Supporting Information

for

Mechanism of H_2 Production by Models for the [NiFe]-Hydrogenases: Role of Reduced Hydrides

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Studies on dppe and dppbz Derivatives

Studies also include the dppe complexes [(dppe)Ni(μ-pdt)(μ-H)Fe(CO)(diphos)]$^{+}$, labeled [H**A**]$^{+}$ and [H**B**]$^{+}$ for diphos = dppe or dppbz, respectively. As revealed by ^{31}P{^{1}H} NMR spectra, samples of [H**A**]BAr$^{F}_{4}$ and [H**B**]BAr$^{F}_{4}$ contain persistent impurities, the concentrations of which increased when these solutions were allowed to stand over the course of 24 h. Also problematic, purification of these salts relied on tedious chromatography using chlorinated solvents, in which these hydrido complexes degrade. Owing to these complications, efforts shifted to the bis(dppv) complex [(dppv)Ni(μ-pdt)Fe(dppv)(CO)] and its hydrides. For completeness, results on the dppe derivatives are included.

The salts *sym*-[H**A**]BAr$^{F}_{4}$ and *sym*-[H**B**]BAr$^{F}_{4}$ were also characterized crystallographically. All feature octahedral iron centers and approximately square pyramidal nickel centers (Figure S1).

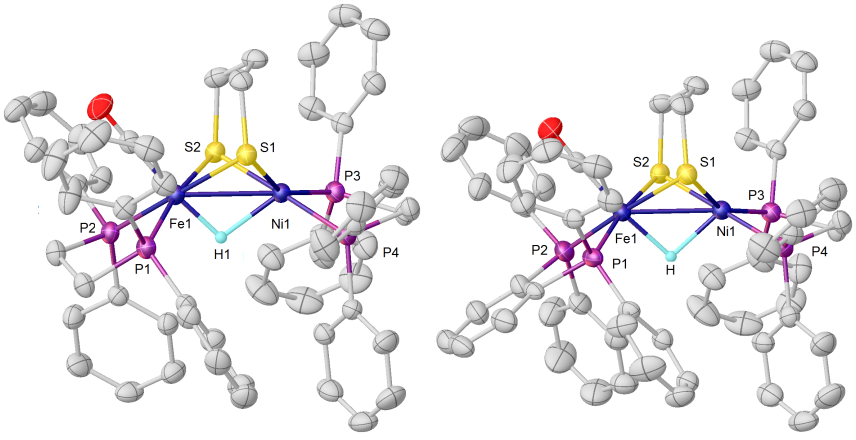


Figure S1. Molecular structures of the cations [H**A**]BAr^F_4 (left) and [H**B**]BAr^F_4 (right) with 50% probability thermal ellipsoids. Hydrogen atoms that were not refined, the counter ion, and solvent molecules have been omitted for clarity.

The structures of [H**A**]$^+$ and [H**B**]$^+$, like the case of [H**1**]$^+$, were also optimized using DFT, and these structures generally agree well with the crystallographic results. Selected bond lengths and angles are provided in Table S1 below. Consistent with the crystal structures, the optimized structures of *sym*-[H**A**]$^+$ and *unsym*-[H**1**]$^+$ feature asymmetrically bound hydrides, which are closer to Fe than to Ni. DFT also predicts an unsymmetrically bridging hydride for *sym*-[H**B**]$^+$. The crystal structure for *sym*-[H**B**]$^+$, however, reveals that the hydride ligand is nearly symmetrically bound. This discrepancy between the computational and experimental result is unusual when redox potentials and CO frequencies match. Consistent with previous DFT calculations on NiFe models, the CO stretching frequencies (ν_{CO}) for the optimized structures agree well with the experimental FT-IR data (Table S2).

Table S1. Selected structural metrics for *sym*-[H**A**]$^+$, *sym*-[H**B**]$^+$, and *unsym*-[H**1**]$^+$.

	sym-[H**A**]$^+$		*sym*-[H**B**]$^+$		*unsym*-[H**1**]$^+$	
	Expt[a]	**Calc**[b]	**Expt**[a]	**Calc**[b]	**Expt**[a]	**Calc**[b]
Fe-Ni (Å)	2.656(4)	2.738	2.671(8)	2.699	2.6461(5)	2.686
Fe-H (Å)	1.555(3)	1.646	1.798(5)	1.654	1.56(3)	1.609
Ni-H (Å)	1.847(3)	1.902	1.788(5)	1.851	1.79(3)	1.812
P_1-Ni-P_2/S_1-Ni-S_2 dihedral angle (°)[c]	28.04	19.82	25.11	26.79	15.97	17.56
P_1-Ni-P_2 bite angle (°)	87.27	88.05	87.01	87.91	87.50	88.67
P_3-Fe-P_4 bite angle (°)	86.73	86.96	87.80	88.00	86.43	87.21

[a]Crystal structures were obtained for [H**A**]BAr^F_4, and [H**B**]BAr^F_4, and [H**1**]BF_4.
[b]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT optimized structure.
[c]Dihedral refers to the angle between the planes formed by the groups of three atoms listed.

Table S2. Experimental and Calculated Values for ν_{CO} (cm^{-1}) of Metal Complexes Discussed.

	ν_{CO} Exp[a]	**ν_{CO} DFT**[b]
[H**A**]$^+$	1938, 1954 (sh)	1936, 1954
[H**A**]^0	1909	1921
[H**B**]$^+$ (as $BAr^F_4{}^-$ salt)	1949, 1935	1945, 1941
[H**B**]^0	1925	1917
[H**1**]$^+$ (as $BAr^F_4{}^-$ salt)	1953, 1960 (sh)	1946, 1957
[H**1**]^0	1920	1922
[**1**]^0	1912, 1897 (sh)	1905
[**1**]$^+$ (as PF_6^- salt)	1950[c] (unstable,	1948

	tent.)	
$[Cl\mathbf{1}]^+$ (as BF_4^- salt)	1946[c]	n/a

[a]Experiments performed in THF solution unless otherwise noted.
[b]No counterions were included in the DFT calculations.
[c]Experiments performed in acetone solution.

Redox Experiments on Hydrides. The main difference in redox behavior of the hydrides is the reversibility or their reduction. The current ratio, $i_{pa}/i_{pc,}$ for the $[H\mathbf{1}]^{+/0}$ couple is 0.94 at 100 mV/s in MeCN (Table S3). DFT was used to calculate the potentials for the $[H\mathbf{A}]^{+/0}$, $[H\mathbf{B}]^{+/0}$, and $[H\mathbf{1}]^{+/0}$ couples, and the calculated potentials agree with the experimental values (Table S3).

Table S3. Current Ratios (i_{pa}/i_{pc}) and Observed and Calculated Redox Potentials (V vs $Fc^{0/+}$) for Ni-H-Fe Complexes.[a]

Redox Couple	$E_{½}$ **EXP**	i_{pa}/i_{pc}	$E_{½}$ **DFT**[b]
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppe)(CO)]^{+/0}$ ($[H\mathbf{A}]^{+/0}$)	–1.50, –1.59[c]	0.52	–1.50, –1.55[c]
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppBz)(CO)]^{+/0}$ ($[H\mathbf{B}]^{+/0}$)	–1.47, –1.57[c]	0.68	–1.50, –1.59[c]
$[(dppv)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppv)(CO)]^{+/0}$ ($[H\mathbf{1}]^{+/0}$)	–1.48	0.94	–1.45

[a] 1 mM complex in MeCN, 0.1 M $[NBu_4]BF_4$ electrolyte, glassy carbon electrode, 100 mV/s scan-rate.
[b] The reference for all the calculated potentials is the experimental $E_{1/2}$ for $[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(CO)_2(P(OPh)_3)]^{+/0}$ from ref. 8. Because the experimental reference is $E_{1/2}$, the calculated potentials are also assumed to be $E_{1/2}$.
[c] Additional reduction attributed to second unsymmetrical isomer.

The spin density plots for $[H\mathbf{A}]^0$ and $[H\mathbf{B}]^0$ also feature similar localization patterns seen for $[H\mathbf{1}]^0$ (Figure S2). Overall, the reduction of the bridging hydride species is predicted to occur primarily at the Ni center with some delocalization of the spin density onto the Fe and S centers (Table S4).

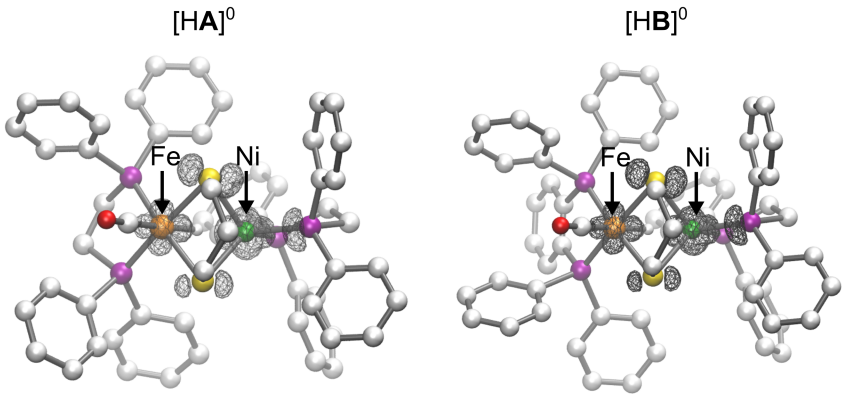


Figure S2. Top-down view of the isocontour plot (isovalue = 0.005) of the unpaired spin density for *sym*-[H**A**]^0 (left) and *sym*-[H**B**]^0 (right) showing predominant localization around the Ni coordination sphere, with some localization near the Fe center as well. The numerical atomic spin densities are provided in Table S4. The hydrogens have been removed for clarity.

Table S4. Calculated Spin Densities for the Reduced Hydride Complexes [H**A**]^0 and [H**B**]^0.

Complex	**Ni**	**Fe**	**2S**	**2P$_{Ni}$** [a]
sym-[H**A**]^0	0.46	0.21	0.17	0.13
unsym-[H**A**]^0	0.44	0.22	0.15	0.14
sym-[H**B**]^0	0.48	0.14	0.19	0.14
unsym-[H**B**]^0	0.41	0.29	0.13	0.13

[a]These values refer to the P atoms of the dppe or dppbz ligand on the Ni center.

Table S5. Calculated Bond Lengths (Å) and Bond Angles (°) for Isomers of [H**A**]$^+$ and [H**A**]^0 [a]

	sym-[H**A**]$^+$	*unsym*-[H**A**]$^+$	*sym*-[H**A**]^0	*unsym*-[H**A**]^0
Ni-Fe	2.738	2.708	2.691	2.651
Fe-H	1.646	1.614	1.628	1.595
Ni-H	1.902	1.833	1.803	1.720
Ni-P [b]	2.211	2.207	2.254	2.245
Ni-S [b]	2.251	2.256	2.359	2.394
Fe-P [b]	2.246	2.277	2.231	2.260
Fe-S [b]	2.317	2.346	2.344	2.365
Fe-C	1.755	1.743	1.758	1.739
P_1-Ni-P_2	88.05	88.84	87.29	89.02
P_3-Fe-P_4	86.96	88.01	87.58	87.87
S_1-Ni-S_2/ P_1-Ni-P_2 [c]	19.82	17.80	81.99	113.46

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures.
[b]These bond lengths are average values.
[c]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S6. Calculated Bond Lengths (Å) and Bond Angles (°) for Isomers of $[H\mathbf{B}]^+$ and $[H\mathbf{B}]^0$ [a]

	sym-$[H\mathbf{B}]^+$	*unsym*-$[H\mathbf{B}]^+$	*sym*-$[H\mathbf{B}]^0$	*unsym*-$[H\mathbf{B}]^0$
Ni-Fe	2.699	2.643	2.691	2.665
Fe-H	1.654	1.614	1.638	1.600
Ni-H	1.851	1.723	1.763	1.730
Ni-P [b]	2.208	2.241	2.269	2.237
Ni-S [b]	2.253	2.370	2.374	2.365
Fe-P [b]	2.239	2.244	2.220	2.263
Fe-S [b]	2.322	2.378	2.342	2.368
Fe-C	1.756	1.745	1.755	1.744
P_1-Ni-P_2	87.91	88.11	87.32	87.88
P_3-Fe-P_4	88.00	87.75	87.92	86.96
S_1-Ni-S_2/ P_1-Ni-P_2 [c]	26.79	47.11	124.87	91.09

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures.
[b]These bond lengths are average values.
[c]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

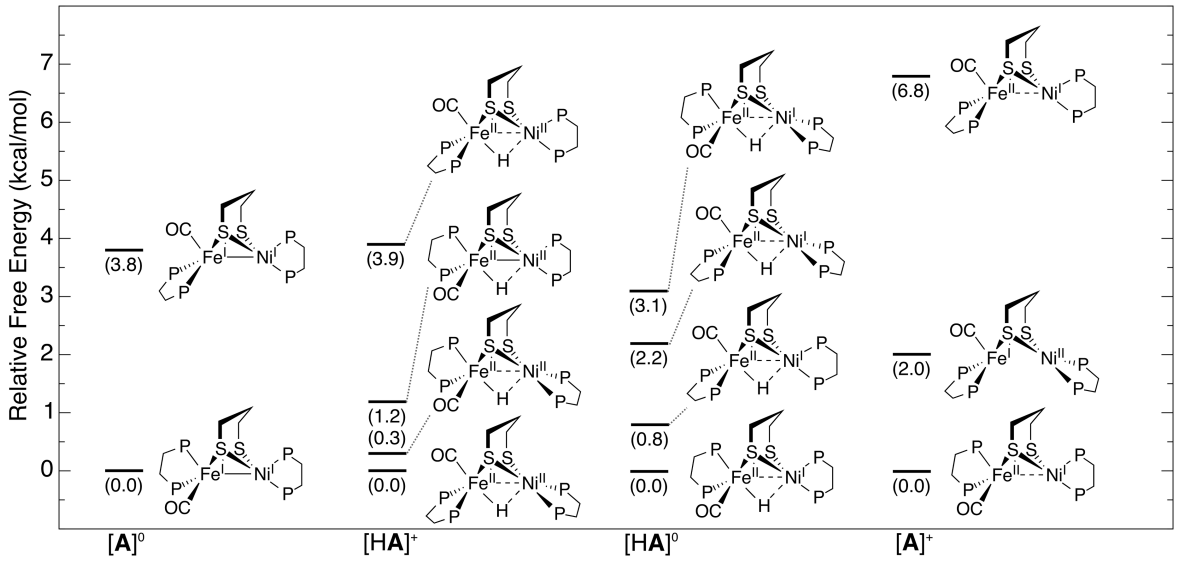


Figure S3. Calculated relative free energies ($\Delta G°$) of **A** in different protonation and redox states as given on the *x*-axis. The free energies are calculated relative to the respective global minimum structure shown at the bottom of each column. The structures and free energies are reported only for the species in which the central CH_2 group of the pdt^{2-} is oriented toward the Ni center, and the Ph groups have been removed in this figure for clarity.

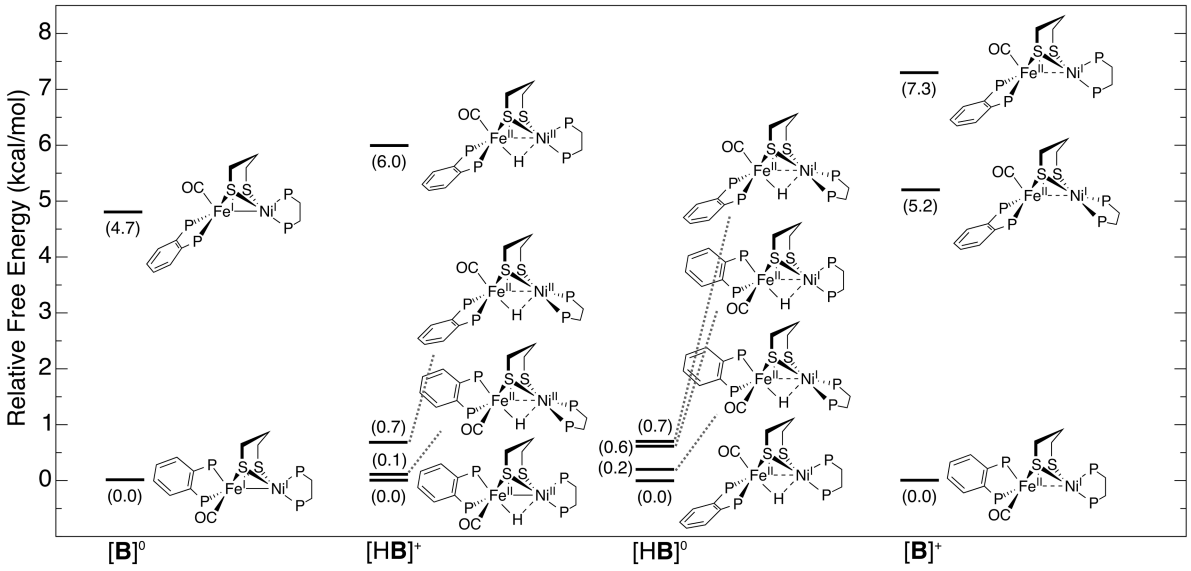


Figure S4. Calculated relative free energies ($\Delta G°$) of **B** in different protonation and redox states as given on the *x*-axis. The free energies are calculated relative to the respective global minimum structure shown at the bottom of each column. The structures and free energies are reported only for the species in which the central CH_2 group of the pdt^{2-} is oriented toward the Ni center, and the Ph groups have been removed in this figure for clarity.

Synthesis of [(dppe)Ni(μ-H)(μ-pdt)Fe(dppe)(CO)]BArF4, [HA]BArF4. In a 250-mL Schlenk tube was dissolved [(dppe)Ni(μ-H)(μ-pdt)Fe(CO)$_3$]BAr$^F_4$ (0.300 g, 0.191 mmol) and dppe (0.080 g, 0.20 mmol) in 120 mL of THF. The solution was photolyzed for 20 h causing the orange solution to darken, which was followed by removal of the solvent in vacuo. The CH_2Cl_2 extract of the red-orange solid was chromatographed on an alumina column, eluting with 6:4 hexanes: CH_2Cl_2. The second band, which was red-orange, contained the product. Evaporation gave a red-orange solid. Yield: 0.135 (37%). Crystals of the symmetric isomer formed upon layering a 10 mL CH_2Cl_2 solution of the product with 10 mL of hexanes at -40 ºC. *Sym* isomer: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ -3.01 (t, $^2J_{PH}$ = 33.2 Hz 1H, Fe(μ-*H)*Ni). ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2): δ 61.03 (s, 2P, Ni*P*), 83.00 (s, 2P, Fe*P*). *Unsym isomer:* ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ -6.34 (t, $^2J_{PH}$ = 37.6 Hz, 1H, Fe(μ-*H)*Ni). ^{31}P{1H} NMR (202.3 MHz, CD_2Cl_2): δ 65.07 (br s, 2P, Ni2*P*), 73.94 (br s, 1P, Fe*P*), 85.47 (s, 1P, Fe*P*). Mixture of isomers: FT-IR (THF): ν_{CO} = 1938 (s), 1954 (sh) cm^{-1}. Anal. Calcd for $C_{88}H_{67}BF_{24}FeNiOP_4S_2$: C, 55.34; H, 3.54. Found: C, 55.51; H, 3.26.

Synthesis of [(dppe)Ni(μ-H)(μ-pdt)Fe(dppbz)(CO)]BArF4, [HB]BArF4. In a 250-mL Schlenk tube was dissolved [(dppe)Ni(μ-H)(μ-pdt)Fe(CO)$_3$]BAr$^F_4$ (0.300 g, 0.191 mmol) and dppbz (0.085 g, 0.191 mmol) in 120 mL of degassed THF. The solution was photolyzed for 5 h causing the orange solution to darken, which was followed by removal of the solvent in vacuo. The CH_2Cl_2 extract of the resulting red-orange solid was chromatographed on a neutral alumina column (1 x 12 cm), eluting with 1:1 hexanes:CH_2Cl_2. The first band, which was red-orange, contained the product, which was obtained as a red-orange solid after evaporation. Yield: 0.251 g (67%). Crystals of the symmetric isomer formed upon layering a 10 mL CH_2Cl_2 solution of the chromatographed product with 10 mL of hexanes at -40 ºC. *Sym* isomer: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.76-7.26 (m, 52 H, Ar), 6.96 (t, J_{PH} = 7.6 Hz, 4H, P(C$_6H_4$)P), 2.67 – 2.40 (m, 4H, P(CH_2)$_2$P), 1.94 (d, J_{HH} = 14.3 Hz, 1H, (SCH$_2$)$_2$CH_2)), 1.67 (d, J_{HH} = 12.4 Hz, 2H, (SCH$_2$)$_2$CH_2)), 1.50 (t, J_{HH} = 12.4 Hz, 2H, (SCH$_2$)$_2$CH_2)), 0.97 (d, J_{HH} = 6.4 Hz, 1H), -3.14 (t, $^2J_{PH}$ = 33.3 Hz, 1H, Fe(μ-*H)*Ni). ^{31}P{1H} NMR (202.3 MHz, CD_2Cl_2): δ 87.1(s, 2P, Fe2*P*), 59.4 (s, 2P, Ni2*P*). *Unsym* isomer: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ -6.01 (t, $^2J_{PH}$ = 36.9 Hz, 1H, Fe(μ-*H)*Ni). ^{31}P{1H} NMR (202.3 MHz, CD_2Cl_2): δ 83.55 (d, J_{PP} = 14.9 Hz, 1P, Fe*P*), 69.45 (d, J_{PP} = 10.3 Hz, 1P, Fe*P*), 65.88 (s, 2P, Ni2*P*). Mixture of isomers: FT-IR (THF): ν_{CO} = 1949 (s), 1935 (m) cm^{-1}. Anal. Calcd. for $C_{92}H_{67}BF_{24}FeNiOP_4S_2 \cdot C_6H_{14}$: C, 57.59; H, 3.99. Found: C, 57.59; H, 4.09.

Calculation of H_2 Production Free Energies

Thermodynamic cycles were used to calculate the free energy of the hydrogen production step in the free energy diagram (Scheme 4 in the main text). The free energy of H_2 elimination from $[H\mathbf{1}]^0$ and CF_3CO_2H acid was calculated using the following cycle:

Reactant		Product	Free Energy
$[H\mathbf{1}]^0$	→	$[H\mathbf{1}]^+ + e^-$	$FE°$
$[H\mathbf{1}]^+$	→	$[\mathbf{1}]^0 + H^+$	$\ln(10)RT\mathrm{p}K_a$
$[\mathbf{1}]^0$	→	$[\mathbf{1}]^+ + e^-$	$FE°$
CF_3CO_2H	→	$CF_3CO_2^- + H^+$	$\ln(10)RT\mathrm{p}K_a$
$2H^+ + 2e^-$	→	H_2	$-2FE°(H^+/H_2)$
$[H\mathbf{1}]^0 + CF_3CO_2H$	→	$[\mathbf{1}]^+ + CF_3CO_2^- + H_2$	$\Delta G°$

In this implementation, the pK_a of CF_3CO_2H is the experimental value in acetonitrile ($\mathrm{p}K_a^{MeCN} = 12.7$)[1] and $E°(H^+/H_2) = -0.14$ V vs. $Fc^{0/+}$ is the chosen value for the experimental potential for the normal hydrogen electrode in acetonitrile.[2-5] Other experimental estimates of the $E°(H^+/H_2)$ potential range from –0.80 to –0.50 V vs. $Fc^{0/+}$.[1,6,7] Since the $E°$ for the $[\mathbf{1}]^{+/0}$ was not calculated, the experimental value of –0.93 V vs. $Fc^{0/+}$ was used.

The free energy of H_2 self-elimination from $[H_2\mathbf{1}]^+$ was calculated using the following thermodynamic cycle:

Reactant		Product	Free Energy
$[H_2\mathbf{1}]^+$	→	$[H\mathbf{1}]^0 + H^+$	$\ln(10)RT\mathrm{p}K_a$
$[H\mathbf{1}]^0$	→	$[H\mathbf{1}]^+ + e^-$	$FE°$
$[H\mathbf{1}]^+$	→	$[\mathbf{1}]^0 + H^+$	$\ln(10)RT\mathrm{p}K_a$
$[\mathbf{1}]^0$	→	$[\mathbf{1}]^+ + e^-$	$FE°$
$2H^+ + 2e^-$	→	H_2	$-2FE°(H^+/H_2)$
$[H_2\mathbf{1}]^+$	→	$[\mathbf{1}]^+ + H_2$	$\Delta G°$

The free energy diagram in Scheme 4 can also be calculated with respect to the HA/H_2 couple in acetonitrile: $HA + e^- \rightarrow \frac{1}{2}H_2 + A^-$, where HA is CF_3CO_2H acid ($\mathrm{p}K_a^{MeCN} = 12.7$).

$$E^\circ_{HA/H_2} = E^\circ_{H^+/H_2} - 0.059\mathrm{p}K_a(CF_3CO_2H) = -0.89 \text{ V vs. } Fc^{0/+}$$

The free energies calculated using this reference are depicted in Figure S5.

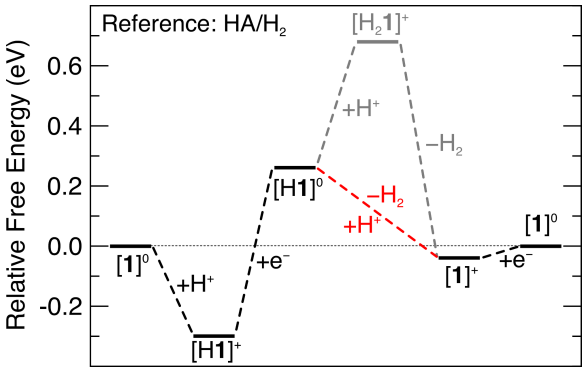


Figure S5. Proposed reaction pathway and corresponding relative free energies for hydrogen evolution catalyzed by **1**. The free energies are calculated with CF_3CO_2H acid (pK_a^{MeCN} = 12.7) and with respect to the HA/H_2 couple in acetonitrile (–0.89 V vs. $Fc^{0/+}$). H_2 evolution is proposed to occur directly from interaction of $[H\mathbf{1}]^0$ and CF_3CO_2H acid under these conditions (red pathway). Protonation of $[H\mathbf{1}]^0$ to form an intermediate dihydrogen complex, $[H_2\mathbf{1}]^+$ (gray pathway) is more thermodynamically favorable when stronger acids are used. In the last step, an alternative mechanism for reduction of $[\mathbf{1}]^+$ by $[H\mathbf{1}]^0$ could also occur under certain experimental conditions. The structures are shown in Scheme 4.

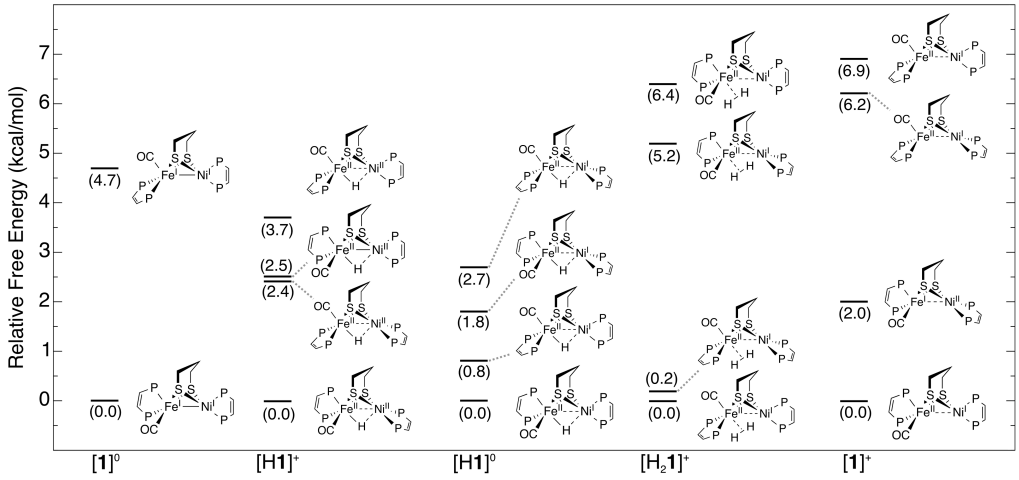


Figure S6. Calculated relative free energies ($\Delta G°$) of **1** in different protonation and redox states as given on the *x*-axis. The free energies are calculated relative to the respective global minimum structure shown at the bottom of each column. The structures and free energies are reported only for the species in which the central CH_2 group of the pdt^{2-} is oriented toward the Ni center, and the Ph groups have been removed in this figure for clarity.

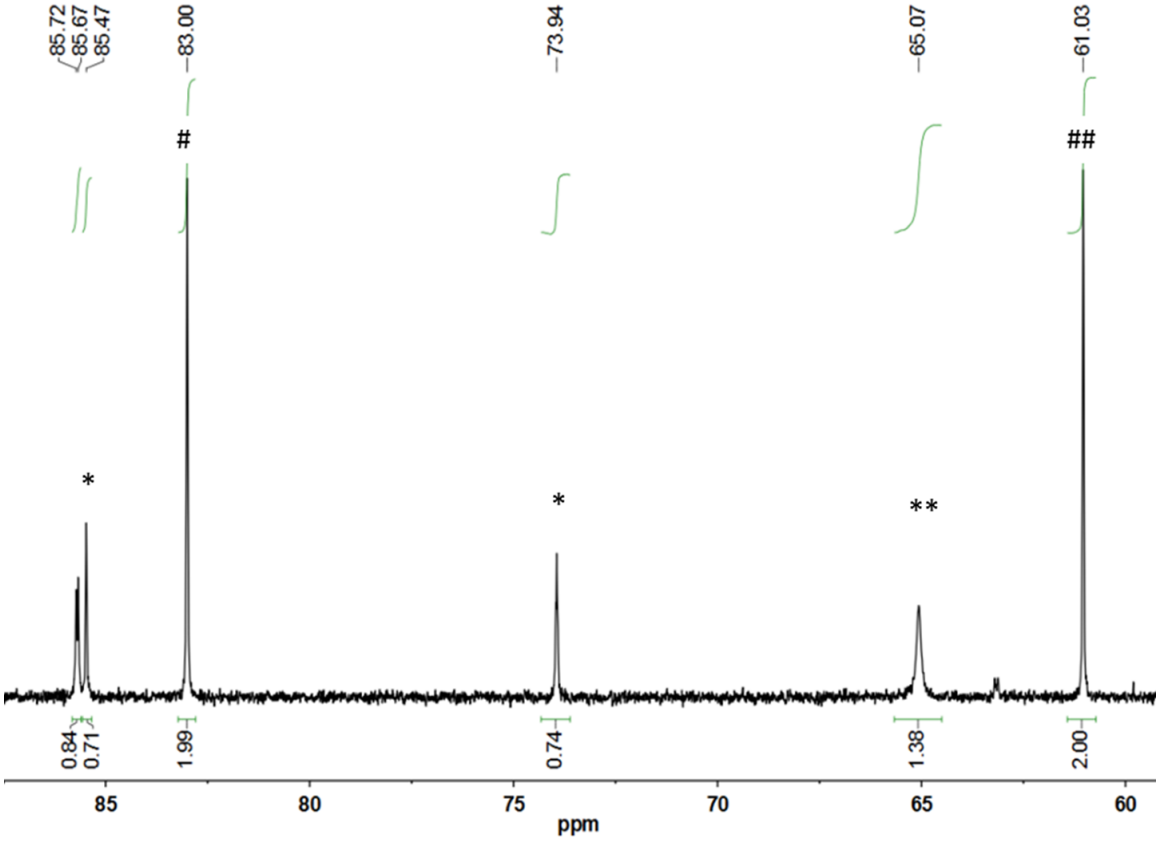


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, CD_2Cl_2, 20 °C) of [(dppe)Ni^{II}(μ-H)(μ-pdt)Fe^{II}(dppe)(CO)]BAr^F_4 ([H**A**]BAr^F_4). # and * refer to Fe(dppe) signals for symmetrical and unsymmetrical isomer respectively. ## and ** refer to Ni(dppe) signals for symmetrical and unsymmetrical isomer respectively. Doublet at 85.67 ppm corresponds to unknown complex.

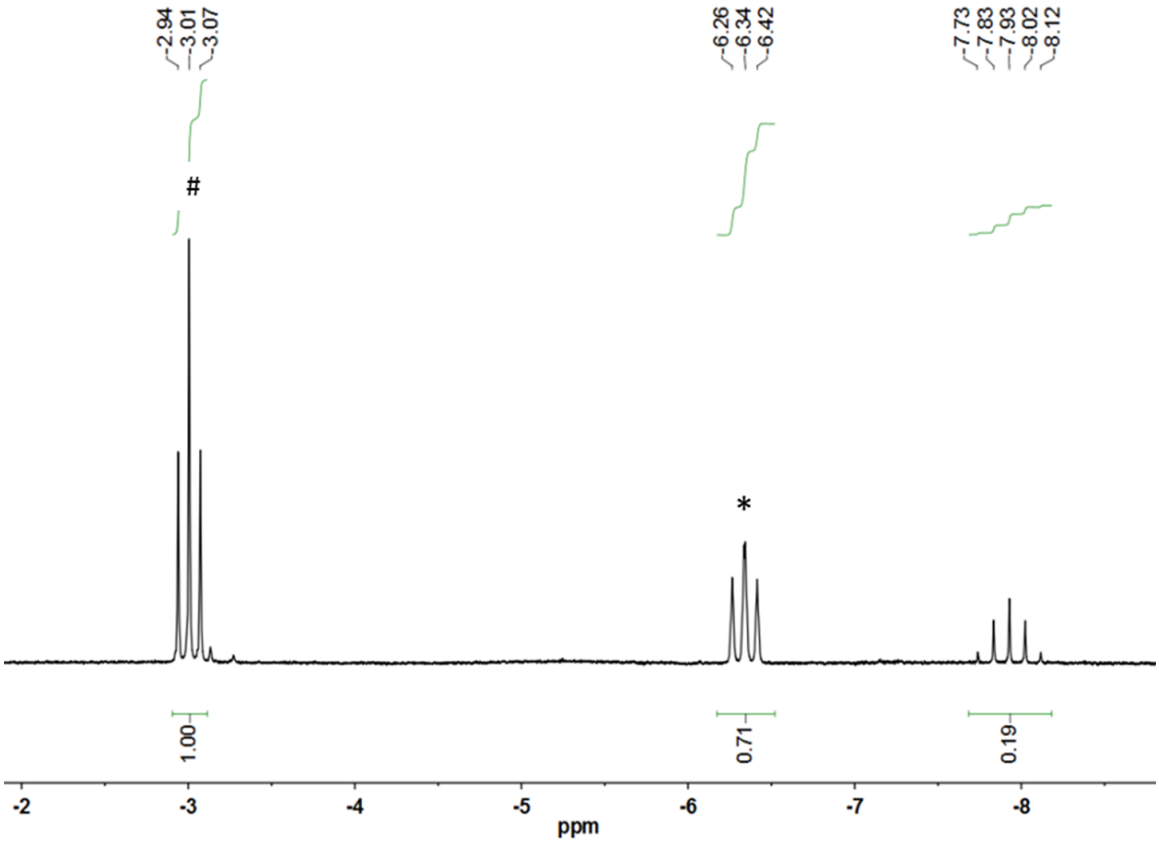


Figure S8. High-field ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 20 °C) of [(dppe)Ni^{II}(μ-H)(μ-pdt)Fe^{II}(dppe)(CO)]BAr$^{F}_{4}$ ([H**A**]BAr$^{F}_{4}$). # and * refer to symmetrical and unsymmetrical isomer respectively. Multiple at 7.93 ppm correspond to unknown complex.

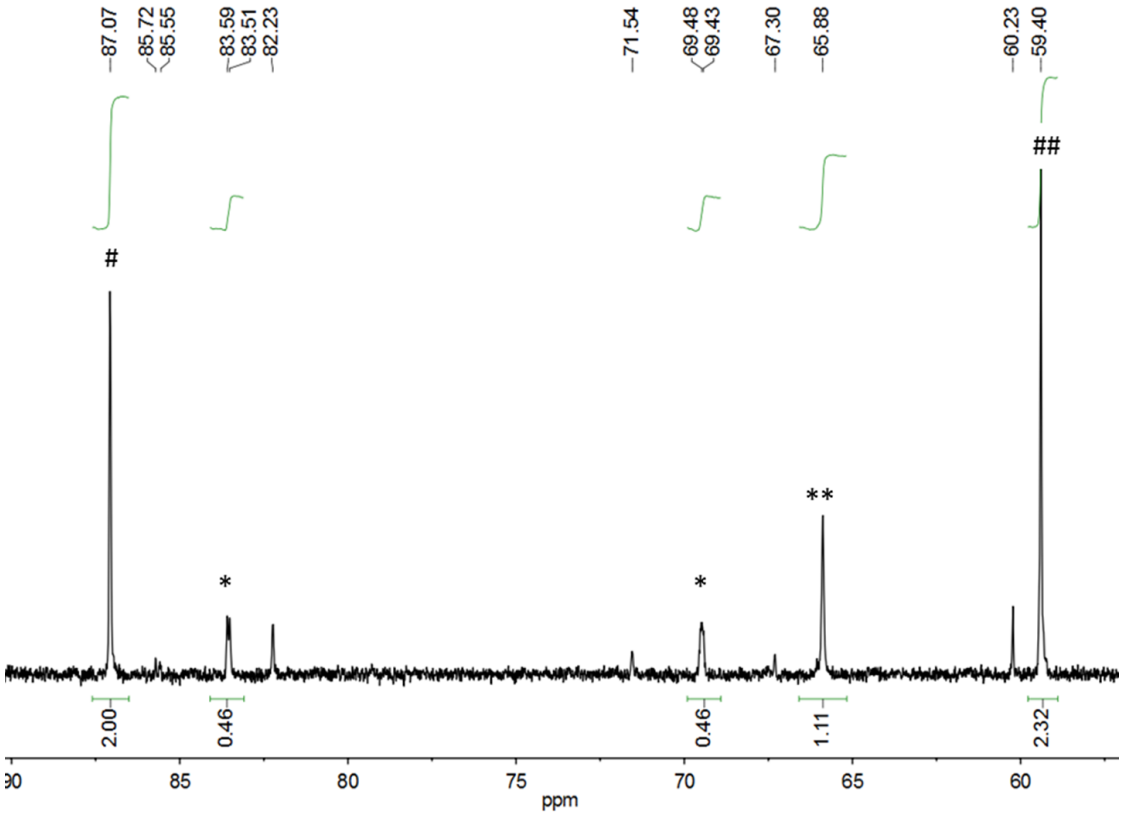


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, CD_2Cl_2) of [(dppe)Ni^{II}(μ-H)(μ-pdt)Fe^{II}(dppbz)(CO)]BAr^{F}_{4} ([H**B**]BAr^{F}_{4}). # and * refer to Fe(dppBz) signals for symmetrical and unsymmetrical isomer respectively. ## and ** refer to Ni(dppe) signals for symmetrical and unsymmetrical isomer respectively. The signals at 85.72-85.55, 82.23, 71.54, 67.30, and 60.23 are proposed to be isomers containing Ni(dppbz) and Fe(dppe) moieties.

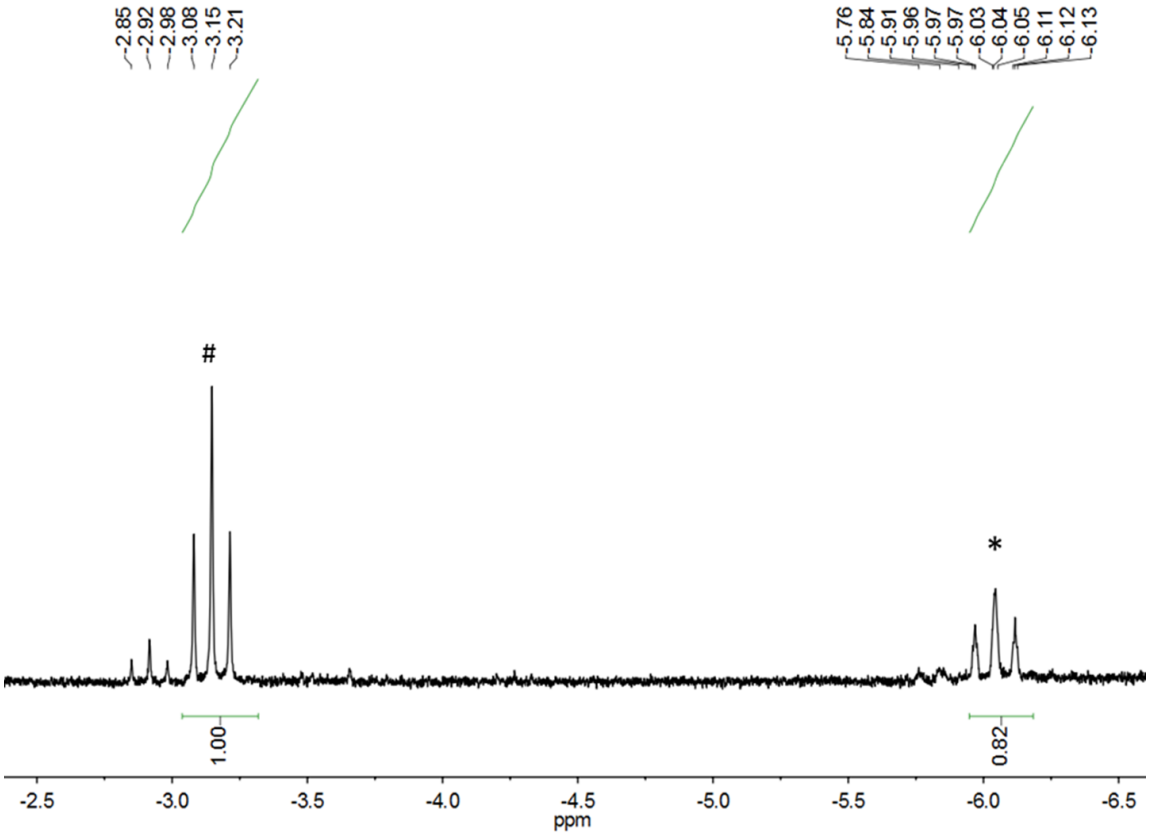


Figure S10. High-field ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of [(dppe)Ni^{II}(μ-H)(μ-pdt)Fe^{II}(dppbz)(CO)]BAr$^{F}_{4}$ ([H**B**]BAr$^{F}_{4}$). # and * refer to symmetrical and unsymmetrical isomer respectively. The signals at –2.92 and –5.9 are proposed to be isomers containing Ni(dppbz) and Fe(dppe) moieties.

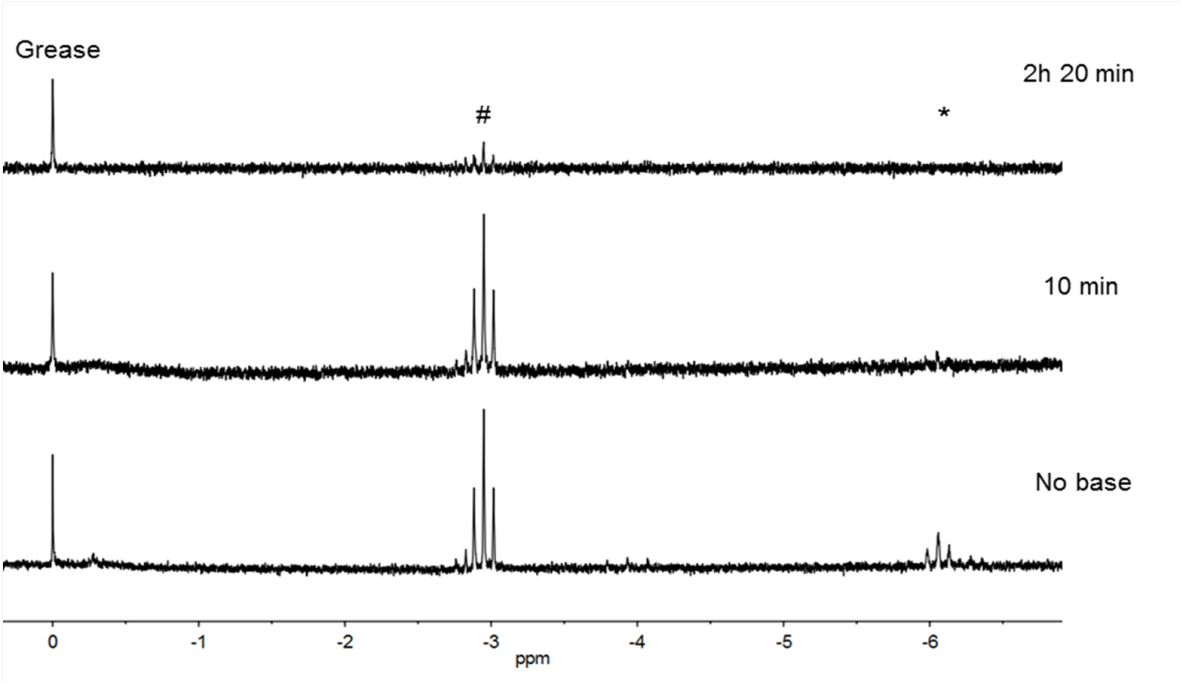


Figure S11. ^{1}H NMR spectrum (500 MHz, CD_3OD) of [(dppe)Ni^{II}(μ-H)(μ-pdt)Fe^{II}(dppbz)(CO) BAr^{F}_{4} ([H**B**]BAr^{F}_{4}) in the absence and presence of 4 equiv of $KO^{t}Bu$. The spectra are referenced to the signal for silicone grease. # and * refer to symmetrical and unsymmetrical isomer respectively.

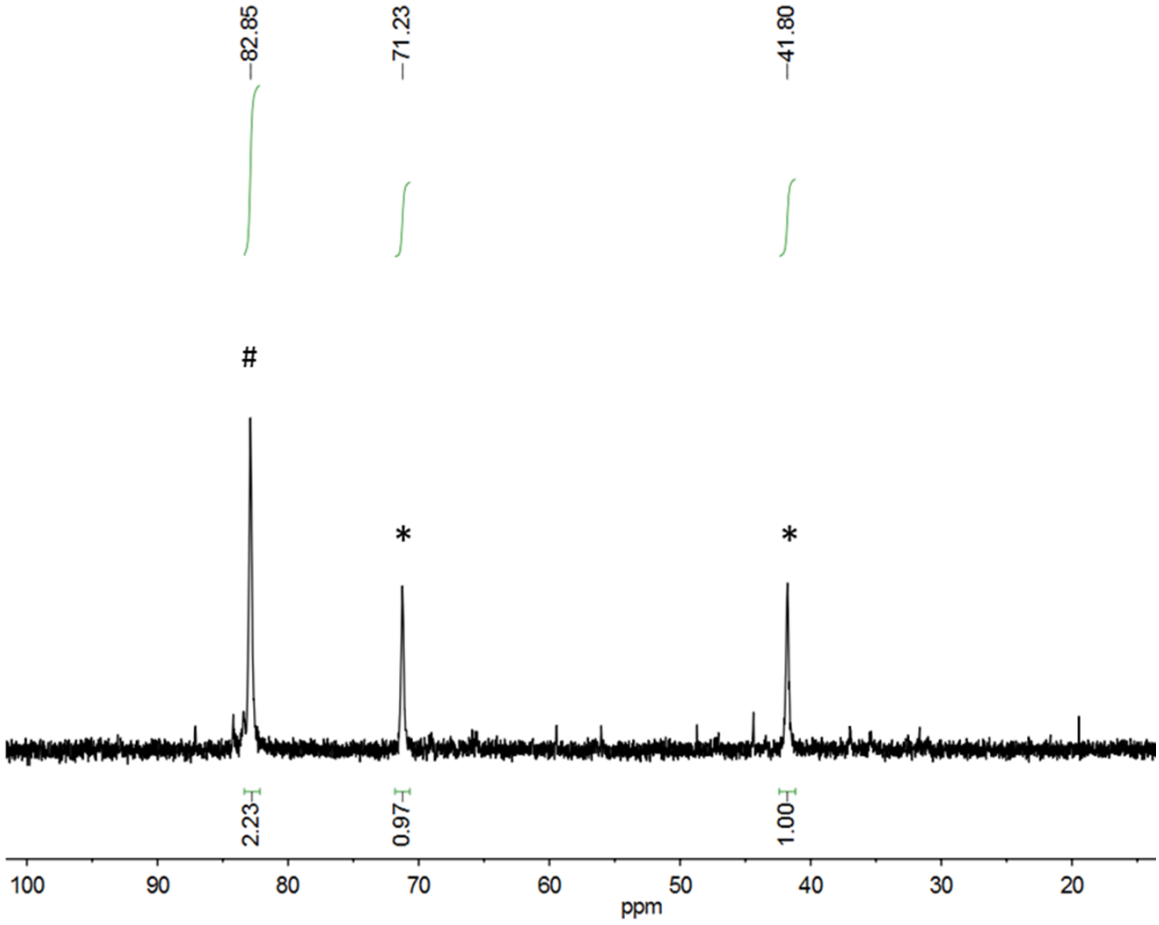


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, CD_2Cl_2) of $[\mathbf{B}]^0$.

