were grown by slow diffusion of diethyl ether into an acetonitrile solution of $[HNi(dmpbz)_2][BF_4]_2$. The crystalline yellow plate (0.06 x 0.04 x 0.02 mm^3) was mounted on a nylon loop. Data were collected at 100(2) Kelvin on a Bruker-AXS Kappa APEX II CCD diffractometer equipped with a 0.71073 Å Mo-Kα radiation source (graphite monochromator).[7]

The data intensity was corrected for absorption and decay using SADABS.[8] Unit cell parameters were obtained from least-squares fits of all measured reflections after integration (SAINT+).[9] The structure was solved in the orthorhombic space group Fddd using OLEX2 and refined using SHELXL-2014[10,11] A direct methods solution was calculated which provided most non-hydrogen atoms from the Emap. Full-matrix least squares / difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed ideally and refined as riding atoms with relative isotropic displacement parameters.

One quarter of the molecule is unique due to crystallographic symmetry. The metal hydride hydrogen atom was not located in the difference map, but dissolution of the crystalline product in acetonitrile confirmed the presence of the hydride ligand (see main text and NMR spectra included in the Supporting Information).

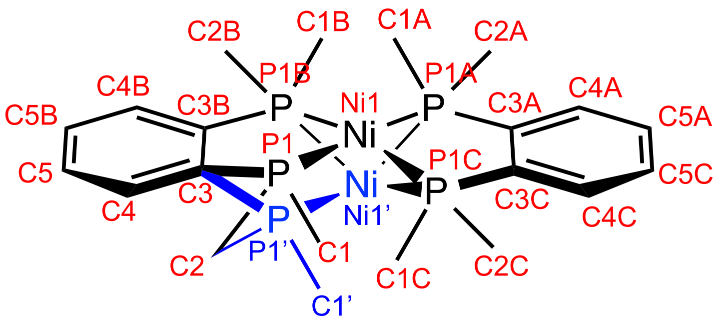
The Ni is disordered over a two-fold rotation axis within the unit cell due to a hydride that could not be located from the electron density map. The two disordered Ni atoms are equivalent due to symmetry, and each was assigned a 50% occupancy. The positions of the phosphorous donor and one of its methyl substituents are also disordered, without crystallographic symmetry. The positions of these disordered atoms were determined from the difference map, and the disorder was also modeled with 50% occupancy at each position. The disordered atoms are shown in blue in the labeling scheme. Only one of the four symmetry-equivalent positions for the disordered atoms are shown.

Crystallographic data are summarized here:

	$[HNi(dmpbz)_2][BF_4]$
Empirical Formula	$C_{20}H_{32}BF_4NiP_4$
Formula Weight (g/mol)	541.85
Crystal System	Orthorhombic
Space Group	Fddd
a, Å	12.354(3)
b, Å	19.109(3)
c, Å	20.927(5)
α, degrees	90
β, degrees	90
γ, degrees	90
Volume, Å^3	4940.2(2)
Z	8
Radiation (λ, Å)	Mo-Kα (0.71073)
Calc'd Density (g/cm^3)	1.457
μ, mm^{-1}	1.081
Temperature, Kelvin	100(2)
Size, mm^3	0.06 x 0.04 x 0.02

Color	yellow
Habit	plate
# of Reflections	13187
# of Independent Reflections (R_{int})	1258 (0.0508)
Θ_{max}, degrees	26.445
Data/Restraints/Parameters	1258 / 0 / 92
R_1	0.0317
wR_2	0.0687
GOF (F^2)	1.039
F(000)	2248

Numbering Scheme for [HNi(dmpbz)$_2$]$^+$



Relevant Bond Lengths

Bond Between:			Length, Å
Ni1	−	P1	2.121(9)
Ni1’	−	P1’	2.218(8)
P1	−	C1	1.838(1)
P1’	−	C1’	1.781(1)
P1	−	C2	1.836(1)
P1’	−	C2	1.821(1)
P1	−	C3	1.799(1)
P1’	−	C3	1.867(1)
C3	−	C4	1.393(3)
C4	−	C5	1.379(3)
C5	−	C5B	1.380(5)
C3	−	C3B	1.388(4)