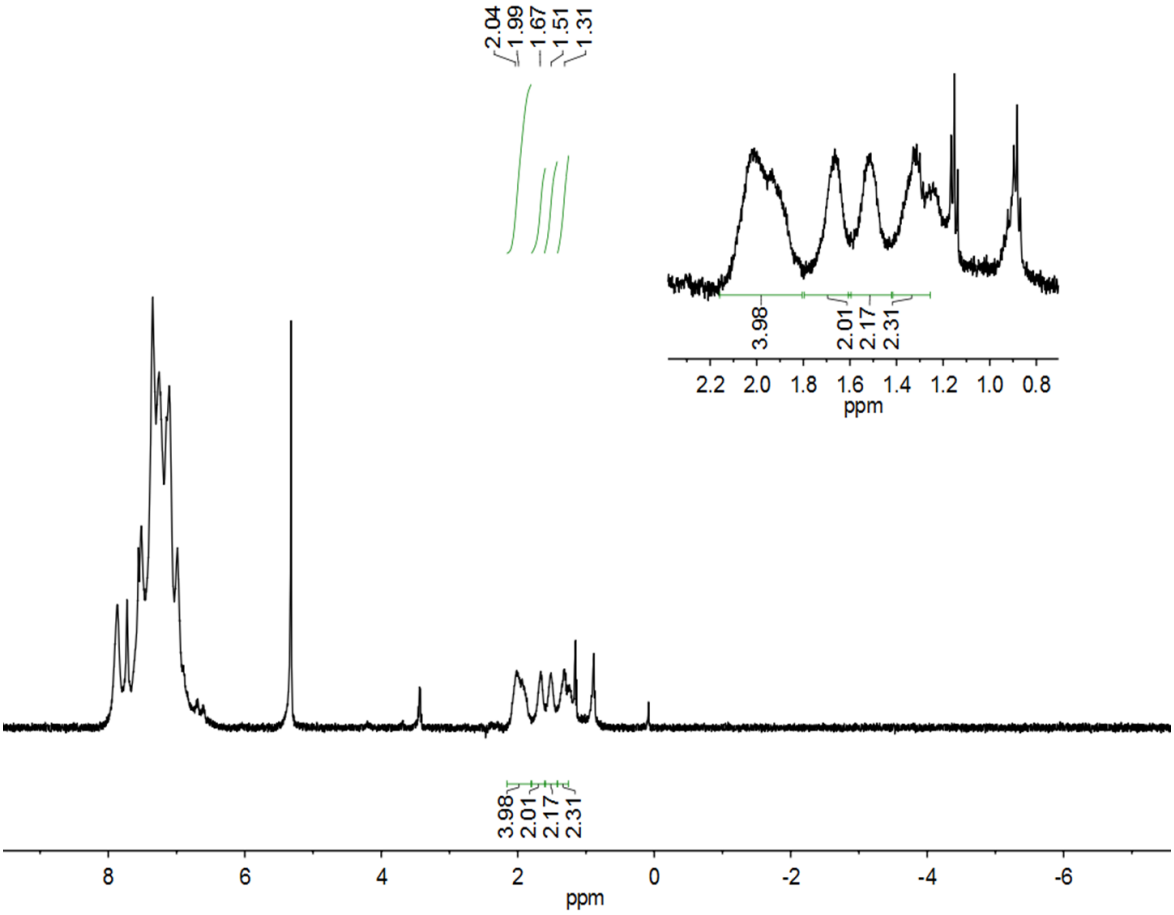


Figure S13. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of $[\mathbf{B}]^0$.

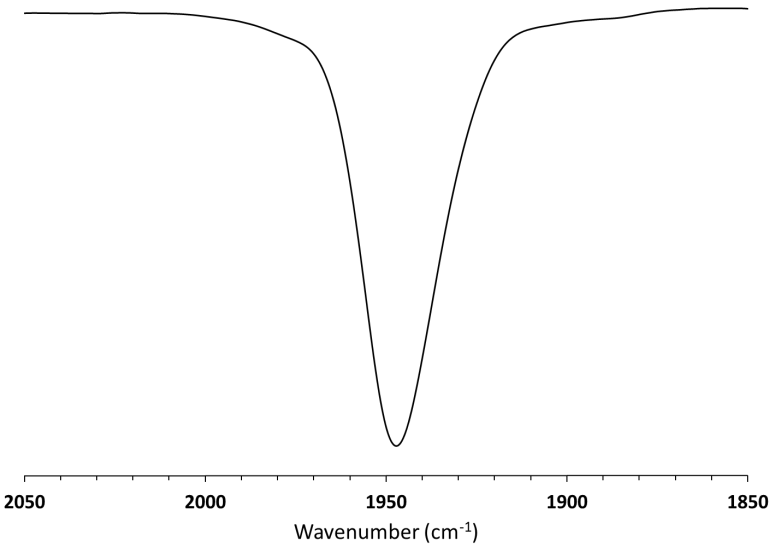


Figure S14. FT-IR spectrum of [Cl**1**]BF_4.

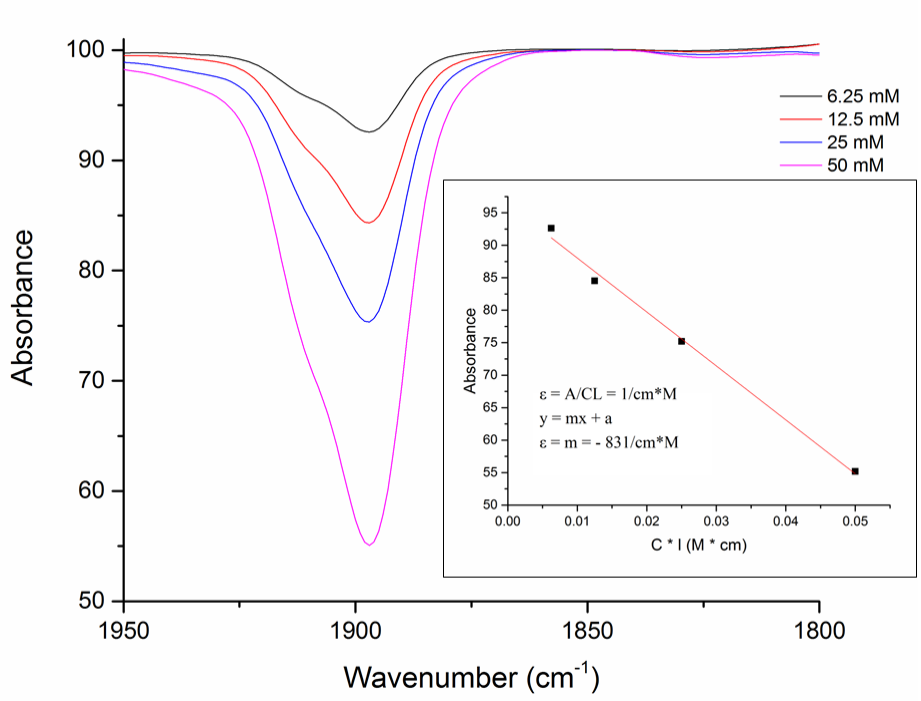


Figure S15. FT-IR of $[\mathbf{1}]^0$ in THF at various concentrations at 26 °C. *Insert:* calibration curve of $[\mathbf{1}]^0$, ε = absorption coefficient.

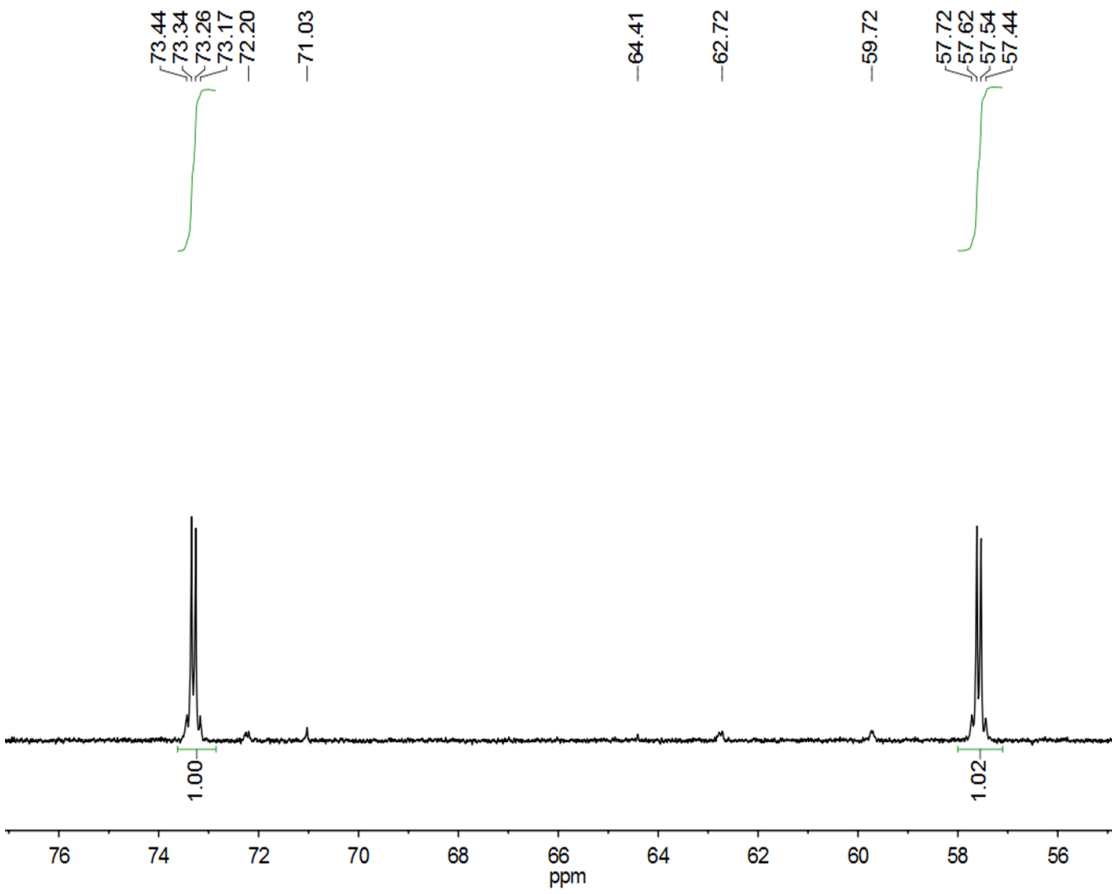


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, CD_2Cl_2) of [Cl**1**]BF_4.

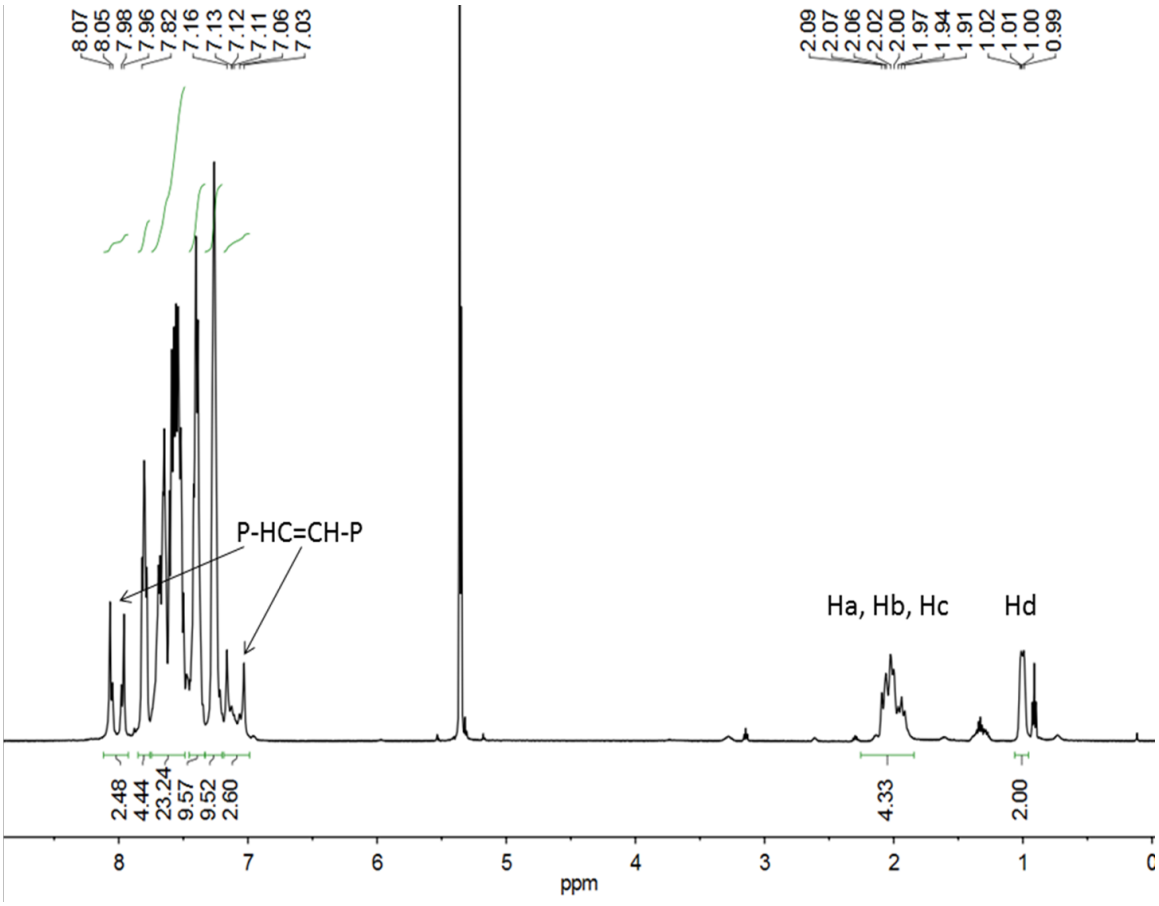


Figure S17. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of [Cl**1**]BF_4.

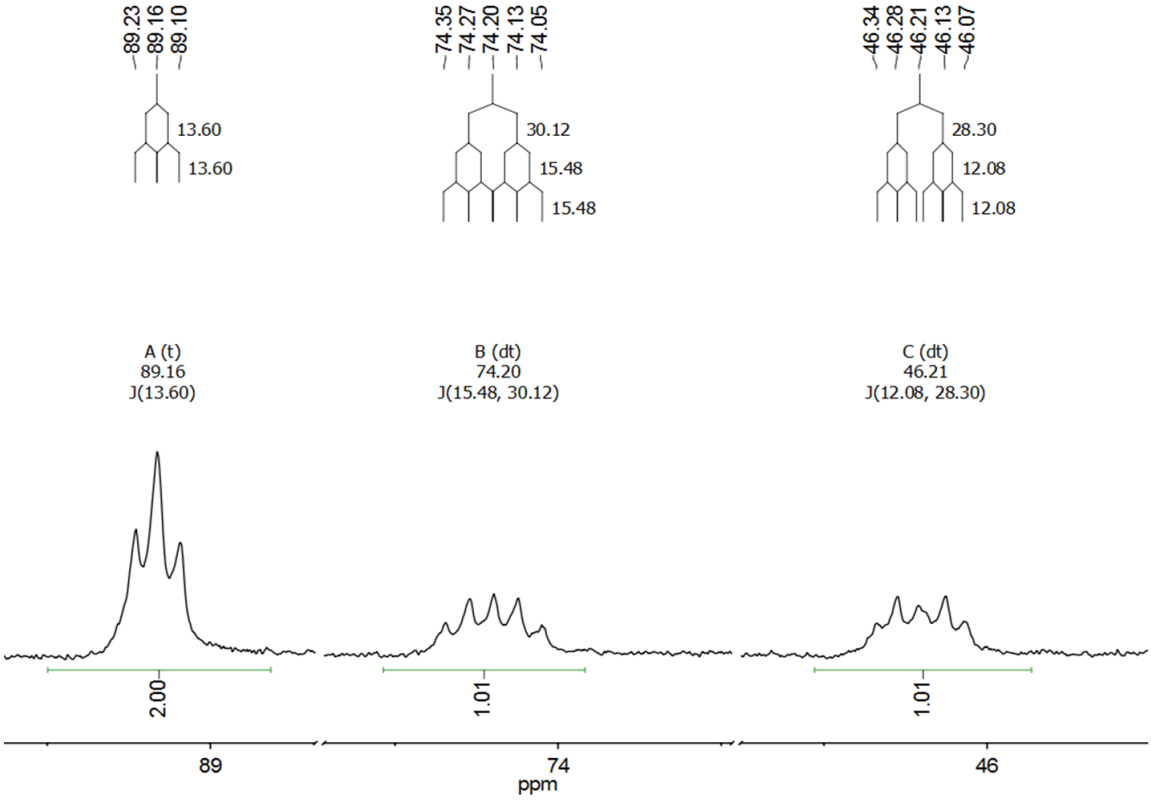


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, C_6D_6) of $[\mathbf{1}]^0$ at 20 ºC.

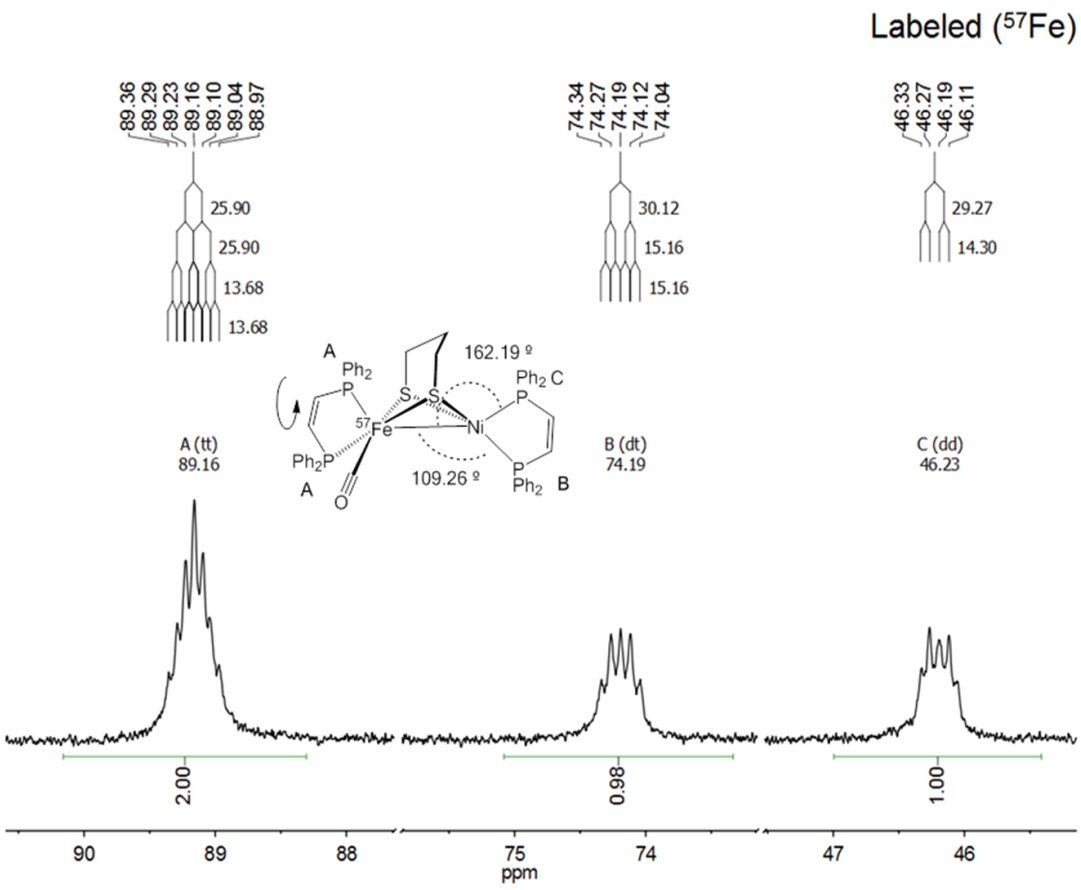


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, C_6D_6) of ^{57}Fe labeled $[\mathbf{1}]^0$ at 20 ºC.

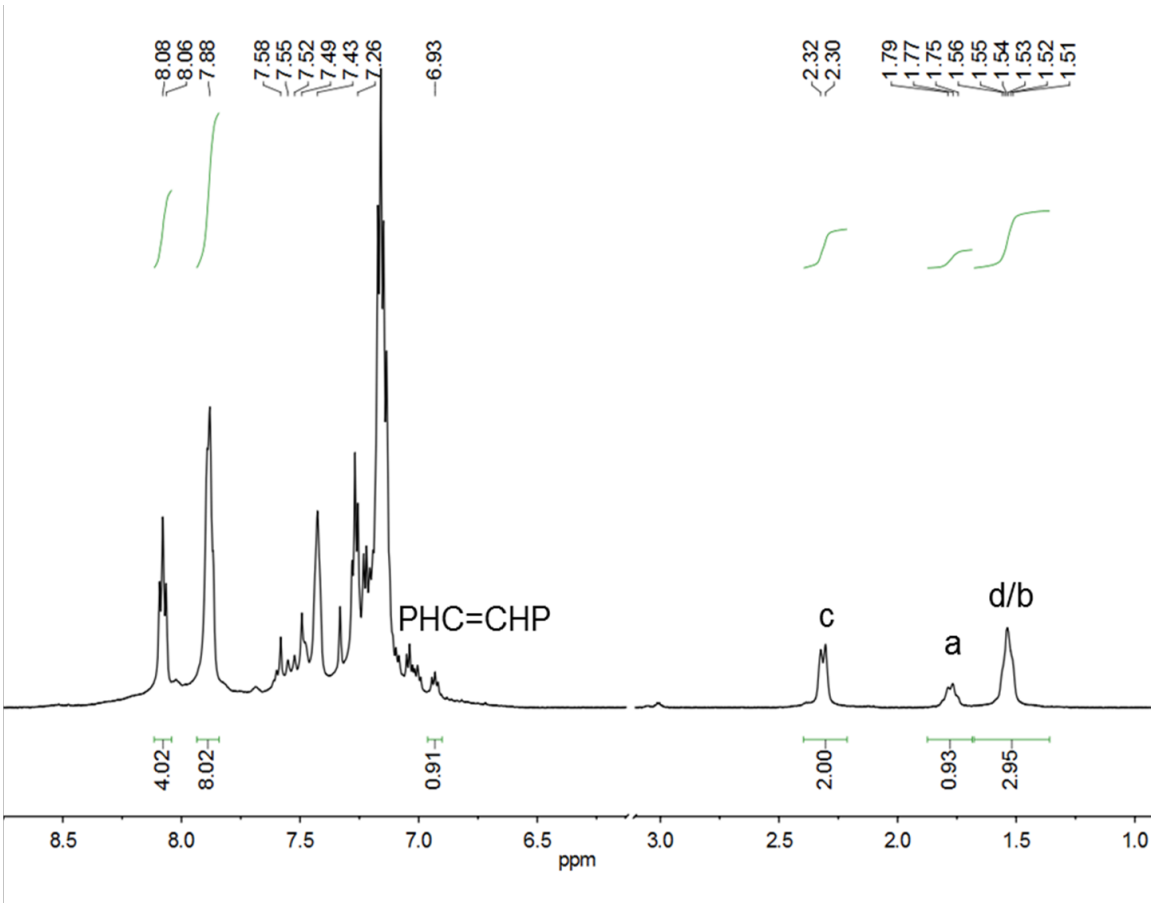


Figure S20. ^{1}H NMR spectrum (500 MHz, C_6D_6) of $[\mathbf{1}]^0$ at 20 ºC.

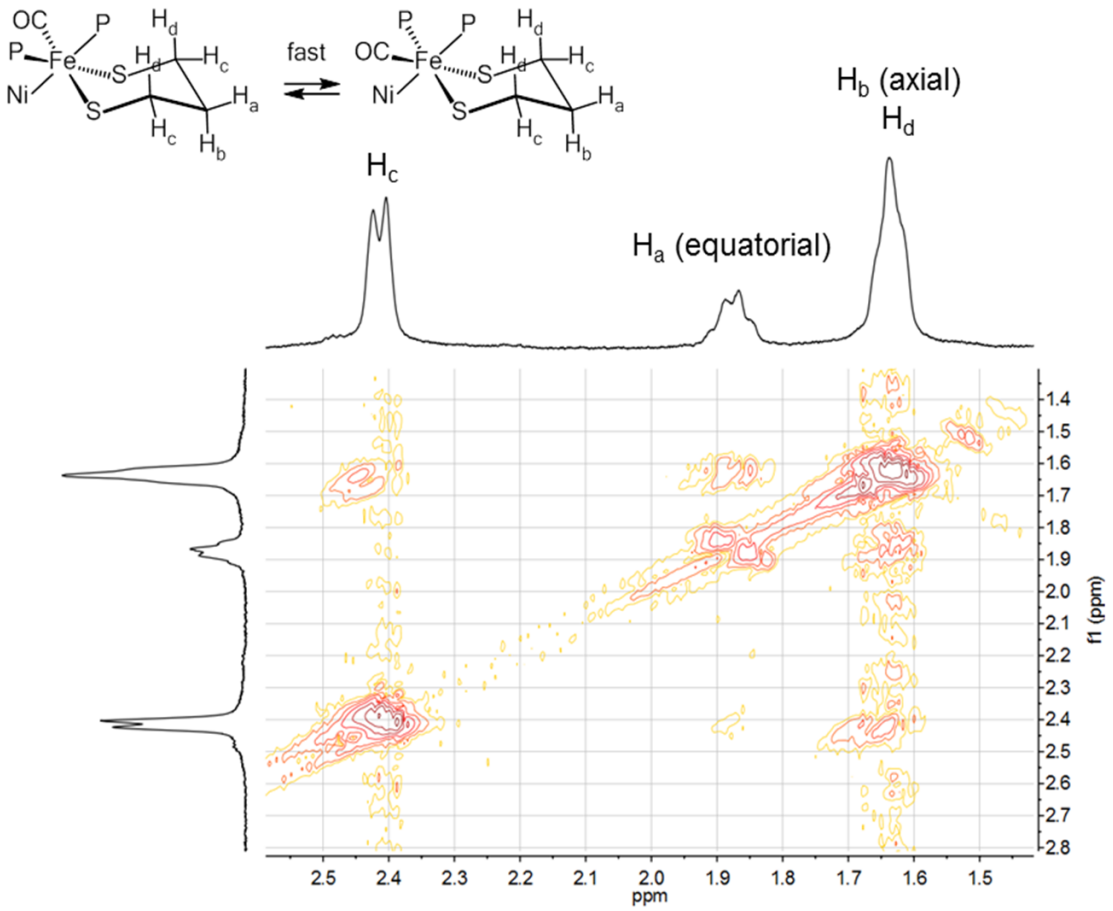


Figure S21. ^{1}H-^{1}H COSY NMR spectrum of [**1**]^{0} in C_6D_6 at 20 ºC.

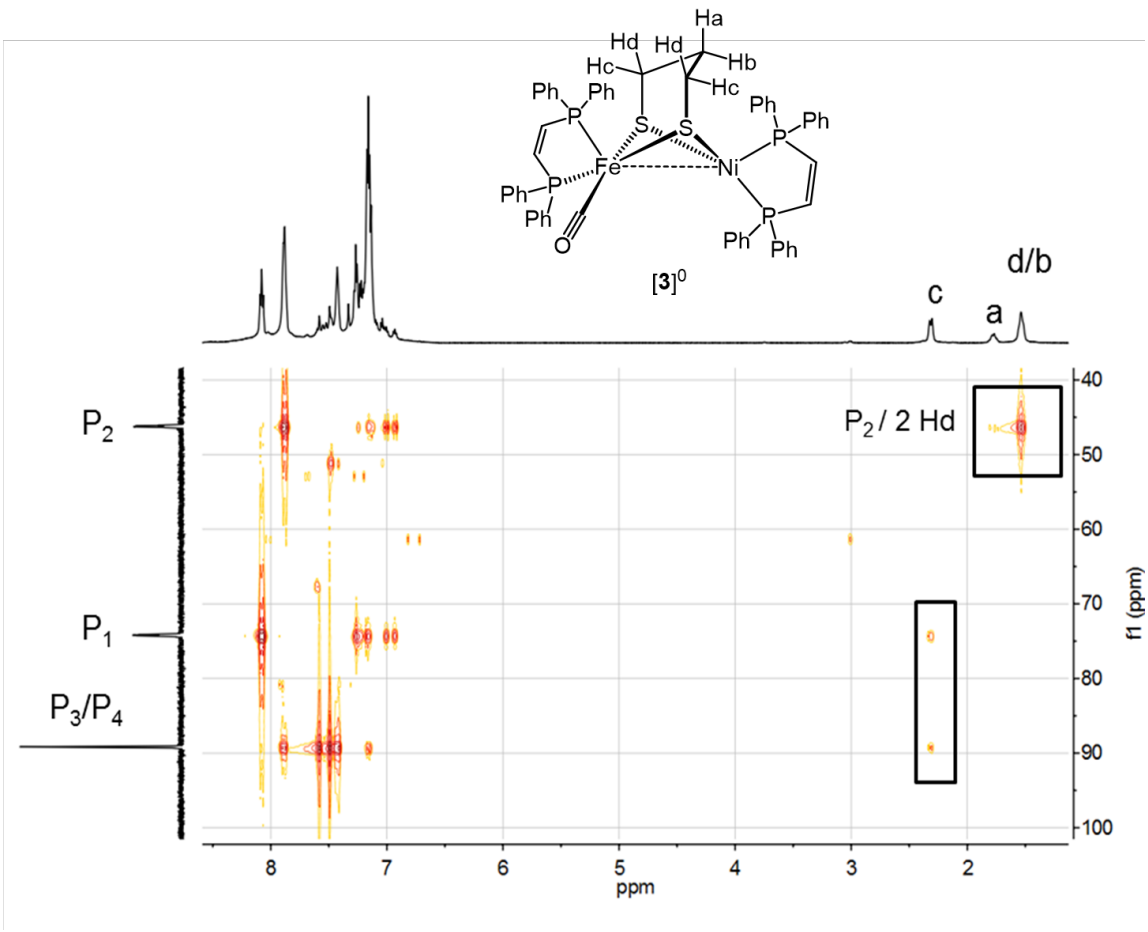


Figure S22. ^{1}H-^{31}P gHMBC NMR spectrum of $[\mathbf{1}]^{0}$ in C_6D_6 at 20 ºC.

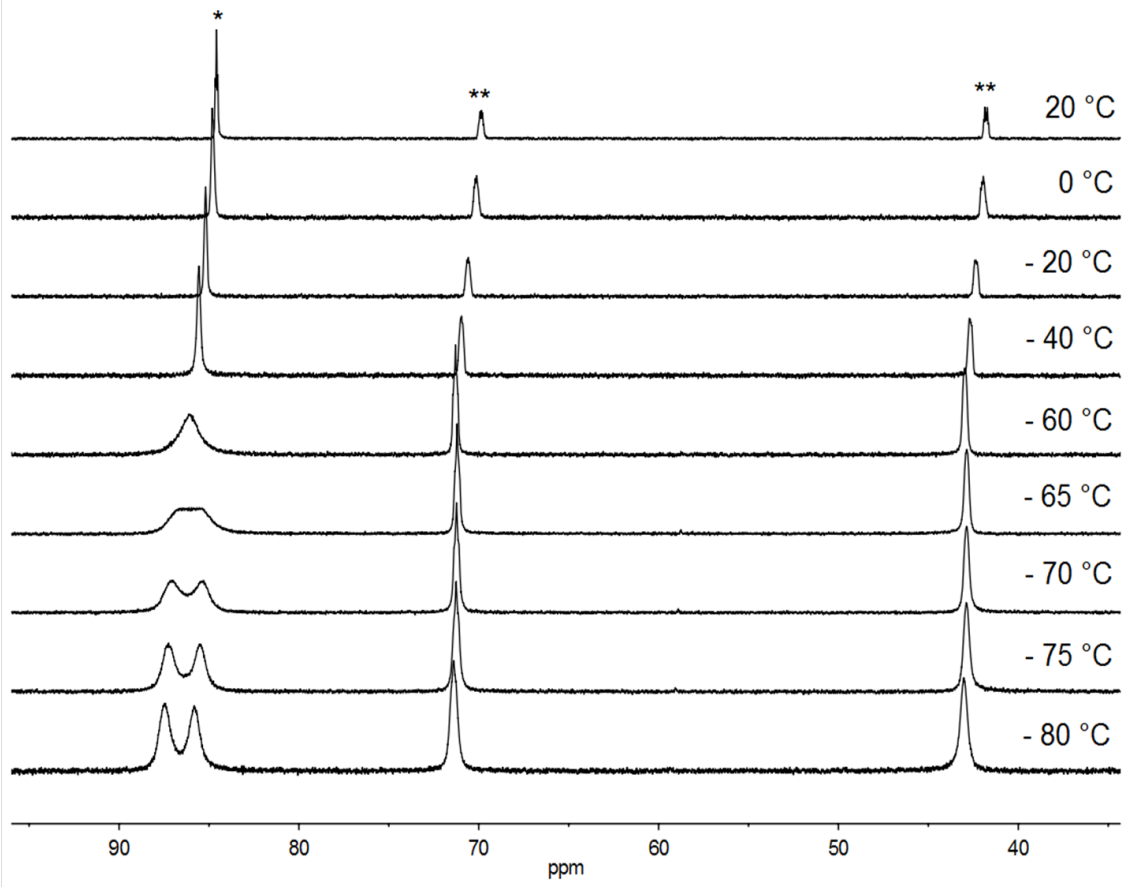


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, toluene-d_8) of $[\mathbf{1}]^0$ at various temperatures. Signals labeled * and ** are assigned to the Fe(dppv) and Ni(dppv) sites, respectively. The two ^{31}P NMR signals assigned to the Ni(dppv) site in $[\mathbf{1}]^0$ are observed even up to 90 ºC, indicating a barrier to rotation at Ni of > 15 kcal/mol. The non-coalesced signals are separated by 5700 Hz or (28 ppm at 202 Hz/ppm), rate of rotation at this Ni center is thus slower than 11,400 Hz. At 363 K, the following arithmetic applies:

Calculation of lower limit for the activation barrier for isomerization of the phosphines on the Ni site in $[1]^0$.

The two ^{31}P signals are separated by 28 ppm at 90 ºC.

28 ppm x 202 MHz = 5700 Hz

at coalescence $k_c = \pi\Delta\nu/\sqrt{2}$,

$\Delta\nu$ =(Δppm)(202 MHz/ppm)

k_c = (3.14)(5700)/(1.41) < 12700 s^{-1}

rate = $(k_B T/h)e^{-\Delta G^*/RT} = k^* e^{-\Delta G^*/RT}$

Solving for ΔG*:

ΔG* = $-RT^*\ln(\text{rate}/k^*)$ > 14.5 kcal/mol

Calculation of activation barrier for isomerization of the Fe site in $[1]^0$.

The two ^{31}P signals are separated by 1.5 ppm in slow exchange limit.

1.5 ppm x 202 MHz = 303 Hz

at coalescence $k_c = \pi\Delta\nu/\sqrt{2}$,

k_c = (3.14)(303)/(1.41) = 674 s^{-1}

Solving ΔG* = –RT*ln(rate/k*) = 9.5 kcal/mol

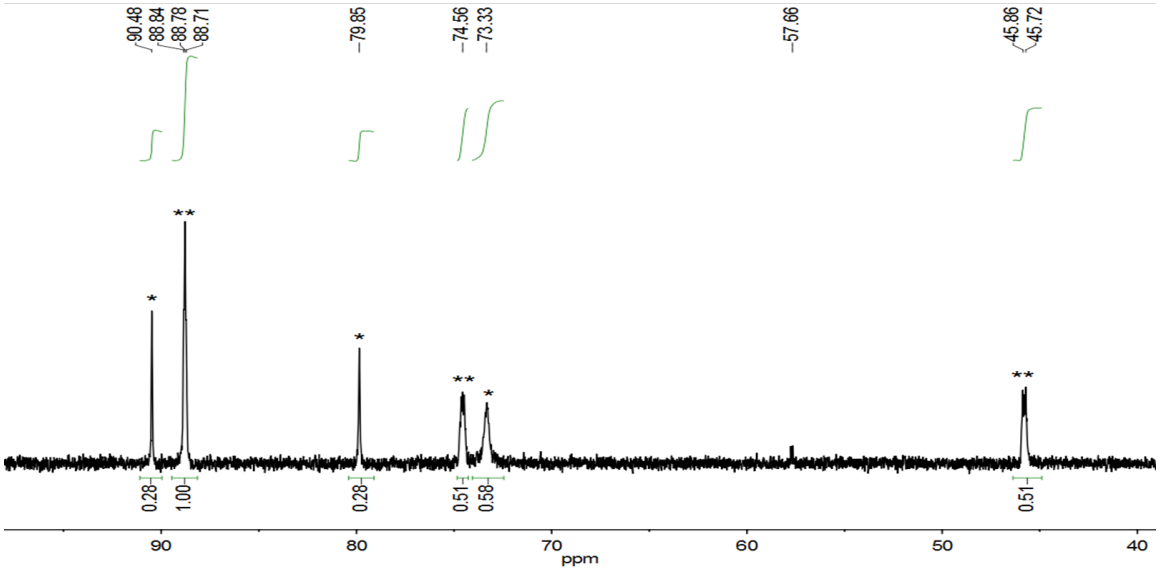


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, benzonitrile) of mixture of $[\mathbf{1}]^{0}$** and $[H\mathbf{1}]^{+}$* used to determine p*K*a.

Table S7. Determination of pK_a of $[\mathbf{1}]^{0}$ ($[H\mathbf{1}]^{+}$) using HOAc in PhCN.

Experiment number	Initial $[\mathbf{1}]^{0}$ (mg, μmol)	Total Volume (mL)	Added HOAc (μmol)	Final $[\mathbf{1}]^{0}$ /$[H3]^{+}$	pK_a Calcd.
1	5.0, 4.8	0.75	24	1.67	16.64
2	5.0, 4.8	0.75	23	0.98	16.65
3	5.1, 4.89	0.75	24.5	1.78	16.65
4	5.0, 4.8	0.75	33.6	0.384	16.60
5	5.1, 4.89	0.75	34.3	0.877	16.72

Numerical analysis method (contributed by Dr. David Schilter) using homoconjugating acid. Done for $[\mathbf{1}]^{0}$ ($[H\mathbf{1}]^{+}$) in PhCN by protonation with CH_3CO_2H .

M = **1**, MH^+ = $[H\mathbf{1}]^{+}$, HA = CH_3CO_2H, A^- = $CH_3CO_2^-$

"HA_{added}" = $[A^-]_{total} \neq [HA]$

$M + HA \rightleftharpoons MH^+ + A^-$: K_{eq} = unknown equilibrium constant

$MH^+ \rightleftharpoons M + H^+$: $K_a(MH^+)$ = unknown metal-hydride dissociation constant

$HA \rightleftharpoons H^+ + A^-$: $K_a(HA)$ = known acid dissociation constant = 21.56 for CH_3CO_2H in MeCN[8]

$HA + A^- \rightleftharpoons AHA^-$: $K_f(HA)$ = known acid homoconjugation constant = 3.21 for CH_3CO_2H in MeCN[8]

1. Add a known amount of acid HA to a known amount of M. Determine $[MH^+]$ and [M] by FT-IR or NMR with an internal standard.

2. Find $[A^-]$ according to the relationship derived from reference (equation 4)[9]:
   $[A^-]^2 + \{[A^-]_{total} - 2[MH^+] + 1/K_f(HA)\}[A^-] - [MH]/K_f(HA) = 0$
   ("HA_{added}" = $[A^-]_{total}$)
   Solving quadratically, one obtains:
   $[A^-] = \{\{\{[A^-]_{total} - 2[MH^+] + 1/K_f(HA)\}^2 + 4[MH^+]/K_f(HA)\}^{1/2} - \{[A^-]_{total} - 2[MH^+] + 1/K_f(HA)\}\}/2$
3. Find $[AHA^-]$ using the mass balance on $[A^-]$:
   $[A^-]_{total} = [A^-] + [HA] + 2[AHA^-]$
   But we don't directly know [HA]. What we DO know is that the $[H^+]$ from reacted [HA] formed either $[MH^+]$ or $[AHA^-]$ (mass balance on $[H^+]$)
   $[MH^+] + [AHA^-] = [A^-]_{total} - [HA]$ and $[HA] = [A^-]_{total} - [MH^+] - [AHA^-]$
   Substituting this expression for [HA] into the mass balance above:
   $[AHA^-] = [MH^+] - [A^-]$
4. Find [HA] from the mass balance:
   $[HA] = [A^-]_{total} - [A^-] - 2[AHA^-]$
5. Compute K_{eq}, $K_{eq} = [A^-][MH^+]/[HA][M]$ and pK_{eq}
6. Find the desired, $pK_a(MH^+)$ from $pK_a(MH^+) = pK_a(HA) - pK_{eq}$

Table S8. Summary of kinetics data for exponential decay of *unsym*-[H**1**]$^+$ and exponential growth of *sym*-[H**1**]$^+$.

Run # (acid used)	**Temp (°C)**	k_{obs} **(s^{-1})**
Run A (HOTf)	22.7	
unsym		-3.04×10^{-4}
sym		2.76×10^{-4}
Run B ($HBAr^F_4 \cdot 2Et_2O$)	26.5	
unsym		-3.10×10^{-4}
sym		3.10×10^{-4}
Run C ($HBAr^F_4 \cdot 2Et_2O$)	24.0	
unsym		-3.34×10^{-4}
sym		3.34×10^{-4}
Average (absolute)		$\mathbf{3.11 \times 10^{-4}}$
stdev		$\mathbf{\pm 1.98 \times 10^{-5}}$

Calculation of the rate constant, k_1, for the isomerization of *unsym*-[H1]$^+$ to *sym*-[H1]$^+$

$$k_{obs} = k_1 + k_{-1}$$

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{1}{5} \; in \; MeCN$$

$$k_{-1} = 5k_1$$

$$k_{obs} = 6k_1$$

$$k_1 = 3.11\ x\ 10^{-4}/6$$

$$k_1 = 5.2\ x\ 10^{-5}\ s^{-1}$$

$$k_{-1} = 2.6\ x\ 10^{-4}\ s^{-1}$$

Calculation of the activation barrier for the isomerization of *unsym*-[H1]$^+$ to *sym*-[H1]$^+$

$$\frac{kh}{k_B T} = e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta G^{\ddagger}}{RT}$$

$$\Delta G^{\ddagger} = -RT \ln\left(\frac{kh}{k_B T}\right)$$

$R = 1.987 \times 10^{-3}$ kcal mol^{-1} K^{-1}

$h = 1.584 \times 10^{-37}$ kcal mol^{-1} s

$k_B = 3.3 \times 10^{-27}$ kcal mol^{-1} K^{-1}

$T = 298$ K

$k = 5.2 \times 10^{-5}$ s^{-1}

$$\Delta G^{\ddagger} = -(1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \ln\left(\frac{(5.2 \times 10^{-5}\ \text{s}^{-1})(1.584 \times 10^{-37}\ \text{kcal mol}^{-1}\text{s})}{(3.3 \times 10^{-27}\ \text{kcal mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}\right)$$

$$\Delta G^{\ddagger} = 23\ \text{kcal mol}^{-1}$$

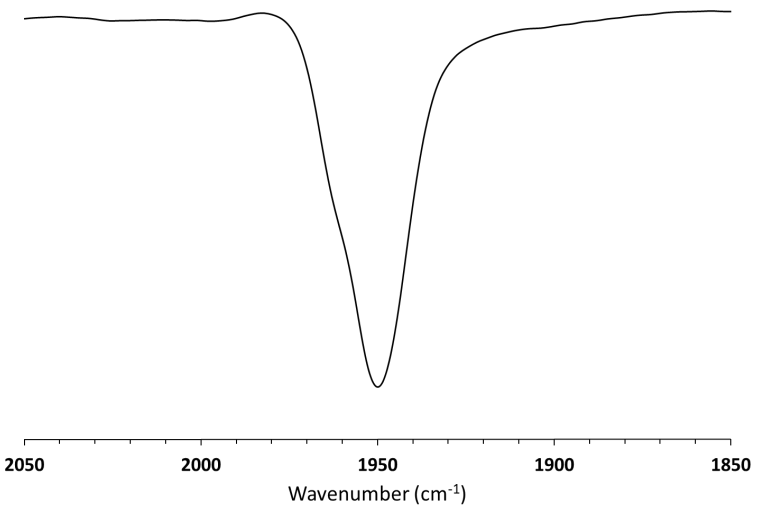


Figure S25. FT-IR spectrum of a thermally equilibrated solution of [H**1**]BF_4 in CH_2Cl_2.

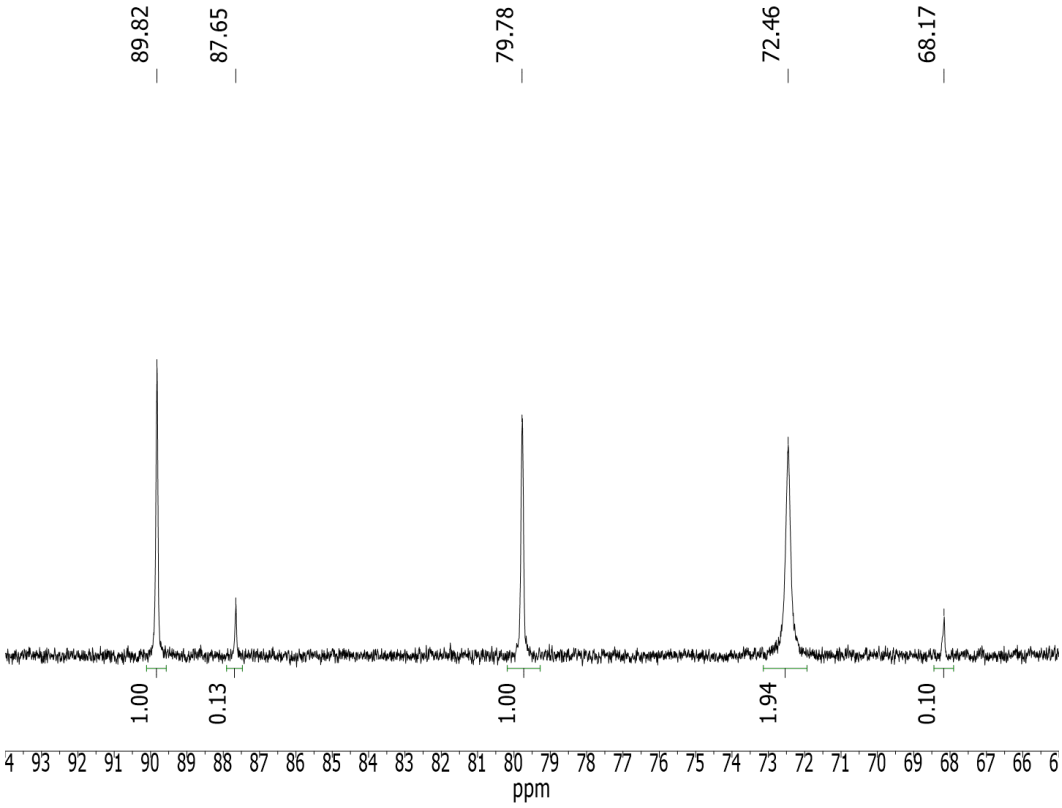


Figure S26. $^{31}P\{^1H\}$ NMR spectrum (202.3 MHz, CD_2Cl_2) of [H**1**]BF_4, thermally equilibrated at 20 ºC.

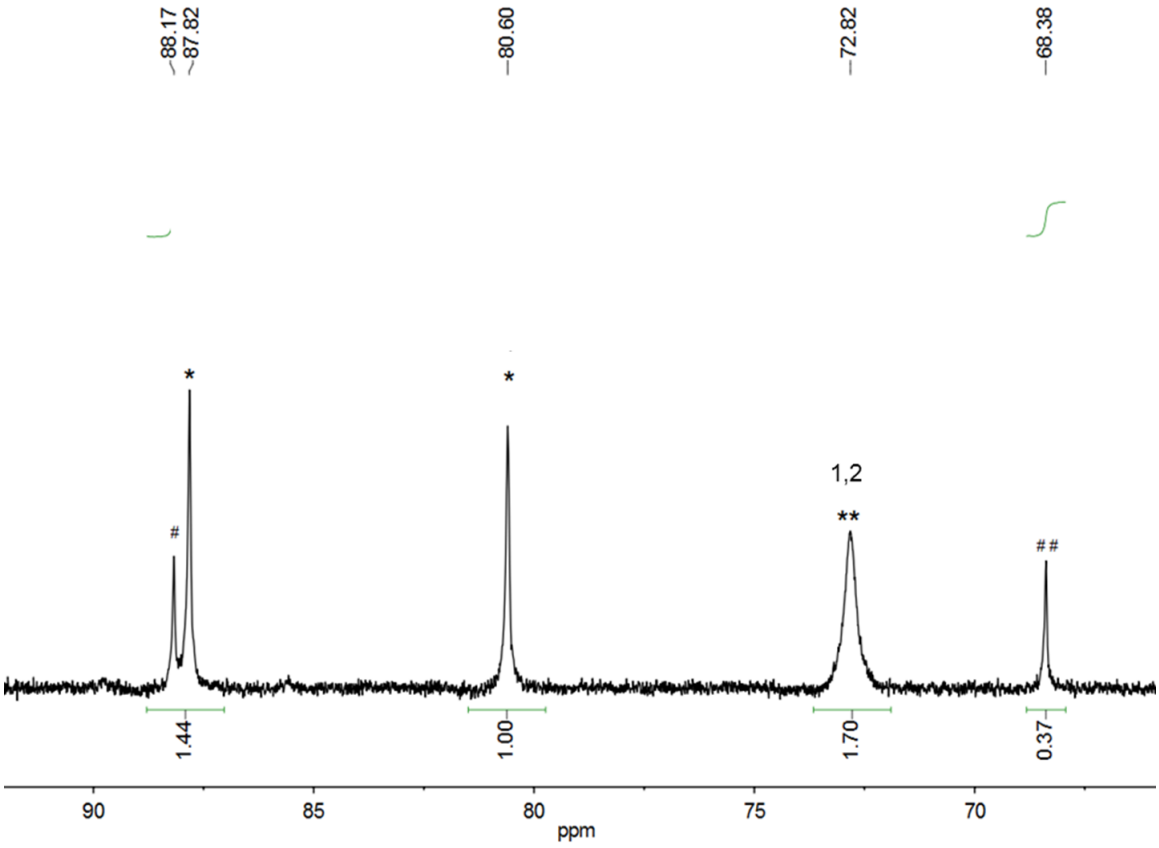


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, C_6D_6) of [H**1**]BAr^F_4, thermally equilibrated at 20 ºC. Signals labeled * are for unsymmetrical Fe(dppv), ** for unsymmetrical Ni(dppv), # is for symmetrical Fe(dppv), and # # for symmetrical Ni(dppv).

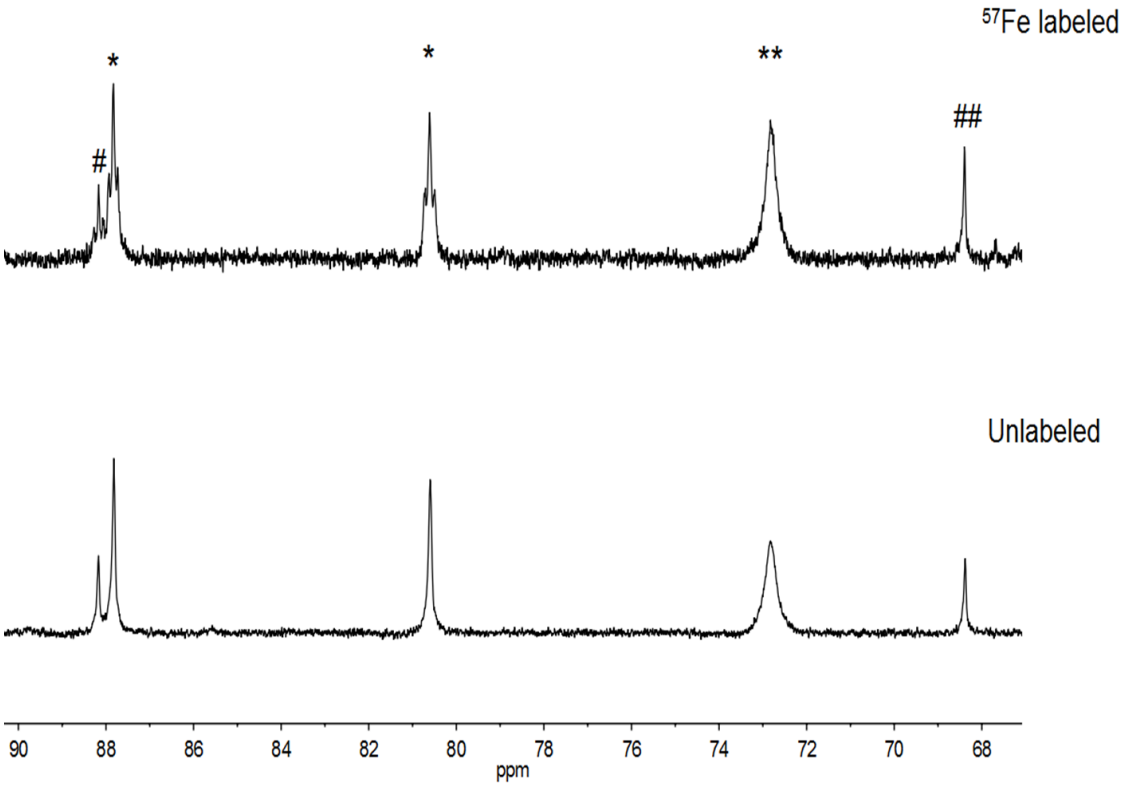


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, C_6D_6) of [H**1**]BAr^F_4 at 20 ºC. Signals labeled * are for unsymmetrical Fe(dppv), ** for unsymmetrical Ni(dppv), # is for symmetrical Fe(dppv), and # # for symmetrical Ni(dppv).

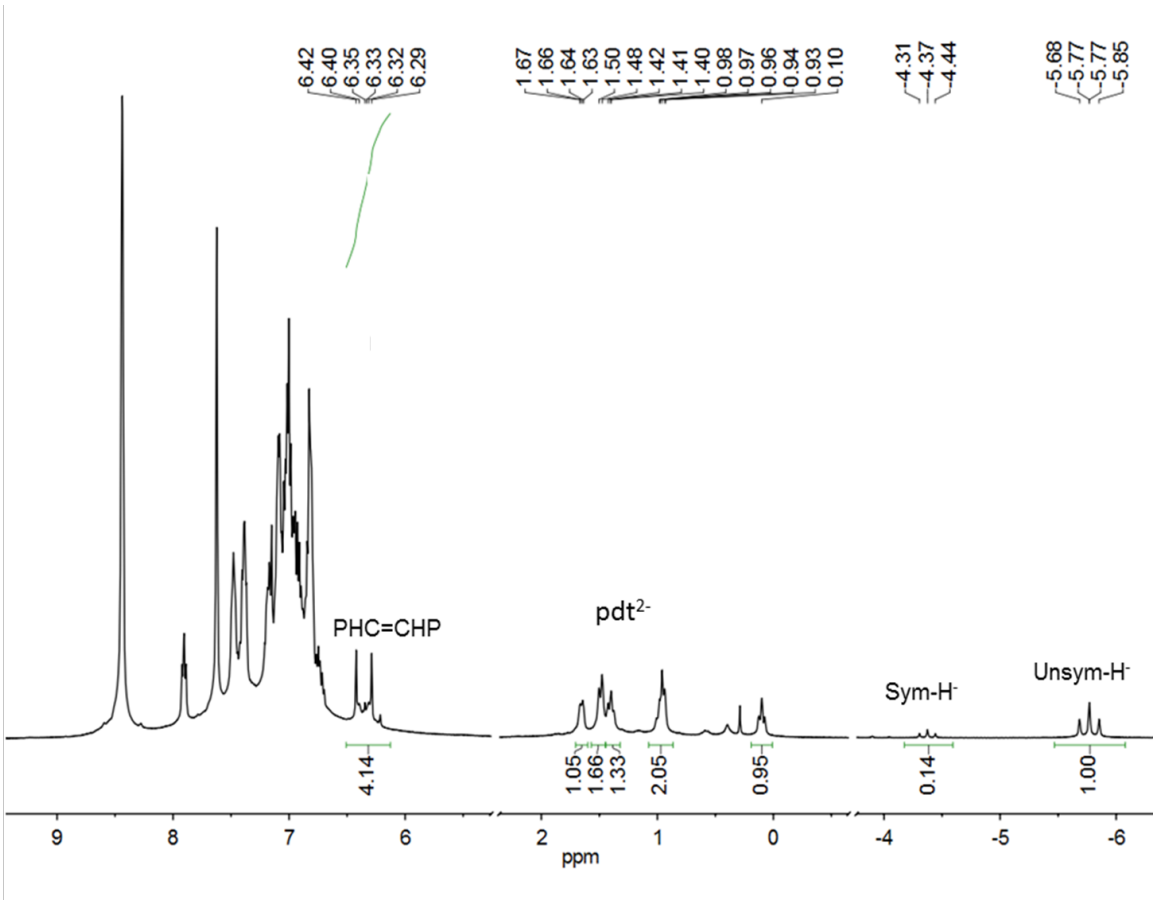


Figure S29. ^{1}H NMR spectrum (500 MHz, C_6D_6) of [H**1**]BAr^F_4 at 20 ºC. Integrations shown are for the hydrides of both isomers.

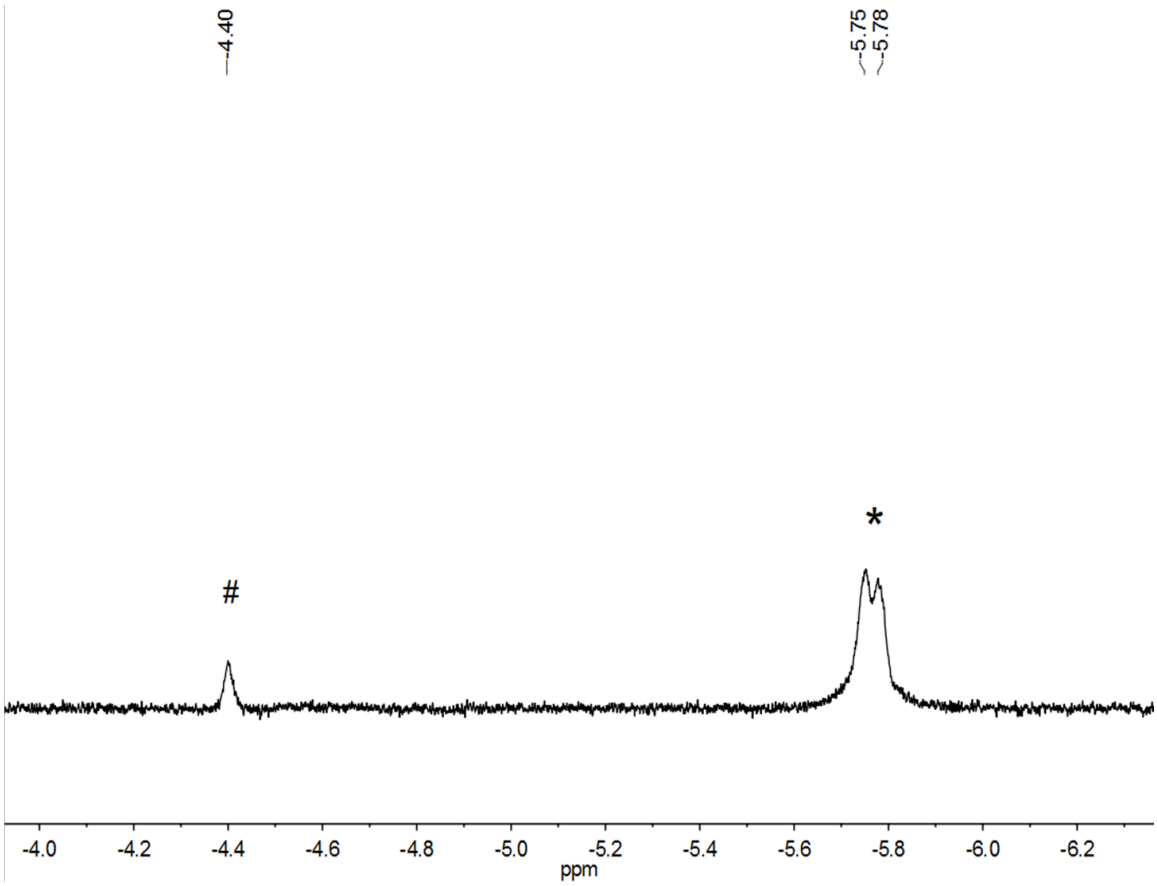


Figure S30. $^{1}H\{^{31}P\}$ NMR spectrum (500 MHz, C_6D_6) of ^{57}Fe-labeled [H**1**]BAr^F_4 at 20 ºC. # refers to *sym*-[H**1**]BAr^F_4, while * refers to *unsym*-[H**1**]BAr^F_4.

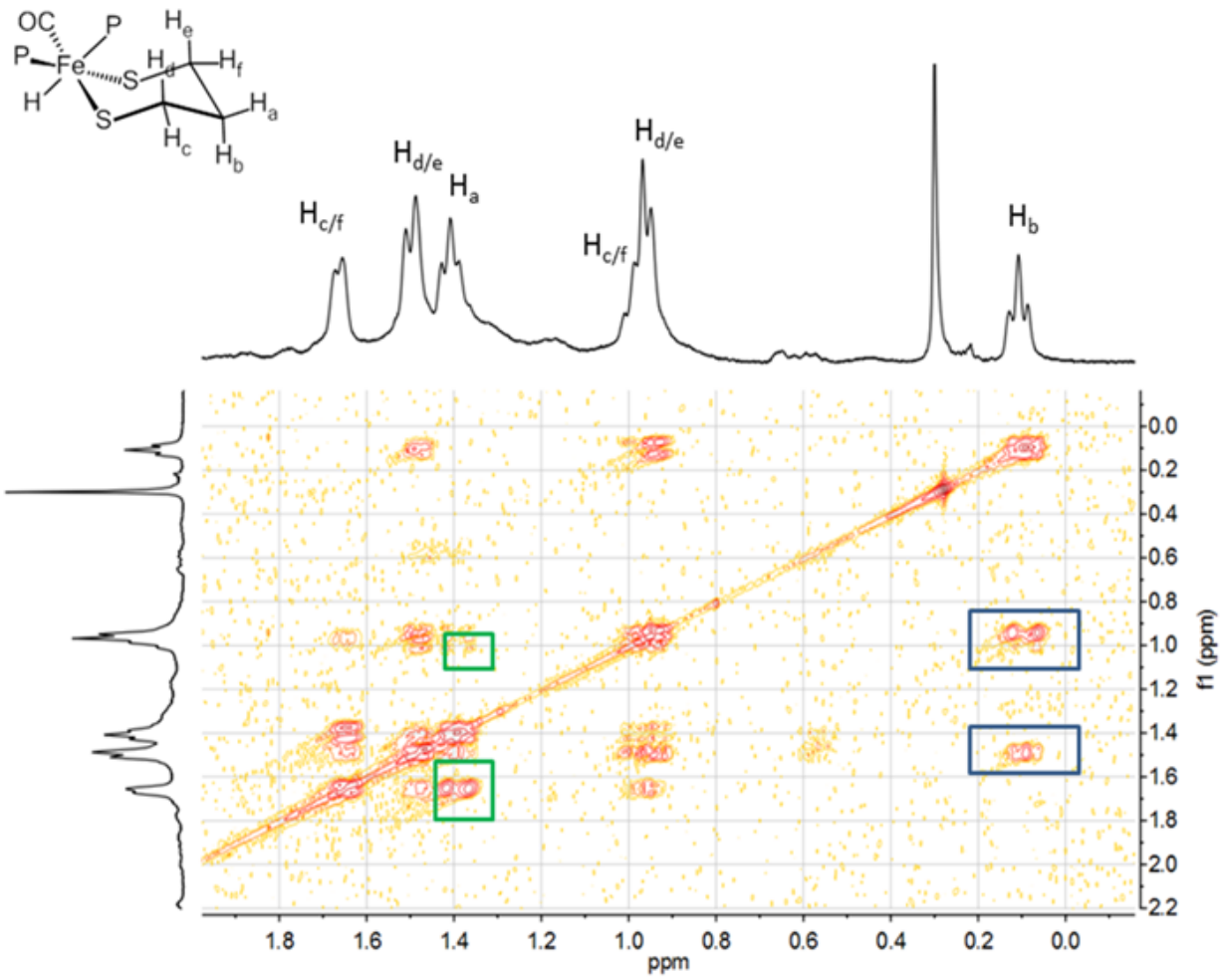


Figure S31. ^{1}H -^{1}H COSY NMR spectrum of [H**1**]BAr$^{F}_{4}$ in C_6D_6 at 20 ºC.

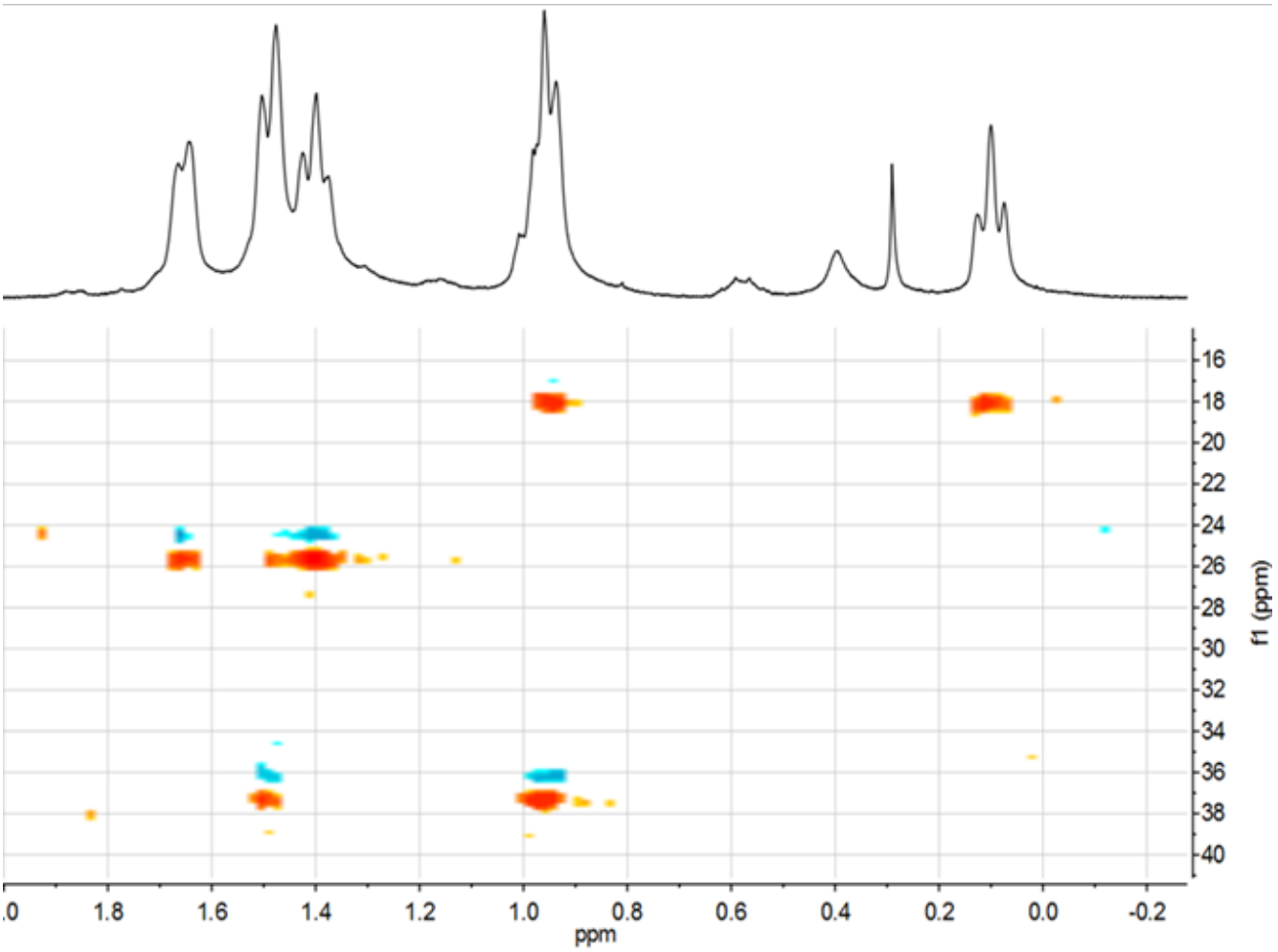


Figure S32. ^{1}H-^{13}C gHSQC NMR spectrum of [H**1**]BAr^{F}_{4} in C_6D_6 at 20 ºC.

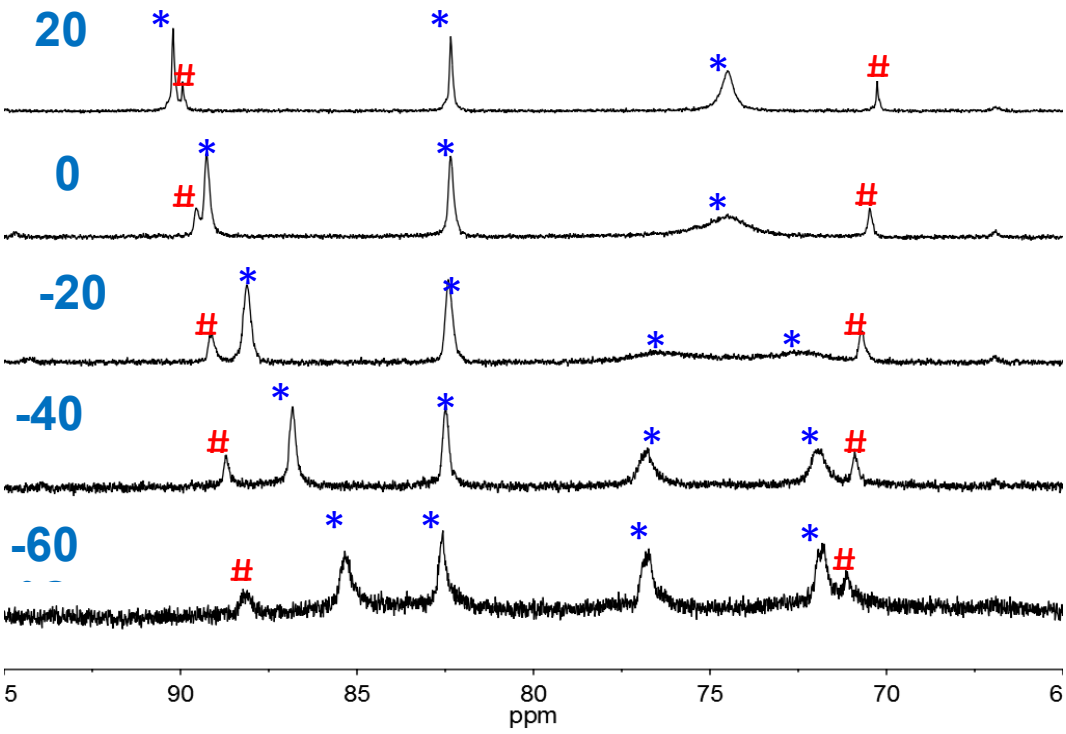


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, d_8-toluene) of [H**1**]BAr^{F}_{4} at various temperatures (in ºC, * denotes the unsym isomer. # for sym isomer).

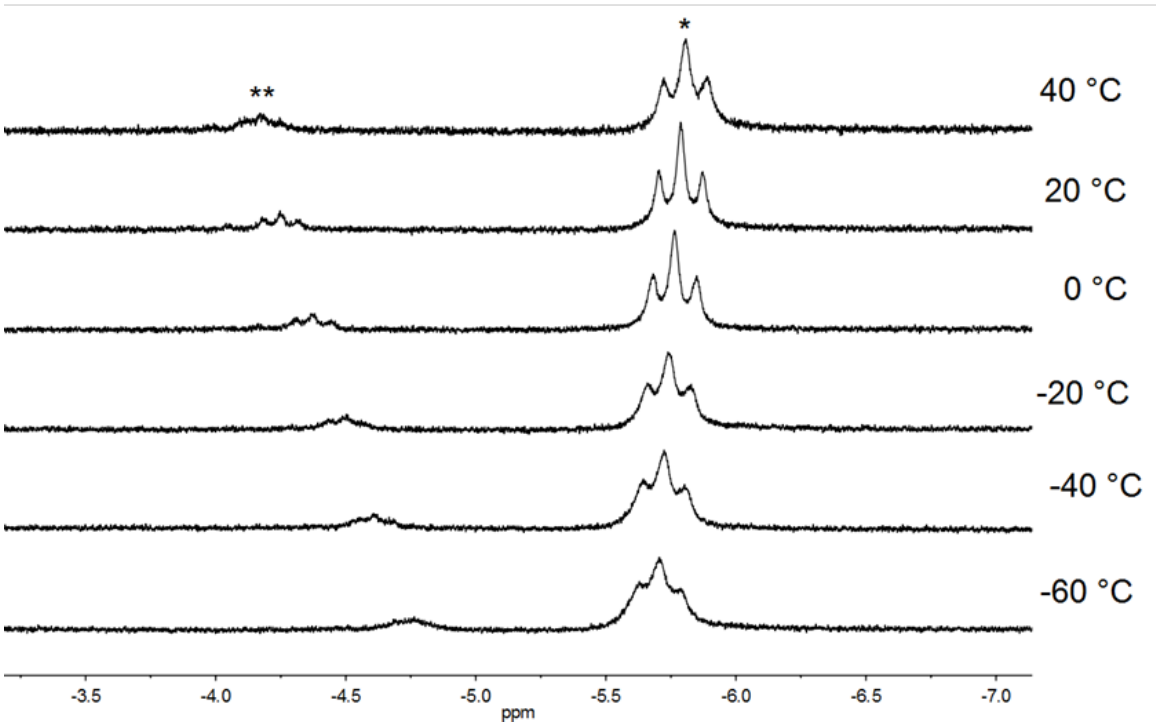


Figure S34. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of $[(dppv)Ni^{II}(\mu\text{-}H)(\mu\text{-}pdt)Fe^{II}(dppv)(CO)]^{+}$, [H**1**]$BAr^{F}_{4}$ showing signals for the two isomers. * refers to the symmetrical isomer, and ** refers to the unsymmetrical isomer.

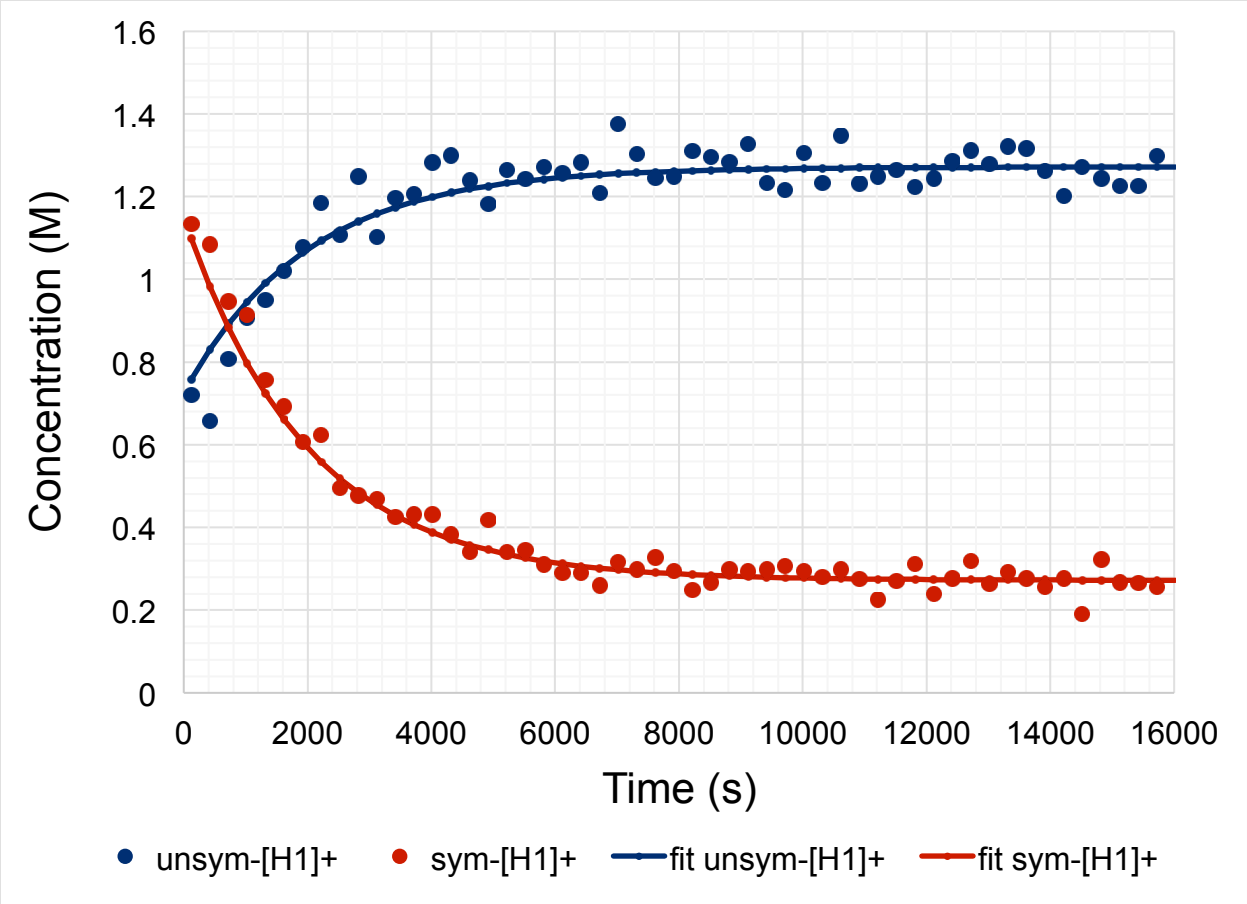


Figure S35. A thermally equilibrated (with respect to sym vs unsym) solution of $[H\mathbf{1}]^0$ in MeCN was treated with a solution of $FcBF_4$ in MeCN at 25 ˚C. The conversion of *sym*-$[H\mathbf{1}]^+$ to *unsym*-$[H\mathbf{1}]^+$ was monitored by $^{31}P\{1H\}$ NMR spectroscopy. The relative $^{31}P\{^1H\}$ NMR intensities for *sym*-$[H\mathbf{1}]^+$ and *unsym*-$[H\mathbf{1}]^+$ were compared to those an internal standard, $[PPh_4]Br$. The initial ratio of *unsym*-$[H\mathbf{1}]^+$ to *sym*-$[H\mathbf{1}]^+$ is approximately 1:1.6. This ratio changes to 4.7:1 over the course of 4 h. The observed half-life for the isomerization of *sym*-$[H\mathbf{1}]^+$ to *unsym*-$[H\mathbf{1}]^+$ is approximately 22 min. The ratio of *unsym*-$[H\mathbf{1}]^+$ to *sym*-$[H\mathbf{1}]^+$ after 17 min is approximately 1:1. The difference between the initial unsym to sym ratio in this plot and the unsym to sym ratio reflected in the EPR simulations of $[H\mathbf{1}]^0$ is likely due to differences in solvent (MeCN vs toluene) and temperature (25 ˚C vs warming to room temperature from frozen solutions). Finally, the presence of reduced species, such as $[H\mathbf{1}]^0$ may catalyze the isomerization of *sym*-$[H\mathbf{1}]^+$ to *unsym*-$[H\mathbf{1}]^+$.

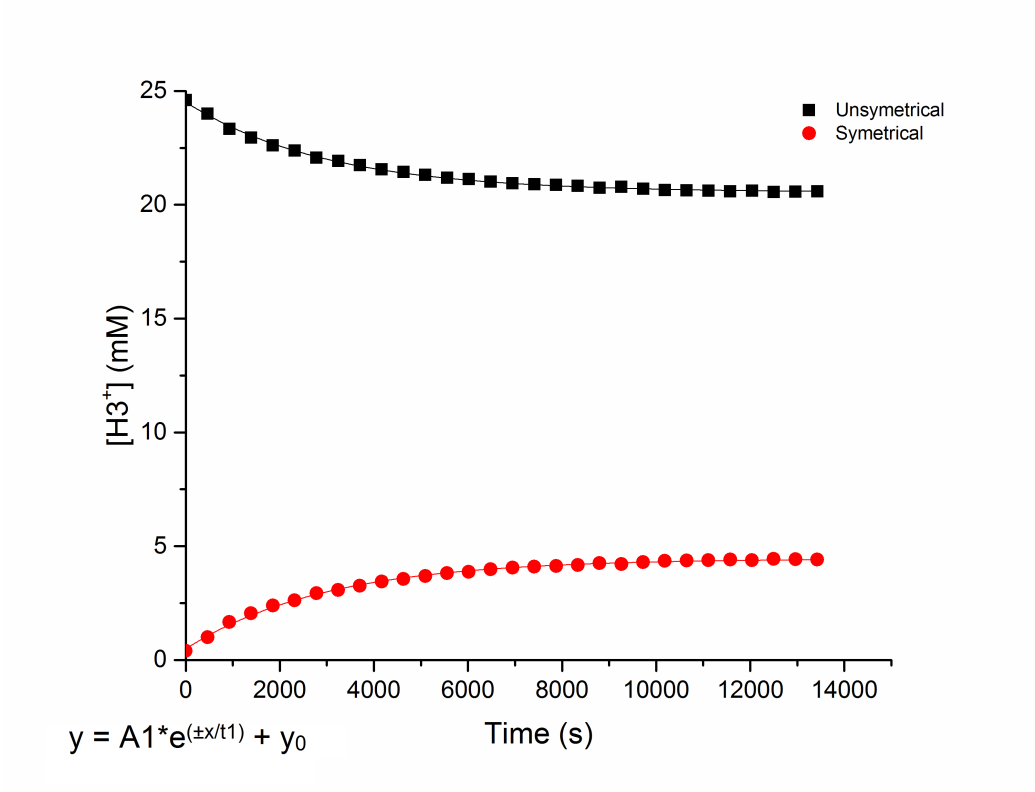


Figure S36. Exponential decay of *unsym*-[H**1**]$^+$ and exponential growth of *sym*-[H**1**]$^+$ determined by ^{1}H NMR spectroscpopy in d_3-MeCN. The conversion follows first-order kinetics with an observed rate constant of 3.1(0.2) x 10^{-4} s^{-1} ($t_{1/2}$ = 37 min). This value is equal to the sum of the rate constants for the forward and reverse reactions. Using an equilibrium constant of 0.2 for *unsym*-[H**1**]$^+$/*sym*-[H**1**]$^+$ in MeCN, a rate constant of 5.2 x 10^{-5} s^{-1} was calculated for the forward reaction.

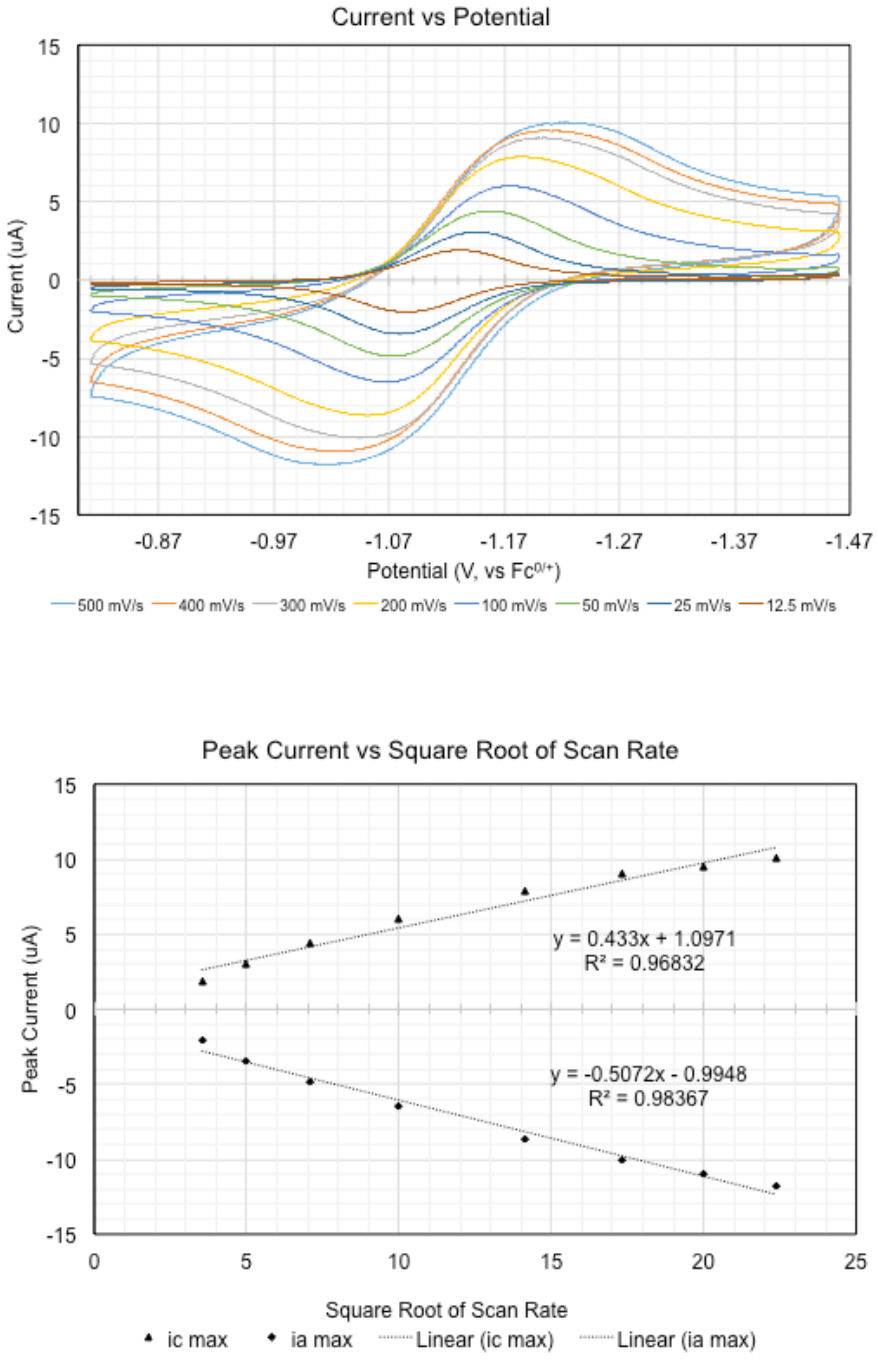


Figure S37. Cyclic voltammetry of 0.001 M $[\mathbf{1}]^0$ in 1,2-$C_6H_4F_2$ and $NBu_4BAr^F{}_4$ electrolyte (0.01 M).

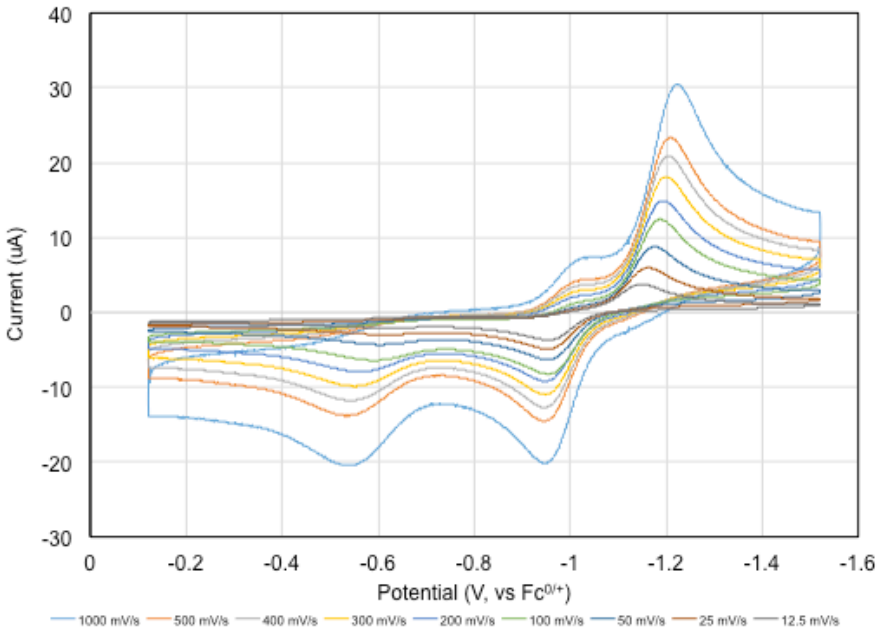


Figure S38. Cyclic voltammogram of $[\mathbf{1}]^0$ in PhCN solution at various scan rates. *Conditions:* 1 mM analyte, 0.1M $[Bu_4N]PF_6$ electrolyte, glassy carbon working electrode, Ag pseudo-reference electrode, Pt wire counter electrode.

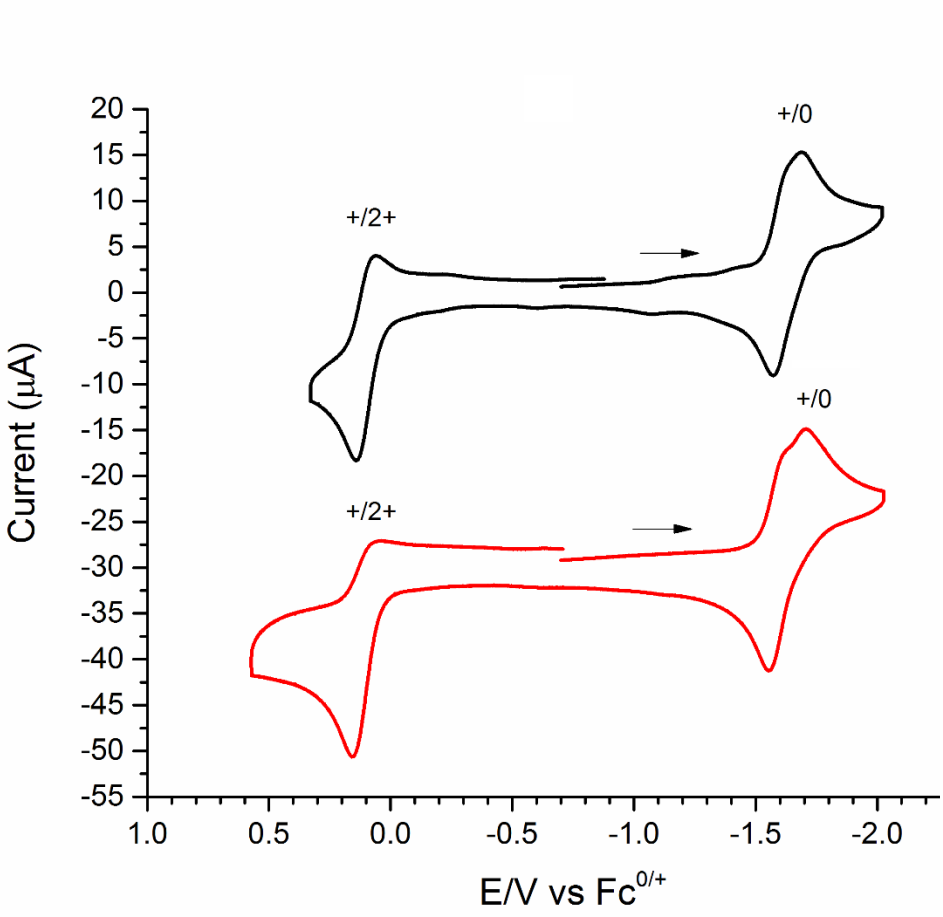


Figure S39. Cyclic voltammograms of [H**A**]BAr^F_4 (top) and [H**B**]BAr^F_4 (bottom) in dichloromethane at 100 mV/s scan rates. *Conditions:* 1 mM analyte, 0.1M $[Bu_4N]PF_6$ electrolyte, glassy carbon working electrode, Ag pseudo-reference electrode, Pt wire counter electrode.

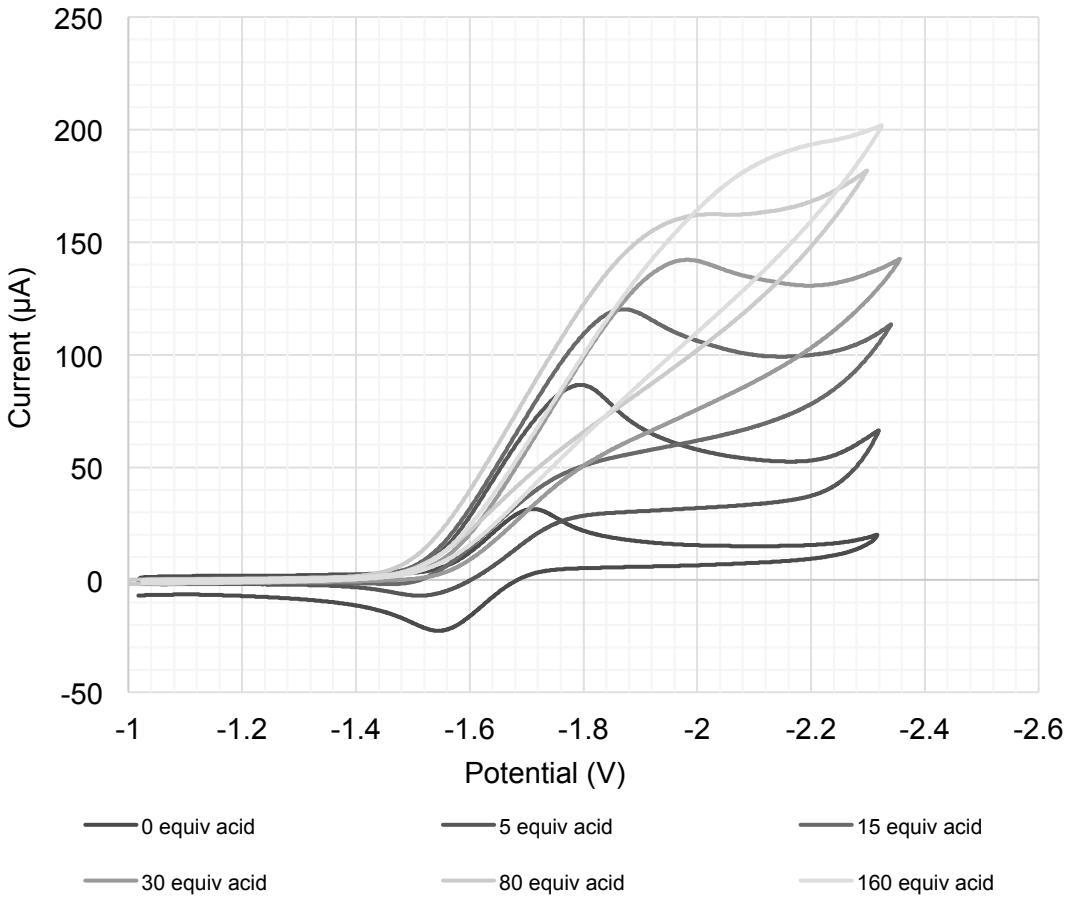


Figure S40. Cyclic voltammograms of $[H\mathbf{1}]^+$ with increasing amounts of added ClH_2CCO_2H. *Conditions:* 0.125 M $[Bu_4N][PF_6]$ in CH_2Cl_2, 1.0 mM $[H\mathbf{1}]^+$, glassy carbon working electrode, Pt counter electrode, Ag pseudo reference electrode, ferrocene internal standard, scan rate = 0.5 V/s.

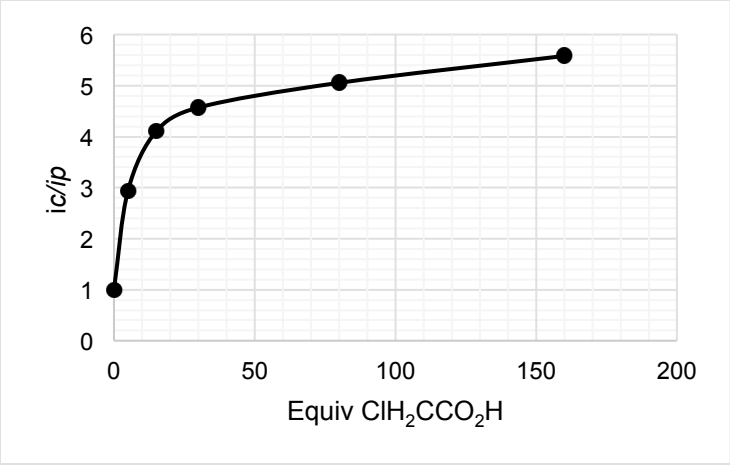


Figure S41. Plot of i_c/i_p vs equiv of added ClH_2CCO_2H. *Conditions*: 0.125 M $[Bu_4N][PF_6]$ in CH_2Cl_2, 1.0 mM $[H\mathbf{1}]^+$, glassy carbon working electrode, Pt counter electrode, Ag pseudo reference electrode, ferrocene internal standard, scan rate = 0.5 V/s.

Determination of the TOF for proton reduction by foot of the wave method.

The method of Savéant and coworkers was followed for the foot of the wave method to determine the turnover frequency (TOF) from CV experiments recorded under electrocatalytic conditions. At the beginning of the catalytic peak, the currents are low and therefore less affected by side phenomena such as depletion of acid or deactivation of the catalyst. Accordingly to the equation below the TOF is directly calculated from the slope (a) of the linear portion of the slope of I/I_p vs. $1/(1+\exp[F(E-E_{cat})/RT])$.[10]

$$\frac{I}{I_p} = \frac{2.24\sqrt{RT \times TOF/Fv}}{1 + \exp\left[F(E - E_{cat})/RT\right]}$$

$$TOF = \left(\frac{a}{2.24}\right)^2 \frac{Fv}{RT}$$

The foot of the wave analysis of the CV at 0.1 V s^{-1} of 0.5 mM of $[H\mathbf{1}]BF_4$ in the presence of 5 and 15 equiv of HOTs is shown below. Deviation from linearity is observed for $I/I_p > 0.5$. From the slope of the linear portion, we calculated a value of $TOF = 490$ s^{-1}. Values of $TOF = 505$ s^{-1} were derived from CV measured at a scan rate of 0.5 V s^{-1} indicating that TOF of **X** can be estimated with a good precision using this method.

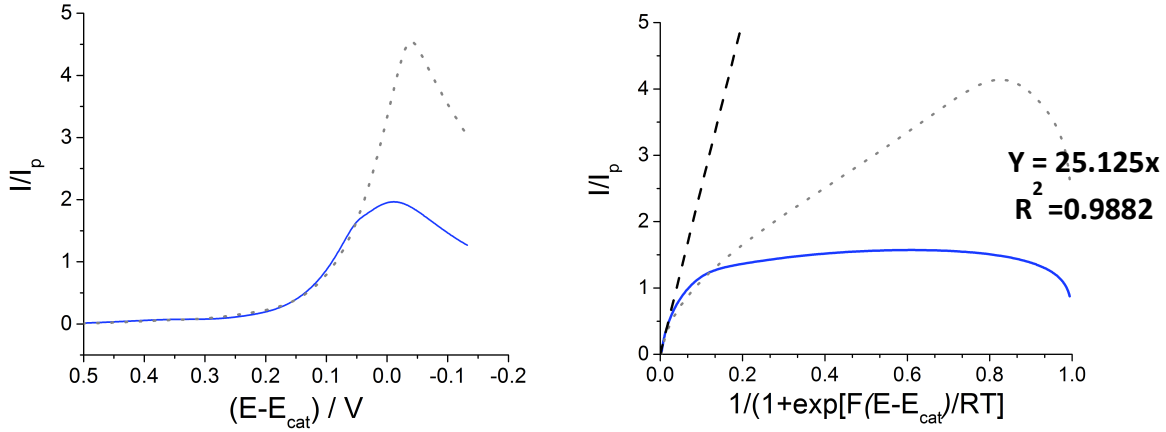


Figure S42. *Left:* Background-corrected catalytic responses of [H**1**]BF_4 derived from CVs recorded at 0.1 V s^{-1} in presence of 5 (blue) and 15 equiv (grey) of HOTs. *Right:* Foot of the wave analyses. Linear fits (dashed line) to the data show deviation from "pure" catalytic conditions at $I/I_p > 0.5$.