Relevant Bond Angles

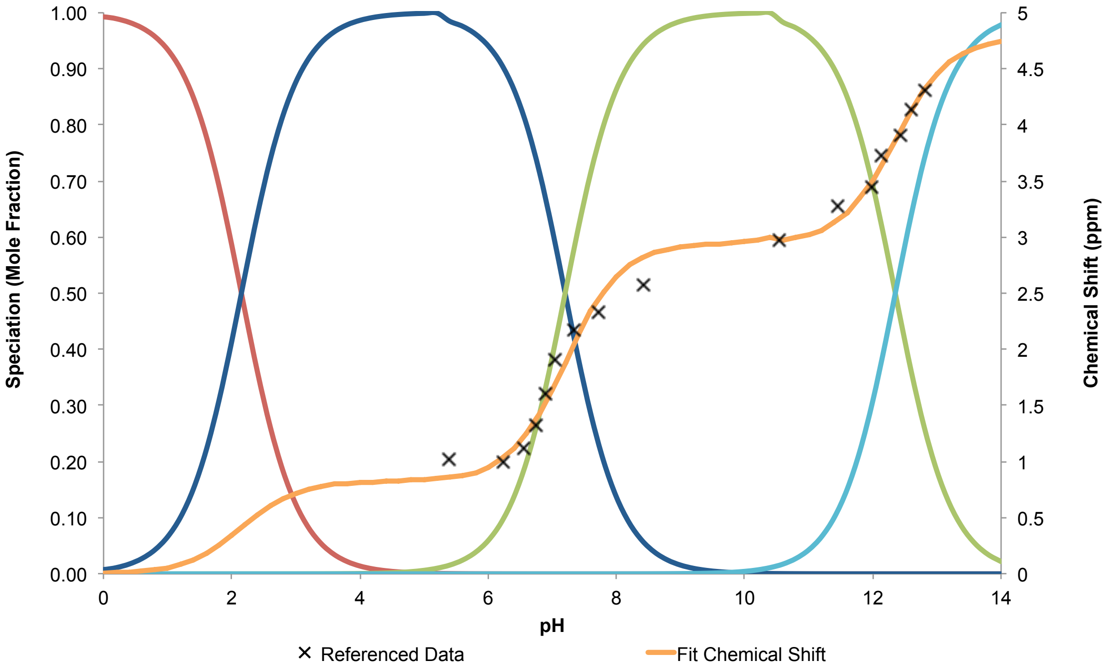
Angle Between:	Angle (Degrees)
P1 – Ni1 – P1B	89.9(6)
P1 – Ni1 – P1C	112.6(5)
P1 – Ni1 – P1A	142.6(6)
P2 – Ni1 – P2’	89.54(5)
C3 – P1 – Ni1	97.9(4)
C1 – P1 – Ni1	118.7(6)
C2 – P1 – Ni1	117.8(4)
C1 – P1 – C3	104.6(15)
C1 – P1 – C2	102.4(5)
C2 – P1 – C3	104.0(5)
C3’ – C3 – P1	121.7(3)
C4 – C3 – P1	118.4(3)
C3’ – C3 – C4	119.83(5)
C3 – C4 – C5	119.8(3)
C4 – C5 – C5’	120.36(1)

Phosphate Buffer pH Calibration Curve.

The pH of the phosphate buffer reaction mixtures could be directly measured using this calibration curve. The red, blue, green, and aqua lines describe the speciation of the phosphate buffer at any aqueous pH (as determined by the Henderson-Hasselbach equation), left vertical axis.

The data points plotted on the right vertical axis are the measured chemical shifts (referenced to a capillary standard containing H_3PO_4) of a solution at a given pH. The orange line was fit to those data points using the Solver function in Microsoft Excel. The function describes the weighted average chemical shift of the two species present in the buffered solution at any pH.

It should be noted that this curve is only valid at 298 K.



Abbreviations.

dmpe = 1,2-bis(dimethylphosphino)ethane
dmpbz = 1,2-bis(dimethylphosphino)benzene

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