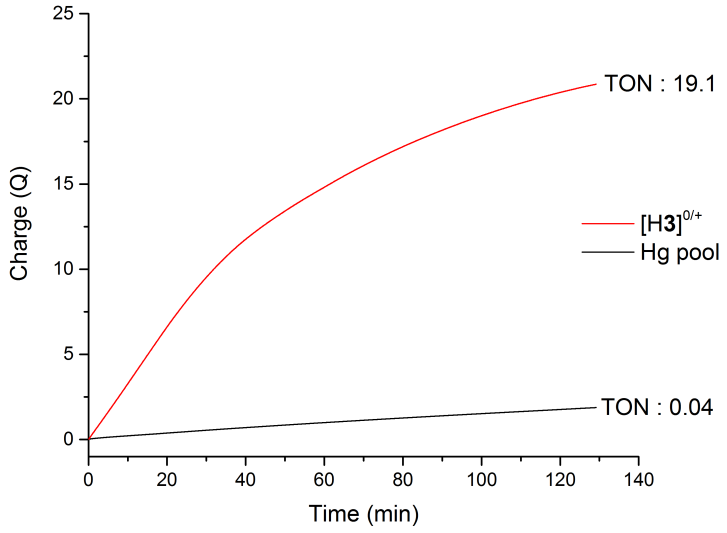


Figure S43. Bulk electrolysis of ClH_2CO_2H in the presence (red) and absence of $[H\mathbf{1}]^{0/+}$ using a Hg pool working electrode (black). *Conditions:* 1 mM [H**1**]BF_4 in MeCN, 0.1 M $[Bu_4N]BF_4$, 50 mM ClH_2CO_2H, -1.8 V vs $Fc^{0/+}$.

Calculating turnover number from charge (Q) obtained during the bulk electrolysis experiment:

A) Determine Faradaic yield at 60 min from charge (Q) measured and by sampling headspace gas.
Expected mmol H_2 at 60 min $= Q_{60min}$ x 1mol e^-/96485 C x 1mol H_2 /2 mol e^- x 1000 = 0.083 mmol H_2

96485 C = 1 Farad (mole of electrons)

Q_{60min} = 16 C (from Figure S37)

Actual mmol H_2 at 60 min = Area H_2/Area CH_4 x 1/γ x mmol CH_4 = 0.077 mmol H_2

γ = ratio of retention factors for CH_4 and H_2 = 4.2 (specific to GC used)

AreaH_2/AreaCH_4 = 3.73

CH_4 added = 0.86 *mmol*

Faradaic yield (**at 60 min**): 0.077/0.083 x 100 = 92.8 %

B) Calculate mmol of H_2 at other times (T) from charge, without sampling headspace gas.
Q_{129min} = 20.86 C

mmol H_2 at 129 min = 2.86 C x 1mol e^-/96485 C x 1mol H_2 /2 mol e^- x 1000 x 0.928 = 0.095 mmol H_2

TON$_{129min}$ = 0.095 mmol H_2/0.005 mmol [H**1**]$^{+/0}$ = 19.1

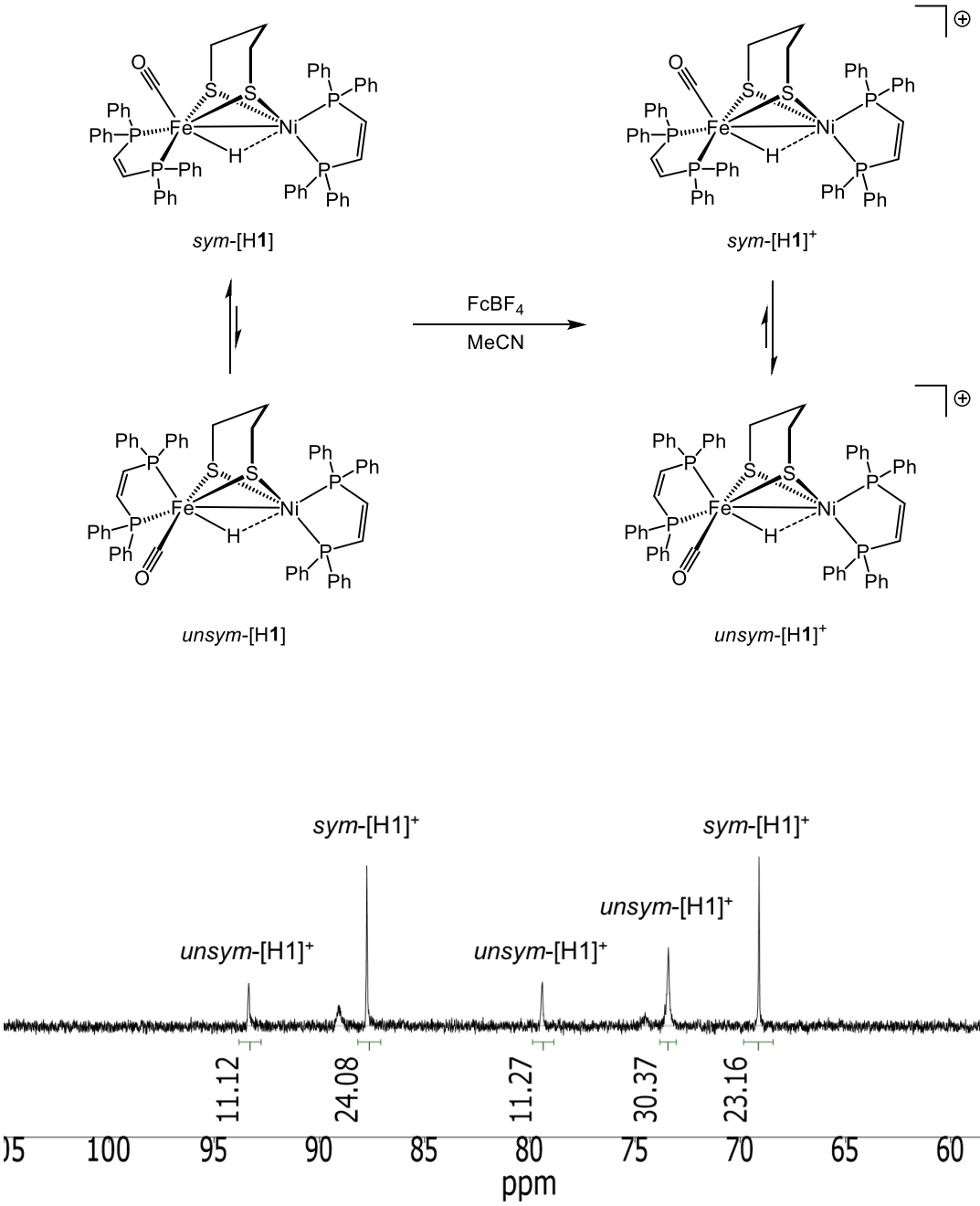
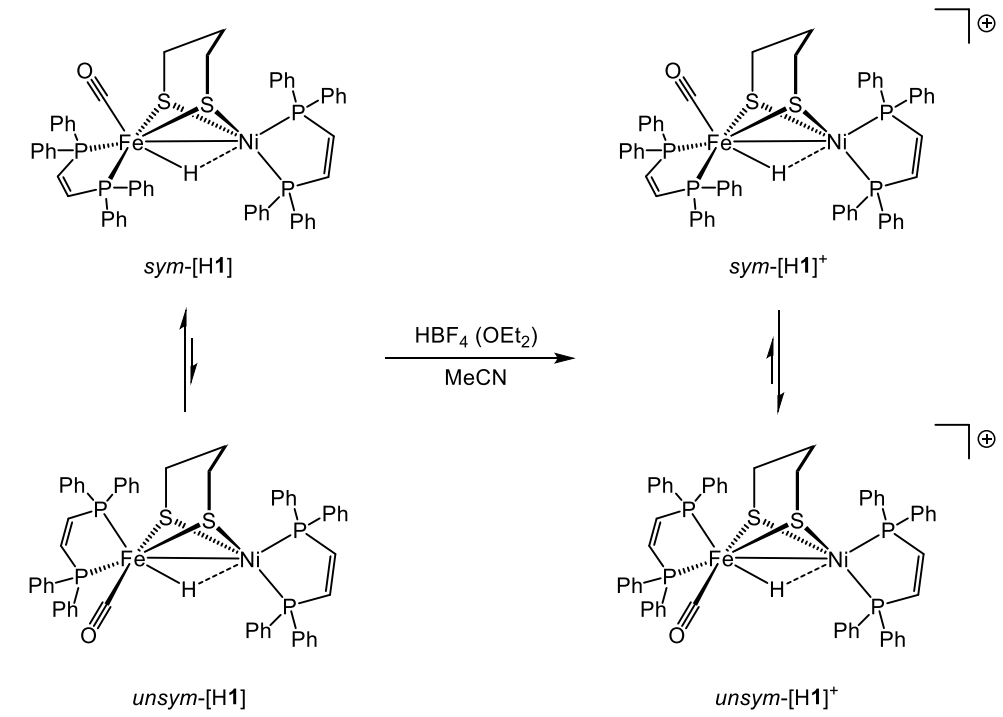


Figure S44. $^{31}P\{1H\}$ NMR spectrum collected 20 minutes after the oxidation of [H**1**]^{0} with $FcBF_4$ in MeCN at room temperature. The ratio of *unsym*-[H**1**]$^{+}$ to *sym*-[H**1**]$^{+}$ equals 53:47.



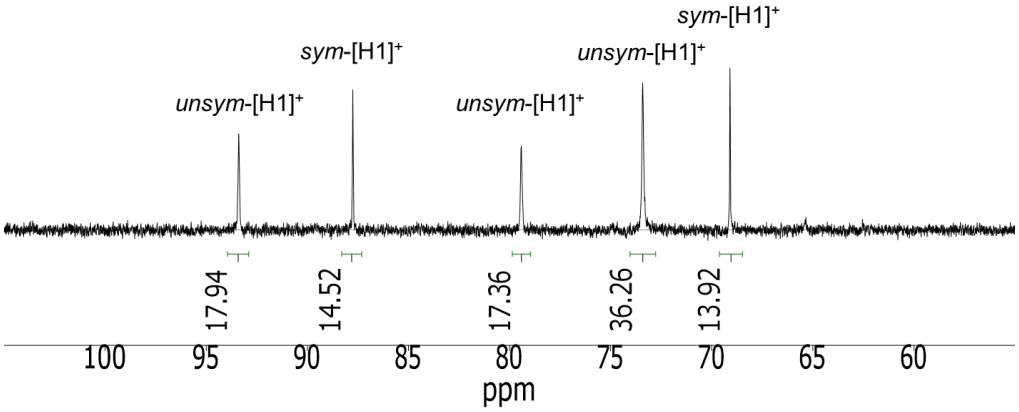


Figure S45. $^{31}P\{1H\}$ NMR spectrum collected 20 minutes after the addition of $HBF_4(OEt_2)$ to a solution of $[H\mathbf{1}]^0$ in MeCN at room temperature. The ratio of *unsym*-$[H\mathbf{1}]^+$ to *sym*-$[H\mathbf{1}]^+$ equals 72:28. The expected *unsym*-$[H\mathbf{1}]^+$ to *sym*-$[H\mathbf{1}]^+$ ratio after 20 min in MeCN according to the mechanism depicted in equations 8-10 and the *unsym*-$[H\mathbf{1}]^+$ to *sym*-$[H\mathbf{1}]^+$ ratio in Figure equals 76.5: 23.5.

The ratio of *unsym*-[H1]$^+$ to *sym*-[H1]$^+$ expected after 20 minutes from the protonation of [H1]^0 at room temperature in MeCN:

Half of the [H**1**]^0 undergoes protonation to [**1**]$^+$, then reduction to [**1**]^0, and a second protonation to [H**1**]$^+$. The ^{31}P NMR data shows that protonation of [**1**]^0 results almost exclusively in *unsym*-[H**1**]$^+$. The other half of [H**1**]^0 is involved in the reduction of [**1**]$^+$ to [**1**], and thus is oxidized by [**1**]$^+$ to [H**1**]$^+$. The ^{31}P NMR data in Figure shows that the ratio of *unsym*-[H**1**]$^+$ to *sym*-[H**1**]$^+$ formed by oxidation of [H**1**]^0 equals 53:47 after 20 min in MeCN. Thus amount of *unsym*-[H**1**]$^+$ expected 20 min after the protonation of [H**1**]^0 with $HBF_4(OEt_2)$ in MeCN is

$$\text{expected amount of } \textit{unsym}\text{-[H}\mathbf{1}\text{]}^+ = 50 + 50*0.53 = 76.5$$

The amount of *sym*-[H**1**]$^+$ expected 20 min after the protonation of [H**1**]^0 with $HBF_4(OEt_2)$ in MeCN is

$$\text{expected amount of } \textit{sym}\text{-[H}\mathbf{1}\text{]}^+ = 50*0.47 = 23.5$$

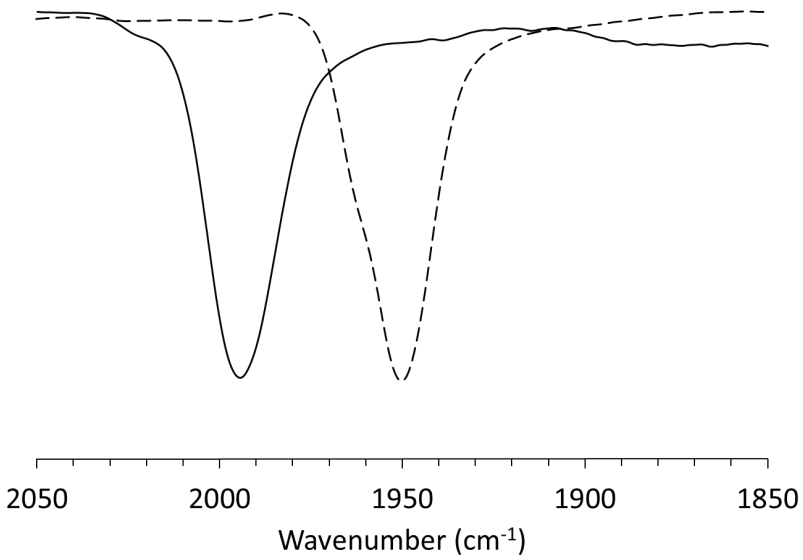


Figure S46. FT-IR spectrum (CH_2Cl_2) of [H**1**H]$(BF_4)_2$ (solid line) and [H**1**]BF_4 (dashed line).

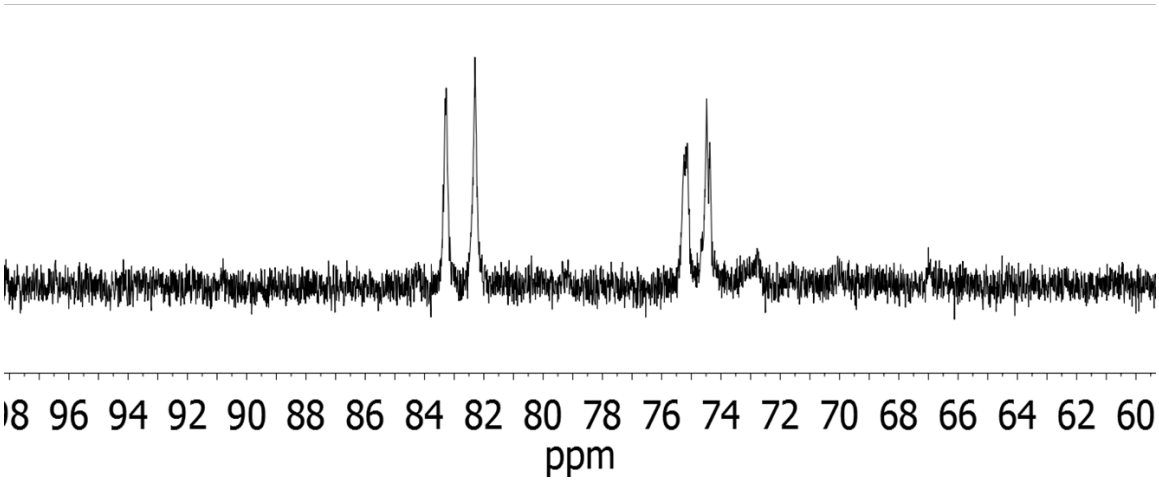


Figure S47. $^{31}P\{^1H\}$ NMR spectrum (202.3 MHz, THF-d_8) of [H**1**H]$(BF_4)_2$.

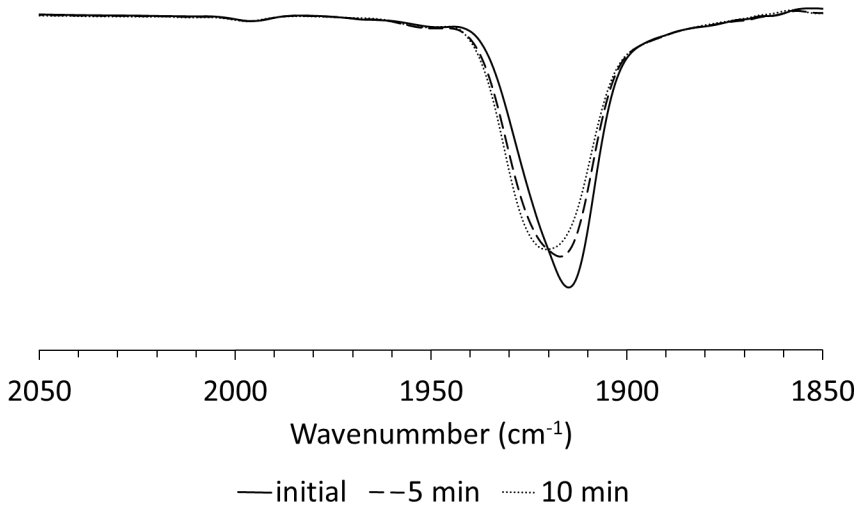


Figure S48. FT-IR spectra (CH_2Cl_2) of the reaction of $CoCp^*_2$ and [H**1**]BF_4 in CH_2Cl_2 immediately upon mixing (solid line), after 5 min. (dashed line), after 10 min. (dotted line).

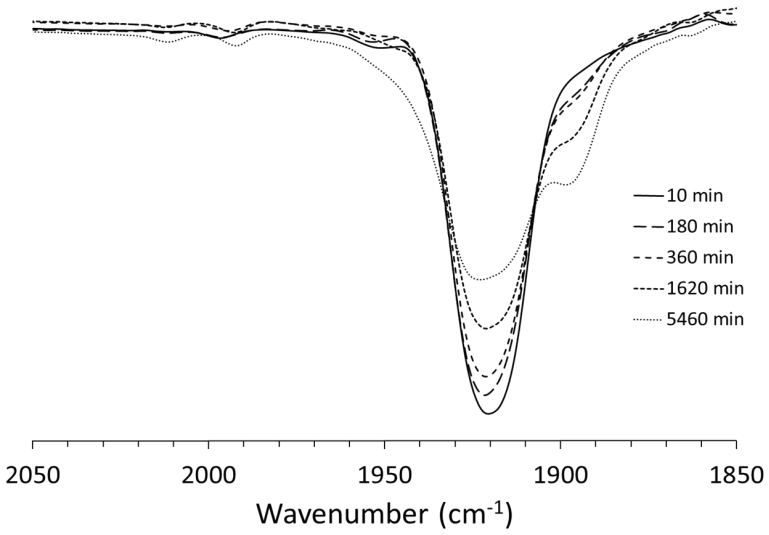


Figure S49. FT-IR spectra (toluene) for the conversion of $[H\mathbf{1}]^0$ to $[\mathbf{1}]^0$ in THF at 26 °C, initial concentration of $[H\mathbf{1}]^0$ was 50 mM. Note that the rates are erratic, but the conversions are clean.

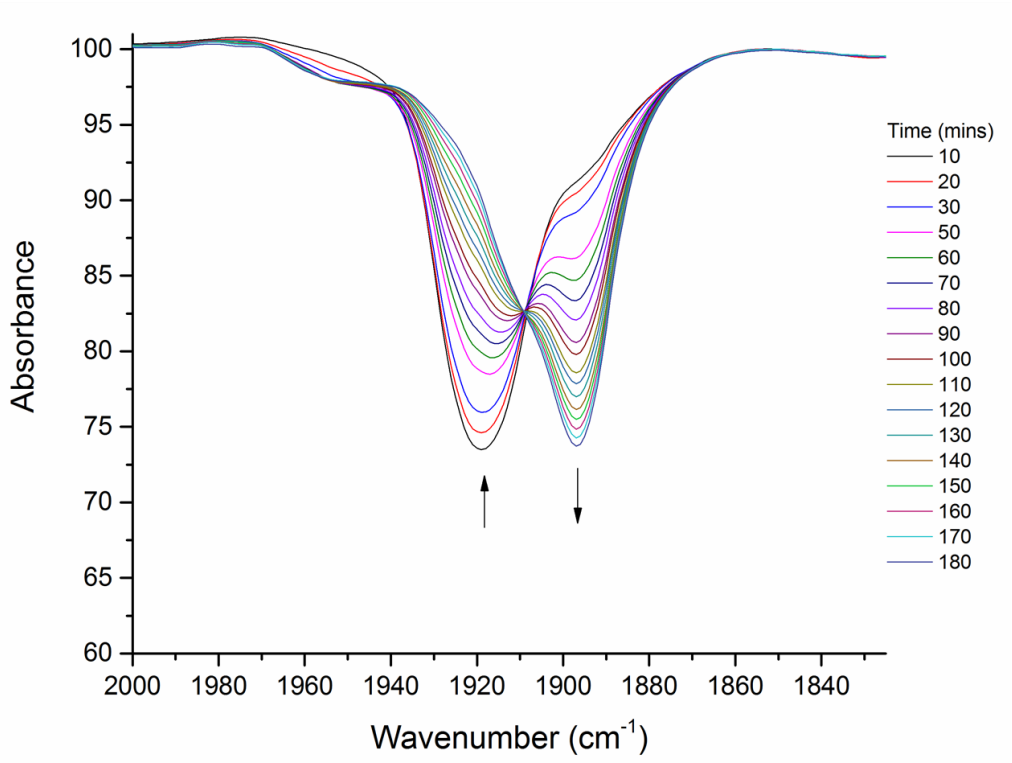


Figure S50. FT-IR spectra for the conversion of a sample of $[H\mathbf{1}]^0$ to $[\mathbf{1}]^0$ in THF at 26 °C, initial concentration of $[H\mathbf{1}]^0$ was 50 mM. Note that the rates are erratic, but the conversions are clean.

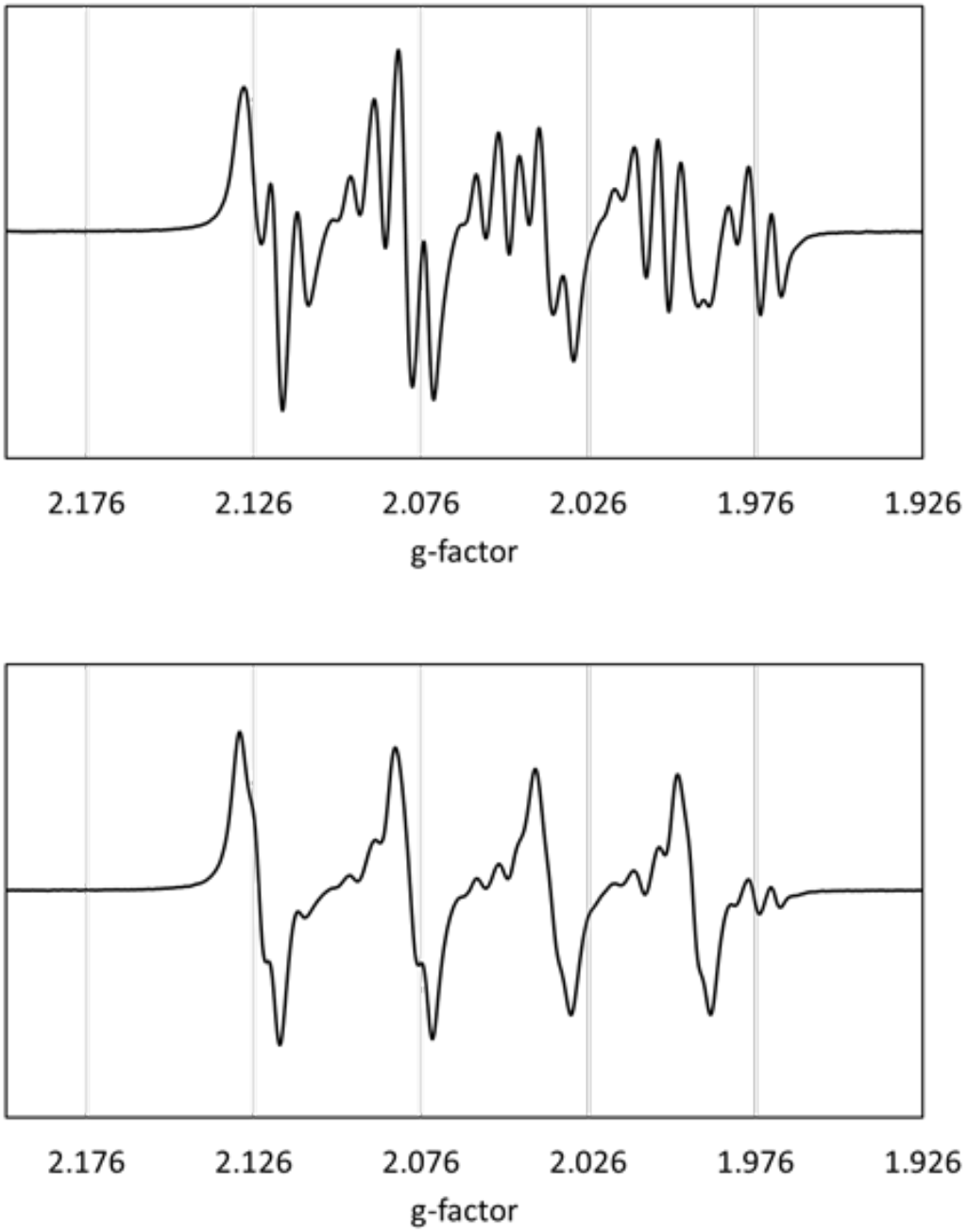


Figure S51. EPR spectra (toluene) of $[H\mathbf{1}]^0$ collected immediately after the addition of $CoCp^*_2$ to $[H\mathbf{1}]BF_4$ (top) and after 10 min. at room temperature (bottom).

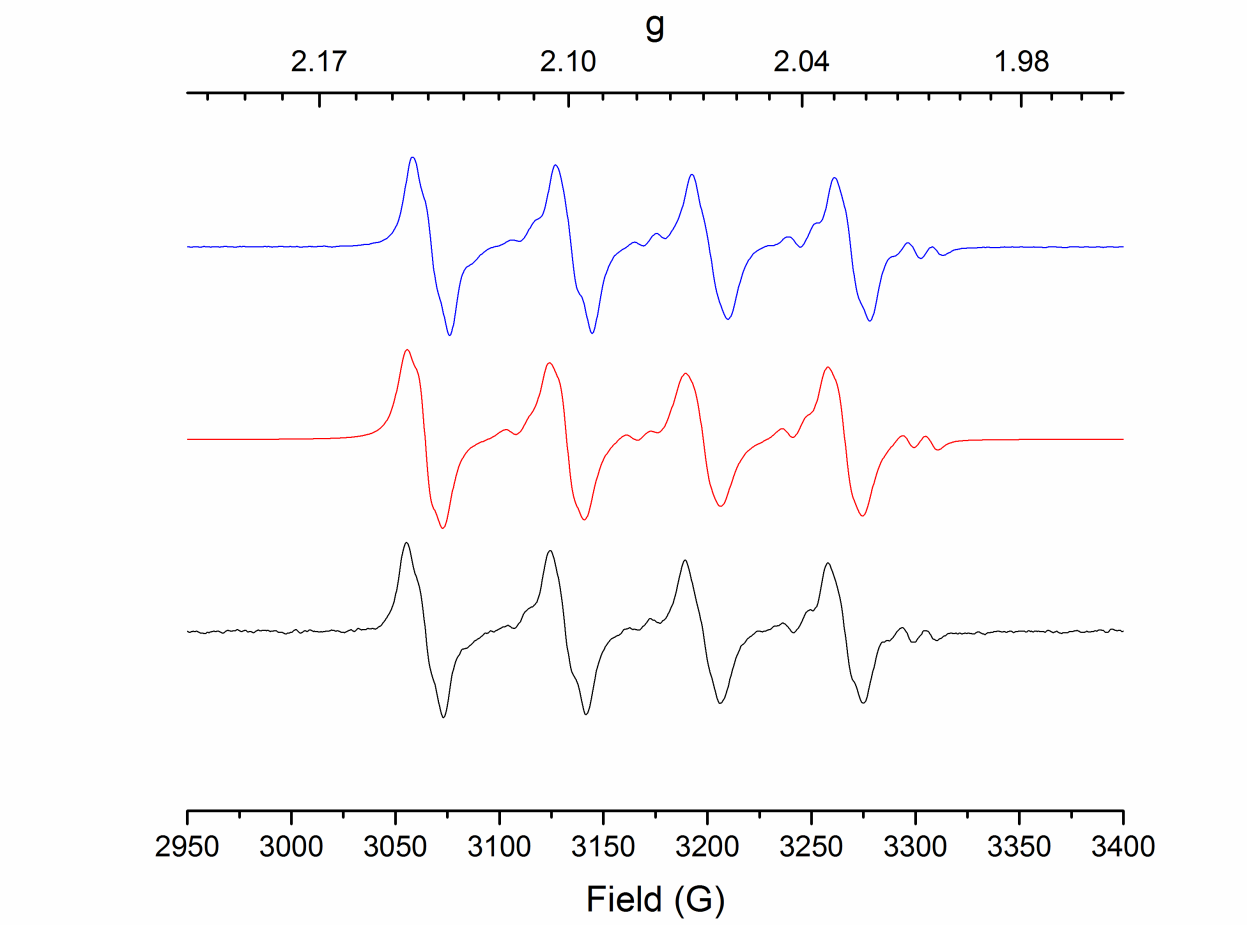


Figure S52. EPR spectrum of $[H\mathbf{1}]^0$ after standing at room temperature for ~ 10 min in THF at 25 °C (black), simulation of the spectra of $[H\mathbf{1}]^0$ (red), and ^{57}Fe-labeled congener $[H\mathbf{1'}]^0$ (blue).

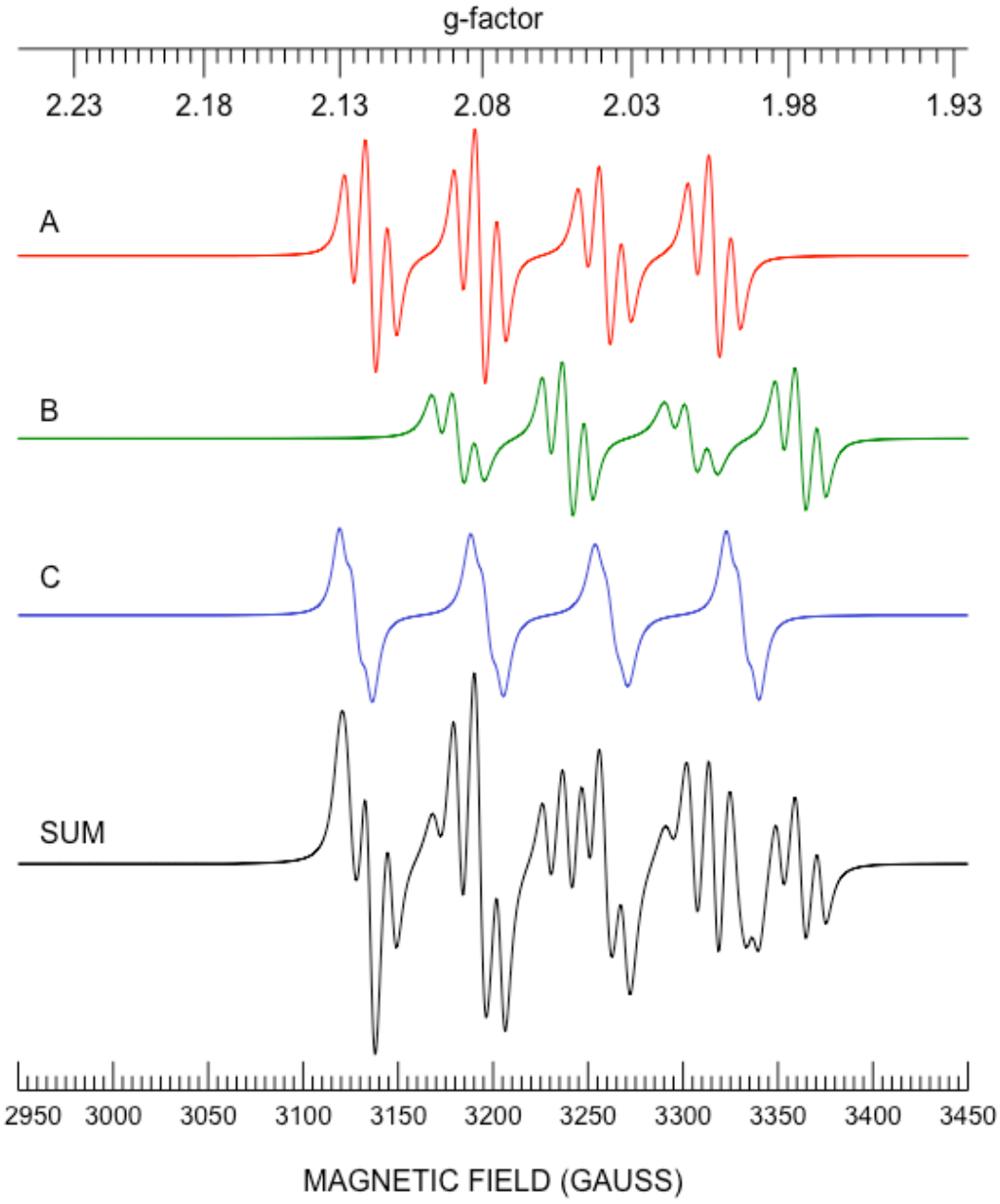


Figure S53. Simulation of the three components X-band EPR spectrum of toluene solution of $[H\mathbf{1}]^0$ (not equilibrated, hence sizable contributions of unsym isomers).

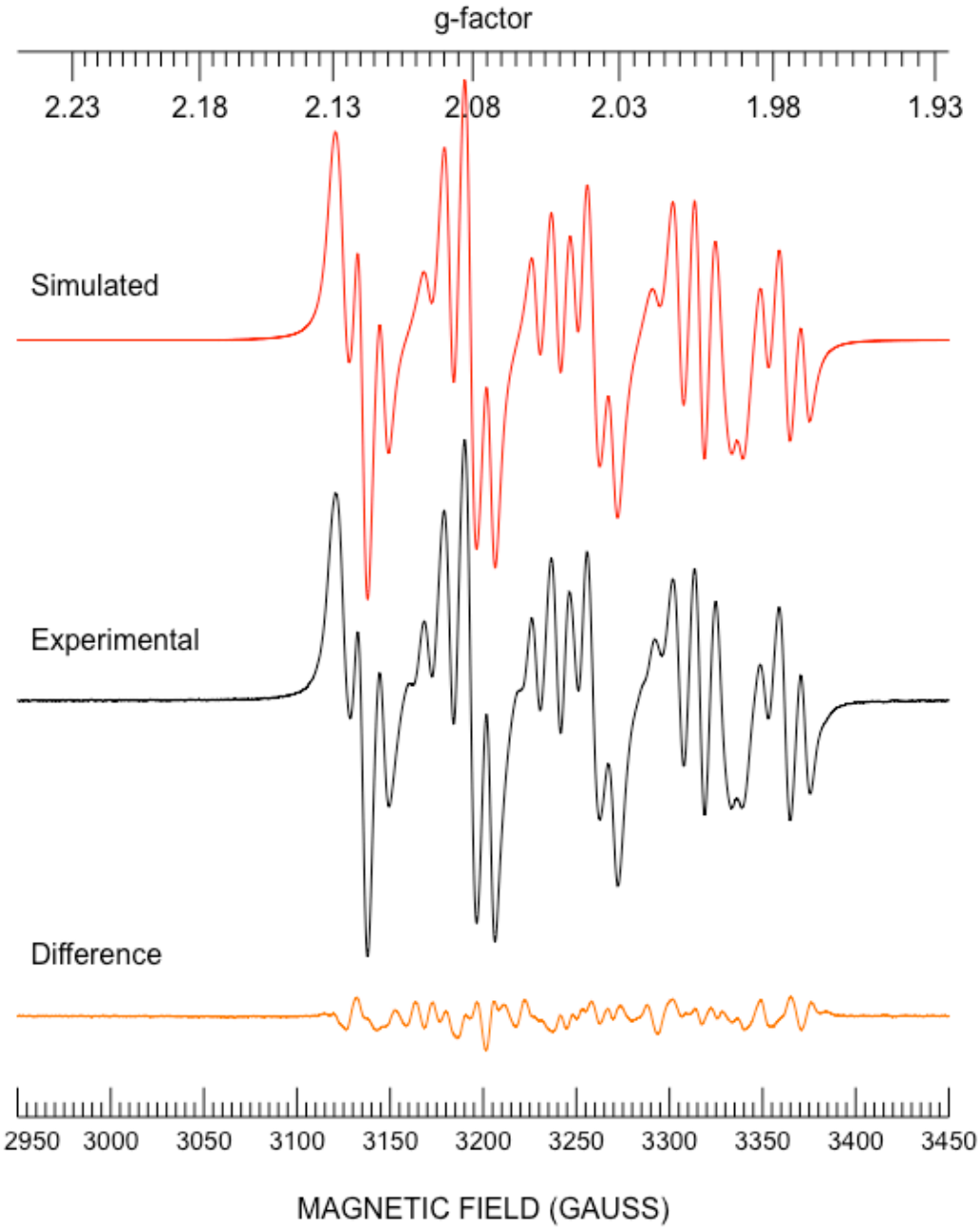


Figure S54. Simulated and experimental X-band EPR spectra of toluene solution of $[\mathbf{H1}]^0$ (not equilibrated, hence sizable contributions of unsym isomers), and the difference between these spectra. Interpretation: the differences are minor that coupling for a fifth spin (such as the hydride) must be negligible.

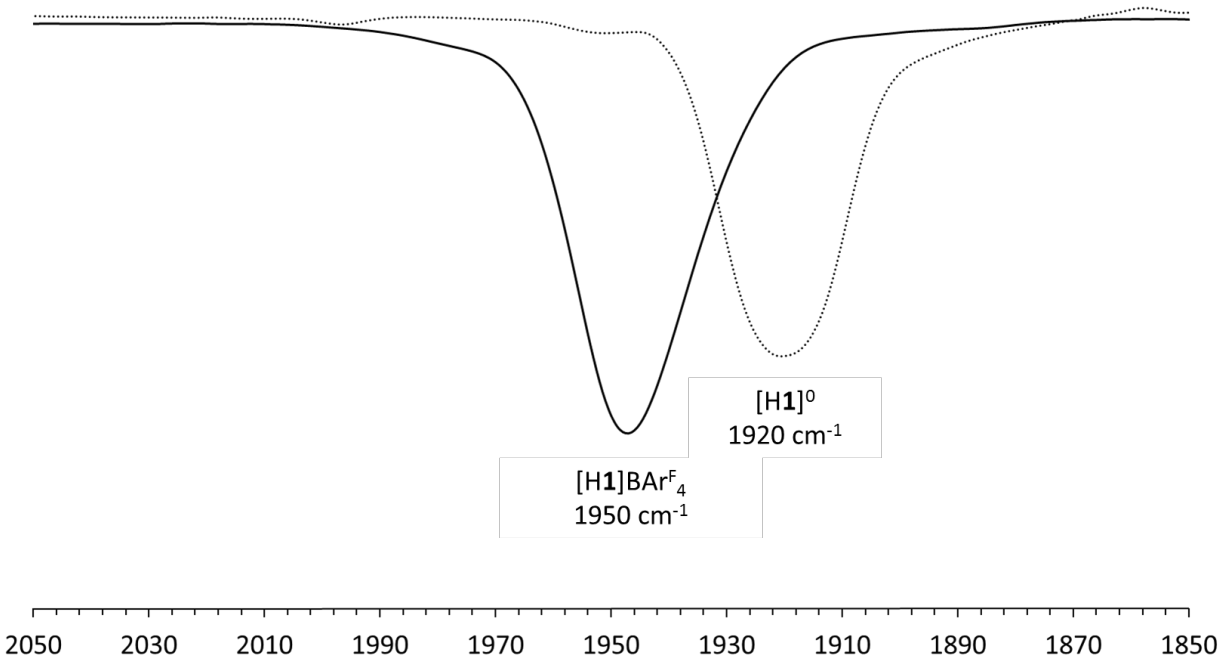


Figure S55. FT-IR spectrum (THF) of $[H\mathbf{1}]^0$ before (dotted line), and immediately after the addition of 5 equiv of $H(OEt_2)_2BAr^F{}_4$ (solid line). All of the starting material has been converted to $[H\mathbf{1}]^+$.

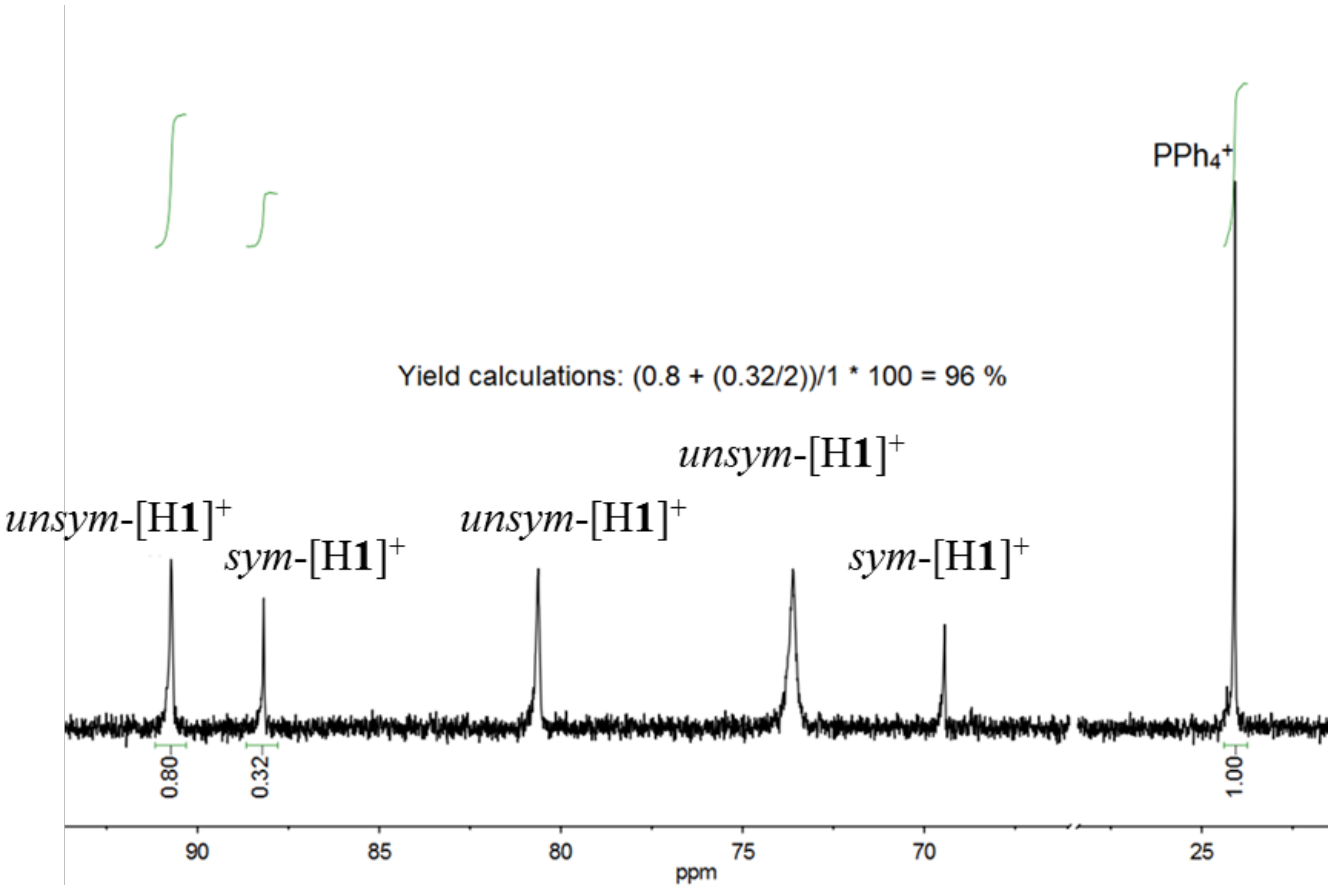


Figure S56. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, THF-d_8) collected immediately after the addition of 5 equiv of $H(OEt_2)_2BAr^F{}_4$ to thermally equilibrated $[H\mathbf{1}]^0$. Only $[H\mathbf{1}]^+$ is visible.

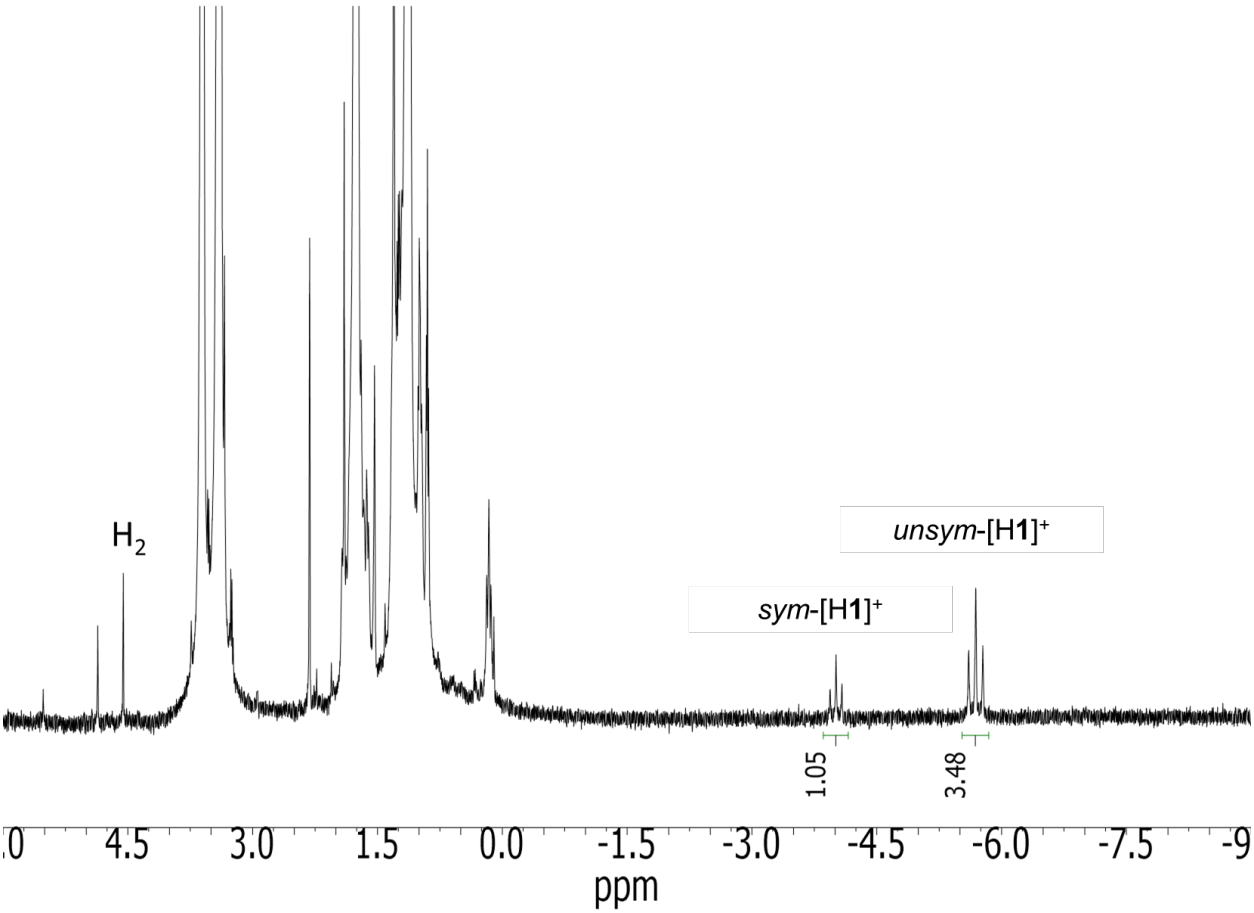


Figure S57. ^{1}H NMR spectrum (500 MHz, THF-d_8) collected immediately after the addition of 5 equiv of $H(OEt_2)_2BAr^F{}_4$ to thermally equilibrated $[H\mathbf{1}]^0$.

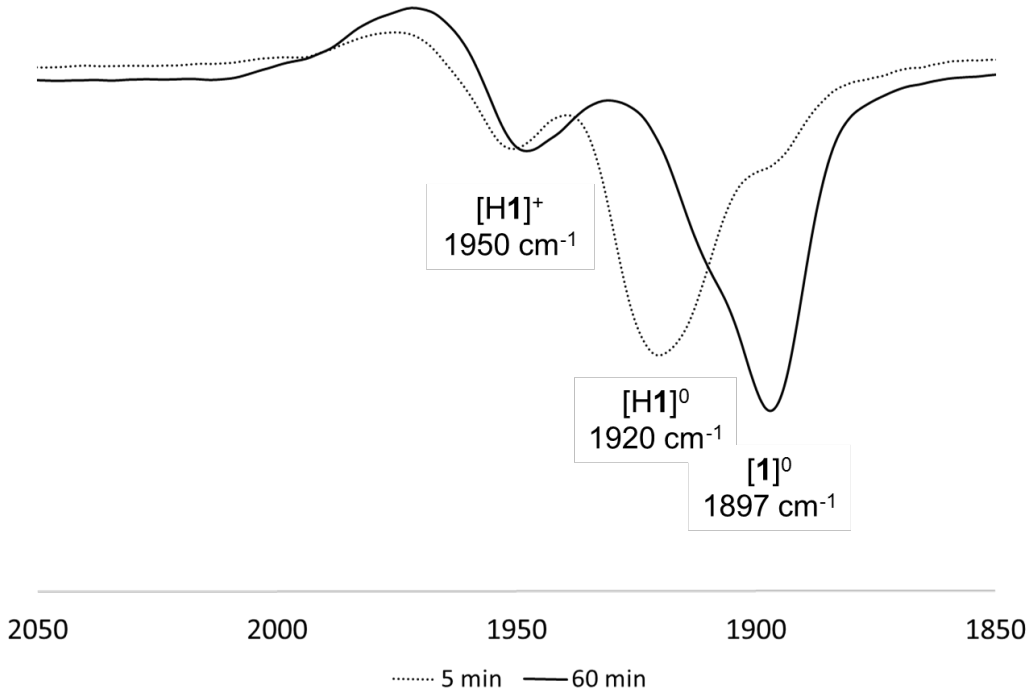


Figure S58. FT-IR spectra (THF) for the reaction of thermally equilibrated $[H\mathbf{1}]^0$ and 0.5 equiv of $H(OEt_2)_2BAr^F{}_4$ recorded at 5 min (dotted line) and 60 min (solid line).

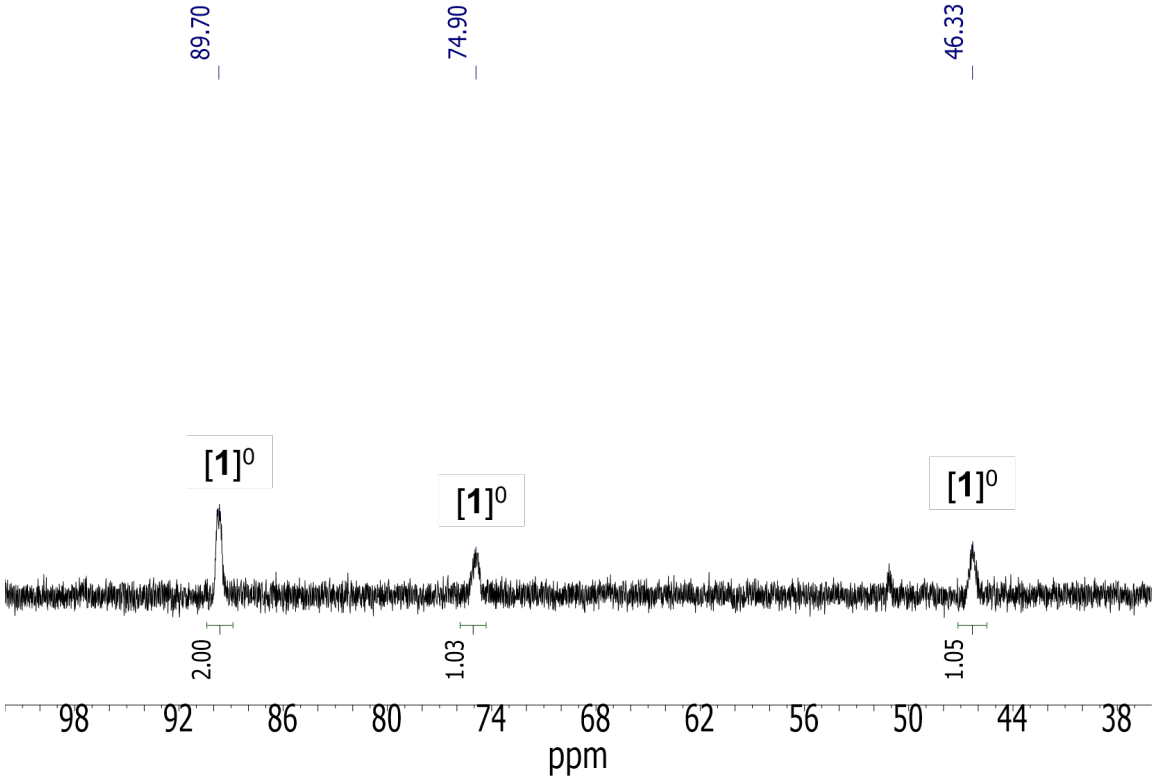


Figure S59. $^{31}P\{^{1}H\}$ NMR spectrum (202.3 MHz, THF-d_8) collected immediately after the addition of 0.5 equiv of $H(OEt_2)_2BAr^F{}_4$ to thermally equilibrated [H**1**]^0.

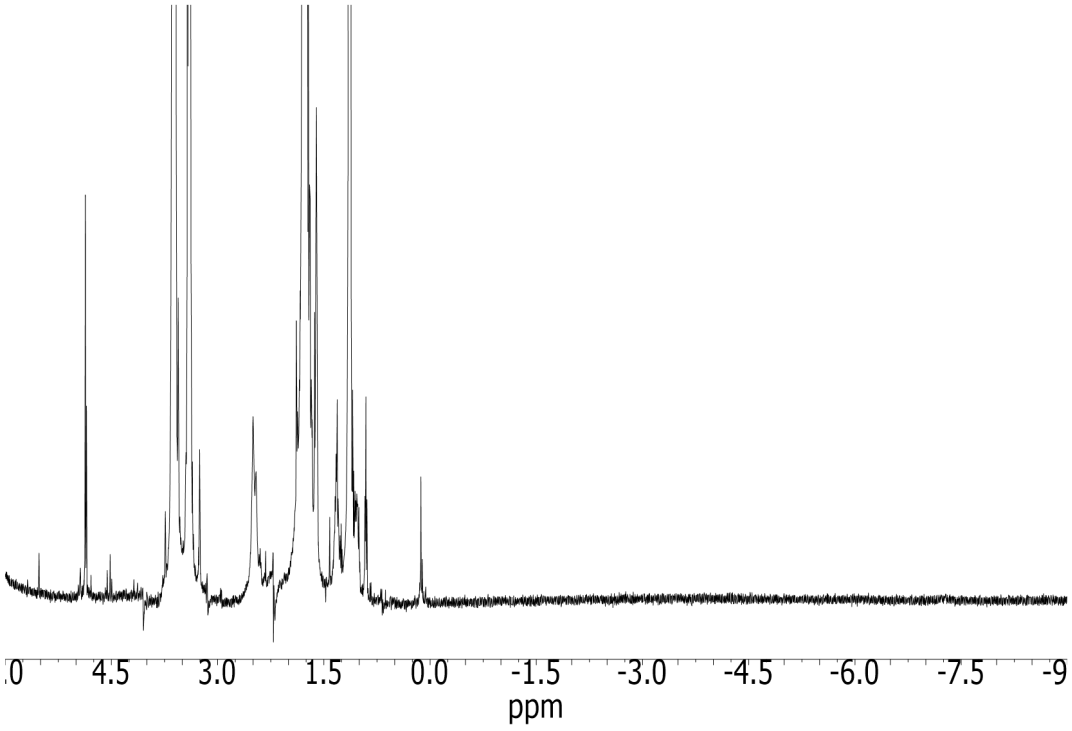


Figure S60. ^{1}H NMR spectrum (500 MHz, THF-d_8) collected immediately after the addition of 0.5 equiv of $H(OEt_2)_2BAr^F{}_4$ to thermally equilibrated $[H\mathbf{1}]^0$.

Experiments on Reduced Hydrides.

Synthesis of [HA]^0 and [HB]^0. A 20-mL vial containing a stirring bar was charged with BAr^F_4 or BF_4 salts of [H**A**]$^+$, [H**B**]$^+$, or [H**1**]$^+$ and $CoCp^*_2$ in a glove box. The solids were stirred in 5 mL of chilled toluene to produce a brown mixture. The mixture was filtered through Celite to remove the BAr^F_4 or BF_4 salts of $[CoCp^*_2]^+$. The filtrate was diluted with 15 mL of cold pentane, and was allowed to stand at –40 ºC to give a brown solid. The precipitate was collected by filtration.

[HA]^0. Using [H**A**]BAr^F_4 (25.7 mg, 0.013 mmol) and $CoCp^*_2$ (4.4 mg, 0.013 mmol). Yield: 10 mg (74 %). FT-IR (THF): ν_{CO} = 1909 cm^{-1}.

[HB]^0. The above general procedure was done with [H**B**]BAr^F_4 (43.3 mg, 0.022 mmol) and $CoCp^*_2$ (7.3 mg, 0.022 mmol). Yield: 13.4 mg (56 %). FT-IR (THF): ν_{CO} = 1925 cm^{-1}. HR ESI-MS: 1093.1348.

Reactions of [H1]^0 with $HBAr^F_4 \cdot 2Et_2O$. 250 uL of 0.2M [H**1**]BAr^F_4 in THF was charged into three vials (0.05 mmol). The vials were sealed with septa and treated with equimolar $CoCp^*_2$ via syringe causing the solution to change color from red-orange to brown. Three control vials were charged with 250 uL of 0.2 M $CoCp^*_2$ in THF. Each vial was treated with equimolar amount of $HBAr^F_4 \cdot 2Et_2O$.

Reductant	Run	H_2 percent yield (%)	Average yield
[H**1**]BAr^F_4 + $CoCp^*_2$	A	32.02	32.15
	B	31.30	
	C	33.19	
$CoCp^*_2$	A	33.45	33.64
	B	33.82	
	C	33.66	

NMR, GC, EPR and FT-IR analysis of Hydrogen Evolution from $[H1]^0$.

NMR analysis: 250 uL of 0.2M [H**1**]BAr^F_4 in THF (0.05 mmol) and $PPh_4BAr^F_4$ (0.05 mmol) were charged into four separate J-young NMR tubes. Each solution was treated with 250 uL of 0.2M $CoCp^*_2$. An equimolar amount of acid was added to the first three samples, and each J-young tube was sealed with a cap. Acid added was varied per sample: $HBAr^F_4{\cdot}2Et_2O$ (a), $[Bu_3NH]BF_4$ (b), ClH_2CO_2H (c), and no acid (d). The internal standard in b and c precipitated as salts of the conjugate bases. Each sample was analyzed by $^{31}P\{^1H\}$ NMR to quantify the products formed, by integration relative to the internal standard. For (b) and (c) the yield were determined by relative product integrations.

FT-IR analysis: 25 uL of 0.1M [H**1**]BAr^F_4 in THF (2.5 umol) was charged into a vial. The solution was treated with 25 uL of 0.1M $CoCp^*_2$ via syringe causing the solution to change color from red-orange to brown. A timer was started upon injection of the reducing agent and an aliquot of the solution was charged into a gas-tight CaF_2 IR cell. FT-IR spectra were recorded for the sample at various time intervals, and the temperate of the spectrometer (~ 26 °) was reported for every collection. The above procedure was repeated with an additional 50 uL of THF added to the solution prior to the reducing agent to achieve an initial concentration of 25 mM.

GC analysis: 25 uL of 0.2M [H**1**]BAr^F_4 in THF (0.005 mmol) was charged into three vials (a, b, c). The vials were sealed with septa and treated with equimolar $CoCp^*_2$ via syringe causing the solution to change color from red-orange to brown. To each reaction vial was injected 100 uL of CH_4 gas (93%) to be used as an internal standard. After >3 h a 500uL sample of the headspace gas was drawn *via* gas-tight syringe from each sample to be analyzed by gas chromatography (see SI for calculation). The yield of H_2 was calculated based on equation 5.

Run	Time (h)	μmol of H_2	Percent H_2
A	3:07	0.25	25
B	3:20	0.29	29
C	3:35	0.35	35

Reactions of $[HA]^0$, $[HB]^0$, and $[H1]^0$ with $HBAr^F_4{\cdot}2Et_2O$. A sample of $[Hn]^0$ (n = **A**, **B**, **1**) (6 umol) was dissolved in 3 mL of THF. The solution was divided into three 5-mL vials (1 mL solution each, 2 umol) and each vial was sealed with a septum. In a separate vial $HBAr^F_4{\cdot}2Et_2O$ (8.1 mg, 8 umol) was dissolved in 3 mL of THF. 0.75 mL of the acid solution (2 umol) was injected into the vial containing the catalyst causing immediate effervesces and a color change from brown to red-orange. Into each reaction vial was injected 60-100 uL of CH_4 gas (93%) as an internal standard. A 500 uL sample of the headspace gas, drawn *via* gas-tight syringe, was analyzed by gas chromatography.

Reductant	Run	H_2 percent yield (%)	Average yield
$[H\mathbf{A}]^0$	A	72.4	70 ± 2.4
	B	67.6	
$[H\mathbf{B}]^0$	A	71.6	71.1 ± 0.6
	B	70.6	
$[H\mathbf{1}]^0$	A	71.2	70.8 ± 0.8
	B	69.8	
	C	71.4	

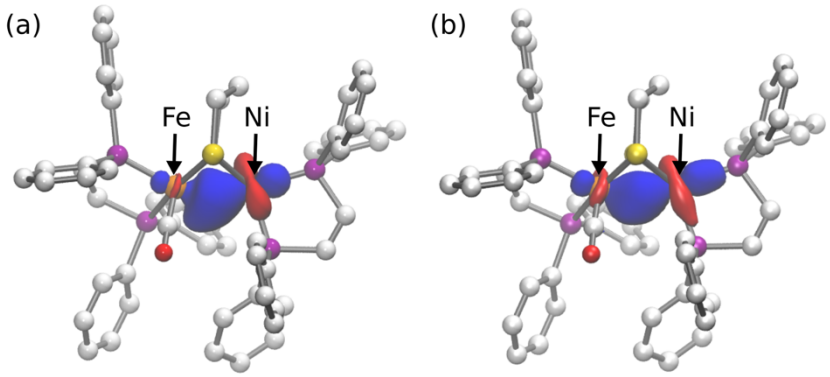


Figure S61. (a) Natural Bond Orbital (NBO) and (b) Pipek-Mezey localized molecular orbital depicting the Ni-Fe σ-bond in $[\mathbf{1}]^0$ (isovalue = 0.05). The hydrogens have been removed for clarity.

Table S9. Comparison of Selected Bond Lengths (Å) and Bond Angles (°) for *unsym*-$[\mathbf{1}]^0$

	Expt	Calc [a]	
		Gas-Opt [b]	Sol-Opt [c]
Ni-Fe	2.526	2.523	2.537
Ni-P [d]	2.159	2.185	2.191
Ni-S [d]	2.273	2.315	2.309
Fe-P [d]	2.205	2.229	2.235
Fe-S [d]	2.265	2.301	2.297
Fe-C	1.763	1.743	1.728
P_1-Ni-P_2	89.54	90.09	90.10
P_3-Fe-P_4	86.27	87.08	86.73
S_1-Ni-S_2/ P_1-Ni-P_2 [e]	80.94	79.19	81.89

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures. [b]Geometries optimized in the gas phase. [c]Geometries optimized in MeCN solvent using C-PCM. [d]These bond lengths are average values. [e]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S10. Comparison of Selected Bond Lengths (Å) and Bond Angles (°) for *unsym*-[H**1**]$^+$

	Expt	Calc [a]	
		Gas-Opt [b]	Sol-Opt [c]
Ni-Fe	2.646	2.686	2.693
Fe-H	1.563	1.609	1.598
Ni-H	1.802	1.812	1.840
Ni-P [d]	2.147	2.199	2.194
Ni-S [d]	2.225	2.255	2.254
Fe-P [d]	2.214	2.267	2.254
Fe-S [d]	2.305	2.349	2.337
Fe-C	1.749	1.743	1.725
P_1-Ni-P_2	87.50	88.67	88.21
P_3-Fe-P_4	86.43	87.21	86.54
S_1-Ni-S_2/ P_1-Ni-P_2 [e]	15.97	17.56	12.13

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures. [b]Geometries optimized in the gas phase. [c]Geometries optimized in MeCN solvent using C-PCM. [d]These bond lengths are average values. [e]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S11. Comparison of Selected Bond Lengths (Å) and Bond Angles (°) for *sym*-[H**A**]$^+$

	Expt	Calc [a]	
		Gas-Opt [b]	Sol-Opt [c]
Ni-Fe	2.656	2.738	2.730
Fe-H	1.555	1.646	1.637
Ni-H	1.847	1.902	1.896
Ni-P [d]	2.176	2.219	2.209
Ni-S [d]	2.227	2.251	2.252
Fe-P [d]	2.225	2.246	2.241
Fe-S [d]	2.300	2.317	2.317
Fe-C	1.763	1.755	1.742
P_1-Ni-P_2	87.27	88.05	87.06
P_3-Fe-P_4	86.73	86.96	86.55
S_1-Ni-S_2/ P_1-Ni-P_2 [e]	28.04	19.82	21.26

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures. [b]Geometries optimized in the gas phase. [c]Geometries optimized in MeCN solvent using C-PCM. [d]These bond lengths are average values. [e]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S12. Comparison of Selected Bond Lengths (Å) and Bond Angles (°) for *sym*-[H**B**]$^+$

	Expt	**Calc** [a]	
		Gas-Opt [b]	**Sol-Opt** [c]
Ni-Fe	2.671	2.699	2.716
Fe-H	1.798	1.654	1.641
Ni-H	1.789	1.851	1.886
Ni-P [d]	2.177	2.217	2.211
Ni-S [d]	2.226	2.253	2.252
Fe-P [d]	2.207	2.239	2.230
Fe-S [d]	2.293	2.322	2.322
Fe-C	1.764	1.756	1.744
P_1-Ni-P_2	87.01	87.91	86.95
P_3-Fe-P_4	87.80	88.00	87.71
S_1-Ni-S_2/ P_1-Ni-P_2 [e]	25.11	26.79	25.14

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures. [b]Geometries optimized in the gas phase. [c]Geometries optimized in MeCN solvent using C-PCM. [d]These bond lengths are average values. [e]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S13. Calculated Bond Lengths (Å) and Bond Angles (°) for Isomers of [H**1**]$^+$ and [H**1**]^0 [a]

	sym-[H**1**]$^+$	*unsym*-[H**1**]$^+$	*sym*-[H**1**]^0	*unsym*-[H**1**]^0
Ni-Fe	2.712	2.686	2.691	2.691
Fe-H	1.653	1.609	1.631	1.631
Ni-H	1.869	1.812	1.808	1.808
Ni-P [b]	2.206	2.199	2.227	2.249
Ni-S [b]	2.257	2.255	2.360	2.355
Fe-P [b]	2.239	2.267	2.260	2.222
Fe-S [b]	2.315	2.349	2.366	2.342
Fe-C	1.756	1.743	1.739	1.761
P_1-Ni-P_2	88.00	88.67	87.26	87.26
P_3-Fe-P_4	87.15	87.21	87.17	87.17
S_1-Ni-S_2/ P_1-Ni-P_2 [c]	26.52	17.56	104.78	104.78

[a]The omission of counterions in the calculations may introduce discrepancies between the crystal structure and DFT-optimized structures. [b]These bond lengths are average values. [c]Dihedral angle defined as the angle between the planes formed by the two groups of three atoms listed.

Table S14. Calculated Spin Densities for Reduced Hydride Species $[H\mathbf{A}]^0$ and $[H\mathbf{B}]^0$

Complex	Ni	Fe	2S	$2P_{Ni}$ [a]
sym-$[H\mathbf{A}]^0$	0.46	0.21	0.17	0.13
unsym-$[H\mathbf{A}]^0$	0.44	0.22	0.15	0.14
sym-$[H\mathbf{B}]^0$	0.48	0.14	0.19	0.14
unsym-$[H\mathbf{B}]^0$	0.41	0.29	0.13	0.13

[a]These values refer to the P atoms of the dppe or dppBz ligand on the Ni center.

Table S15. Experimental and Calculated ν_{CO} (cm^{-1}) for $[H\mathbf{1}]^+$, $[H\mathbf{1}]^0$, and $[\mathbf{1}]^0$ where the pdt is Oriented toward the Fe Center

	ν_{CO} Expt [a,b]	ν_{CO} Calc
$[H\mathbf{1}]^+$	1953, 1960 (sh) [c]	1942 (sym) 1958 (unsym)
$[H\mathbf{1}]^0$	1920	1924
$[\mathbf{1}]^0$	1912 (sh) [c], 1897	1908

[a]Experiments performed in THF solution unless otherwise noted. [b]Counterions for salts are $BAr^F{}_4^-$. [c]sh = shoulder.

Table S16. Calculated Spin Densities for Reduced Hydride Species $[H\mathbf{1}]^0$ for Geometries where the pdt is Oriented toward the Fe Center

Complex	Ni	Fe	2S	$2P_{Ni}$ [a]
sym-$[H\mathbf{1}]^0$	0.46	0.21	0.18	0.11
unsym-$[H\mathbf{1}]^0$	0.48	0.22	0.14	0.10

[a]These values refer to the P atoms of the dppv ligand on the Ni center.

Table S17. Calculated Spin Densities and Select Bond Lengths (Å) and Bond Angles (°) for Dihydrogen Species *unsym*-$[H_2\mathbf{1}]^+$

	Ni(dppv): apical-basal	Ni(dppv): dibasal
ρ(Ni)	0.60	0.57
ρ(Fe)	0.01	0.00
ρ(2S)	0.18	0.19
$\rho(P_{Ni})$ [a]	0.15	0.17
Ni-Fe	3.051	3.044
Fe-H [b]	1.695	1.703
H-H [c]	0.847	0.854

[a]These values refer to the P atoms of the dppv ligand on the Ni center. [b]These bond lengths are average values. [c]For comparison, the H-H bond length in molecular H_2 is 0.74 Å.

Table S18. Calculated pK_a's of Hydride Species

	Expt	Calc
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(CO)_2(PPh_3)]^+$	14.9 [a]	14.9 [b]
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(CO)_3]^+$	10.7 [a]	10.5
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppe)(CO)]^+$ ($[H\mathbf{A}]^+$)	n/a	15.9
$[(dppe)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppBz)(CO)]^+$ ($[H\mathbf{B}]^+$)	n/a	15.9
$[(dppv)Ni(\mu\text{-}pdt)(\mu\text{-}H)Fe(dppv)(CO)]^+$ ($[H\mathbf{1}]^+$)	16.6	17.7
$[(dppv)Ni(\mu\text{-}pdt)(\mu\text{-}H_2)Fe(dppv)(CO)]^+$ ($[H_2\mathbf{1}]^+$)	n/a	5.6

[a]Experimental value from ref. [11]. [b]This species was used as the reference for all calculated pK_a's, so the calculated and experimental values agree by construction.

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Optimized Cartesian Coordinates of Species Studied

The following tables provide the optimized Cartesian coordinates of all species studied. The geometries were optimized in the gas phase using the BP86 functional with the SDD pseudopotential and associated basis set for the Ni and Fe centers, the 6-31G** basis set the μ-H ligands, and the 6-31G* basis set for all other atoms.

Table S19. Cartesian Coordinates for *unsym*-[(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*unsym*-[**1**]^{0}, –4696.35317317 E_h)

atom	x	y	z
Ni	1.602547	8.718879	9.899522
Fe	1.195300	9.719577	12.179973
O	3.136622	11.900750	11.997651
C	2.341022	11.030379	12.093510
P	3.676478	9.173333	9.389298
P	1.364978	7.657641	8.002783
C	5.173500	8.594610	10.326760
C	5.739419	7.327854	10.054598
H	5.312286	6.701750	9.262160
C	6.845149	6.864676	10.786154
H	7.278710	5.884946	10.552401
C	7.400070	7.658195	11.803931
H	8.266512	7.300065	12.371595
C	6.835362	8.912477	12.091612
H	7.251248	9.533502	12.892083
C	5.727974	9.377284	11.364905
H	5.297001	10.356514	11.599497
C	4.202825	10.894747	8.872966
C	3.198849	11.847883	8.605207
H	2.149702	11.589539	8.792835
C	3.538973	13.121325	8.119577
H	2.747949	13.855024	7.925279
C	4.883620	13.457213	7.896000
H	5.148875	14.452823	7.521590
C	5.889859	12.512148	8.158011
H	6.942482	12.766721	7.986515
C	5.552679	11.238036	8.640633
H	6.346205	10.511161	8.846979
C	4.010659	8.348799	7.757698
H	5.010208	8.434906	7.307099
C	2.998902	7.715071	7.136630
H	3.112526	7.246154	6.148967
C	0.278771	8.375676	6.669719

C	-0.958511	7.809051	6.293897
H	-1.280500	6.858286	6.732820
C	-1.779443	8.448197	5.349624
H	-2.736250	7.992651	5.068656
C	-1.377317	9.660135	4.766617
H	-2.017328	10.156001	4.027999
C	-0.148923	10.234289	5.137232
H	0.174129	11.180795	4.688546
C	0.669437	9.601732	6.084343
H	1.618697	10.064565	6.378402
C	1.015967	5.830033	7.898104
C	0.960851	5.078269	9.089819
H	1.066589	5.594611	10.051959
C	0.779045	3.685396	9.043259
H	0.734882	3.115079	9.978147
C	0.656039	3.028968	7.808758
H	0.513328	1.942656	7.773446
C	0.718080	3.769176	6.615324
H	0.626353	3.262395	5.647495
C	0.898792	5.159929	6.658407
H	0.937064	5.728450	5.721924
P	2.283252	8.697879	13.871610
P	-0.156965	10.556171	13.704637
C	2.569489	6.868131	13.841517
C	1.864670	5.976931	14.676320
H	1.125204	6.358614	15.388584
C	2.089098	4.593106	14.592195
H	1.531611	3.912489	15.246183
C	3.021658	4.084448	13.674333
H	3.199481	3.004633	13.611960
C	3.721777	4.965420	12.832985
H	4.448173	4.580112	12.108893
C	3.492129	6.347768	12.907721
H	4.030553	7.023395	12.234543
C	3.865387	9.345310	14.637704
C	4.917083	8.504279	15.057309
H	4.863098	7.427140	14.874666
C	6.040282	9.039209	15.710350
H	6.846822	8.369254	16.030521
C	6.130386	10.418699	15.953011
H	7.007298	10.833788	16.463066
C	5.084747	11.263341	15.543926
H	5.139960	12.341748	15.730938
C	3.959298	10.731189	14.897454

H	3.147169	11.401175	14.599034
C	1.259765	8.931142	15.402213
H	1.565213	8.448139	16.341384
C	0.236771	9.805826	15.350759
H	-0.370322	10.037773	16.236806
C	-0.076945	12.385923	14.019308
C	-0.164966	12.946032	15.312560
H	-0.279768	12.300545	16.189557
C	-0.100593	14.337161	15.491217
H	-0.159482	14.757338	16.501975
C	0.035706	15.186201	14.380717
H	0.084037	16.271973	14.522100
C	0.115696	14.637766	13.090437
H	0.227738	15.292929	12.219119
C	0.068931	13.246163	12.908359
H	0.149604	12.815130	11.902416
C	-2.002654	10.274294	13.718829
C	-2.503680	9.017375	14.126771
H	-1.805937	8.231099	14.438830
C	-3.885340	8.769092	14.143516
H	-4.256880	7.791406	14.471652
C	-4.787195	9.768106	13.740438
H	-5.865624	9.574030	13.751948
C	-4.298616	11.017611	13.326265
H	-4.994717	11.804589	13.013911
C	-2.917037	11.271848	13.318177
H	-2.548833	12.256761	13.011240
S	0.210578	10.573702	10.257508
S	0.435907	7.664096	11.554393
C	-1.552489	10.019075	10.064932
H	-2.124095	10.383884	10.936467
H	-1.918704	10.564869	9.176048
C	-1.767925	8.519398	9.861905
H	-2.848764	8.346890	9.668809
H	-1.230221	8.204414	8.951398
C	-1.352528	7.624912	11.029862
H	-1.545561	6.567582	10.769995
H	-1.947006	7.858860	11.930655

Table S20. *unsym*-[(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*unsym*-[**1**]^{0}, – 4696.34940037 E_h)

atom	x	y	z
Ni	1.665290	8.740437	9.902309
Fe	1.106742	9.697414	12.154608
O	3.091187	11.835325	11.979397
C	2.274205	10.985624	12.074880
P	3.746266	9.205033	9.379942
P	1.428514	7.670326	8.019337
C	5.239887	8.587438	10.295598
C	5.801177	7.326566	9.987691
H	5.380465	6.730594	9.168983
C	6.895375	6.831851	10.715691
H	7.325318	5.857596	10.453862
C	7.444983	7.587436	11.764818
H	8.303343	7.205020	12.328936
C	6.884911	8.835270	12.087988
H	7.296591	9.427406	12.912200
C	5.787608	9.330659	11.366494
H	5.358393	10.303433	11.630493
C	4.287676	10.930999	8.895595
C	3.286687	11.884289	8.615561
H	2.234403	11.619715	8.774951
C	3.634119	13.164714	8.154621
H	2.845501	13.898096	7.949410
C	4.982777	13.508223	7.969146
H	5.253491	14.509496	7.614156
C	5.985667	12.563351	8.243963
H	7.041290	12.823740	8.101895
C	5.641492	11.281558	8.701052
H	6.432233	10.554312	8.916341
C	4.051132	8.419734	7.722724
H	5.040068	8.524818	7.252926
C	3.031461	7.793113	7.105925
H	3.128673	7.347154	6.105854
C	0.247896	8.328870	6.743663
C	-1.028758	7.762314	6.531354
H	-1.312347	6.843296	7.056662
C	-1.934528	8.356291	5.636850
H	-2.919164	7.900172	5.480967
C	-1.581869	9.526376	4.945384
H	-2.288827	9.988240	4.246961

C	-0.317317	10.102653	5.156187
H	-0.033239	11.016666	4.621961
C	0.588127	9.512919	6.050624
H	1.567477	9.976140	6.218605
C	1.156433	5.828374	7.921103
C	1.250040	5.062265	9.101461
H	1.407746	5.572621	10.059109
C	1.133449	3.662695	9.050347
H	1.201912	3.081777	9.977145
C	0.928230	3.014208	7.822559
H	0.836303	1.922528	7.783936
C	0.840234	3.769540	6.640257
H	0.682285	3.269272	5.677586
C	0.954547	5.167157	6.687747
H	0.875683	5.747636	5.761275
P	2.187308	8.671549	13.841187
P	-0.228195	10.561594	13.695406
C	2.484660	6.845235	13.791747
C	1.786059	5.942821	14.619319
H	1.045199	6.314144	15.335741
C	2.019315	4.561191	14.522762
H	1.466816	3.871130	15.170988
C	2.955204	4.067020	13.600402
H	3.141172	2.989074	13.529742
C	3.649485	4.959653	12.766099
H	4.379234	4.585438	12.039626
C	3.410452	6.339796	12.852217
H	3.942664	7.025256	12.183514
C	3.771949	9.322595	14.599760
C	4.834623	8.485013	14.997635
H	4.789842	7.410466	14.798489
C	5.957249	9.020011	15.651831
H	6.771995	8.352398	15.955584
C	6.036079	10.395993	15.916456
H	6.912533	10.811051	16.427294
C	4.979674	11.237198	15.528487
H	5.026067	12.312896	15.732521
C	3.854628	10.704938	14.881799
H	3.033423	11.372120	14.602230
C	1.175159	8.901782	15.377830
H	1.478465	8.409497	16.312809
C	0.171362	9.798997	15.335966
H	-0.424004	10.041498	16.227178
C	-0.085667	12.388428	14.005527

C	-0.126202	12.954446	15.298385
H	-0.238498	12.314631	16.179938
C	-0.017683	14.343775	15.470092
H	-0.039796	14.768705	16.480345
C	0.115318	15.185066	14.353317
H	0.197939	16.269447	14.489352
C	0.148284	14.630715	13.063433
H	0.257972	15.279818	12.187307
C	0.057736	13.240459	12.887908
H	0.104713	12.803927	11.882145
C	-2.082201	10.341407	13.760663
C	-2.613041	9.105235	14.194184
H	-1.934289	8.300056	14.498902
C	-3.999880	8.896101	14.226317
H	-4.395971	7.933529	14.570221
C	-4.877167	9.914760	13.817023
H	-5.960428	9.750539	13.839015
C	-4.358092	11.144443	13.381278
H	-5.035328	11.945661	13.063506
C	-2.970500	11.360109	13.356821
H	-2.577155	12.327490	13.026727
S	0.232576	10.572745	10.173775
S	0.432409	7.635932	11.455202
C	-1.443277	9.925829	9.681145
H	-2.116276	10.802655	9.664767
H	-1.342420	9.560958	8.643637
C	-2.055384	8.847017	10.574884
H	-2.225532	9.259267	11.580881
H	-3.058718	8.599852	10.165399
C	-1.271727	7.540173	10.697452
H	-1.146537	7.055572	9.711833
H	-1.835103	6.839069	11.340864

Table S21. *sym*-[(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*sym*-[**1**]^{0}, –4696.34382101 E_h)

atom	x	y	z
Fe	4.210303	2.475814	7.436273
Ni	3.500164	1.830744	4.981307
S	4.463888	0.400817	6.521336
S	5.067425	3.376716	5.557283
P	2.965804	1.674003	9.145893
P	3.516186	4.510133	8.105363
P	3.771870	1.247813	2.877979
P	1.335286	1.831631	4.701582
O	6.761932	2.549197	8.821801
C	3.977838	1.056878	10.587905
C	3.717278	1.435495	11.921744
H	2.901218	2.128670	12.151081
C	4.502188	0.932953	12.972616
H	4.291180	1.243595	14.002537
C	5.548066	0.035248	12.707057
H	6.158304	-0.357683	13.528118
C	5.811778	-0.351114	11.382912
H	6.631064	-1.045576	11.164591
C	5.039390	0.162191	10.329827
H	5.262232	-0.122489	9.294595
C	1.661489	0.339625	9.131229
C	0.289078	0.664770	9.082283
H	-0.024159	1.712655	9.015727
C	-0.690186	-0.338898	9.144963
H	-1.750342	-0.064181	9.112787
C	-0.311496	-1.685611	9.251167
H	-1.075128	-2.469141	9.308858
C	1.051490	-2.022602	9.277379
H	1.357655	-3.072150	9.356927
C	2.031026	-1.020988	9.214164
H	3.088254	-1.299105	9.256292
C	4.838030	5.481381	8.983247
C	5.069404	5.324992	10.365372
H	4.425740	4.664154	10.956832
C	6.129438	6.002033	10.989963
H	6.294134	5.874177	12.066028
C	6.976718	6.832663	10.239981
H	7.805303	7.358507	10.727767
C	6.760464	6.982314	8.859736

H	7.421433	7.623901	8.265597
C	5.697890	6.313875	8.233325
H	5.534111	6.436715	7.157101
C	2.768476	5.864564	7.070300
C	2.477101	5.651592	5.710008
H	2.669519	4.669531	5.261904
C	1.944545	6.693607	4.931279
H	1.729303	6.517681	3.872146
C	1.683240	7.946032	5.506163
H	1.266563	8.755866	4.896004
C	1.958547	8.161850	6.867630
H	1.757891	9.138334	7.323721
C	2.506087	7.130334	7.643265
H	2.752618	7.318860	8.694753
C	5.689097	2.529837	8.325807
C	6.261732	0.197989	6.066982
H	6.845382	0.314507	6.997842
H	6.362367	-0.851778	5.736367
C	6.797211	1.122514	4.969718
H	7.856548	0.846350	4.776929
H	6.245883	0.917158	4.036436
C	6.750633	2.625212	5.254482
H	7.159534	3.174545	4.386589
H	7.364244	2.885666	6.134504
C	4.323182	-0.481485	2.458505
C	5.632169	-0.780957	2.019814
H	6.340817	0.029748	1.817903
C	6.032899	-2.112315	1.819602
H	7.052375	-2.324053	1.476457
C	5.133754	-3.165214	2.051488
H	5.446709	-4.203268	1.891784
C	3.829007	-2.878144	2.487674
H	3.117505	-3.692157	2.668764
C	3.427950	-1.549960	2.694100
H	2.411691	-1.338987	3.046544
C	4.681473	2.288472	1.622625
C	4.872047	1.857891	0.289416
H	4.553550	0.853591	-0.012483
C	5.479607	2.702354	-0.652384
H	5.623740	2.353444	-1.681663
C	5.900136	3.990240	-0.278410
H	6.376177	4.647907	-1.014846
C	5.706194	4.430117	1.040296
H	6.028106	5.434327	1.339356

C	5.098759	3.585647	1.985049
H	4.937650	3.928135	3.014494
C	0.303462	0.353159	5.224900
C	-1.103139	0.332818	5.102590
H	-1.641576	1.249345	4.835570
C	-1.817813	-0.857039	5.311888
H	-2.909536	-0.861150	5.207762
C	-1.136009	-2.040375	5.641711
H	-1.693968	-2.971555	5.795289
C	0.261103	-2.023238	5.781125
H	0.797860	-2.937669	6.057640
C	0.978751	-0.832694	5.578692
H	2.069541	-0.811663	5.692585
C	0.125040	3.214017	5.006518
C	-0.308481	3.478425	6.324305
H	0.055464	2.849304	7.143750
C	-1.201899	4.525134	6.591606
H	-1.531447	4.709530	7.620829
C	-1.672778	5.337662	5.545782
H	-2.369977	6.156867	5.754437
C	-1.237462	5.095991	4.233762
H	-1.595542	5.725631	3.410599
C	-0.344466	4.044543	3.965988
H	-0.009956	3.872597	2.936380
C	2.256367	4.316573	9.445750
C	2.013964	3.071418	9.900979
C	2.095474	1.252709	2.099062
C	1.045716	1.557864	2.883604
H	1.984842	1.005294	1.033769
H	0.015609	1.556926	2.498365
H	1.745718	5.198653	9.857210
H	1.281109	2.880483	10.697505

Table S22. *sym*-[(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*sym*-[**1**]^{0}, –4696.34288488 E_h)

atom	x	y	z
Fe	4.273165	2.440396	7.473723
Ni	3.450583	1.823143	5.052385
S	4.385921	0.346323	6.556445
S	5.098906	3.292360	5.562523
P	3.002601	1.690056	9.183728
P	3.618997	4.502296	8.093345
P	3.757082	1.278734	2.946627
P	1.274415	1.794415	4.740041
O	6.716486	2.569131	9.048548
C	3.978270	0.993674	10.613919
C	3.733586	1.356916	11.954860
H	2.955219	2.087530	12.198203
C	4.487889	0.791397	12.995959
H	4.290453	1.090517	14.031933
C	5.486571	-0.153446	12.712839
H	6.072898	-0.595306	13.526425
C	5.734891	-0.523349	11.381064
H	6.518778	-1.253485	11.149404
C	4.993490	0.051875	10.337881
H	5.206490	-0.217543	9.296407
C	1.626448	0.433782	9.144715
C	0.273306	0.833492	9.145223
H	0.016788	1.898729	9.138950
C	-0.757067	-0.119565	9.179822
H	-1.801572	0.211490	9.185135
C	-0.448762	-1.487582	9.212777
H	-1.251710	-2.232021	9.246150
C	0.894675	-1.896422	9.196551
H	1.145138	-2.963225	9.219139
C	1.925133	-0.946483	9.158911
H	2.966861	-1.280622	9.160714
C	4.967102	5.502390	8.893072
C	5.202938	5.449137	10.281892
H	4.550497	4.848233	10.925396
C	6.278376	6.153201	10.848009
H	6.447086	6.105681	11.929963
C	7.135893	6.907507	10.032352
H	7.976294	7.454544	10.474484
C	6.915096	6.953631	8.645234

H	7.584155	7.535415	8.000729
C	5.837932	6.257894	8.076925
H	5.670796	6.298062	6.994885
C	2.840672	5.821635	7.035423
C	2.468854	5.553029	5.705058
H	2.621421	4.547379	5.292817
C	1.908672	6.568977	4.911279
H	1.629058	6.349450	3.875732
C	1.699375	7.850068	5.442516
H	1.260203	8.638990	4.820839
C	2.055229	8.121360	6.775080
H	1.895604	9.120448	7.197118
C	2.630330	7.116002	7.564814
H	2.938453	7.346412	8.591325
C	5.704858	2.508961	8.440165
C	6.087735	0.005005	5.868522
H	6.511699	-0.811463	6.482273
H	5.935432	-0.391429	4.849384
C	7.073600	1.177841	5.852783
H	7.300922	1.484293	6.886732
H	8.028854	0.803202	5.425386
C	6.664591	2.409515	5.039081
H	6.532234	2.156436	3.971476
H	7.465331	3.168807	5.104213
C	4.414327	-0.404158	2.505697
C	5.779783	-0.617774	2.208310
H	6.461825	0.237046	2.132712
C	6.270359	-1.914811	1.986234
H	7.331139	-2.059323	1.750264
C	5.408024	-3.020490	2.064463
H	5.791336	-4.032120	1.889761
C	4.050758	-2.820406	2.368430
H	3.369102	-3.676657	2.430629
C	3.558026	-1.525540	2.590719
H	2.499338	-1.381714	2.836064
C	4.615878	2.382315	1.705879
C	4.918370	1.946351	0.395511
H	4.727777	0.906546	0.106931
C	5.471638	2.833150	-0.540925
H	5.702975	2.479593	-1.552584
C	5.726808	4.168374	-0.184463
H	6.161275	4.859022	-0.916397
C	5.422728	4.612390	1.111939
H	5.619208	5.651870	1.398892

C	4.868711	3.726440	2.051185
H	4.633931	4.070169	3.065536
C	0.252722	0.296792	5.234533
C	-1.156856	0.274536	5.155985
H	-1.706682	1.197907	4.941761
C	-1.860742	-0.926072	5.340253
H	-2.955286	-0.930148	5.271323
C	-1.165894	-2.119296	5.599170
H	-1.715934	-3.058383	5.732104
C	0.235108	-2.101696	5.692347
H	0.783704	-3.025283	5.910418
C	0.942147	-0.900908	5.515777
H	2.035943	-0.880131	5.595849
C	0.037418	3.159918	5.011740
C	-0.411856	3.435552	6.322368
H	-0.055181	2.814442	7.151122
C	-1.314475	4.479372	6.569507
H	-1.656988	4.671580	7.593158
C	-1.778560	5.279246	5.510831
H	-2.482576	6.096488	5.703848
C	-1.328190	5.026450	4.205873
H	-1.681846	5.645111	3.372446
C	-0.426685	3.977412	3.958086
H	-0.080970	3.796879	2.933608
C	2.399735	4.360128	9.475748
C	2.130951	3.129334	9.953908
C	2.091144	1.216644	2.151376
C	1.023369	1.504097	2.918456
H	2.003302	0.962263	1.085530
H	-0.000428	1.477547	2.517343
H	1.927911	5.262791	9.889106
H	1.414143	2.973760	10.772323

Table S23. *unsym*-[(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} transition state to interconvert the Fe(dppv) enantiomers with Ni(dppv) apical basal and pdt oriented toward Ni (TS-*unsym*-[**1**]^{0}, –4696.33809725 E_h)

atom	x	y	z
Ni	1.880238	8.844054	9.862385
Fe	1.246512	10.072953	12.035005
O	4.077415	10.695208	12.283128
C	2.930224	10.425923	12.113557
P	4.016107	9.022179	9.363248
P	1.599149	7.538578	8.132479
C	4.298016	7.934990	7.883247
H	5.312507	7.856330	7.466729
C	3.261300	7.236379	7.385200
H	3.362199	6.548344	6.533819
P	1.103009	9.539113	14.172370
P	0.737404	12.113276	12.657571
C	1.203570	11.108518	15.155074
H	1.353047	11.072034	16.243373
C	1.064892	12.264759	14.476581
H	1.083990	13.247677	14.968537
S	0.523491	10.734576	9.916556
S	0.621496	7.928883	11.523461
C	-1.231773	10.167465	9.654991
H	-1.853363	10.658752	10.424208
H	-1.530907	10.592909	8.678925
C	-1.475415	8.657145	9.627651
H	-2.551376	8.489300	9.402623
H	-0.914022	8.230965	8.777994
C	-1.138638	7.868089	10.894568
H	-1.343423	6.797278	10.713952
H	-1.771382	8.184871	11.743876
C	-0.492367	8.816641	14.813717
C	-0.732443	7.429391	14.678995
C	-1.489314	9.624629	15.401063
C	-1.942150	6.871144	15.118158
H	0.030235	6.789009	14.224462
C	-2.698662	9.061092	15.843104
H	-1.321855	10.701094	15.515532
C	-2.929600	7.683951	15.701809
H	-2.111774	5.793933	15.006436
H	-3.458440	9.704001	16.302632
H	-3.872084	7.244168	16.047654
C	2.332993	8.481693	15.095478

C	2.094845	8.115256	16.440118
C	3.545557	8.104383	14.488597
C	3.056377	7.394059	17.162601
H	1.147845	8.385506	16.921432
C	4.507989	7.382337	15.214775
H	3.743339	8.383400	13.450042
C	4.267411	7.027141	16.550504
H	2.858612	7.116554	18.204602
H	5.448091	7.103597	14.726281
H	5.019779	6.464772	17.115648
C	-1.019345	12.745052	12.626534
C	-1.346100	14.118285	12.608982
C	-2.060904	11.796943	12.711133
C	-2.687848	14.529399	12.662472
H	-0.551053	14.868728	12.546399
C	-3.401746	12.209738	12.772026
H	-1.806090	10.730647	12.738271
C	-3.718109	13.577767	12.742639
H	-2.927674	15.598941	12.642679
H	-4.198609	11.460141	12.838492
H	-4.764306	13.902183	12.782065
C	1.701034	13.528412	11.957537
C	2.860571	13.985750	12.620720
C	1.348193	14.108950	10.718034
C	3.637016	15.017358	12.070114
H	3.165591	13.528374	13.568558
C	2.129855	15.137202	10.169435
H	0.465604	13.747108	10.181950
C	3.271982	15.597778	10.844943
H	4.530321	15.365412	12.601507
H	1.844894	15.577665	9.207170
H	3.877656	16.403949	10.415424
C	0.711919	8.090262	6.583875
C	0.406746	7.208620	5.522664
C	0.437975	9.466024	6.432465
C	-0.176142	7.694321	4.341583
H	0.617869	6.137703	5.620678
C	-0.140389	9.949327	5.247159
H	0.683973	10.149673	7.255650
C	-0.452063	9.065122	4.201749
H	-0.412817	6.999526	3.527224
H	-0.348906	11.020449	5.143186
H	-0.907560	9.441808	3.278670
C	0.994842	5.803785	8.394101

C	1.884851	4.861816	8.957345
C	-0.340949	5.414377	8.152769
C	1.452966	3.562321	9.261208
H	2.921927	5.152618	9.161784
C	-0.771962	4.113602	8.461209
H	-1.046996	6.124612	7.708709
C	0.122359	3.183752	9.015487
H	2.159152	2.843493	9.692520
H	-1.811476	3.827140	8.263394
H	-0.215267	2.168835	9.253896
C	4.774117	10.595439	8.721067
C	5.443263	11.515927	9.558419
C	4.592432	10.927275	7.358574
C	5.934333	12.723445	9.036917
H	5.566104	11.294276	10.621818
C	5.082474	12.136607	6.842592
H	4.062625	10.233577	6.695343
C	5.760158	13.037806	7.679477
H	6.451318	13.424646	9.701937
H	4.935665	12.371857	5.781837
H	6.145888	13.981565	7.276983
C	5.359021	8.245017	10.404910
C	6.730276	8.556734	10.296109
C	4.963178	7.177927	11.239041
C	7.684972	7.819741	11.016065
H	7.055198	9.378257	9.648549
C	5.921167	6.428347	11.941252
H	3.894159	6.940617	11.325292
C	7.284847	6.751072	11.835190
H	8.747110	8.077253	10.928675
H	5.598909	5.593666	12.574626
H	8.033496	6.170860	12.386997

Table S24. [(dppv)Ni^{I}(μ-pdt)Fe^{I}(dppv)(CO)]^{0} transition state to interconvert the unsym and sym isomers with Ni(dppv) apical-basal and pdt oriented toward Ni (TS-[**1**]^{0}, –4696.31303163 E_h)

atom	x	y	z
Ni	1.617109	8.815398	9.794580
Fe	1.391623	9.555479	12.397213
O	0.026912	11.956345	13.334050
C	0.616277	11.004443	12.944030
P	3.654929	8.764065	8.973862
P	0.849204	8.339588	7.803699
C	4.652809	7.236435	9.338400
C	4.580077	6.105220	8.495555
H	3.988578	6.148339	7.574203
C	5.255569	4.919628	8.827749
H	5.189533	4.053781	8.158421
C	6.013532	4.844381	10.007011
H	6.543362	3.919961	10.264439
C	6.086181	5.962106	10.855092
H	6.673626	5.920094	11.779177
C	5.407785	7.146564	10.528911
H	5.474339	8.006656	11.201966
C	4.949352	10.110198	8.922701
C	6.319969	9.864581	8.693363
H	6.686950	8.834514	8.628033
C	7.218777	10.935408	8.559099
H	8.281614	10.732882	8.380401
C	6.760028	12.261157	8.650783
H	7.464662	13.094820	8.550854
C	5.395797	12.513274	8.872556
H	5.029898	13.542135	8.960396
C	4.496835	11.442488	9.006051
H	3.432602	11.631316	9.188585
C	3.480639	8.613553	7.129344
H	4.384846	8.639718	6.504380
C	2.246367	8.497593	6.605410
H	2.062340	8.415552	5.524791
C	-0.447554	9.414346	7.035066
C	-1.819029	9.078813	7.064923
H	-2.136684	8.111207	7.469420
C	-2.781684	9.969940	6.563854
H	-3.841973	9.693106	6.590960
C	-2.389809	11.207819	6.028725
H	-3.142402	11.902007	5.638330

C	-1.027968	11.551691	5.998064
H	-0.713144	12.515979	5.582829
C	-0.064562	10.664585	6.501078
H	0.995361	10.944881	6.486091
C	0.318033	6.607730	7.341120
C	0.679577	5.554987	8.208336
H	1.189993	5.795247	9.150519
C	0.385892	4.223879	7.870043
H	0.671046	3.415439	8.553123
C	-0.273638	3.930627	6.665329
H	-0.508056	2.892199	6.404241
C	-0.632941	4.973124	5.794116
H	-1.145135	4.749992	4.850820
C	-0.335749	6.304399	6.126073
H	-0.620959	7.110136	5.440190
P	3.287815	10.518590	13.047505
P	1.235805	8.789915	14.470381
C	5.057604	9.898787	13.075310
C	5.408425	8.866912	13.976045
H	4.651095	8.444618	14.644485
C	6.723856	8.381693	14.035401
H	6.975158	7.589647	14.750470
C	7.713866	8.917196	13.193436
H	8.743076	8.543653	13.243293
C	7.374187	9.936585	12.290034
H	8.132417	10.359097	11.621708
C	6.057754	10.424435	12.228077
H	5.815280	11.222357	11.520051
C	3.553555	12.302542	12.546232
C	2.716243	12.885957	11.575414
H	1.953940	12.268453	11.087001
C	2.844737	14.244724	11.240986
H	2.177570	14.682408	10.489563
C	3.813990	15.038086	11.874588
H	3.909918	16.100108	11.620586
C	4.658890	14.465823	12.841165
H	5.419319	15.077910	13.340007
C	4.529698	13.108930	13.173909
H	5.205971	12.673203	13.918514
C	3.096477	10.740001	14.890610
H	3.748475	11.443024	15.427166
C	2.175034	9.989388	15.524461
H	2.020431	10.028839	16.611842
C	-0.449549	8.790570	15.253291

C	-1.243356	7.620531	15.272841
H	-0.824375	6.671929	14.918664
C	-2.554062	7.653579	15.773180
H	-3.152891	6.735465	15.784719
C	-3.093141	8.854493	16.264060
H	-4.116200	8.879722	16.656023
C	-2.311808	10.021491	16.252542
H	-2.722119	10.962761	16.635842
C	-1.001889	9.992779	15.748639
H	-0.411486	10.914562	15.728435
C	1.951489	7.198938	15.148919
C	1.654961	6.798484	16.472574
H	0.931219	7.366537	17.067184
C	2.272255	5.669962	17.033921
H	2.029708	5.374291	18.061262
C	3.194885	4.923907	16.281723
H	3.672094	4.038667	16.717962
C	3.501541	5.318348	14.970254
H	4.216673	4.741505	14.372932
C	2.888751	6.450797	14.406106
H	3.117627	6.742542	13.378210
S	-0.017017	10.089972	10.633138
S	1.363756	7.342009	11.542529
C	-1.544896	9.018343	10.780219
H	-1.982523	9.265850	11.763922
H	-2.230576	9.399734	10.002305
C	-1.369972	7.508480	10.619547
H	-2.373780	7.041818	10.722936
H	-1.026804	7.283987	9.594147
C	-0.427710	6.826953	11.613953
H	-0.428807	5.737158	11.426959
H	-0.783185	6.985744	12.647089

Table S25. Cartesian Coordiantes for *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Ni **(***unsym*-[H1]$^+$, –4696.79312917 E_h)

atom	x	y	z
Fe	3.935659	2.409113	7.512015
H	2.962713	2.655973	6.253970
Ni	3.398431	1.310788	5.120679
S	3.479525	0.156980	7.064298
S	5.408144	2.141365	5.690216
P	4.021425	4.648581	7.779906
P	5.300232	2.251436	9.327790
P	3.658719	1.893310	3.028824
P	1.456886	0.407334	4.573694
O	1.491948	2.378665	9.104610
C	2.372911	5.488533	7.868547
C	1.776265	5.800501	9.107788
H	2.295059	5.565700	10.043557
C	0.508984	6.405258	9.155583
H	0.059585	6.642861	10.125830
C	-0.174918	6.706367	7.967837
H	-1.158036	7.188029	8.006245
C	0.408033	6.389648	6.727780
H	-0.118360	6.623040	5.795598
C	1.669901	5.777976	6.677530
H	2.112622	5.539525	5.703942
C	5.040990	5.884963	6.822539
C	6.257195	5.486706	6.226350
H	6.543697	4.431201	6.230628
C	7.089821	6.432806	5.606729
H	8.026754	6.106567	5.141820
C	6.723352	7.787555	5.578715
H	7.374934	8.524878	5.097254
C	5.517146	8.194290	6.173169
H	5.226114	9.250589	6.162533
C	4.679370	7.251953	6.791401
H	3.744548	7.584381	7.253717
C	4.858992	1.171981	10.771110
C	5.590945	1.262917	11.979043
H	6.451961	1.936983	12.053914
C	5.236817	0.477847	13.084868
H	5.809709	0.560122	14.014988
C	4.152229	-0.412801	12.998884
H	3.876512	-1.025280	13.864211

C	3.427227	-0.516207	11.802645
H	2.583039	-1.210359	11.728318
C	3.776072	0.272808	10.693159
H	3.205673	0.185683	9.763501
C	7.132832	1.965912	9.177630
C	7.958537	2.994117	8.670992
H	7.529913	3.974074	8.432766
C	9.332663	2.775776	8.483441
H	9.962854	3.586505	8.101277
C	9.899661	1.528823	8.794931
H	10.972428	1.360828	8.651247
C	9.086879	0.502055	9.303071
H	9.523415	-0.469502	9.559811
C	7.712557	0.717496	9.495118
H	7.093155	-0.084570	9.911250
C	2.491171	2.420431	8.487232
C	5.011225	-0.889854	7.082906
H	5.524089	-0.712771	8.045796
H	4.636422	-1.928591	7.079426
C	5.960287	-0.667079	5.905912
H	6.777938	-1.414315	5.969840
H	5.421385	-0.852475	4.957038
C	6.595718	0.723667	5.872697
H	7.268265	0.810262	5.002155
H	7.183319	0.911518	6.787434
C	5.055180	1.045034	2.169081
C	6.306227	1.686861	2.035492
H	6.433148	2.716375	2.386343
C	7.383360	1.010499	1.441700
H	8.348493	1.517867	1.335269
C	7.223948	-0.305751	0.976222
H	8.064985	-0.827852	0.507524
C	5.981903	-0.948554	1.107666
H	5.850119	-1.972344	0.740866
C	4.902916	-0.279709	1.705846
H	3.938002	-0.788666	1.808376
C	3.831184	3.656028	2.520961
C	3.934921	4.004383	1.155013
H	3.965026	3.225816	0.384084
C	4.018614	5.353045	0.780311
H	4.093696	5.618255	-0.279841
C	4.013687	6.359370	1.762251
H	4.085915	7.411396	1.465594
C	3.925697	6.016844	3.120687

H	3.945487	6.794944	3.891124
C	3.827892	4.667873	3.499264
H	3.764649	4.388761	4.556195
C	1.312170	-1.423642	4.729042
C	1.600630	-2.264958	3.633145
H	1.859209	-1.831096	2.660592
C	1.543140	-3.660598	3.775241
H	1.759794	-4.303016	2.914803
C	1.200350	-4.228573	5.012513
H	1.152546	-5.317303	5.122209
C	0.910345	-3.396810	6.107643
H	0.634327	-3.835102	7.072868
C	0.966286	-2.001713	5.972153
H	0.732103	-1.361760	6.828515
C	-0.104649	1.061858	5.307274
C	-1.306459	0.321451	5.224895
H	-1.307942	-0.684356	4.791667
C	-2.502042	0.870503	5.710414
H	-3.429140	0.290503	5.646586
C	-2.509457	2.155688	6.279161
H	-3.444577	2.577748	6.663141
C	-1.318970	2.895148	6.358721
H	-1.313612	3.893689	6.808001
C	-0.118608	2.353039	5.873458
H	0.811791	2.926660	5.944396
C	2.171947	1.342441	2.091350
C	1.206562	0.693899	2.770716
C	5.299342	3.926454	10.113494
C	4.728804	4.955084	9.458154
H	5.784389	4.061609	11.089683
H	4.732850	5.977630	9.860921
H	2.084853	1.571486	1.020603
H	0.273519	0.358808	2.297033

Table S26. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Fe (*unsym*-[H**1**]$^+$, –4696.78764349 E_h)

atom	x	y	z
Fe	3.952452	2.346952	7.532793
H	2.972714	2.634633	6.296578
Ni	3.351795	1.300115	5.103218
S	3.349441	0.119439	7.018112
S	5.401221	2.011874	5.704926
P	4.015506	4.586094	7.784109
P	5.367361	2.234347	9.336393
P	3.654887	1.895508	3.020141
P	1.398118	0.450717	4.521701
O	1.573050	2.293387	9.219169
C	2.358592	5.414759	7.848509
C	1.721621	5.666463	9.081682
H	2.210126	5.385723	10.021110
C	0.454840	6.272928	9.117992
H	-0.024845	6.465358	10.083743
C	-0.189439	6.634152	7.924657
H	-1.171893	7.117861	7.954489
C	0.433177	6.376343	6.690305
H	-0.062570	6.655501	5.753998
C	1.695855	5.765618	6.651290
H	2.170410	5.577489	5.682060
C	5.026883	5.828082	6.826157
C	6.175855	5.424552	6.113255
H	6.412961	4.360228	6.022507
C	7.001809	6.379408	5.496663
H	7.885999	6.050205	4.939705
C	6.693864	7.745671	5.586590
H	7.340310	8.489088	5.107547
C	5.550643	8.156789	6.293086
H	5.303621	9.221441	6.370351
C	4.720713	7.206918	6.909027
H	3.833041	7.541314	7.456007
C	4.990718	1.117774	10.768024
C	5.678028	1.256790	11.997310
H	6.480109	1.996315	12.101994
C	5.355419	0.437012	13.087846
H	5.893263	0.556504	14.034703
C	4.346436	-0.534456	12.965854
H	4.094763	-1.172846	13.819693

C	3.664139	-0.683478	11.749289
H	2.876311	-1.437965	11.648525
C	3.982402	0.138771	10.655194
H	3.441055	0.023829	9.710458
C	7.221303	2.098792	9.178917
C	7.927420	3.144988	8.544100
H	7.393810	4.037477	8.199537
C	9.317108	3.061812	8.366248
H	9.851379	3.887328	7.882954
C	10.020973	1.931993	8.815571
H	11.106024	1.869117	8.679524
C	9.328003	0.889039	9.450737
H	9.869881	0.008769	9.813910
C	7.937905	0.970757	9.634647
H	7.413425	0.156766	10.146163
C	2.544072	2.349611	8.559594
C	4.746820	-1.097373	6.854590
H	4.596462	-1.822678	7.674240
H	4.580978	-1.627510	5.899786
C	6.147572	-0.503549	6.943127
H	6.285030	-0.054113	7.939213
H	6.882633	-1.331827	6.873371
C	6.505385	0.523769	5.869455
H	6.525050	0.066461	4.863446
H	7.509510	0.935824	6.072911
C	5.040100	1.006090	2.184640
C	6.310385	1.611867	2.064839
H	6.461037	2.639976	2.409786
C	7.377265	0.901444	1.492332
H	8.357565	1.381188	1.397563
C	7.189276	-0.413918	1.036007
H	8.022629	-0.962746	0.584432
C	5.928650	-1.022346	1.155997
H	5.774738	-2.045864	0.797134
C	4.859700	-0.319068	1.731931
H	3.880407	-0.801331	1.825588
C	3.881604	3.652601	2.516077
C	4.044120	4.001487	1.155996
H	4.096408	3.223457	0.385728
C	4.156632	5.349905	0.787979
H	4.277506	5.616232	-0.267660
C	4.120777	6.355025	1.770765
H	4.214455	7.406715	1.479005
C	3.974478	6.011647	3.123917

H	3.970088	6.788861	3.895560
C	3.848846	4.662901	3.494915
H	3.739953	4.380509	4.547253
C	1.213001	-1.380774	4.640404
C	1.510594	-2.208714	3.536434
H	1.801164	-1.763224	2.578264
C	1.417790	-3.605065	3.650281
H	1.641602	-4.236235	2.783355
C	1.030196	-4.187764	4.867355
H	0.954517	-5.276922	4.954933
C	0.730958	-3.369786	5.970186
H	0.419858	-3.819168	6.919519
C	0.822152	-1.974012	5.862934
H	0.579435	-1.344604	6.724626
C	-0.154237	1.119204	5.259826
C	-1.377015	0.423607	5.117067
H	-1.402206	-0.556588	4.628968
C	-2.563012	0.982834	5.613885
H	-3.506830	0.438045	5.502499
C	-2.539432	2.233409	6.255062
H	-3.467438	2.663442	6.647420
C	-1.327850	2.928078	6.395584
H	-1.299229	3.899907	6.899164
C	-0.136683	2.375892	5.898430
H	0.809798	2.915207	6.013871
C	2.166348	1.391862	2.058447
C	1.172796	0.767693	2.720051
C	5.273638	3.900886	10.135945
C	4.687303	4.913997	9.471287
H	5.737749	4.049260	11.120235
H	4.652969	5.935641	9.874720
H	2.101153	1.632223	0.988589
H	0.237279	0.463313	2.230819

Table S27. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ transition state interconverting the Fe(dppv) enantiomers with Ni(dppv) dibasal and pdt oriented toward Ni (TS-*unsym*-[H**1**]$^+$, –4696.75406846 E_h)

atom	x	y	z
Fe	4.175580	2.486253	7.197032
H	2.977235	2.418758	6.041236
Ni	3.511063	1.175903	4.940507
S	3.960486	0.054435	6.889931
S	5.418001	2.269804	5.222078
P	2.629873	3.940205	7.742715
P	5.630272	4.027510	7.836979
P	3.688747	1.220403	2.750604
P	1.503499	0.269446	4.674866
O	4.066802	1.407073	9.907829
C	1.164065	3.328265	8.692222
C	1.268961	3.138876	10.087949
H	2.199488	3.386521	10.609867
C	0.184489	2.627763	10.818146
H	0.277843	2.492435	11.901151
C	-1.012576	2.294536	10.164273
H	-1.859313	1.899341	10.736115
C	-1.122625	2.476919	8.775466
H	-2.054880	2.227214	8.257324
C	-0.041882	2.990107	8.040354
H	-0.146556	3.144663	6.961693
C	1.879485	5.137886	6.536510
C	2.412236	5.258062	5.238069
H	3.217538	4.585151	4.922111
C	1.912062	6.227773	4.352205
H	2.329865	6.301424	3.342263
C	0.881200	7.090258	4.760666
H	0.494299	7.849955	4.072261
C	0.348191	6.979694	6.056965
H	-0.455296	7.650127	6.381465
C	0.843396	6.009652	6.941556
H	0.412993	5.923489	7.945400
C	7.134712	3.590147	8.836877
C	8.032481	4.605903	9.241105
H	7.872379	5.642166	8.922089
C	9.142250	4.293923	10.039101
H	9.828669	5.089583	10.348726
C	9.374602	2.965812	10.437807
H	10.242937	2.724562	11.060383

C	8.491509	1.951764	10.037926
H	8.665102	0.915706	10.348548
C	7.375970	2.263271	9.242394
H	6.677731	1.475299	8.945217
C	6.349531	5.194669	6.582067
C	5.646937	6.356486	6.199840
H	4.687934	6.597640	6.669653
C	6.177108	7.218281	5.225421
H	5.629021	8.126934	4.952720
C	7.407709	6.924931	4.615877
H	7.825061	7.602954	3.863255
C	8.110399	5.765893	4.986873
H	9.075481	5.534600	4.522544
C	7.587378	4.906639	5.965115
H	8.157551	4.021206	6.266327
C	4.120085	1.856472	8.816913
C	5.658665	-0.676380	6.914245
H	6.170334	-0.336196	7.832524
H	5.494803	-1.765281	7.007572
C	6.497966	-0.383058	5.670311
H	7.450885	-0.946185	5.746565
H	5.972435	-0.761358	4.774840
C	6.847870	1.090666	5.467064
H	7.464289	1.208788	4.559372
H	7.418418	1.481952	6.329436
C	5.189104	0.415530	2.021387
C	6.191649	1.136680	1.341221
H	6.095035	2.217704	1.200782
C	7.311134	0.465874	0.821233
H	8.082293	1.035166	0.290869
C	7.436293	-0.924906	0.966319
H	8.307145	-1.444403	0.552489
C	6.436615	-1.649988	1.637001
H	6.523240	-2.736542	1.746468
C	5.322144	-0.984577	2.168569
H	4.547347	-1.556291	2.693238
C	3.520313	2.822479	1.846699
C	2.543665	2.999729	0.841739
H	1.857659	2.186231	0.584864
C	2.439480	4.224262	0.162894
H	1.679567	4.346388	-0.616523
C	3.308944	5.282069	0.473661
H	3.233426	6.231715	-0.067079
C	4.274930	5.117600	1.481451

H	4.954284	5.938269	1.736339
C	4.377361	3.900048	2.173169
H	5.122082	3.786779	2.968871
C	1.061349	-1.185160	5.697495
C	1.223494	-2.496776	5.202913
H	1.567694	-2.662433	4.175623
C	0.943594	-3.599209	6.025301
H	1.062264	-4.614202	5.630854
C	0.508536	-3.400556	7.345758
H	0.290057	-4.262151	7.985712
C	0.356622	-2.096493	7.846201
H	0.025540	-1.937150	8.877790
C	0.636344	-0.989676	7.031412
H	0.519026	0.023425	7.432779
C	-0.000521	1.346424	4.684254
C	-1.284954	0.836446	4.973925
H	-1.407548	-0.205913	5.284952
C	-2.409575	1.670699	4.867997
H	-3.403573	1.268900	5.093459
C	-2.262975	3.010570	4.470466
H	-3.143532	3.657330	4.391011
C	-0.986606	3.519415	4.175422
H	-0.860498	4.565384	3.877277
C	0.141206	2.690910	4.280755
H	1.136967	3.092922	4.065418
C	2.355116	0.148796	2.070951
C	1.432707	-0.324758	2.931405
C	4.737317	5.183044	8.968234
C	3.392642	5.134081	8.938311
H	5.299313	5.882619	9.600988
H	2.757080	5.795574	9.542641
H	2.347848	-0.105714	1.002598
H	0.598678	-0.962858	2.608406

Table S28. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*unsym*-[H**1**]$^+$, –4696.78736885 E_h)

atom	x	y	z
Ni	1.727450	8.831712	9.852870
Fe	1.264185	9.797111	12.155967
O	3.194200	11.984873	12.298750
C	2.396183	11.123009	12.310620
P	3.750485	9.376554	9.112831
P	1.476147	7.569361	8.063312
C	5.172779	8.718037	10.088362
C	5.767241	7.483818	9.744634
H	5.405976	6.922780	8.875573
C	6.828982	6.972327	10.508810
H	7.292199	6.021248	10.223579
C	7.302485	7.683165	11.623489
H	8.135160	7.286350	12.214253
C	6.707227	8.906364	11.977118
H	7.065486	9.462818	12.849066
C	5.645500	9.422854	11.218576
H	5.195514	10.380777	11.500455
C	4.233023	11.117651	8.711534
C	3.228637	12.035084	8.335700
H	2.175718	11.739484	8.389067
C	3.577997	13.331114	7.924403
H	2.791041	14.039459	7.643334
C	4.926293	13.719678	7.881247
H	5.196725	14.732331	7.562843
C	5.929860	12.807472	8.248444
H	6.983661	13.104871	8.214995
C	5.589631	11.510487	8.660809
H	6.380345	10.809338	8.946428
C	3.974950	8.562393	7.478803
H	4.901366	8.739481	6.915541
C	2.974731	7.794028	7.012532
H	3.020664	7.289831	6.037743
C	0.142857	7.995541	6.850803
C	-1.002014	7.189670	6.671460
H	-1.107189	6.251577	7.226452
C	-2.006930	7.583321	5.772974
H	-2.889940	6.949194	5.637735
C	-1.879942	8.779588	5.048476
H	-2.663834	9.081431	4.345620

C	-0.743682	9.587602	5.225426
H	-0.637383	10.519825	4.660032
C	0.261244	9.202239	6.124792
H	1.140577	9.841646	6.264618
C	1.397483	5.727304	8.199650
C	1.509085	5.103443	9.458259
H	1.588661	5.714328	10.362686
C	1.511017	3.701400	9.550422
H	1.589373	3.229890	10.535670
C	1.413546	2.915160	8.392418
H	1.414804	1.822217	8.467344
C	1.314487	3.531759	7.132811
H	1.241227	2.923105	6.224976
C	1.305661	4.930212	7.033488
H	1.212415	5.399409	6.047607
P	2.159958	8.585195	13.845790
P	-0.192164	10.600642	13.690967
C	2.387333	6.768836	13.625368
C	1.616304	5.827206	14.338445
H	0.840006	6.161648	15.034645
C	1.834614	4.451309	14.161635
H	1.232880	3.730454	14.725805
C	2.827056	4.003133	13.275384
H	3.010842	2.929765	13.154406
C	3.586973	4.935444	12.547553
H	4.358945	4.594598	11.849533
C	3.362866	6.311496	12.710874
H	3.958837	7.029219	12.135545
C	3.730211	9.126280	14.692543
C	4.782075	8.238762	15.001767
H	4.728150	7.190320	14.695545
C	5.905505	8.693065	15.712876
H	6.712008	7.990508	15.950581
C	5.992067	10.032170	16.124405
H	6.868191	10.382043	16.681175
C	4.942967	10.919176	15.829940
H	4.994907	11.963854	16.155065
C	3.817632	10.469312	15.124321
H	2.999536	11.168813	14.923414
C	1.046153	8.738477	15.305321
H	1.259621	8.162736	16.216347
C	0.076257	9.671878	15.263113
H	-0.578501	9.862993	16.123823
C	0.011275	12.379096	14.156980

C	-0.039084	12.817111	15.498807
H	-0.181070	12.101353	16.314722
C	0.098166	14.180770	15.802010
H	0.066018	14.508523	16.846809
C	0.272038	15.119900	14.772215
H	0.375857	16.183559	15.012333
C	0.316991	14.691398	13.435763
H	0.457984	15.418352	12.628543
C	0.195008	13.327474	13.125611
H	0.252170	12.993038	12.081822
C	-2.041996	10.428433	13.585631
C	-2.631861	9.173305	13.858889
H	-1.999683	8.316267	14.120480
C	-4.026757	9.018774	13.816916
H	-4.471680	8.043602	14.043650
C	-4.847616	10.111578	13.491695
H	-5.935790	9.991230	13.460943
C	-4.268493	11.360936	13.217153
H	-4.903138	12.220026	12.973805
C	-2.874125	11.522749	13.266917
H	-2.435614	12.508162	13.076889
S	0.488407	10.933171	10.236819
S	0.247315	7.931117	11.278939
C	-1.329441	10.678664	10.008947
H	-1.855096	11.011445	10.919956
H	-1.603897	11.377645	9.197781
C	-1.745944	9.263368	9.616567
H	-2.835934	9.263326	9.407162
H	-1.244123	8.991271	8.674750
C	-1.493101	8.180610	10.666667
H	-1.784006	7.193120	10.265644
H	-2.096696	8.362715	11.573037
H	2.491684	9.137601	11.287727

Table S29. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*unsym*-[H**1**]$^+$, –4696.78606484 E_h)

atom	x	y	z
Ni	1.915485	9.049865	9.887880
Fe	1.196280	10.135908	12.069323
O	2.382739	12.785836	12.459376
C	1.931992	11.709345	12.325942
P	4.045690	9.143282	9.307230
P	1.512538	8.013067	7.998761
C	5.228903	7.937390	10.068885
C	5.201266	6.589013	9.643337
H	4.526753	6.280780	8.836763
C	6.040670	5.637967	10.243334
H	6.021813	4.600926	9.890026
C	6.908272	6.015274	11.282971
H	7.564661	5.272308	11.748752
C	6.932490	7.350019	11.718276
H	7.600901	7.654881	12.530472
C	6.100461	8.307701	11.115956
H	6.136370	9.344126	11.463404
C	4.942095	10.758375	9.300538
C	4.194022	11.945757	9.444654
H	3.112871	11.888887	9.612017
C	4.829379	13.195618	9.357398
H	4.240340	14.111229	9.475999
C	6.211111	13.268138	9.120075
H	6.705870	14.243125	9.051841
C	6.960182	12.088445	8.964904
H	8.037560	12.141799	8.773360
C	6.331724	10.837360	9.052310
H	6.925145	9.923661	8.936207
C	4.140590	8.652143	7.533090
H	5.095333	8.741151	6.997258
C	3.023770	8.175372	6.954894
H	2.988046	7.845047	5.907964
C	0.213565	8.676459	6.866461
C	-1.029442	8.034103	6.677885
H	-1.234402	7.076056	7.167465
C	-2.001010	8.608183	5.841019
H	-2.959981	8.098801	5.696561
C	-1.742592	9.824633	5.189236
H	-2.500495	10.268343	4.534827

C	-0.508219	10.471159	5.376219
H	-0.300999	11.419466	4.868795
C	0.464055	9.904924	6.213457
H	1.418125	10.422186	6.366990
C	1.255671	6.179921	7.986875
C	1.383019	5.439702	9.180544
H	1.561704	5.963197	10.125676
C	1.266774	4.039669	9.156305
H	1.355918	3.474909	10.090607
C	1.034303	3.369518	7.945280
H	0.943664	2.277948	7.929180
C	0.917077	4.101033	6.750537
H	0.737977	3.582803	5.802227
C	1.027046	5.498878	6.767443
H	0.923991	6.059053	5.831367
P	2.345676	9.212856	13.793200
P	-0.383332	10.695422	13.591502
C	2.357316	7.375426	14.005812
C	1.584638	6.733456	14.996425
H	0.969047	7.324201	15.684120
C	1.609466	5.333613	15.117955
H	1.014027	4.846804	15.898238
C	2.403232	4.565252	14.252448
H	2.427118	3.474644	14.353176
C	3.175061	5.200077	13.263884
H	3.806958	4.610407	12.591103
C	3.152840	6.596725	13.136515
H	3.767494	7.079941	12.369001
C	4.121816	9.643247	14.133647
C	4.788597	8.982823	15.192010
H	4.287935	8.174923	15.737409
C	6.096602	9.344370	15.544740
H	6.598797	8.825007	16.368276
C	6.757828	10.369935	14.846896
H	7.776547	10.657810	15.128677
C	6.106946	11.023991	13.789536
H	6.614619	11.821827	13.236774
C	4.797032	10.660620	13.430619
H	4.312650	11.175127	12.598160
C	1.561342	9.817559	15.345207
H	2.058618	9.642875	16.309171
C	0.402890	10.496748	15.252456
H	-0.107452	10.884297	16.143656
C	-1.011932	12.435338	13.626707

C	-1.568365	12.986842	14.805237
H	-1.652486	12.387149	15.717763
C	-2.039895	14.307547	14.815968
H	-2.463351	14.723865	15.736392
C	-1.968952	15.091715	13.651978
H	-2.335686	16.123774	13.663788
C	-1.426185	14.549408	12.477374
H	-1.365482	15.155957	11.567278
C	-0.947349	13.229201	12.462702
H	-0.508557	12.815552	11.546945
C	-1.915287	9.667460	13.869717
C	-1.768456	8.278030	14.079499
H	-0.775450	7.816949	14.040862
C	-2.893181	7.475128	14.321893
H	-2.764295	6.399817	14.487644
C	-4.177169	8.046146	14.350647
H	-5.054420	7.417906	14.539162
C	-4.330255	9.424332	14.135448
H	-5.327335	9.877781	14.153687
C	-3.207136	10.234639	13.898079
H	-3.341587	11.308362	13.735174
S	0.555442	11.005722	9.984637
S	0.424933	8.096428	11.336929
C	-1.175079	10.562376	9.482043
H	-1.736103	11.513689	9.455965
H	-1.115472	10.183578	8.448375
C	-1.904073	9.572800	10.388156
H	-2.051248	10.026279	11.381818
H	-2.920359	9.416264	9.970095
C	-1.266789	8.192194	10.555930
H	-1.190749	7.669849	9.585895
H	-1.905885	7.576678	11.213185
H	2.566578	9.660628	11.247799

Table S30. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ transition state to interconvert Ni(dppv) site between apical-basal and dibasal with Fe(dppv) apical-basal and pdt oriented toward Ni (TS-*unsym*-[H**1**]$^+$, –4696.78443302 E_h)

atom	x	y	z
Ni	1.833680	8.783384	9.975697
Fe	1.364539	9.700866	12.289178
O	3.278118	11.890009	12.560197
C	2.490986	11.017635	12.514764
P	3.817989	9.345374	9.145624
P	1.564852	7.498526	8.224785
C	5.340086	9.206900	10.189013
C	5.768042	7.910562	10.555969
H	5.199246	7.033266	10.224697
C	6.933133	7.737925	11.316471
H	7.265894	6.727770	11.579532
C	7.675271	8.857206	11.730321
H	8.586485	8.723230	12.322774
C	7.249859	10.146476	11.375708
H	7.826356	11.022703	11.691033
C	6.089787	10.325279	10.604222
H	5.782082	11.334825	10.316238
C	3.954280	10.976254	8.293292
C	3.686350	12.160241	9.017874
H	3.405801	12.113023	10.074124
C	3.778609	13.409671	8.385558
H	3.577312	14.320237	8.960028
C	4.117823	13.492177	7.025231
H	4.184589	14.468719	6.533635
C	4.365872	12.318686	6.295531
H	4.625807	12.374554	5.232850
C	4.285968	11.065781	6.923429
H	4.478227	10.160677	6.338438
C	4.203504	8.118070	7.826641
H	5.203404	8.103396	7.372778
C	3.227223	7.267478	7.458134
H	3.358376	6.521958	6.661733
C	0.650368	8.174333	6.757832
C	0.233979	7.342725	5.694155
H	0.366075	6.257206	5.755998
C	-0.359878	7.906499	4.554328
H	-0.685847	7.255604	3.735691
C	-0.534430	9.297645	4.462779
H	-0.999376	9.733132	3.571644

C	-0.111729	10.128521	5.513560
H	-0.243567	11.213862	5.444857
C	0.479187	9.571956	6.658770
H	0.803580	10.215117	7.486836
C	0.936344	5.780414	8.427091
C	-0.443922	5.495931	8.335298
H	-1.152420	6.290590	8.076475
C	-0.911347	4.189005	8.541648
H	-1.982966	3.977311	8.459031
C	-0.008982	3.154769	8.840685
H	-0.375523	2.134276	8.994676
C	1.364605	3.431145	8.933790
H	2.073444	2.626383	9.157089
C	1.836152	4.737623	8.733600
H	2.909909	4.945064	8.810152
P	2.248036	8.467408	13.967404
P	-0.104998	10.503920	13.806763
C	2.284537	6.631106	13.796729
C	1.554464	5.783592	14.655835
H	0.938142	6.204113	15.457051
C	1.606620	4.390063	14.491133
H	1.036178	3.743420	15.166742
C	2.390555	3.828784	13.471597
H	2.436276	2.741207	13.349852
C	3.112422	4.666874	12.605553
H	3.721117	4.233789	11.804288
C	3.052386	6.060200	12.757578
H	3.602458	6.710591	12.067763
C	3.913416	8.888914	14.680603
C	4.974222	7.963069	14.753887
H	4.852080	6.951786	14.355332
C	6.189734	8.327666	15.355686
H	7.003211	7.595980	15.411923
C	6.358682	9.612524	15.893598
H	7.305806	9.890506	16.368660
C	5.304349	10.538320	15.829067
H	5.423318	11.541632	16.252256
C	4.089184	10.180370	15.228083
H	3.271965	10.908912	15.199014
C	1.233947	8.761173	15.476686
H	1.495999	8.251398	16.413898
C	0.257770	9.687023	15.421792
H	-0.351117	9.929244	16.302815
C	-0.035383	12.314604	14.188494

C	-0.245262	12.812100	15.494470
H	-0.434895	12.130634	16.329531
C	-0.213785	14.193366	15.738856
H	-0.368833	14.566192	16.757170
C	0.011024	15.093034	14.683654
H	0.031941	16.170927	14.877518
C	0.209236	14.606258	13.382137
H	0.384548	15.302423	12.554603
C	0.193119	13.224242	13.132667
H	0.360358	12.845745	12.116394
C	-1.936360	10.188881	13.734940
C	-2.428538	8.903223	14.055002
H	-1.731641	8.104484	14.335184
C	-3.807969	8.643680	14.026590
H	-4.177832	7.646339	14.288913
C	-4.709608	9.659798	13.667342
H	-5.785766	9.457119	13.646991
C	-4.227117	10.938207	13.343942
H	-4.925399	11.737428	13.072417
C	-2.848631	11.205774	13.380830
H	-2.485070	12.213853	13.154471
S	0.636601	10.864289	10.350817
S	0.352217	7.851159	11.373815
C	-1.176910	10.614238	10.069446
H	-1.727399	10.959137	10.962157
H	-1.426005	11.305770	9.243792
C	-1.601365	9.195684	9.689719
H	-2.685962	9.208620	9.453887
H	-1.080244	8.897287	8.762678
C	-1.383717	8.136541	10.770256
H	-1.707025	7.147085	10.402020
H	-1.978264	8.366196	11.671320
H	2.598329	9.044873	11.419078

Table S31. *sym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*sym*-[H**1**]$^+$, –4696.78456783 E_h)

atom	x	y	z
Ni	9.053196	10.159373	3.211532
Fe	6.874501	11.526473	2.994252
P	10.417366	10.327476	4.968179
S	8.727600	12.046779	1.684295
P	10.301044	8.496956	2.494255
S	7.094279	9.369937	2.410949
O	5.003981	12.147235	0.846175
C	8.349984	11.448733	-0.032937
H	7.436160	11.968526	-0.368679
H	9.181067	11.815680	-0.662019
C	8.218707	9.933022	-0.214200
H	9.182478	9.455958	0.036119
H	8.047512	9.734713	-1.292810
C	7.094119	9.233253	0.553026
H	7.125135	8.149197	0.348501
H	6.102809	9.606091	0.239631
C	5.730112	11.930395	1.742575
C	11.820318	11.547808	4.984650
C	12.288206	12.057285	3.755339
H	11.753108	11.813610	2.831450
C	13.425483	12.880143	3.717942
H	13.780897	13.272223	2.758857
C	14.101145	13.202292	4.907177
H	14.989514	13.842517	4.877705
C	13.632659	12.705361	6.135749
H	14.153190	12.958268	7.065933
C	12.497249	11.881182	6.178367
H	12.138390	11.499760	7.140111
C	9.747052	10.432571	6.683764
C	9.159316	11.639929	7.123711
H	9.114014	12.506314	6.454742
C	8.652487	11.744644	8.427025
H	8.209087	12.689519	8.759462
C	8.719344	10.648762	9.304497
H	8.324950	10.734642	10.322639
C	9.295403	9.444694	8.872167
H	9.354084	8.586941	9.551003
C	9.805794	9.334211	7.568231
H	10.250351	8.386455	7.245303

C	11.598657	8.776465	1.199368
C	12.488852	7.734399	0.848759
H	12.377369	6.737323	1.289324
C	13.512703	7.965772	-0.081562
H	14.195698	7.152210	-0.348747
C	13.660395	9.234136	-0.668842
H	14.460043	9.410509	-1.396222
C	12.781378	10.272426	-0.323025
H	12.891444	11.261871	-0.780257
C	11.755817	10.046784	0.609629
H	11.063688	10.852389	0.883947
C	9.478150	6.916554	2.006895
C	8.798287	6.185110	3.006106
H	8.780966	6.554410	4.037875
C	8.137089	4.991953	2.682049
H	7.619191	4.428556	3.465670
C	8.136163	4.523298	1.356855
H	7.618445	3.591676	1.104761
C	8.801057	5.251140	0.357486
H	8.805099	4.890026	-0.676694
C	9.471373	6.444002	0.677706
H	9.998966	6.995970	-0.107098
P	6.731005	13.635482	3.846533
P	5.261568	10.972364	4.483078
C	8.122796	14.649782	4.531878
C	9.454396	14.199856	4.473743
C	7.844358	15.915949	5.097357
C	10.494544	14.994851	4.987379
H	9.681528	13.234996	4.010138
C	8.881417	16.701864	5.617429
H	6.818760	16.302445	5.109855
C	10.208701	16.240883	5.564307
H	11.526608	14.635177	4.929296
H	8.654253	17.680132	6.055119
H	11.019220	16.859628	5.964719
C	5.948106	14.877542	2.717306
C	4.604652	15.281161	2.854800
C	6.725018	15.401756	1.659791
C	4.045527	16.198979	1.949867
H	3.990338	14.884681	3.670964
C	6.160143	16.313686	0.756887
H	7.770433	15.092907	1.545250
C	4.820572	16.714814	0.899992
H	3.002105	16.510932	2.069039

H	6.769831	16.715622	-0.059784
H	4.383178	17.429839	0.194944
C	3.611997	10.629082	3.715873
C	3.341007	9.333497	3.221100
C	2.653127	11.648096	3.543362
C	2.129190	9.068288	2.566446
H	4.074769	8.531013	3.356164
C	1.438622	11.375459	2.892863
H	2.851863	12.658574	3.916794
C	1.175336	10.087288	2.402028
H	1.927287	8.060026	2.188408
H	0.698106	12.173419	2.770835
H	0.228219	9.876190	1.894058
C	5.378944	9.587192	5.707803
C	4.244269	9.254172	6.484172
C	6.570262	8.857910	5.879175
C	4.306441	8.210568	7.417597
H	3.303070	9.798120	6.345839
C	6.622750	7.803359	6.806503
H	7.454143	9.114072	5.283691
C	5.495807	7.478501	7.575897
H	3.422100	7.962430	8.014588
H	7.552120	7.237120	6.929632
H	5.540331	6.655423	8.297621
C	11.359199	7.976678	3.910151
C	11.409717	8.775049	4.991700
H	11.983402	7.078781	3.808643
H	12.098182	8.584617	5.826282
C	5.570537	13.584898	5.282016
C	4.933285	12.430702	5.559556
H	5.424955	14.485363	5.894586
H	4.239989	12.334974	6.406609
H	8.068794	11.118538	4.132498

Table S32. *unsym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ transition state to interconvert Ni(dppv) site between apical-basal and dibasal with Fe(dppv) apical-basal and pdt oriented toward Ni (TS-*unsym*-[H**1**]$^+$, –4696.78443302 E_h)

atom	x	y	z
Ni	1.833680	8.783384	9.975697
Fe	1.364539	9.700866	12.289178
O	3.278118	11.890009	12.560197
C	2.490986	11.017635	12.514764
P	3.817989	9.345374	9.145624
P	1.564852	7.498526	8.224785
C	5.340086	9.206900	10.189013
C	5.768042	7.910562	10.555969
H	5.199246	7.033266	10.224697
C	6.933133	7.737925	11.316471
H	7.265894	6.727770	11.579532
C	7.675271	8.857206	11.730321
H	8.586485	8.723230	12.322774
C	7.249859	10.146476	11.375708
H	7.826356	11.022703	11.691033
C	6.089787	10.325279	10.604222
H	5.782082	11.334825	10.316238
C	3.954280	10.976254	8.293292
C	3.686350	12.160241	9.017874
H	3.405801	12.113023	10.074124
C	3.778609	13.409671	8.385558
H	3.577312	14.320237	8.960028
C	4.117823	13.492177	7.025231
H	4.184589	14.468719	6.533635
C	4.365872	12.318686	6.295531
H	4.625807	12.374554	5.232850
C	4.285968	11.065781	6.923429
H	4.478227	10.160677	6.338438
C	4.203504	8.118070	7.826641
H	5.203404	8.103396	7.372778
C	3.227223	7.267478	7.458134
H	3.358376	6.521958	6.661733
C	0.650368	8.174333	6.757832
C	0.233979	7.342725	5.694155
H	0.366075	6.257206	5.755998
C	-0.359878	7.906499	4.554328
H	-0.685847	7.255604	3.735691
C	-0.534430	9.297645	4.462779
H	-0.999376	9.733132	3.571644

C	-0.111729	10.128521	5.513560
H	-0.243567	11.213862	5.444857
C	0.479187	9.571956	6.658770
H	0.803580	10.215117	7.486836
C	0.936344	5.780414	8.427091
C	-0.443922	5.495931	8.335298
H	-1.152420	6.290590	8.076475
C	-0.911347	4.189005	8.541648
H	-1.982966	3.977311	8.459031
C	-0.008982	3.154769	8.840685
H	-0.375523	2.134276	8.994676
C	1.364605	3.431145	8.933790
H	2.073444	2.626383	9.157089
C	1.836152	4.737623	8.733600
H	2.909909	4.945064	8.810152
P	2.248036	8.467408	13.967404
P	-0.104998	10.503920	13.806763
C	2.284537	6.631106	13.796729
C	1.554464	5.783592	14.655835
H	0.938142	6.204113	15.457051
C	1.606620	4.390063	14.491133
H	1.036178	3.743420	15.166742
C	2.390555	3.828784	13.471597
H	2.436276	2.741207	13.349852
C	3.112422	4.666874	12.605553
H	3.721117	4.233789	11.804288
C	3.052386	6.060200	12.757578
H	3.602458	6.710591	12.067763
C	3.913416	8.888914	14.680603
C	4.974222	7.963069	14.753887
H	4.852080	6.951786	14.355332
C	6.189734	8.327666	15.355686
H	7.003211	7.595980	15.411923
C	6.358682	9.612524	15.893598
H	7.305806	9.890506	16.368660
C	5.304349	10.538320	15.829067
H	5.423318	11.541632	16.252256
C	4.089184	10.180370	15.228083
H	3.271965	10.908912	15.199014
C	1.233947	8.761173	15.476686
H	1.495999	8.251398	16.413898
C	0.257770	9.687023	15.421792
H	-0.351117	9.929244	16.302815
C	-0.035383	12.314604	14.188494

C	-0.245262	12.812100	15.494470
H	-0.434895	12.130634	16.329531
C	-0.213785	14.193366	15.738856
H	-0.368833	14.566192	16.757170
C	0.011024	15.093034	14.683654
H	0.031941	16.170927	14.877518
C	0.209236	14.606258	13.382137
H	0.384548	15.302423	12.554603
C	0.193119	13.224242	13.132667
H	0.360358	12.845745	12.116394
C	-1.936360	10.188881	13.734940
C	-2.428538	8.903223	14.055002
H	-1.731641	8.104484	14.335184
C	-3.807969	8.643680	14.026590
H	-4.177832	7.646339	14.288913
C	-4.709608	9.659798	13.667342
H	-5.785766	9.457119	13.646991
C	-4.227117	10.938207	13.343942
H	-4.925399	11.737428	13.072417
C	-2.848631	11.205774	13.380830
H	-2.485070	12.213853	13.154471
S	0.636601	10.864289	10.350817
S	0.352217	7.851159	11.373815
C	-1.176910	10.614238	10.069446
H	-1.727399	10.959137	10.962157
H	-1.426005	11.305770	9.243792
C	-1.601365	9.195684	9.689719
H	-2.685962	9.208620	9.453887
H	-1.080244	8.897287	8.762678
C	-1.383717	8.136541	10.770256
H	-1.707025	7.147085	10.402020
H	-1.978264	8.366196	11.671320
H	2.598329	9.044873	11.419078

Table S33. *sym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*sym*-[H**1**]$^+$, –4696.77979712 E_h)

atom	x	y	z
Ni	9.048659	10.170933	3.183808
Fe	6.877434	11.537304	2.899320
P	10.393180	10.395216	4.953895
S	8.764962	12.076618	1.625823
P	10.291099	8.464670	2.551112
S	7.140427	9.399287	2.261876
O	4.837617	12.360585	0.979931
C	8.546961	11.482557	-0.128188
H	8.423629	12.389328	-0.745767
H	9.502321	11.011532	-0.421497
C	7.387384	10.522354	-0.411441
H	7.459982	10.222431	-1.477712
H	6.426433	11.049661	-0.313451
C	7.358285	9.237178	0.414490
H	8.271264	8.636236	0.258661
H	6.504273	8.610033	0.102177
C	5.663283	12.037503	1.748669
C	11.807251	11.603552	4.953004
C	12.293710	12.075840	3.716247
H	11.763931	11.816439	2.793789
C	13.441940	12.883023	3.669242
H	13.811666	13.245798	2.704012
C	14.110692	13.226206	4.856527
H	15.007812	13.853730	4.819760
C	13.624309	12.765735	6.092216
H	14.139582	13.034531	7.020874
C	12.478155	11.957180	6.144240
H	12.106081	11.604157	7.111744
C	9.705958	10.545867	6.660004
C	9.171882	11.780887	7.090867
H	9.183318	12.648532	6.422460
C	8.648097	11.910090	8.385456
H	8.247725	12.876202	8.711487
C	8.644935	10.812101	9.262852
H	8.238126	10.917359	10.274309
C	9.168736	9.581204	8.839567
H	9.173032	8.721452	9.518303
C	9.695510	9.446390	7.544730
H	10.100563	8.478882	7.227982

C	11.576695	8.684691	1.237012
C	12.437478	7.620636	0.878510
H	12.311519	6.629387	1.328078
C	13.453969	7.825621	-0.065919
H	14.115739	6.996238	-0.337903
C	13.623775	9.088591	-0.659482
H	14.417292	9.243392	-1.398405
C	12.777566	10.149799	-0.302265
H	12.907462	11.136207	-0.760732
C	11.760082	9.950319	0.645507
H	11.100079	10.774227	0.941296
C	9.462439	6.863488	2.145745
C	8.759291	6.204098	3.178545
H	8.728340	6.640584	4.183280
C	8.091405	4.998592	2.922933
H	7.555322	4.492890	3.733187
C	8.105589	4.444340	1.631068
H	7.582231	3.503041	1.432110
C	8.791623	5.099873	0.597359
H	8.806192	4.673527	-0.411552
C	9.469274	6.304777	0.850074
H	10.014554	6.797950	0.038609
P	6.749840	13.616861	3.839457
P	5.292145	10.913499	4.393220
C	8.147957	14.619924	4.531664
C	9.488954	14.227930	4.367193
C	7.859389	15.835329	5.195695
C	10.528556	15.029645	4.871923
H	9.723500	13.305348	3.828137
C	8.896727	16.626247	5.707332
H	6.824273	16.182809	5.290162
C	10.234137	16.223188	5.546779
H	11.567235	14.714407	4.731465
H	8.660870	17.564461	6.221434
H	11.044694	16.846500	5.939904
C	5.936983	14.906275	2.786878
C	4.600507	15.308950	2.980147
C	6.687633	15.471789	1.731915
C	4.022720	16.269686	2.133391
H	4.005293	14.876097	3.791951
C	6.103877	16.426200	0.886995
H	7.727189	15.161881	1.574070
C	4.771697	16.828095	1.086422
H	2.984697	16.580588	2.294830

H	6.692721	16.860577	0.071666
H	4.319444	17.576367	0.426713
C	3.625307	10.596720	3.654431
C	3.372133	9.340545	3.058695
C	2.632233	11.595966	3.608190
C	2.142965	9.093979	2.430304
H	4.134605	8.554101	3.093763
C	1.400592	11.341553	2.982582
H	2.817258	12.576800	4.059705
C	1.154590	10.092697	2.391891
H	1.954576	8.116319	1.973222
H	0.633695	12.123349	2.957718
H	0.194272	9.896155	1.903252
C	5.436064	9.481582	5.562544
C	4.306057	9.103921	6.325490
C	6.638636	8.766239	5.711999
C	4.383981	8.031186	7.224059
H	3.356387	9.636842	6.203979
C	6.707116	7.683490	6.605147
H	7.518968	9.055439	5.124830
C	5.585025	7.314317	7.361421
H	3.502678	7.748985	7.810267
H	7.645860	7.128912	6.712785
H	5.642510	6.469278	8.056351
C	11.346628	8.005745	3.988132
C	11.383043	8.842379	5.040795
H	11.974158	7.106720	3.923748
H	12.059897	8.683535	5.891459
C	5.622681	13.492301	5.296611
C	4.990977	12.326471	5.535310
H	5.489073	14.361449	5.955143
H	4.318715	12.193145	6.394194
H	8.052034	11.12555	4.063133

Table S34. *sym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) dibasal, and pdt oriented toward Ni (*sym*-[H**1**]$^+$, –4696.79188666 E_h)

atom	x	y	z
Fe	4.099682	2.192923	7.588187
H	2.883239	2.507694	6.514750
Ni	3.289975	1.278140	5.166574
S	3.474712	-0.003121	7.057003
S	5.302958	2.089275	5.647035
P	2.814058	2.183610	9.425898
P	4.403089	4.377239	7.947084
P	3.673694	1.712476	3.053616
P	1.302673	0.492651	4.563853
O	6.445089	1.490174	9.201623
C	3.243511	0.922896	10.707078
C	4.169557	1.217409	11.730039
H	4.608470	2.218881	11.803339
C	4.536274	0.231578	12.660222
H	5.251555	0.474368	13.453563
C	3.989083	-1.058170	12.572773
H	4.275740	-1.826477	13.298984
C	3.070652	-1.360278	11.553028
H	2.639464	-2.364994	11.482043
C	2.697551	-0.377678	10.623704
H	1.977326	-0.619015	9.835075
C	0.961280	2.127235	9.432109
C	0.244606	2.289827	8.231773
H	0.795428	2.382908	7.289458
C	-1.160644	2.326108	8.241931
H	-1.705670	2.452781	7.300762
C	-1.857194	2.198713	9.454053
H	-2.952340	2.228258	9.464186
C	-1.148436	2.030401	10.656298
H	-1.688333	1.927364	11.604022
C	0.253485	1.992676	10.648363
H	0.797216	1.847637	11.588407
C	6.150810	4.965465	7.923900
C	6.894268	5.074500	9.118074
H	6.417101	4.872735	10.083603
C	8.251050	5.434755	9.079229
H	8.816243	5.518134	10.013815
C	8.878898	5.687132	7.849535
H	9.936609	5.970208	7.820899

C	8.146854	5.575620	6.655061
H	8.631932	5.772782	5.692668
C	6.792246	5.211729	6.688078
H	6.230292	5.127019	5.751361
C	3.463351	5.738788	7.090195
C	2.105531	5.518136	6.772670
H	1.667636	4.527206	6.933600
C	1.313491	6.562647	6.271615
H	0.256086	6.381660	6.049314
C	1.869018	7.837906	6.070298
H	1.249075	8.653888	5.683011
C	3.220819	8.063420	6.377171
H	3.661136	9.055784	6.229490
C	4.014131	7.023532	6.891005
H	5.061306	7.217817	7.142824
C	5.483906	1.776595	8.585987
C	5.022728	-1.020482	6.977859
H	5.562949	-0.883250	7.931520
H	4.675595	-2.067779	6.929288
C	5.928282	-0.722344	5.780963
H	6.773138	-1.441555	5.795829
H	5.368548	-0.899781	4.843514
C	6.526033	0.687516	5.751435
H	7.166881	0.805445	4.861401
H	7.138419	0.882220	6.650035
C	5.202748	0.978854	2.322032
C	6.378325	1.747432	2.175371
H	6.378718	2.806152	2.454414
C	7.544325	1.158449	1.660770
H	8.450125	1.763491	1.544480
C	7.548710	-0.196365	1.287807
H	8.458617	-0.650635	0.881317
C	6.381863	-0.965302	1.431191
H	6.377600	-2.020145	1.135755
C	5.214847	-0.383586	1.950427
H	4.307822	-0.989586	2.059637
C	3.686582	3.456911	2.457575
C	3.876221	3.761357	1.090583
H	4.067260	2.962109	0.365441
C	3.837100	5.094972	0.658751
H	3.980679	5.326486	-0.402247
C	3.618527	6.130377	1.584840
H	3.592218	7.170776	1.242779
C	3.437857	5.832922	2.944929

H	3.272062	6.634292	3.672491
C	3.468174	4.497973	3.381363
H	3.327501	4.260110	4.442187
C	0.774205	-1.156948	5.173054
C	1.040228	-2.316585	4.414145
H	1.520691	-2.234486	3.432291
C	0.688125	-3.581814	4.910039
H	0.890887	-4.475479	4.309928
C	0.071334	-3.699098	6.166058
H	-0.207317	-4.686393	6.549773
C	-0.189393	-2.548129	6.928921
H	-0.671123	-2.635558	7.908812
C	0.165143	-1.281157	6.442092
H	-0.040341	-0.389765	7.045460
C	-0.214594	1.556388	4.667683
C	-1.513665	1.002627	4.651407
H	-1.650677	-0.082347	4.701806
C	-2.635713	1.843130	4.567832
H	-3.639660	1.404953	4.554458
C	-2.472169	3.236622	4.493189
H	-3.349138	3.888835	4.420168
C	-1.180815	3.791008	4.507867
H	-1.047372	4.876115	4.440347
C	-0.055444	2.957094	4.597228
H	0.951705	3.389957	4.602801
C	2.354740	0.899265	2.060296
C	1.346671	0.308752	2.729569
C	3.834598	4.727569	9.670855
C	3.117804	3.779816	10.306133
H	4.004726	5.723638	10.102729
H	2.672891	3.949781	11.296348
H	2.401465	0.920170	0.963174
H	0.499849	-0.172068	2.220643

Table S35. *sym*-[(dppv)Ni^{II}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) dibasal, and pdt oriented toward Fe (*sym*-[H**1**]$^+$, –4696.7867114 E_h)

atom	x	y	z
Fe	4.145918	2.168174	7.599967
H	2.925618	2.505829	6.537936
Ni	3.288682	1.296405	5.164568
S	3.480183	-0.018803	7.017035
S	5.329709	2.038583	5.645258
P	2.847394	2.149474	9.427308
P	4.414758	4.359846	7.938565
P	3.669568	1.750423	3.055081
P	1.294011	0.529228	4.556575
O	6.444017	1.734828	9.374007
C	3.263834	0.884214	10.707533
C	4.155736	1.178873	11.760121
H	4.581780	2.183723	11.856339
C	4.506692	0.186886	12.690133
H	5.195959	0.429203	13.506298
C	3.977517	-1.107910	12.573301
H	4.251956	-1.880621	13.299568
C	3.092563	-1.409670	11.524033
H	2.674917	-2.418265	11.430462
C	2.735337	-0.421526	10.594661
H	2.041347	-0.662391	9.782508
C	0.994398	2.096990	9.425403
C	0.279146	2.253769	8.223618
H	0.830664	2.337650	7.280797
C	-1.126055	2.295407	8.233226
H	-1.670376	2.417991	7.291197
C	-1.823533	2.178244	9.445804
H	-2.918548	2.212108	9.455154
C	-1.116012	2.014054	10.649310
H	-1.656589	1.917995	11.597362
C	0.285698	1.971463	10.642147
H	0.828570	1.829617	11.583181
C	6.149064	4.984124	7.892711
C	6.892817	5.162603	9.078098
H	6.425905	4.986933	10.053381
C	8.239353	5.557029	9.017882
H	8.805480	5.693309	9.945633
C	8.855971	5.774759	7.776083
H	9.905671	6.084322	7.731063

C	8.123397	5.593823	6.590329
H	8.599831	5.763353	5.618410
C	6.779458	5.195260	6.644607
H	6.217116	5.055730	5.714617
C	3.440545	5.700226	7.086552
C	2.074914	5.468399	6.813427
H	1.645816	4.478662	7.001191
C	1.262761	6.502027	6.322474
H	0.200078	6.312131	6.136016
C	1.804807	7.777135	6.086974
H	1.168904	8.584599	5.707850
C	3.163894	8.013642	6.349678
H	3.594176	9.006265	6.176242
C	3.978285	6.984741	6.853050
H	5.031264	7.187905	7.070843
C	5.515322	1.862107	8.661818
C	4.937830	-1.146440	6.755079
H	4.903687	-1.870425	7.588474
H	4.728480	-1.697693	5.820920
C	6.316654	-0.486260	6.713583
H	6.562514	-0.082850	7.707562
H	7.066622	-1.279039	6.511911
C	6.506159	0.593172	5.646762
H	6.440810	0.169855	4.628541
H	7.504572	1.054657	5.752179
C	5.182933	0.977674	2.330777
C	6.360513	1.726391	2.117552
H	6.373605	2.799721	2.332304
C	7.513834	1.098107	1.620562
H	8.421434	1.688206	1.453088
C	7.504559	-0.277006	1.334278
H	8.404792	-0.762274	0.942312
C	6.336618	-1.028475	1.548824
H	6.322154	-2.100375	1.323194
C	5.182214	-0.407047	2.049556
H	4.274590	-0.998798	2.216245
C	3.717448	3.492918	2.456619
C	3.906576	3.794638	1.088862
H	4.079065	2.992273	0.362479
C	3.890338	5.128905	0.657444
H	4.033684	5.358138	-0.404092
C	3.693868	6.167711	1.584617
H	3.684501	7.208530	1.242932
C	3.512606	5.872951	2.945195

H	3.362968	6.676919	3.673328
C	3.520736	4.537540	3.381372
H	3.376854	4.301329	4.442192
C	0.763429	-1.129223	5.141617
C	1.021707	-2.276918	4.362105
H	1.495753	-2.179589	3.378484
C	0.668780	-3.549590	4.838327
H	0.865582	-4.433440	4.221878
C	0.058262	-3.686569	6.095276
H	-0.221516	-4.679401	6.463593
C	-0.194700	-2.547828	6.878926
H	-0.671410	-2.650412	7.859830
C	0.161383	-1.273933	6.411862
H	-0.037147	-0.392536	7.031890
C	-0.224903	1.591094	4.671180
C	-1.524018	1.037508	4.656569
H	-1.660704	-0.047677	4.703356
C	-2.646502	1.878164	4.579038
H	-3.650451	1.439906	4.567067
C	-2.483320	3.271859	4.508090
H	-3.360512	3.924240	4.439297
C	-1.191911	3.826140	4.520636
H	-1.058434	4.911351	4.454979
C	-0.066178	2.992107	4.604710
H	0.940878	3.425585	4.608835
C	2.340906	0.961711	2.055105
C	1.332060	0.367820	2.719986
C	3.851547	4.702170	9.665966
C	3.147016	3.747782	10.305464
H	4.010922	5.700545	10.096510
H	2.704089	3.916599	11.296731
H	2.386109	0.994221	0.958244
H	0.482239	-0.104082	2.207733

Table S36. Cartesian Coordinates for *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Ni (*unsym*-[H**1**]^{0}, –4696.93489816 E_h)

atom	x	y	z
Fe	4.043280	2.337410	7.533572
H	3.074370	2.574834	6.245571
Ni	3.449349	1.313393	5.148359
S	3.689250	0.034174	7.085173
S	5.624345	2.206714	5.772024
P	4.027552	4.564634	7.804032
P	5.371431	2.230173	9.357804
P	3.700541	1.815088	3.004106
P	1.387654	0.486227	4.631473
O	1.580535	2.144984	9.091093
C	2.351176	5.361864	7.856581
C	1.691366	5.610842	9.077640
H	2.173561	5.343206	10.024329
C	0.412991	6.193828	9.093163
H	-0.085038	6.380863	10.051303
C	-0.221247	6.536404	7.889130
H	-1.213844	7.000918	7.901771
C	0.422162	6.277663	6.665488
H	-0.068134	6.533946	5.719520
C	1.694923	5.687637	6.648430
H	2.184218	5.490213	5.687948
C	5.009665	5.887971	6.907748
C	6.224463	5.553718	6.270824
H	6.524282	4.501727	6.203953
C	7.019492	6.554085	5.686040
H	7.952550	6.274638	5.183340
C	6.619653	7.898349	5.733771
H	7.241532	8.676750	5.276799
C	5.413824	8.241045	6.368810
H	5.092597	9.288257	6.414313
C	4.613726	7.245286	6.951456
H	3.676309	7.528020	7.441498
C	4.959456	1.129397	10.803090
C	5.610616	1.286189	12.049250
H	6.404232	2.033433	12.165823
C	5.267537	0.475171	13.140381
H	5.779123	0.609734	14.100479
C	4.272884	-0.508751	13.000871
H	4.004814	-1.142402	13.854137

C	3.629939	-0.678566	11.765842
H	2.858071	-1.447437	11.647263
C	3.968196	0.135841	10.671022
H	3.473182	-0.007210	9.703442
C	7.227667	2.058511	9.286590
C	7.996205	3.115107	8.749069
H	7.505876	4.045546	8.442305
C	9.386395	2.984518	8.605589
H	9.968138	3.815746	8.190743
C	10.029836	1.797482	8.992793
H	11.115214	1.696777	8.880003
C	9.274394	0.741381	9.528648
H	9.767614	-0.187634	9.837154
C	7.883702	0.869312	9.673868
H	7.306151	0.041458	10.099231
C	2.586076	2.250267	8.483760
C	5.288923	-0.899649	7.115076
H	5.792646	-0.715133	8.083112
H	4.989096	-1.963672	7.093656
C	6.230270	-0.598279	5.947798
H	7.069744	-1.326109	5.975603
H	5.689483	-0.754487	4.994782
C	6.827580	0.810583	5.976874
H	7.533619	0.929828	5.135364
H	7.390646	0.969351	6.912774
C	5.008950	0.950761	2.018662
C	6.320467	1.478507	1.974488
H	6.532252	2.443282	2.448831
C	7.347508	0.777880	1.324703
H	8.357851	1.202663	1.295329
C	7.085787	-0.458991	0.710363
H	7.889318	-1.003190	0.201321
C	5.787085	-0.993237	0.753527
H	5.572027	-1.956324	0.275757
C	4.757926	-0.296957	1.405932
H	3.749247	-0.725097	1.440163
C	3.910751	3.573553	2.435187
C	4.022715	3.920715	1.070969
H	4.036911	3.136255	0.304956
C	4.134432	5.266417	0.689566
H	4.214844	5.526887	-0.372370
C	4.151461	6.277200	1.666959
H	4.246803	7.327195	1.366767
C	4.056937	5.939547	3.026411

H	4.093998	6.719445	3.795342
C	3.931016	4.592726	3.406719
H	3.863054	4.311994	4.464168
C	1.120148	-1.340692	4.770872
C	1.332796	-2.211556	3.680574
H	1.592130	-1.800568	2.698037
C	1.211094	-3.601838	3.840235
H	1.374963	-4.262753	2.980934
C	0.876206	-4.141904	5.091827
H	0.779881	-5.226476	5.216514
C	0.666627	-3.282845	6.185020
H	0.407623	-3.695804	7.166819
C	0.792003	-1.895085	6.030086
H	0.635853	-1.235869	6.890701
C	-0.233438	1.160029	5.247867
C	-1.456497	0.475077	5.068933
H	-1.466402	-0.510108	4.589102
C	-2.658341	1.042862	5.517099
H	-3.601394	0.501762	5.375581
C	-2.652899	2.299368	6.147490
H	-3.592517	2.738376	6.502667
C	-1.441918	2.985774	6.327967
H	-1.424152	3.959895	6.828544
C	-0.236700	2.419115	5.881612
H	0.711828	2.947063	6.033142
C	2.158845	1.332593	2.106244
C	1.164184	0.756172	2.813049
C	5.270171	3.897310	10.169464
C	4.669664	4.904336	9.507333
H	5.722515	4.048396	11.159414
H	4.612911	5.922241	9.919244
H	2.054558	1.537752	1.030685
H	0.211144	0.473105	2.341862

Table S37. *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Fe (*unsym*-[H**1**]^{0}, –4696.92707267 E_h)

atom	x	y	z
Fe	4.065116	2.267079	7.550141
H	3.075549	2.540807	6.286484
Ni	3.409309	1.319875	5.135440
S	3.620495	-0.033467	7.013779
S	5.621663	2.114680	5.780113
P	4.004659	4.490034	7.825154
P	5.427902	2.206241	9.371484
P	3.695733	1.804585	2.996281
P	1.321516	0.567473	4.603139
O	1.656130	2.010061	9.180858
C	2.320351	5.275356	7.843555
C	1.603152	5.432433	9.047678
H	2.038497	5.087558	9.992024
C	0.330254	6.027348	9.048433
H	-0.211303	6.145622	9.993822
C	-0.242348	6.470622	7.846091
H	-1.230063	6.945694	7.848072
C	0.456688	6.299837	6.637708
H	0.013478	6.632987	5.692521
C	1.725680	5.701767	6.635286
H	2.261103	5.579237	5.687287
C	4.979717	5.831866	6.948912
C	6.110766	5.510344	6.169543
H	6.360790	4.457471	5.991206
C	6.892880	6.529877	5.598481
H	7.760405	6.261954	4.984590
C	6.561404	7.877955	5.800796
H	7.172961	8.670692	5.354629
C	5.435887	8.207504	6.576002
H	5.167195	9.257647	6.739653
C	4.650044	7.194013	7.145081
H	3.771560	7.465346	7.740559
C	5.095778	1.044586	10.786787
C	5.688884	1.231471	12.057499
H	6.402416	2.047968	12.218549
C	5.390005	0.364067	13.118265
H	5.855915	0.521833	14.097880
C	4.496828	-0.704154	12.924039
H	4.262707	-1.380769	13.753985

C	3.908734	-0.900539	11.665598
H	3.211944	-1.731295	11.506390
C	4.203938	-0.031631	10.601022
H	3.743470	-0.184768	9.616886
C	7.296190	2.211891	9.288866
C	7.930386	3.274066	8.606325
H	7.330264	4.086943	8.184108
C	9.326320	3.301224	8.466350
H	9.800495	4.136581	7.938433
C	10.111355	2.265025	8.999209
H	11.201518	2.286349	8.888994
C	9.490280	1.202990	9.675656
H	10.093132	0.389884	10.096454
C	8.093394	1.175405	9.820510
H	7.623346	0.342229	10.353478
C	2.638010	2.142968	8.541154
C	5.137540	-1.100026	6.844313
H	5.050051	-1.887349	7.615710
H	5.062089	-1.586684	5.855241
C	6.477150	-0.387597	6.997817
H	6.534283	0.061211	8.002874
H	7.284925	-1.149849	6.955666
C	6.791040	0.674056	5.942093
H	6.828507	0.212586	4.937628
H	7.785450	1.107387	6.151467
C	4.973651	0.868228	2.036005
C	6.322502	1.294034	2.073065
H	6.583547	2.219365	2.599010
C	7.324141	0.541214	1.442579
H	8.363945	0.887024	1.477809
C	7.000187	-0.648343	0.766932
H	7.784321	-1.234022	0.273954
C	5.664312	-1.080927	0.727931
H	5.400449	-2.005410	0.200861
C	4.659565	-0.331208	1.359471
H	3.620729	-0.679778	1.325660
C	3.991792	3.543822	2.404578
C	4.201172	3.858170	1.044014
H	4.251417	3.055938	0.298223
C	4.362462	5.192974	0.642521
H	4.519506	5.428246	-0.416743
C	4.329552	6.225283	1.596730
H	4.462223	7.266722	1.281315
C	4.137466	5.919740	2.953533

H	4.135884	6.716808	3.705432
C	3.964977	4.583867	3.353286
H	3.822945	4.326423	4.409597
C	1.018668	-1.256629	4.720102
C	1.265964	-2.122836	3.633634
H	1.575961	-1.708364	2.667472
C	1.114204	-3.511992	3.776276
H	1.305200	-4.169187	2.919701
C	0.714807	-4.055553	5.007286
H	0.594632	-5.139206	5.118694
C	0.471429	-3.201152	6.097065
H	0.162601	-3.616768	7.063210
C	0.626480	-1.814580	5.959025
H	0.442066	-1.159110	6.816843
C	-0.296931	1.255977	5.211666
C	-1.531554	0.612026	4.969649
H	-1.553206	-0.348165	4.441718
C	-2.730171	1.186739	5.417060
H	-3.682331	0.677833	5.225769
C	-2.709618	2.409248	6.111023
H	-3.646879	2.853820	6.465600
C	-1.487397	3.054577	6.354820
H	-1.458809	4.002488	6.902608
C	-0.285175	2.481010	5.908033
H	0.671534	2.978099	6.105514
C	2.141880	1.389611	2.085724
C	1.118347	0.855492	2.784378
C	5.208489	3.845965	10.214432
C	4.588707	4.837137	9.546899
H	5.626086	4.002053	11.218623
H	4.477342	5.846092	9.969271
H	2.054620	1.605109	1.010565
H	0.157293	0.614476	2.306272

Table S38. *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*unsym*-[H**1**]^{0}, –4696.93777738 E_h)

atom	x	y	z
Ni	1.861735	8.879577	9.878850
Fe	1.279394	10.050774	12.186692
O	2.500015	12.702731	12.234054
C	2.014661	11.625665	12.255733
P	3.985635	8.850261	9.305700
P	1.370908	8.015495	7.856269
C	5.217401	7.697212	10.087232
C	5.197125	6.327772	9.731483
H	4.503405	5.979370	8.957105
C	6.058482	5.412172	10.354156
H	6.038189	4.358033	10.053138
C	6.950082	5.845199	11.351516
H	7.626413	5.131571	11.835481
C	6.965867	7.199246	11.722899
H	7.655075	7.548591	12.500332
C	6.105910	8.119561	11.101062
H	6.134131	9.172330	11.401325
C	4.939835	10.442717	9.173564
C	4.228418	11.650474	9.323556
H	3.161794	11.614913	9.572281
C	4.879096	12.884392	9.155520
H	4.315622	13.814539	9.287907
C	6.243972	12.922114	8.830664
H	6.752544	13.884548	8.701537
C	6.959979	11.722260	8.673458
H	8.025959	11.746956	8.418226
C	6.313089	10.489042	8.843497
H	6.881699	9.558671	8.730263
C	4.098631	8.273650	7.551609
H	5.079997	8.231514	7.057682
C	2.962507	7.930791	6.915745
H	2.956625	7.595523	5.868757
C	0.349672	8.998398	6.658618
C	-0.930705	8.604680	6.212683
H	-1.339187	7.632463	6.508869
C	-1.685909	9.447365	5.379948
H	-2.676830	9.124215	5.040036
C	-1.175802	10.693572	4.982582
H	-1.765624	11.348470	4.331268

C	0.094174	11.098191	5.429151
H	0.498606	12.072076	5.130363
C	0.847884	10.262609	6.265759
H	1.828263	10.594116	6.626692
C	0.790020	6.261679	7.626914
C	0.659272	5.452210	8.775156
H	0.848737	5.894976	9.761664
C	0.295280	4.100372	8.652380
H	0.193873	3.483045	9.552441
C	0.062522	3.543502	7.385013
H	-0.221949	2.489157	7.290138
C	0.196677	4.341322	6.235231
H	0.019637	3.910548	5.242781
C	0.560311	5.691405	6.353679
H	0.656595	6.306331	5.451272
P	2.433570	9.336348	13.970404
P	-0.371984	10.622631	13.648416
C	2.619769	7.525094	14.312739
C	2.223996	6.938044	15.533096
H	1.785638	7.555267	16.324843
C	2.384450	5.558800	15.745218
H	2.071171	5.116763	16.698241
C	2.950920	4.752867	14.744957
H	3.081461	3.677755	14.913882
C	3.343995	5.328630	13.525633
H	3.782712	4.710175	12.735250
C	3.168303	6.703145	13.303200
H	3.455344	7.136938	12.338727
C	4.146745	9.982534	14.341070
C	5.281068	9.147796	14.414673
H	5.183769	8.073481	14.232088
C	6.540545	9.684319	14.731225
H	7.409717	9.018889	14.793733
C	6.686511	11.057845	14.979560
H	7.669974	11.472826	15.227945
C	5.561509	11.895648	14.913456
H	5.660265	12.969516	15.108601
C	4.301970	11.363549	14.599214
H	3.436171	12.030916	14.555286
C	1.587981	9.976997	15.486593
H	2.084779	9.907654	16.464700
C	0.393949	10.581927	15.337278
H	-0.146368	11.006155	16.194857
C	-1.117052	12.327177	13.623847

C	-1.849532	12.835117	14.721999
H	-2.022264	12.210534	15.606097
C	-2.383201	14.131400	14.684465
H	-2.945861	14.513386	15.544183
C	-2.199754	14.935750	13.545911
H	-2.616947	15.948956	13.517544
C	-1.485473	14.435543	12.447046
H	-1.342808	15.054478	11.553987
C	-0.944006	13.138847	12.483818
H	-0.388433	12.748027	11.622503
C	-1.863157	9.565898	14.019060
C	-1.664362	8.288727	14.592642
H	-0.652584	7.956750	14.849147
C	-2.752831	7.432064	14.815878
H	-2.581340	6.445086	15.260623
C	-4.053723	7.832880	14.467415
H	-4.902546	7.162049	14.641957
C	-4.259701	9.097669	13.892246
H	-5.270758	9.419375	13.616603
C	-3.173430	9.958879	13.668137
H	-3.347277	10.944419	13.223144
S	0.439648	10.739723	10.098011
S	0.588089	7.855503	11.591830
C	-1.329479	10.192729	9.939134
H	-1.887593	10.622329	10.792880
H	-1.699517	10.683660	9.020657
C	-1.577256	8.685787	9.839377
H	-2.663051	8.532934	9.657096
H	-1.056686	8.294119	8.949222
C	-1.193323	7.851653	11.062622
H	-1.426898	6.789990	10.859682
H	-1.795364	8.154282	11.934520
H	2.533195	9.588152	11.306076

Table S39. *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*unsym*-[H**1**]^{0}, –4696.93828203 E_h)

atom	x	y	z
Ni	1.907601	9.041593	9.868492
Fe	1.206671	10.180934	12.145772
O	2.287678	12.877135	12.468354
C	1.869353	11.777888	12.358251
P	4.034461	8.987749	9.327958
P	1.436520	8.090190	7.885056
C	5.204686	7.733721	10.051496
C	5.152278	6.395818	9.593882
H	4.485732	6.130626	8.765041
C	5.944407	5.402835	10.189566
H	5.898485	4.375104	9.810242
C	6.796505	5.723088	11.261288
H	7.415845	4.947392	11.725777
C	6.846123	7.045258	11.732249
H	7.499131	7.308102	12.572212
C	6.058774	8.042906	11.134591
H	6.111846	9.067546	11.516345
C	5.048715	10.548935	9.319813
C	4.364025	11.771392	9.485952
H	3.281150	11.757943	9.658608
C	5.059916	12.990839	9.424345
H	4.515876	13.931570	9.563844
C	6.444551	13.000290	9.191043
H	6.988096	13.951052	9.143747
C	7.133276	11.786840	9.016013
H	8.213583	11.789635	8.828694
C	6.440646	10.567728	9.079290
H	6.987260	9.626130	8.952638
C	4.142176	8.522507	7.541010
H	5.114266	8.549415	7.028122
C	3.010146	8.154959	6.910573
H	2.998042	7.867664	5.849352
C	0.277303	8.856505	6.657529
C	-0.997972	8.322149	6.365859
H	-1.303583	7.366944	6.807119
C	-1.875244	9.000139	5.504585
H	-2.858153	8.567926	5.283554
C	-1.497756	10.224961	4.928934
H	-2.184338	10.753271	4.257884

C	-0.236637	10.770698	5.222623
H	0.064460	11.728441	4.782767
C	0.642870	10.096099	6.082660
H	1.618378	10.536716	6.319325
C	1.069016	6.269089	7.745234
C	1.082297	5.490973	8.922106
H	1.246492	5.986917	9.887163
C	0.875151	4.102365	8.855422
H	0.879518	3.510544	9.777963
C	0.660468	3.477605	7.617037
H	0.499779	2.394437	7.566451
C	0.650849	4.245363	6.439096
H	0.485622	3.762702	5.468716
C	0.854217	5.632029	6.501120
H	0.835670	6.223248	5.578277
P	2.357673	9.390011	13.877053
P	-0.445464	10.675243	13.650325
C	2.452337	7.569002	14.227459
C	1.819598	6.976474	15.340433
H	1.250273	7.596528	16.042363
C	1.912808	5.590802	15.557631
H	1.420270	5.144462	16.429492
C	2.638713	4.785309	14.666699
H	2.714235	3.705414	14.838736
C	3.268116	5.368933	13.553793
H	3.837950	4.751367	12.851020
C	3.172903	6.750043	13.330560
H	3.662696	7.191604	12.455933
C	4.135648	9.878082	14.158069
C	4.827021	9.390044	15.290199
H	4.335876	8.680630	15.966715
C	6.147306	9.787258	15.546628
H	6.669520	9.400494	16.429423
C	6.798749	10.674711	14.672180
H	7.830045	10.986559	14.873604
C	6.124489	11.155475	13.539215
H	6.623965	11.839691	12.844437
C	4.800642	10.757327	13.281693
H	4.289441	11.130609	12.390889
C	1.587495	10.058177	15.419402
H	2.118671	9.993196	16.379693
C	0.378765	10.644200	15.313628
H	-0.130820	11.066873	16.190464
C	-1.227957	12.361175	13.652754

C	-1.876368	12.895446	14.790290
H	-1.961246	12.302156	15.707955
C	-2.436920	14.180955	14.753671
H	-2.934099	14.583173	15.643939
C	-2.361285	14.948895	13.578801
H	-2.797767	15.953933	13.551830
C	-1.724133	14.425296	12.443666
H	-1.657860	15.019753	11.525422
C	-1.157777	13.139935	12.478803
H	-0.645014	12.737367	11.596133
C	-1.886458	9.549140	14.029645
C	-1.608349	8.187132	14.290131
H	-0.574836	7.826277	14.273846
C	-2.651932	7.283905	14.543674
H	-2.417178	6.232302	14.744672
C	-3.987306	7.720961	14.532170
H	-4.801081	7.013515	14.728487
C	-4.272753	9.068611	14.261364
H	-5.311189	9.419583	14.244530
C	-3.231403	9.977552	14.010818
H	-3.469992	11.024770	13.799010
S	0.556601	10.956900	10.001295
S	0.509212	8.025493	11.460345
C	-1.165989	10.427447	9.545782
H	-1.771193	11.351709	9.496434
H	-1.109850	10.013504	8.524209
C	-1.847575	9.435409	10.488226
H	-1.977738	9.900260	11.479502
H	-2.872531	9.254018	10.098184
C	-1.174810	8.069063	10.657646
H	-1.069970	7.569784	9.675545
H	-1.821032	7.432485	11.287996
H	2.506395	9.743771	11.297979

Table S40. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*sym*-[H**1**]^{0}, –4696.93781793 E_h)

atom	x	y	z
Ni	9.063529	10.182714	3.208156
Fe	6.768419	11.574391	3.016937
P	10.412004	10.260213	4.979851
S	8.696111	11.984254	1.718839
P	10.382204	8.512957	2.413881
S	6.993810	9.312925	2.533067
O	4.919682	12.095378	0.792130
C	8.274069	11.338649	0.025212
H	7.364696	11.866544	-0.312249
H	9.102704	11.659038	-0.633628
C	8.099260	9.820306	-0.104645
H	9.049259	9.328955	0.170477
H	7.932906	9.593795	-1.180110
C	6.948689	9.172895	0.678190
H	6.942757	8.087773	0.470057
H	5.977162	9.583460	0.349037
C	5.647499	11.900726	1.698861
C	11.828400	11.490850	5.028160
C	12.215923	12.096015	3.814276
H	11.623958	11.901879	2.911610
C	13.330082	12.949774	3.766771
H	13.617904	13.414376	2.816762
C	14.064290	13.216808	4.934649
H	14.931508	13.886219	4.899321
C	13.677331	12.627648	6.150896
H	14.242214	12.836226	7.067173
C	12.568219	11.767456	6.198439
H	12.273727	11.313183	7.151016
C	9.862706	10.285267	6.752569
C	9.269650	11.460670	7.269775
H	9.177928	12.350115	6.636391
C	8.808880	11.505517	8.593453
H	8.357745	12.427846	8.976976
C	8.924542	10.378009	9.424510
H	8.563715	10.414992	10.458507
C	9.500618	9.202406	8.918726
H	9.595513	8.316598	9.557873
C	9.962444	9.154337	7.592658
H	10.402079	8.225422	7.211930

C	11.701250	8.791124	1.124378
C	12.620557	7.784945	0.749237
H	12.543538	6.781790	1.184346
C	13.625759	8.054987	-0.191634
H	14.332578	7.266159	-0.474237
C	13.726715	9.332667	-0.769295
H	14.512465	9.541515	-1.504325
C	12.818411	10.337966	-0.402805
H	12.890754	11.335487	-0.851399
C	11.811697	10.069576	0.539921
H	11.097011	10.848993	0.833232
C	9.632936	6.894608	1.910341
C	8.948284	6.152735	2.900107
H	8.924939	6.521563	3.931980
C	8.290370	4.959104	2.570239
H	7.768859	4.393707	3.351048
C	8.289885	4.495654	1.243372
H	7.771712	3.565256	0.984916
C	8.952391	5.234292	0.249773
H	8.954880	4.882115	-0.788360
C	9.619179	6.426372	0.578779
H	10.140325	6.987620	-0.204164
P	6.652048	13.662755	3.781046
P	5.163706	11.072846	4.462575
C	8.037028	14.659949	4.522063
C	9.330506	14.118072	4.630703
C	7.798354	15.973921	4.985436
C	10.369377	14.870523	5.208518
H	9.522638	13.109024	4.249936
C	8.832061	16.720126	5.568132
H	6.804945	16.423916	4.871488
C	10.119725	16.167237	5.682248
H	11.372341	14.438210	5.281471
H	8.634347	17.737330	5.925984
H	10.929511	16.752119	6.133571
C	5.962284	14.927305	2.608298
C	4.633437	15.390513	2.684843
C	6.792697	15.391280	1.563188
C	4.143753	16.308159	1.739857
H	3.973670	15.031847	3.483237
C	6.299552	16.304489	0.620438
H	7.822352	15.022815	1.486343
C	4.975117	16.767739	0.707174
H	3.108673	16.661757	1.812517

H	6.952686	16.655447	-0.186849
H	4.592419	17.482283	-0.030405
C	3.509388	10.670139	3.721518
C	3.279877	9.366159	3.227350
C	2.507080	11.648696	3.563009
C	2.069045	9.053613	2.592028
H	4.057341	8.601822	3.335046
C	1.293460	11.330154	2.931399
H	2.675321	12.667401	3.930406
C	1.071509	10.032637	2.444739
H	1.904233	8.039174	2.210912
H	0.522022	12.100660	2.818483
H	0.125389	9.784741	1.950254
C	5.268723	9.755772	5.769380
C	4.128477	9.434065	6.540866
C	6.475519	9.070707	6.004356
C	4.197599	8.446776	7.533725
H	3.176738	9.943950	6.351232
C	6.536454	8.072253	6.991675
H	7.362101	9.314696	5.407065
C	5.403336	7.760032	7.757432
H	3.307024	8.207220	8.126381
H	7.480016	7.544650	7.164584
H	5.456269	6.981406	8.527346
C	11.454219	7.979217	3.820976
C	11.463462	8.738957	4.934259
H	12.103114	7.098417	3.714083
H	12.142207	8.522376	5.771894
C	5.435671	13.708534	5.179158
C	4.784355	12.568733	5.483688
H	5.285219	14.635265	5.751221
H	4.069010	12.506602	6.316114
H	7.893765	11.20132	4.136688

Table S41. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Fe (*sym*-[H**1**]^{0}, –4696.93158536 E_h)

atom	x	y	z
Ni	9.007992	10.182947	3.187169
Fe	6.717196	11.556208	2.966594
P	10.337395	10.247530	4.974001
S	8.633837	11.905516	1.621392
P	10.369353	8.545581	2.364717
S	6.938561	9.273175	2.545446
O	4.653956	12.239539	0.983106
C	8.387394	11.074683	-0.034636
H	8.356128	11.886637	-0.783999
H	9.301159	10.482512	-0.227684
C	7.150540	10.187923	-0.217475
H	7.184808	9.797066	-1.257903
H	6.239184	10.801192	-0.158168
C	7.026062	8.973641	0.709149
H	7.875663	8.285180	0.552108
H	6.105813	8.418408	0.451788
C	5.495321	11.945446	1.754905
C	11.787655	11.441167	5.059980
C	12.254107	11.997889	3.851004
H	11.702464	11.795322	2.925847
C	13.398409	12.811832	3.832808
H	13.748116	13.235611	2.884464
C	14.083970	13.090770	5.027289
H	14.974582	13.729595	5.015563
C	13.618005	12.551721	6.238843
H	14.144263	12.769339	7.175804
C	12.479884	11.728934	6.256238
H	12.127029	11.311622	7.205672
C	9.759846	10.292690	6.736821
C	9.147469	11.473079	7.218978
H	9.052696	12.345215	6.562113
C	8.673148	11.545096	8.536592
H	8.207549	12.470997	8.893308
C	8.793908	10.439526	9.396000
H	8.421965	10.497152	10.425116
C	9.389512	9.259347	8.925089
H	9.487919	8.390501	9.586552
C	9.866182	9.184750	7.605441
H	10.321236	8.252200	7.253109

C	11.746234	8.880591	1.150173
C	12.698625	7.899644	0.790088
H	12.618031	6.883381	1.192648
C	13.743032	8.211322	-0.093469
H	14.474531	7.440953	-0.363967
C	13.852376	9.506777	-0.628481
H	14.668428	9.747897	-1.319253
C	12.914003	10.488438	-0.274716
H	12.991982	11.500268	-0.688815
C	11.868263	10.178067	0.611399
H	11.136910	10.943504	0.899619
C	9.698653	6.910012	1.801248
C	8.963282	6.152257	2.741891
H	8.850121	6.525338	3.766138
C	8.369077	4.936781	2.371023
H	7.806206	4.359908	3.113828
C	8.486803	4.465036	1.052736
H	8.020141	3.516761	0.763040
C	9.200056	5.219063	0.106403
H	9.292737	4.861590	-0.925741
C	9.799101	6.434798	0.475092
H	10.354267	7.012202	-0.272088
P	6.670096	13.655143	3.721731
P	5.162176	11.084164	4.482871
C	8.088953	14.635581	4.420271
C	9.380224	14.083341	4.498274
C	7.872083	15.953770	4.883581
C	10.438241	14.831257	5.047042
H	9.555515	13.070536	4.118357
C	8.925417	16.694715	5.436317
H	6.879944	16.411402	4.791693
C	10.210979	16.131868	5.520624
H	11.439114	14.391707	5.098003
H	8.744466	17.715199	5.793668
H	11.036610	16.711816	5.949017
C	5.969236	14.930043	2.567414
C	4.661299	15.438102	2.696227
C	6.770649	15.358581	1.485340
C	4.164528	16.367853	1.766895
H	4.022466	15.103995	3.521803
C	6.270350	16.284070	0.558616
H	7.782410	14.953143	1.367043
C	4.967598	16.793726	0.698093
H	3.145691	16.756346	1.879522

H	6.900506	16.607962	-0.277703
H	4.579225	17.517612	-0.027315
C	3.473635	10.699345	3.812081
C	3.218367	9.400040	3.318349
C	2.466848	11.680606	3.712094
C	1.977012	9.094224	2.741832
H	3.999371	8.634073	3.381291
C	1.222569	11.368545	3.139380
H	2.654557	12.696329	4.078176
C	0.974706	10.075647	2.653441
H	1.791610	8.083310	2.360819
H	0.447883	12.141013	3.071104
H	0.004643	9.833035	2.204857
C	5.285829	9.775007	5.796452
C	4.169398	9.502047	6.620130
C	6.471016	9.037961	5.975661
C	4.241102	8.511313	7.609124
H	3.232147	10.051403	6.473398
C	6.532606	8.034255	6.957720
H	7.339825	9.244134	5.339318
C	5.423871	7.770390	7.775250
H	3.369249	8.310118	8.242446
H	7.457733	7.462662	7.084511
H	5.477567	6.987261	8.540502
C	11.386923	7.982875	3.802866
C	11.364429	8.711774	4.936090
H	12.032641	7.099917	3.694228
H	12.014704	8.466143	5.788042
C	5.500338	13.724838	5.157680
C	4.846274	12.597153	5.498676
H	5.382828	14.658302	5.726447
H	4.162504	12.555078	6.358435
H	7.868779	11.206313	4.079202

Table S42. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) dibasal, and pdt oriented toward Ni (*sym*-[H**1**]^{0}, –4696.79188666 E_h)

atom	x	y	z
Fe	4.216739	2.230792	7.604972
H	2.974742	2.516243	6.548846
Ni	3.361887	1.449403	5.180995
S	3.918835	-0.007867	6.900097
S	5.421706	2.563108	5.650914
P	2.837271	2.008295	9.337283
P	4.397505	4.370024	8.154719
P	3.604209	1.545501	2.975052
P	1.258418	0.648589	4.807428
O	6.528696	1.507068	9.258874
C	3.215395	0.669617	10.553747
C	3.954407	0.934967	11.725865
H	4.262569	1.960793	11.958094
C	4.310327	-0.107926	12.596289
H	4.884265	0.114332	13.503192
C	3.935405	-1.428522	12.303063
H	4.213744	-2.242780	12.981846
C	3.206942	-1.702928	11.133326
H	2.917894	-2.732685	10.894085
C	2.851175	-0.664689	10.258796
H	2.296264	-0.890308	9.342548
C	0.976043	1.960102	9.239107
C	0.343338	2.656447	8.188977
H	0.956115	3.109787	7.402971
C	-1.056660	2.755159	8.137900
H	-1.530275	3.291457	7.308784
C	-1.840737	2.148140	9.132845
H	-2.933713	2.218224	9.090605
C	-1.219433	1.446166	10.179432
H	-1.825252	0.969955	10.959330
C	0.180852	1.355932	10.237570
H	0.655665	0.811483	11.060269
C	6.111489	5.024716	8.407287
C	6.720578	4.993012	9.679211
H	6.156335	4.630620	10.546145
C	8.049722	5.415468	9.844041
H	8.508337	5.387394	10.839090
C	8.787681	5.866780	8.738398
H	9.825435	6.195065	8.866635

C	8.191473	5.893299	7.466294
H	8.763496	6.240038	6.597997
C	6.862823	5.474654	7.297980
H	6.406924	5.491550	6.302880
C	3.593601	5.791625	7.254434
C	2.592620	5.536539	6.297911
H	2.353901	4.495234	6.050105
C	1.924881	6.599353	5.665352
H	1.151309	6.386380	4.918922
C	2.251141	7.927246	5.983164
H	1.729896	8.756053	5.490419
C	3.251140	8.190622	6.935161
H	3.513305	9.224906	7.186297
C	3.919221	7.130912	7.566566
H	4.706457	7.345662	8.297956
C	5.594198	1.808197	8.603739
C	5.617863	-0.718489	6.676430
H	6.162862	-0.623636	7.632925
H	5.452002	-1.796543	6.494467
C	6.434178	-0.131439	5.520516
H	7.373854	-0.718402	5.432185
H	5.877564	-0.271640	4.576529
C	6.826245	1.344839	5.660553
H	7.463110	1.633233	4.804990
H	7.405539	1.513022	6.586830
C	5.068389	0.783811	2.128475
C	6.229664	1.545497	1.866010
H	6.235811	2.619168	2.084565
C	7.369692	0.939246	1.315771
H	8.261347	1.544705	1.115068
C	7.368640	-0.433457	1.015193
H	8.258399	-0.903594	0.581407
C	6.220068	-1.199869	1.275427
H	6.209241	-2.271372	1.043641
C	5.082371	-0.598603	1.835356
H	4.195241	-1.207213	2.048515
C	3.505136	3.179534	2.083690
C	3.440994	3.272443	0.675729
H	3.487755	2.364509	0.063137
C	3.332056	4.524158	0.051323
H	3.274506	4.584504	-1.041831
C	3.302426	5.698123	0.824891
H	3.222397	6.675209	0.334377
C	3.382297	5.615695	2.223946

H	3.370618	6.525065	2.835587
C	3.478031	4.361143	2.850072
H	3.545049	4.285932	3.941534
C	0.669432	-0.907479	5.615348
C	1.009144	-2.160515	5.059130
H	1.551472	-2.203586	4.107216
C	0.666794	-3.352359	5.716453
H	0.934793	-4.315843	5.267276
C	-0.015639	-3.311398	6.943040
H	-0.284090	-4.241965	7.456014
C	-0.347948	-2.069333	7.510540
H	-0.877909	-2.024400	8.468857
C	-0.003137	-0.875440	6.858111
H	-0.265169	0.084616	7.315442
C	-0.275056	1.712581	4.730896
C	-1.588555	1.204713	4.833453
H	-1.748172	0.138836	5.027189
C	-2.694784	2.058205	4.693808
H	-3.708367	1.648656	4.777621
C	-2.507165	3.427396	4.439282
H	-3.372047	4.090985	4.326072
C	-1.203046	3.939281	4.324635
H	-1.048274	5.004516	4.116962
C	-0.095785	3.089322	4.473196
H	0.923334	3.483928	4.376057
C	2.226108	0.588343	2.210199
C	1.238243	0.156324	3.021656
C	3.639797	4.596857	9.830150
C	2.974824	3.550656	10.359079
H	3.697268	5.571188	10.336121
H	2.448915	3.616996	11.322346
H	2.220331	0.371563	1.132426
H	0.378675	-0.413549	2.639387

Table S43. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H)Fe^{II}(dppv)(CO)]^{0} with Fe(dppv) dibasal, Ni(dppv) dibasal, and pdt oriented toward Fe (*sym*-[H**1**]^{0}, –4696.93762211 E_h)

atom	x	y	z
Fe	4.145918	2.168174	7.599967
H	2.925618	2.505829	6.537936
Ni	3.288682	1.296405	5.164568
S	3.480183	-0.018803	7.017035
S	5.329709	2.038583	5.645258
P	2.847394	2.149474	9.427308
P	4.414758	4.359846	7.938565
P	3.669568	1.750423	3.055081
P	1.294011	0.529228	4.556575
O	6.444017	1.734828	9.374007
C	3.263834	0.884214	10.707533
C	4.155736	1.178873	11.760121
H	4.581780	2.183723	11.856339
C	4.506692	0.186886	12.690133
H	5.195959	0.429203	13.506298
C	3.977517	-1.107910	12.573301
H	4.251956	-1.880621	13.299568
C	3.092563	-1.409670	11.524033
H	2.674917	-2.418265	11.430462
C	2.735337	-0.421526	10.594661
H	2.041347	-0.662391	9.782508
C	0.994398	2.096990	9.425403
C	0.279146	2.253769	8.223618
H	0.830664	2.337650	7.280797
C	-1.126055	2.295407	8.233226
H	-1.670376	2.417991	7.291197
C	-1.823533	2.178244	9.445804
H	-2.918548	2.212108	9.455154
C	-1.116012	2.014054	10.649310
H	-1.656589	1.917995	11.597362
C	0.285698	1.971463	10.642147
H	0.828570	1.829617	11.583181
C	6.149064	4.984124	7.892711
C	6.892817	5.162603	9.078098
H	6.425905	4.986933	10.053381
C	8.239353	5.557029	9.017882
H	8.805480	5.693309	9.945633
C	8.855971	5.774759	7.776083
H	9.905671	6.084322	7.731063

C	8.123397	5.593823	6.590329
H	8.599831	5.763353	5.618410
C	6.779458	5.195260	6.644607
H	6.217116	5.055730	5.714617
C	3.440545	5.700226	7.086552
C	2.074914	5.468399	6.813427
H	1.645816	4.478662	7.001191
C	1.262761	6.502027	6.322474
H	0.200078	6.312131	6.136016
C	1.804807	7.777135	6.086974
H	1.168904	8.584599	5.707850
C	3.163894	8.013642	6.349678
H	3.594176	9.006265	6.176242
C	3.978285	6.984741	6.853050
H	5.031264	7.187905	7.070843
C	5.515322	1.862107	8.661818
C	4.937830	-1.146440	6.755079
H	4.903687	-1.870425	7.588474
H	4.728480	-1.697693	5.820920
C	6.316654	-0.486260	6.713583
H	6.562514	-0.082850	7.707562
H	7.066622	-1.279039	6.511911
C	6.506159	0.593172	5.646762
H	6.440810	0.169855	4.628541
H	7.504572	1.054657	5.752179
C	5.182933	0.977674	2.330777
C	6.360513	1.726391	2.117552
H	6.373605	2.799721	2.332304
C	7.513834	1.098107	1.620562
H	8.421434	1.688206	1.453088
C	7.504559	-0.277006	1.334278
H	8.404792	-0.762274	0.942312
C	6.336618	-1.028475	1.548824
H	6.322154	-2.100375	1.323194
C	5.182214	-0.407047	2.049556
H	4.274590	-0.998798	2.216245
C	3.717448	3.492918	2.456619
C	3.906576	3.794638	1.088862
H	4.079065	2.992273	0.362479
C	3.890338	5.128905	0.657444
H	4.033684	5.358138	-0.404092
C	3.693868	6.167711	1.584617
H	3.684501	7.208530	1.242932
C	3.512606	5.872951	2.945195

H	3.362968	6.676919	3.673328
C	3.520736	4.537540	3.381372
H	3.376854	4.301329	4.442192
C	0.763429	-1.129223	5.141617
C	1.021707	-2.276918	4.362105
H	1.495753	-2.179589	3.378484
C	0.668780	-3.549590	4.838327
H	0.865582	-4.433440	4.221878
C	0.058262	-3.686569	6.095276
H	-0.221516	-4.679401	6.463593
C	-0.194700	-2.547828	6.878926
H	-0.671410	-2.650412	7.859830
C	0.161383	-1.273933	6.411862
H	-0.037147	-0.392536	7.031890
C	-0.224903	1.591094	4.671180
C	-1.524018	1.037508	4.656569
H	-1.660704	-0.047677	4.703356
C	-2.646502	1.878164	4.579038
H	-3.650451	1.439906	4.567067
C	-2.483320	3.271859	4.508090
H	-3.360512	3.924240	4.439297
C	-1.191911	3.826140	4.520636
H	-1.058434	4.911351	4.454979
C	-0.066178	2.992107	4.604710
H	0.940878	3.425585	4.608835
C	2.340906	0.961711	2.055105
C	1.332060	0.367820	2.719986
C	3.851547	4.702170	9.665966
C	3.147016	3.747782	10.305464
H	4.010922	5.700545	10.096510
H	2.704089	3.916599	11.296731
H	2.386109	0.994221	0.958244
H	0.482239	-0.104082	2.207733

Table S44. Cartesian Coordinates for *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H_2)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Ni **(***unsym*-[H_2**1**]$^+$, –4697.34214064 E_h**)**

atom	x	y	z
Fe	3.931654	2.504537	7.587310
H	2.933947	2.466030	6.075852
Ni	3.481054	1.195108	5.047800
S	3.591055	0.178000	7.138389
S	5.515633	2.304874	5.803088
P	4.048038	4.767786	7.959605
P	5.309459	2.279463	9.399708
P	3.723800	1.769889	2.870785
P	1.391953	0.416711	4.530679
O	1.586163	2.301444	9.338020
C	2.379443	5.561655	8.022823
C	1.696775	5.739904	9.243657
H	2.165102	5.438325	10.187042
C	0.409547	6.302626	9.259099
H	-0.108645	6.440686	10.214037
C	-0.207052	6.688462	8.058850
H	-1.206950	7.135280	8.074357
C	0.464028	6.505390	6.836569
H	-0.008538	6.811501	5.896788
C	1.748477	5.941247	6.816247
H	2.269034	5.820030	5.858478
C	5.053404	6.036551	7.044887
C	6.211304	5.661981	6.329436
H	6.463741	4.602312	6.219051
C	7.016466	6.643974	5.727837
H	7.905595	6.340453	5.164401
C	6.682039	8.002303	5.839658
H	7.313106	8.765457	5.371264
C	5.532436	8.381611	6.553934
H	5.265431	9.439950	6.647474
C	4.719610	7.407725	7.152907
H	3.824401	7.716953	7.702107
C	4.889529	1.124420	10.788598
C	5.595910	1.225639	12.012057
H	6.418354	1.941500	12.121363
C	5.268239	0.393593	13.091107
H	5.821228	0.483853	14.032312
C	4.236764	-0.553131	12.963764
H	3.981429	-1.201910	13.808539

C	3.540694	-0.667042	11.751653
H	2.740360	-1.406921	11.643124
C	3.862184	0.166855	10.667135
H	3.322070	0.060664	9.720951
C	7.146950	2.076009	9.237777
C	7.914686	3.140157	8.714306
H	7.433970	4.086408	8.443853
C	9.300205	2.995902	8.544693
H	9.886485	3.830973	8.146122
C	9.933586	1.790615	8.891096
H	11.015411	1.681160	8.759815
C	9.176819	0.729486	9.414522
H	9.665283	-0.210041	9.694894
C	7.790467	0.868490	9.588144
H	7.213084	0.040255	10.011973
C	2.536810	2.409251	8.662001
C	5.185708	-0.767238	7.197186
H	5.678700	-0.579195	8.167689
H	4.864614	-1.824367	7.189404
C	6.132700	-0.497427	6.027889
H	6.975555	-1.216928	6.090322
H	5.603483	-0.698885	5.076100
C	6.724517	0.912821	6.001930
H	7.388212	1.018580	5.125722
H	7.329177	1.101111	6.903287
C	5.010856	0.833044	1.939286
C	6.300565	1.381470	1.754567
H	6.509828	2.407592	2.076205
C	7.309648	0.621895	1.142707
H	8.302986	1.060492	0.995807
C	7.047956	-0.689601	0.711686
H	7.836347	-1.277647	0.229742
C	5.769612	-1.242304	0.897057
H	5.556892	-2.262432	0.558639
C	4.757496	-0.489675	1.511589
H	3.764354	-0.930424	1.655569
C	3.961377	3.518457	2.319117
C	4.066546	3.849067	0.949084
H	4.061924	3.058453	0.189950
C	4.194883	5.188605	0.553677
H	4.272490	5.435997	-0.510714
C	4.229164	6.209315	1.519866
H	4.334408	7.254108	1.207629
C	4.137150	5.888280	2.883320

H	4.185469	6.678066	3.640951
C	3.999571	4.548059	3.280784
H	3.941676	4.291987	4.344093
C	1.213986	-1.417650	4.640489
C	1.315217	-2.241956	3.499048
H	1.439397	-1.793326	2.507125
C	1.245583	-3.639642	3.621662
H	1.319749	-4.266339	2.726070
C	1.072498	-4.229327	4.883262
H	1.014384	-5.319036	4.977624
C	0.970348	-3.415731	6.025137
H	0.830953	-3.869676	7.012514
C	1.046252	-2.020185	5.909318
H	0.971137	-1.396194	6.806236
C	-0.193622	1.069251	5.232450
C	-1.357469	0.277235	5.345270
H	-1.336681	-0.775269	5.044603
C	-2.543355	0.833171	5.849551
H	-3.439722	0.208935	5.934357
C	-2.583179	2.181298	6.242154
H	-3.509911	2.609680	6.639120
C	-1.431698	2.976892	6.127232
H	-1.450012	4.027068	6.437615
C	-0.242800	2.423990	5.627718
H	0.652082	3.051351	5.543395
C	2.154130	1.316660	2.016251
C	1.159828	0.745563	2.729371
C	5.254267	3.910823	10.269013
C	4.701211	4.977325	9.663391
H	5.711684	3.986303	11.264340
H	4.688122	5.973735	10.126178
H	2.031299	1.544014	0.947830
H	0.194714	0.493874	2.266605
H	2.934058	3.236634	6.532465

Table S45. *unsym*-[(dppv)Ni^{I}(μ-pdt)(μ-H_2)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*unsym*-[H_2**1**]$^+$, –4697.34357912 E_h)

atom	x	y	z
Ni	1.826411	9.034909	9.669653
Fe	1.625873	9.808736	12.544145
O	3.366642	12.036790	13.317003
C	2.663110	11.135851	13.056067
P	3.878514	9.556960	8.893848
P	1.655719	7.529569	7.966846
C	5.333642	9.362688	10.011070
C	6.027648	8.134614	10.084433
H	5.746378	7.305623	9.424351
C	7.087465	7.972678	10.990935
H	7.629928	7.021230	11.025387
C	7.457179	9.027625	11.840950
H	8.285992	8.901436	12.545330
C	6.761549	10.247579	11.784131
H	7.044361	11.074032	12.444793
C	5.704365	10.416949	10.877332
H	5.178470	11.377325	10.830873
C	4.187939	11.170767	8.038142
C	3.084509	11.936281	7.604856
H	2.069655	11.602094	7.845400
C	3.287601	13.125630	6.886361
H	2.424933	13.716575	6.559283
C	4.590828	13.560405	6.596966
H	4.748583	14.490643	6.040352
C	5.694098	12.802073	7.024794
H	6.712597	13.138020	6.801134
C	5.496988	11.611445	7.739987
H	6.362986	11.030065	8.074869
C	4.254141	8.364004	7.537749
H	5.241673	8.402542	7.056009
C	3.295888	7.510006	7.123342
H	3.469344	6.810664	6.293468
C	0.530685	8.117899	6.618627
C	-0.785448	7.613511	6.510595
H	-1.115589	6.798958	7.164877
C	-1.666940	8.135194	5.551251
H	-2.681543	7.729195	5.471612
C	-1.249747	9.164492	4.690677
H	-1.937981	9.565238	3.938736

C	0.056175	9.671915	4.793680
H	0.392288	10.467488	4.119432
C	0.941549	9.157395	5.753444
H	1.958905	9.558773	5.822498
C	1.262792	5.724613	8.082167
C	1.034876	5.139066	9.344554
H	1.055362	5.765958	10.242781
C	0.757232	3.764721	9.444531
H	0.564392	3.322473	10.428278
C	0.716479	2.965724	8.291700
H	0.501081	1.894536	8.371778
C	0.945019	3.543189	7.030102
H	0.909600	2.924108	6.126938
C	1.211680	4.915516	6.923211
H	1.364029	5.360785	5.933242
P	2.202868	8.494578	14.313911
P	-0.053532	10.606925	13.888760
C	1.854810	6.686493	14.246625
C	1.160584	6.018608	15.277724
H	0.784143	6.574213	16.143058
C	0.951256	4.631789	15.206719
H	0.413050	4.123769	16.014236
C	1.440462	3.898861	14.113927
H	1.285912	2.815501	14.067398
C	2.127465	4.557848	13.080578
H	2.507273	3.993818	12.221867
C	2.322640	5.946442	13.137452
H	2.841711	6.453323	12.315491
C	3.952993	8.582847	14.926702
C	4.859066	7.511594	14.784890
H	4.544164	6.581260	14.302454
C	6.166129	7.622452	15.285573
H	6.857115	6.779360	15.177641
C	6.580315	8.796214	15.934346
H	7.597272	8.874478	16.333827
C	5.682778	9.866828	16.079041
H	5.994715	10.784114	16.590062
C	4.376992	9.764259	15.577236
H	3.685545	10.603564	15.706316
C	1.307003	9.117224	15.789211
H	1.579666	8.750411	16.787854
C	0.378895	10.073782	15.605184
H	-0.175097	10.508547	16.447459
C	-0.305506	12.429528	14.100229

C	-1.076527	12.915232	15.184064
H	-1.561065	12.219850	15.878516
C	-1.251103	14.293669	15.367913
H	-1.846833	14.656631	16.212396
C	-0.666735	15.204466	14.470412
H	-0.803652	16.281324	14.616590
C	0.086203	14.730478	13.386163
H	0.538479	15.434128	12.679090
C	0.269115	13.349825	13.199398
H	0.851203	12.989382	12.344547
C	-1.786606	9.942484	13.836508
C	-2.005674	8.585368	14.166087
H	-1.165920	7.946052	14.458626
C	-3.298710	8.044384	14.105981
H	-3.457718	6.992178	14.365638
C	-4.383899	8.847200	13.715032
H	-5.392704	8.422987	13.670764
C	-4.172281	10.195850	13.385556
H	-5.014601	10.828358	13.084942
C	-2.880725	10.744183	13.445160
H	-2.729173	11.800143	13.198677
S	1.159352	11.084804	10.565640
S	0.402897	8.129906	11.347530
C	-0.676111	11.151999	10.280110
H	-1.170048	11.483161	11.210638
H	-0.805913	11.959168	9.536572
C	-1.286613	9.855144	9.749165
H	-2.347992	10.051832	9.490385
H	-0.773843	9.575126	8.809579
C	-1.262618	8.674995	10.724568
H	-1.654093	7.772952	10.220482
H	-1.907383	8.869622	11.594358
H	2.673497	9.150347	11.316191
H	3.018661	9.092991	12.129996

Table S46. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H_2)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*sym*-[H_2**1**]$^+$, –4697.35313063 E_h)

atom	x	y	z
Ni	9.397117	10.146711	2.969584
Fe	6.789940	11.706258	3.255568
P	10.792600	10.366669	4.719885
S	8.770120	12.178357	1.996579
P	10.526745	8.287870	2.377203
S	7.201459	9.493480	2.568856
O	5.110289	12.296993	0.949299
C	8.358066	11.716352	0.233200
H	7.483573	12.311801	-0.077123
H	9.222071	12.080052	-0.351141
C	8.158907	10.222990	-0.051515
H	9.114231	9.699565	0.133641
H	7.943320	10.119320	-1.135792
C	7.043982	9.494206	0.711334
H	7.061105	8.424071	0.439418
H	6.044925	9.883219	0.452306
C	5.792174	12.052987	1.870356
C	12.037521	11.743265	4.804978
C	12.233619	12.542716	3.658918
H	11.600198	12.382755	2.778374
C	13.219762	13.543641	3.652509
H	13.363109	14.160329	2.758355
C	14.015410	13.754959	4.790520
H	14.785360	14.534259	4.785512
C	13.821864	12.965130	5.937970
H	14.440281	13.127603	6.827711
C	12.839486	11.963097	5.947335
H	12.691819	11.356616	6.847878
C	10.178097	10.255124	6.467788
C	9.690146	11.405088	7.129733
H	9.716375	12.380713	6.631955
C	9.198372	11.316650	8.441322
H	8.833707	12.219799	8.943050
C	9.188177	10.082928	9.113533
H	8.814408	10.018597	10.140981
C	9.667023	8.934369	8.462846
H	9.677123	7.970390	8.984295
C	10.150901	9.016212	7.146585
H	10.525608	8.113219	6.651414

C	11.615082	8.382122	0.877473
C	12.200553	7.239261	0.288885
H	11.971647	6.241244	0.678298
C	13.070142	7.376711	-0.803977
H	13.517627	6.484711	-1.256038
C	13.368862	8.651268	-1.315055
H	14.048435	8.753759	-2.168022
C	12.796075	9.792557	-0.730600
H	13.028231	10.788033	-1.125041
C	11.921608	9.659143	0.359489
H	11.470027	10.546705	0.820857
C	9.674747	6.660279	2.229902
C	9.466481	5.867063	3.379081
H	9.886680	6.180487	4.341973
C	8.730884	4.674703	3.296640
H	8.586997	4.062656	4.193915
C	8.186769	4.264141	2.068759
H	7.615501	3.331836	2.004816
C	8.382663	5.050831	0.921315
H	7.967069	4.732493	-0.041190
C	9.119269	6.242898	0.999174
H	9.283015	6.838431	0.093684
P	6.474110	13.834325	3.980205
P	4.961749	11.103385	4.421571
C	7.761179	14.723751	4.967715
C	9.109277	14.316844	4.911636
C	7.414867	15.864780	5.727190
C	10.096247	15.031922	5.612966
H	9.398680	13.456001	4.299680
C	8.399159	16.566098	6.437585
H	6.380362	16.223636	5.754303
C	9.740758	16.150266	6.382374
H	11.141236	14.710697	5.548741
H	8.118313	17.445242	7.027574
H	10.508691	16.705539	6.931700
C	6.002008	15.104202	2.727041
C	4.650472	15.396615	2.449494
C	7.020178	15.750652	1.991498
C	4.321213	16.330453	1.454226
H	3.851578	14.899524	3.011241
C	6.683650	16.677584	0.994117
H	8.072600	15.532869	2.202975
C	5.335820	16.970022	0.724708
H	3.269182	16.557711	1.250695

H	7.478250	17.177348	0.429561
H	5.077074	17.698247	-0.051357
C	3.495523	10.557496	3.446074
C	3.420393	9.212387	3.019175
C	2.483693	11.464788	3.069008
C	2.343542	8.788258	2.226769
H	4.200014	8.500464	3.310963
C	1.405514	11.031404	2.280841
H	2.532108	12.510787	3.392189
C	1.335095	9.694859	1.857478
H	2.289781	7.743626	1.901545
H	0.619930	11.740871	1.999263
H	0.493417	9.358483	1.242648
C	5.030333	9.845284	5.772733
C	3.840076	9.525648	6.467447
C	6.232758	9.201900	6.124887
C	3.859912	8.586705	7.507176
H	2.892099	9.996743	6.183652
C	6.243868	8.254509	7.162422
H	7.160814	9.419724	5.587376
C	5.063298	7.949002	7.855368
H	2.933562	8.347471	8.040512
H	7.184201	7.761008	7.426074
H	5.076321	7.209980	8.663888
C	11.798865	7.994810	3.679718
C	11.927884	8.906803	4.664223
H	12.474486	7.131633	3.597400
H	12.718154	8.828644	5.424657
C	5.018083	13.782006	5.114779
C	4.367345	12.614507	5.298344
H	4.695584	14.694831	5.633679
H	3.506286	12.539903	5.977138
H	8.053933	11.197493	4.305474
H	7.463607	11.579597	4.778354

Table S47. *sym*-[(dppv)Ni^{I}(μ-pdt)(μ-H_2)Fe^{II}(dppv)(CO)]$^+$ with Fe(dppv) dibasal, Ni(dppv) dibasal, and pdt oriented toward Ni (*sym*-[H_2**1**]$^+$, –4697.35358442 E_h)

atom	x	y	z
Fe	3.966993	2.418547	7.686728
H	2.678228	2.499733	6.520799
Ni	3.321789	1.395471	4.893060
S	3.725726	0.197198	6.860781
S	5.077052	2.777128	5.642914
P	2.781990	2.060878	9.581553
P	4.209366	4.564224	8.327075
P	3.592152	1.513528	2.641717
P	1.180322	0.778205	4.541208
O	6.411762	1.701860	9.102592
C	3.473363	0.856216	10.790232
C	3.979812	1.271818	12.040264
H	3.944781	2.327373	12.329987
C	4.543541	0.335198	12.921478
H	4.934540	0.669233	13.888560
C	4.605093	-1.021000	12.565193
H	5.043741	-1.749865	13.255047
C	4.107071	-1.440513	11.320085
H	4.157131	-2.497138	11.035417
C	3.548062	-0.510113	10.430984
H	3.179432	-0.838919	9.452881
C	0.966920	1.685755	9.512514
C	0.139440	2.512065	8.719448
H	0.570260	3.330575	8.131004
C	-1.247361	2.304780	8.681638
H	-1.871842	2.949131	8.054638
C	-1.823799	1.268171	9.435609
H	-2.906500	1.105118	9.406700
C	-1.008481	0.444848	10.228417
H	-1.452606	-0.358293	10.826777
C	0.380782	0.650082	10.270443
H	1.004443	0.007935	10.899341
C	5.914610	5.169734	8.674308
C	6.481390	5.034611	9.959476
H	5.892249	4.611127	10.780823
C	7.803036	5.445887	10.192827
H	8.233096	5.345028	11.195102
C	8.569048	5.983427	9.146032
H	9.600193	6.303468	9.330139

C	8.010819	6.113206	7.863018
H	8.605026	6.534208	7.044760
C	6.688622	5.710230	7.623436
H	6.256061	5.819368	6.623343
C	3.480361	5.945880	7.333150
C	2.918964	5.707681	6.063137
H	2.934351	4.697903	5.640646
C	2.363938	6.764612	5.321201
H	1.943215	6.567364	4.328930
C	2.361419	8.066457	5.845512
H	1.926811	8.890419	5.269355
C	2.928619	8.314413	7.107717
H	2.938834	9.330483	7.516567
C	3.492062	7.263622	7.845326
H	3.956772	7.475718	8.814831
C	5.431765	1.986931	8.526211
C	5.449660	-0.475461	6.639963
H	5.978583	-0.408169	7.605810
H	5.292991	-1.547168	6.423583
C	6.261592	0.153486	5.503196
H	7.235163	-0.377492	5.451197
H	5.743439	-0.035032	4.544994
C	6.563322	1.652592	5.618696
H	7.135875	1.976857	4.731939
H	7.174230	1.880892	6.508999
C	4.884712	0.415130	1.906390
C	6.148117	0.928217	1.535092
H	6.338381	2.005938	1.588724
C	7.154583	0.065186	1.074261
H	8.127114	0.475918	0.780940
C	6.915201	-1.315924	0.978356
H	7.700836	-1.985946	0.613042
C	5.662393	-1.833846	1.347951
H	5.466560	-2.908989	1.268805
C	4.654732	-0.976653	1.815424
H	3.680830	-1.389401	2.103888
C	3.810024	3.099491	1.710789
C	3.831021	3.126948	0.297539
H	3.761595	2.193811	-0.273110
C	3.959207	4.345775	-0.384065
H	3.971422	4.357327	-1.479455
C	4.077083	5.547858	0.335708
H	4.181833	6.497833	-0.199740
C	4.069055	5.527367	1.739037

H	4.176228	6.459657	2.304711
C	3.932227	4.308785	2.425125
H	3.944430	4.286176	3.519668
C	0.612884	-0.840833	5.221528
C	0.794567	-2.030035	4.483196
H	1.205055	-1.987188	3.467726
C	0.446628	-3.272152	5.037833
H	0.585048	-4.186533	4.450325
C	-0.083855	-3.340416	6.335754
H	-0.359479	-4.309147	6.766490
C	-0.262004	-2.161058	7.078678
H	-0.676745	-2.204474	8.091604
C	0.088650	-0.918032	6.531074
H	-0.059373	-0.006686	7.121019
C	-0.265358	1.913417	4.814605
C	-1.598533	1.449400	4.851220
H	-1.808141	0.376698	4.781020
C	-2.659661	2.358736	4.984695
H	-3.690708	1.988466	5.006515
C	-2.404110	3.737791	5.082385
H	-3.235435	4.444458	5.181422
C	-1.080329	4.207463	5.044848
H	-0.872692	5.280752	5.118128
C	-0.018238	3.298895	4.910603
H	1.015365	3.662469	4.866988
C	2.041799	0.841183	1.902597
C	1.019829	0.513313	2.719375
C	3.349253	4.744038	9.950787
C	2.751768	3.664745	10.496334
H	3.315491	5.725972	10.442462
H	2.193071	3.732157	11.440237
H	1.958843	0.732058	0.812133
H	0.067012	0.131248	2.325502
H	2.501623	3.023188	7.171774

Table S48. Cartesian Coordinates for *unsym*-[(dppv)Ni^{I}(μ-pdt)Fe^{II}(dppv)(CO)]$^{+}$ with Fe(dppv) apical-basal, Ni(dppv) apical-basal, and pdt oriented toward Ni (*unsym*-[1]$^{+}$, –4696.19127505 E_h)

atom	x	y	z
Ni	1.607410	8.680344	9.949976
Fe	1.178222	9.764594	12.179240
O	3.232243	11.843199	12.103688
C	2.393937	11.017483	12.163496
P	3.677751	9.350128	9.276770
P	1.376955	7.547547	7.985774
C	5.119463	8.660687	10.206808
C	5.657587	7.402321	9.854323
H	5.238259	6.842378	9.010942
C	6.739992	6.867891	10.572546
H	7.158100	5.898253	10.280028
C	7.293236	7.580953	11.648340
H	8.143283	7.167572	12.201871
C	6.755343	8.828096	12.010159
H	7.176007	9.387132	12.852019
C	5.670394	9.365798	11.300772
H	5.262048	10.339439	11.590251
C	4.174191	11.088078	8.873236
C	3.171874	12.038369	8.584648
H	2.116070	11.769851	8.695704
C	3.525322	13.333845	8.174726
H	2.739502	14.066257	7.959367
C	4.876968	13.691079	8.048222
H	5.151099	14.703224	7.731452
C	5.878649	12.746963	8.329215
H	6.935211	13.019204	8.230811
C	5.532902	11.449722	8.736449
H	6.322923	10.723755	8.955218
C	3.925539	8.569890	7.621180
H	4.874854	8.757807	7.099392
C	2.951830	7.821890	7.067426
H	3.069987	7.369757	6.072766
C	0.146950	8.117550	6.723986
C	-0.987900	7.355255	6.372158
H	-1.141093	6.362847	6.809409
C	-1.919266	7.860132	5.449993
H	-2.793077	7.257088	5.179790
C	-1.729711	9.125820	4.872404
H	-2.455256	9.514127	4.149638

C	-0.604163	9.891432	5.221866
H	-0.447544	10.877604	4.771166
C	0.327427	9.394764	6.145522
H	1.202162	9.999003	6.412971
C	1.249708	5.704073	7.977727
C	1.213057	5.009962	9.205242
H	1.214061	5.570975	10.146754
C	1.175435	3.605426	9.221123
H	1.144246	3.077355	10.180208
C	1.178012	2.885610	8.016549
H	1.147747	1.790642	8.030167
C	1.218741	3.570871	6.789274
H	1.221366	3.012410	5.846853
C	1.255618	4.972328	6.766720
H	1.274770	5.496321	5.804331
P	2.236646	8.655830	13.879436
P	-0.162506	10.622650	13.744291
C	2.493370	6.834045	13.738100
C	1.725999	5.911388	14.478860
H	0.959533	6.264194	15.176962
C	1.930768	4.530837	14.322168
H	1.330846	3.824689	14.906651
C	2.902054	4.058873	13.425206
H	3.068110	2.981865	13.312361
C	3.662648	4.972444	12.675190
H	4.423394	4.614020	11.973492
C	3.455781	6.352633	12.822459
H	4.053527	7.054997	12.230672
C	3.808159	9.271342	14.670330
C	4.862727	8.410523	15.040827
H	4.811513	7.343347	14.807182
C	5.984025	8.916247	15.719611
H	6.792318	8.234329	16.006409
C	6.066218	10.281182	16.036653
H	6.940728	10.671637	16.568458
C	5.014987	11.142420	15.679924
H	5.064022	12.207474	15.931067
C	3.891019	10.641607	15.007058
H	3.071831	11.323423	14.756679
C	1.161263	8.843219	15.369494
H	1.422246	8.303481	16.290433
C	0.165716	9.750363	15.335446
H	-0.458729	9.954419	16.215579
C	0.040169	12.419655	14.134788

C	-0.053312	12.917548	15.453328
H	-0.230748	12.239139	16.293905
C	0.083302	14.292233	15.701127
H	0.017360	14.665906	16.728766
C	0.298883	15.184448	14.637885
H	0.402632	16.256931	14.834661
C	0.384772	14.697766	13.323625
H	0.556212	15.388026	12.490548
C	0.264134	13.321880	13.071391
H	0.349442	12.943185	12.046271
C	-2.008293	10.440032	13.653876
C	-2.603044	9.212385	14.024408
H	-1.974618	8.383429	14.371538
C	-3.996977	9.052604	13.969545
H	-4.446529	8.101188	14.274686
C	-4.811570	10.110093	13.531140
H	-5.898932	9.985423	13.490465
C	-4.227446	11.330811	13.155724
H	-4.857693	12.163024	12.823551
C	-2.834353	11.499109	13.218924
H	-2.392035	12.464682	12.950651
S	0.337916	10.605807	10.249735
S	0.299213	7.764583	11.549567
C	-1.457291	10.192848	9.993333
H	-2.006618	10.600388	10.859946
H	-1.749834	10.773679	9.100781
C	-1.785311	8.716281	9.775325
H	-2.872618	8.634007	9.568972
H	-1.269524	8.361489	8.868412
C	-1.461840	7.793294	10.949724
H	-1.687664	6.746421	10.678681
H	-2.070473	8.051611	11.833908

Table S49. *unsym*-[(dppv)Ni^{II}(μ-pdt)Fe^{I}(dppv)(CO)]$^{+}$ with Fe(dppv) apical-basal, Ni(dppv) dibasal, and pdt oriented toward Ni (*unsym*-[**1**]$^{+}$, –4696.18580761 E_h)

atom	x	y	z
Fe	3.974233	2.416438	7.592664
Ni	3.404854	1.216603	5.018421
S	3.398363	0.256916	7.058443
S	5.306179	2.226996	5.692821
P	4.049290	4.672236	7.821414
P	5.317155	2.287607	9.422979
P	3.617298	1.876022	2.930174
P	1.474651	0.294356	4.475393
O	1.486462	2.504999	9.136231
C	2.414380	5.543299	7.910404
C	1.841221	5.913688	9.144477
H	2.374772	5.716105	10.080356
C	0.577142	6.525477	9.188531
H	0.146289	6.806780	10.155565
C	-0.128272	6.776857	8.001857
H	-1.109516	7.262542	8.037146
C	0.430573	6.402826	6.766628
H	-0.112368	6.596562	5.834747
C	1.688492	5.782723	6.721582
H	2.110969	5.496717	5.751397
C	5.083765	5.880110	6.840429
C	6.335418	5.468960	6.330795
H	6.649122	4.426639	6.435964
C	7.177128	6.385512	5.680429
H	8.142777	6.048635	5.287207
C	6.785231	7.725612	5.533816
H	7.443958	8.440433	5.028670
C	5.546426	8.146764	6.044448
H	5.237148	9.193472	5.946561
C	4.699918	7.233021	6.693865
H	3.741542	7.578618	7.093721
C	4.868918	1.233895	10.883370
C	5.613815	1.302975	12.083960
H	6.493226	1.953991	12.150339
C	5.247746	0.525987	13.191871
H	5.830527	0.590266	14.117359
C	4.138489	-0.334668	13.113868
H	3.853923	-0.940999	13.980742
C	3.399567	-0.416261	11.924179

H	2.535479	-1.086416	11.857333
C	3.760939	0.365160	10.813380
H	3.178741	0.301757	9.888692
C	7.141542	1.961507	9.267963
C	8.010254	2.982318	8.820516
H	7.622248	3.992141	8.645629
C	9.374258	2.719022	8.616354
H	10.037640	3.525282	8.283719
C	9.890005	1.433508	8.850434
H	10.955108	1.230682	8.694992
C	9.034911	0.412498	9.298118
H	9.431419	-0.589568	9.496509
C	7.671162	0.672805	9.506840
H	7.019429	-0.125303	9.879959
C	2.490557	2.494280	8.518279
C	4.902324	-0.847174	7.004764
H	5.407445	-0.730375	7.980158
H	4.496554	-1.872124	6.945617
C	5.870287	-0.594599	5.849495
H	6.691363	-1.338486	5.921261
H	5.354892	-0.776986	4.886354
C	6.501018	0.798911	5.836592
H	7.170780	0.899057	4.965643
H	7.088442	0.978769	6.753283
C	5.041862	1.072309	2.079952
C	6.290194	1.731987	2.022543
H	6.392466	2.745414	2.424945
C	7.394440	1.093400	1.437869
H	8.357174	1.613769	1.388889
C	7.265618	-0.202158	0.908337
H	8.128535	-0.694537	0.447415
C	6.026968	-0.861999	0.964560
H	5.919823	-1.868689	0.546216
C	4.919142	-0.231237	1.551788
H	3.954993	-0.750621	1.589996
C	3.740457	3.648488	2.455846
C	3.813057	4.019606	1.093826
H	3.838865	3.253840	0.310029
C	3.872049	5.374870	0.739636
H	3.923943	5.657983	-0.317195
C	3.873160	6.364852	1.738003
H	3.926958	7.422316	1.457397
C	3.816067	5.999919	3.092243
H	3.843313	6.765240	3.874923

C	3.743642	4.644337	3.451800
H	3.710946	4.352411	4.506892
C	1.338929	-1.532084	4.646735
C	1.640633	-2.380755	3.559459
H	1.899060	-1.953776	2.583691
C	1.596644	-3.774993	3.716094
H	1.822321	-4.424479	2.863397
C	1.256476	-4.333112	4.958898
H	1.219509	-5.421066	5.079585
C	0.956335	-3.493763	6.045377
H	0.683607	-3.925349	7.014477
C	0.997462	-2.099379	5.896133
H	0.756917	-1.451948	6.745147
C	-0.039675	0.980398	5.259669
C	-1.276690	0.301517	5.180383
H	-1.338330	-0.683390	4.704675
C	-2.428327	0.885493	5.727182
H	-3.385257	0.355844	5.667079
C	-2.353781	2.142010	6.353394
H	-3.255380	2.590387	6.784692
C	-1.126456	2.819061	6.433043
H	-1.058752	3.792527	6.929333
C	0.030219	2.242074	5.886301
H	0.993165	2.762455	5.959055
C	2.142544	1.281602	1.999061
C	1.206016	0.586452	2.675426
C	5.338090	3.979642	10.173210
C	4.773056	4.997463	9.494671
H	5.821864	4.137854	11.146946
H	4.787959	6.028500	9.875678
H	2.034818	1.521597	0.932512
H	0.285372	0.224023	2.197475

Table S50. *unsym*-[(dppv)Ni^{II}(μ-pdt)Fe^{I}(dppv)(CO)]$^{+}$ transition state interconverting Ni(dppv) between apical-basal and dibasal with Fe(dppv) apical-basal and pdt oriented toward Ni (TS-*unsym*-[**1**]$^{+}$, –4696.18471842 E_h)

atom	x	y	z
Ni	1.518698	8.477553	9.815832
Fe	1.172471	9.838144	12.146240
O	3.026837	12.087661	11.904061
C	2.284425	11.180483	12.038184
P	2.937411	9.316419	8.314129
P	1.951954	6.458767	8.997471
C	4.636179	9.789060	8.856121
C	5.597040	10.233226	7.919122
H	5.328398	10.352048	6.863392
C	6.896991	10.542171	8.343745
H	7.638363	10.886731	7.614638
C	7.245592	10.414717	9.700149
H	8.261564	10.661701	10.027090
C	6.292828	9.981657	10.635501
H	6.552941	9.896598	11.695759
C	4.989612	9.668574	10.215166
H	4.234014	9.351055	10.944852
C	2.385261	10.703180	7.241204
C	1.595199	10.441081	6.101038
H	1.354245	9.408016	5.823266
C	1.123149	11.500967	5.311620
H	0.521644	11.289019	4.420903
C	1.427548	12.827565	5.659259
H	1.061089	13.653790	5.040574
C	2.204521	13.093134	6.799149
H	2.444288	14.126188	7.073175
C	2.681373	12.038138	7.591899
H	3.289611	12.252885	8.477024
C	3.259765	7.960211	7.104901
H	3.843926	8.171178	6.198599
C	2.812684	6.720384	7.390519
H	3.025924	5.857476	6.744259
C	0.475412	5.448019	8.575490
C	-0.193988	4.716639	9.584875
H	0.196563	4.713191	10.608833
C	-1.353240	3.989278	9.275758
H	-1.857934	3.415669	10.060860
C	-1.864431	3.993514	7.966028
H	-2.769357	3.424229	7.728515

C	-1.211613	4.727802	6.963017
H	-1.604445	4.733622	5.940549
C	-0.047783	5.453316	7.263822
H	0.454442	6.023078	6.473718
C	3.129543	5.299465	9.830884
C	4.259614	5.861847	10.465635
H	4.377751	6.951124	10.506154
C	5.239994	5.031636	11.030144
H	6.115152	5.478466	11.513842
C	5.099218	3.634690	10.972142
H	5.864285	2.986849	11.413376
C	3.978808	3.070423	10.340011
H	3.868540	1.981934	10.284232
C	2.998212	3.895752	9.765641
H	2.135767	3.444355	9.265241
P	2.296089	9.064378	13.973405
P	-0.237657	10.836896	13.577924
C	2.083901	7.311111	14.535031
C	1.515341	6.988035	15.786340
H	1.188278	7.781564	16.466231
C	1.366848	5.646929	16.176939
H	0.928363	5.413935	17.153571
C	1.788083	4.611838	15.327403
H	1.677864	3.567058	15.637761
C	2.349937	4.922219	14.078310
H	2.680865	4.124214	13.404799
C	2.485902	6.261123	13.679765
H	2.908818	6.485358	12.694919
C	4.120190	9.365600	14.213946
C	5.076685	8.328079	14.207967
H	4.761384	7.288899	14.072409
C	6.436606	8.613926	14.414656
H	7.165055	7.795299	14.423056
C	6.859368	9.935669	14.632086
H	7.918722	10.153997	14.805951
C	5.913594	10.974449	14.638871
H	6.230417	12.008319	14.814175
C	4.554761	10.693640	14.429717
H	3.830857	11.514877	14.445738
C	1.645458	10.023111	15.416133
H	2.172604	9.964112	16.378573
C	0.549409	10.788333	15.249664
H	0.124605	11.375253	16.075163
C	-0.668226	12.631600	13.416105

C	-1.369331	13.298951	14.448275
H	-1.701976	12.748852	15.336123
C	-1.664808	14.664813	14.336895
H	-2.205166	15.171396	15.144067
C	-1.271298	15.379880	13.192021
H	-1.502679	16.447226	13.106946
C	-0.585483	14.723200	12.159335
H	-0.280491	15.274464	11.263178
C	-0.282418	13.355391	12.269474
H	0.251508	12.847432	11.460571
C	-1.885757	10.051347	13.923346
C	-1.931832	8.814619	14.606087
H	-1.006133	8.353717	14.969262
C	-3.157698	8.165948	14.818975
H	-3.179473	7.213393	15.359946
C	-4.351843	8.735471	14.343678
H	-5.308132	8.228516	14.511900
C	-4.313743	9.959451	13.656739
H	-5.240411	10.412563	13.287331
C	-3.089629	10.616800	13.448177
H	-3.074870	11.581843	12.930230
S	0.390819	10.446741	10.071607
S	0.365996	7.769232	11.613784
C	-1.417313	10.041412	9.889656
H	-1.949364	10.506010	10.738919
H	-1.722142	10.562296	8.964797
C	-1.742457	8.553325	9.793517
H	-2.828964	8.444605	9.594244
H	-1.209883	8.109216	8.930603
C	-1.417738	7.763133	11.061197
H	-1.667247	6.698670	10.916760
H	-1.993200	8.139840	11.924954

Table S51. *sym*-[(dppv)Ni^{I}(μ-pdt)Fe^{II}(dppv)(CO)]$^{+}$ with Fe(dppv) dibasal, Ni(dppv) apical-basal, and and pdt oriented toward Ni (*sym*-[**1**]$^{+}$, –4696.1779561 E_h)

atom	x	y	z
Ni	9.039279	10.095936	3.106895
Fe	6.792968	11.630239	2.964516
P	10.455395	10.412370	4.889560
S	8.731024	12.028862	1.875484
P	10.365902	8.339314	2.454333
S	7.016953	9.472485	2.354255
O	4.988842	12.275342	0.786495
C	8.493657	11.509505	0.093260
H	7.629982	12.090063	-0.273420
H	9.390504	11.872712	-0.439569
C	8.313020	10.013307	-0.174580
H	9.237070	9.481150	0.110400
H	8.203788	9.878638	-1.271227
C	7.112440	9.341469	0.497158
H	7.123184	8.258124	0.284788
H	6.158485	9.751904	0.123922
C	5.682345	12.052958	1.710297
C	11.820423	11.670455	4.859730
C	12.181815	12.258426	3.629293
H	11.589228	12.044744	2.733516
C	13.282847	13.127284	3.556963
H	13.553260	13.582769	2.598112
C	14.031066	13.414350	4.710879
H	14.891975	14.089186	4.653251
C	13.670346	12.837298	5.940923
H	14.247782	13.061965	6.844374
C	12.570289	11.969200	6.018581
H	12.293227	11.528049	6.982063
C	9.848696	10.476972	6.637615
C	9.273377	11.670542	7.129340
H	9.204538	12.553900	6.485649
C	8.808733	11.740547	8.450485
H	8.375736	12.675986	8.821160
C	8.903028	10.622106	9.296485
H	8.540884	10.680528	10.328446
C	9.464473	9.430542	8.813596
H	9.545283	8.554998	9.467186
C	9.933147	9.355295	7.491091
H	10.367961	8.416892	7.129514

C	11.647322	8.508875	1.125887
C	12.422155	7.404359	0.704487
H	12.229900	6.407075	1.115278
C	13.432643	7.577503	-0.253000
H	14.026958	6.715742	-0.575600
C	13.681991	8.849641	-0.796147
H	14.470718	8.980104	-1.544823
C	12.918593	9.951682	-0.379448
H	13.109087	10.944263	-0.802102
C	11.905632	9.782657	0.578012
H	11.304696	10.639360	0.904833
C	9.575480	6.704837	2.130147
C	9.127189	5.928427	3.221197
H	9.317288	6.264639	4.247316
C	8.441932	4.724015	3.000659
H	8.107466	4.125974	3.855320
C	8.188207	4.285892	1.690524
H	7.654468	3.344982	1.519568
C	8.625694	5.055622	0.599957
H	8.437634	4.715329	-0.424264
C	9.314590	6.259818	0.815159
H	9.668318	6.841752	-0.043229
P	6.659366	13.696272	3.926032
P	5.152976	11.026760	4.417751
C	8.015725	14.708812	4.690691
C	9.359409	14.299582	4.615546
C	7.703181	15.936190	5.320383
C	10.378046	15.093045	5.173300
H	9.613740	13.365817	4.104929
C	8.717806	16.720032	5.886238
H	6.668570	16.296611	5.348466
C	10.057423	16.298362	5.814718
H	11.419326	14.763422	5.100178
H	8.463356	17.667079	6.374669
H	10.849652	16.916364	6.251208
C	5.918009	14.968613	2.798867
C	4.534850	15.238607	2.787403
C	6.761931	15.637820	1.884954
C	4.003229	16.169955	1.880224
H	3.868226	14.723406	3.487610
C	6.225236	16.561468	0.976496
H	7.840281	15.441636	1.889940
C	4.845666	16.830598	0.972938
H	2.927626	16.377752	1.884578

H	6.887822	17.076990	0.272622
H	4.429531	17.555429	0.265093
C	3.520647	10.683467	3.616060
C	3.317759	9.435357	2.984627
C	2.501024	11.655761	3.563900
C	2.114740	9.171819	2.313857
H	4.099546	8.668623	3.024237
C	1.296314	11.385122	2.893993
H	2.641623	12.627354	4.050263
C	1.101857	10.145165	2.266612
H	1.966421	8.200303	1.829691
H	0.509211	12.146498	2.865357
H	0.162528	9.935522	1.743815
C	5.285876	9.613201	5.608063
C	4.130939	9.114661	6.253178
C	6.540162	9.046246	5.902735
C	4.235023	8.063762	7.175387
H	3.146850	9.537336	6.023369
C	6.638501	7.987446	6.820101
H	7.439573	9.435597	5.410412
C	5.488832	7.494715	7.456063
H	3.334027	7.684308	7.669658
H	7.618403	7.552800	7.041357
H	5.567273	6.667529	8.170160
C	11.447065	7.996063	3.904899
C	11.494264	8.882436	4.919748
H	12.101027	7.112738	3.884954
H	12.206213	8.757284	5.748215
C	5.442999	13.608127	5.313743
C	4.787613	12.450874	5.528138
H	5.276837	14.490593	5.946484
H	4.061611	12.331448	6.344342

Table S52. *sym*-[(dppv)Ni^{I}(μ-pdt)Fe^{II}(dppv)(CO)]$^{+}$ with Fe(dppv) dibasal, Ni(dppv) dibasal, and and pdt oriented toward Ni (*sym*-[**1**]$^{+}$, –4696.18180502 E_h)

atom	x	y	z
Fe	4.237555	2.204466	7.699224
Ni	3.417710	1.477436	5.148857
S	3.857534	0.088688	6.957536
S	5.275845	2.590237	5.756733
P	2.816554	1.997330	9.447537
P	4.351779	4.395112	8.258380
P	3.708986	1.487369	2.888654
P	1.303559	0.735363	4.791737
O	6.564944	1.516627	9.291118
C	3.204759	0.634986	10.624412
C	3.966930	0.882999	11.786021
H	4.283914	1.903199	12.030001
C	4.331545	-0.174750	12.634320
H	4.921272	0.030968	13.534151
C	3.942949	-1.488545	12.329189
H	4.227492	-2.312935	12.991896
C	3.189848	-1.743773	11.170614
H	2.886320	-2.767868	10.927059
C	2.824345	-0.691764	10.317047
H	2.242297	-0.902487	9.413584
C	0.964071	1.968914	9.302452
C	0.366817	2.753820	8.293116
H	0.998797	3.284282	7.572053
C	-1.029994	2.861820	8.207235
H	-1.478604	3.470733	7.415467
C	-1.844633	2.178926	9.126370
H	-2.935041	2.260070	9.059914
C	-1.257623	1.394554	10.133327
H	-1.888244	0.866171	10.857048
C	0.140260	1.291894	10.227537
H	0.587967	0.686109	11.021667
C	6.056012	5.072135	8.468973
C	6.720014	4.961321	9.709224
H	6.204365	4.525206	10.572321
C	8.043730	5.408669	9.846118
H	8.546869	5.323723	10.815377
C	8.718458	5.960945	8.745805
H	9.751082	6.309814	8.853988
C	8.065393	6.067572	7.506176

H	8.587019	6.500332	6.645422
C	6.741224	5.625882	7.364578
H	6.236881	5.720190	6.397044
C	3.497247	5.746700	7.319830
C	2.589234	5.415682	6.295936
H	2.436576	4.358821	6.038395
C	1.893607	6.425744	5.609943
H	1.193572	6.159805	4.810626
C	2.098069	7.773383	5.945682
H	1.553612	8.561216	5.413741
C	3.003935	8.111414	6.966164
H	3.168029	9.161834	7.230043
C	3.703096	7.105509	7.648803
H	4.420101	7.378912	8.430832
C	5.604278	1.828126	8.684454
C	5.520516	-0.685719	6.626802
H	6.105820	-0.598298	7.558287
H	5.308861	-1.756786	6.459790
C	6.279466	-0.120951	5.425635
H	7.221301	-0.697616	5.311104
H	5.691214	-0.298780	4.508993
C	6.662396	1.360084	5.499880
H	7.148446	1.665269	4.557285
H	7.367546	1.557164	6.326466
C	5.147746	0.675673	2.063436
C	6.295832	1.423964	1.719453
H	6.312929	2.507516	1.881971
C	7.406664	0.787415	1.144489
H	8.288570	1.377987	0.873237
C	7.384891	-0.597301	0.906057
H	8.251235	-1.089816	0.451890
C	6.246806	-1.347243	1.246043
H	6.221039	-2.425745	1.055577
C	5.135410	-0.717475	1.827427
H	4.251922	-1.311067	2.091369
C	3.604025	3.121098	2.028766
C	3.509311	3.199111	0.620553
H	3.532066	2.287203	0.013410
C	3.402864	4.447005	-0.009846
H	3.328074	4.499181	-1.101448
C	3.397878	5.626825	0.755422
H	3.319261	6.599912	0.258532
C	3.501241	5.556522	2.153299
H	3.507691	6.471515	2.755542

C	3.601239	4.307833	2.789818
H	3.695850	4.253551	3.879743
C	0.773480	-0.795963	5.668575
C	1.134366	-2.055946	5.143639
H	1.674067	-2.119578	4.191619
C	0.803324	-3.233570	5.831811
H	1.081836	-4.205358	5.409694
C	0.111843	-3.165414	7.051894
H	-0.152532	-4.084885	7.585327
C	-0.243121	-1.914282	7.583732
H	-0.785916	-1.851666	8.533066
C	0.089996	-0.732679	6.902576
H	-0.194389	0.235040	7.328009
C	-0.203393	1.818198	4.734069
C	-1.511976	1.302996	4.858392
H	-1.667134	0.241929	5.077814
C	-2.621110	2.149674	4.704380
H	-3.632121	1.739426	4.803272
C	-2.437996	3.512286	4.415966
H	-3.305545	4.169155	4.290769
C	-1.138088	4.027791	4.277753
H	-0.992089	5.087096	4.039302
C	-0.025930	3.186510	4.437622
H	0.987425	3.585910	4.309810
C	2.287324	0.544686	2.199645
C	1.280808	0.192539	3.024352
C	3.617932	4.586262	9.939655
C	2.973391	3.528473	10.469788
H	3.679798	5.554151	10.455895
H	2.464379	3.579555	11.442370
H	2.264871	0.300215	1.128593
H	0.392239	-0.339863	2.656218

Table S53. Cartesian Coordiantes for *unsym*-[(dppv)Ni^{II}(μ-pdtH)(μ-H)Fe^{II}(dppv)(CO)]$^{2+}$ with Fe(dppv) apical-basal, Ni(dppv) dibasal, and and pdt oriented toward Ni (*unsym*-[H1H]$^{2+}$, –4697.11739653 E_h)

atom	x	y	z
Fe	4.449781	2.482988	7.249561
H	3.883893	2.779840	5.725622
Ni	3.063916	1.413521	5.260923
S	3.621707	0.380860	7.120638
S	6.534157	2.055688	6.220756
P	5.095336	4.703226	7.333186
P	5.367533	2.278234	9.331263
P	2.914971	2.388078	3.295759
P	1.648777	-0.122529	4.558968
O	1.846128	3.265031	8.315781
C	3.760227	5.947292	7.586656
C	3.806214	6.869600	8.654760
H	4.626019	6.847340	9.379170
C	2.788895	7.825013	8.804484
H	2.831422	8.532298	9.639216
C	1.726101	7.875730	7.888899
H	0.937052	8.625655	8.006416
C	1.674580	6.958771	6.826352
H	0.847658	6.989572	6.109538
C	2.679240	5.991164	6.678304
H	2.614626	5.268933	5.855825
C	6.192045	5.488730	6.056978
C	7.587999	5.263506	6.103494
H	8.018351	4.617776	6.876028
C	8.439537	5.892317	5.180583
H	9.520478	5.726945	5.242100
C	7.909744	6.747216	4.199972
H	8.576385	7.252355	3.493032
C	6.523277	6.972026	4.145364
H	6.106342	7.654149	3.396858
C	5.666272	6.349258	5.067205
H	4.593701	6.566035	5.035974
C	4.233928	2.062402	10.768837
C	4.480837	2.728499	11.991055
H	5.328892	3.411293	12.098263
C	3.633781	2.520875	13.089810
H	3.831382	3.046205	14.029945
C	2.542163	1.643405	12.986475
H	1.885157	1.482741	13.847450

C	2.294101	0.975597	11.776793
H	1.443088	0.291842	11.689981
C	3.129859	1.186427	10.668902
H	2.918971	0.668659	9.726956
C	6.670368	0.990188	9.574893
C	8.016193	1.268741	9.243167
H	8.302457	2.261467	8.877684
C	9.002054	0.280259	9.403413
H	10.045392	0.511240	9.163247
C	8.654042	-0.991650	9.888014
H	9.425258	-1.757365	10.021306
C	7.317725	-1.272538	10.222224
H	7.046579	-2.255098	10.622854
C	6.327965	-0.288680	10.068815
H	5.296069	-0.505549	10.366487
C	2.900530	2.963427	7.906277
C	4.822169	-0.949747	6.633384
H	5.353182	-1.219738	7.565305
H	4.176220	-1.799890	6.356235
C	5.810363	-0.643669	5.505703
H	6.263929	-1.605245	5.192003
H	5.274651	-0.246358	4.621753
C	6.962312	0.279666	5.901843
H	7.736150	0.317928	5.116522
H	7.447066	-0.056728	6.834121
C	4.558569	2.416534	2.474564
C	5.508708	3.403853	2.829184
H	5.246059	4.203284	3.531901
C	6.785428	3.395512	2.242618
H	7.503238	4.177311	2.511539
C	7.130588	2.399285	1.312233
H	8.124170	2.398558	0.852081
C	6.193617	1.413018	0.963223
H	6.453158	0.642918	0.229151
C	4.913515	1.417036	1.541599
H	4.188134	0.648435	1.253123
C	2.129389	4.031888	3.055836
C	2.574183	4.949818	2.079598
H	3.473497	4.741565	1.490972
C	1.850109	6.131277	1.852755
H	2.195904	6.839777	1.092748
C	0.678898	6.395904	2.582062
H	0.110604	7.311868	2.389591
C	0.230022	5.480526	3.550328

H	-0.692152	5.676045	4.108031
C	0.954794	4.303977	3.794943
H	0.597581	3.587098	4.544335
C	2.085029	-1.904815	4.601383
C	2.853315	-2.464084	3.555204
H	3.150354	-1.848616	2.697836
C	3.219766	-3.818167	3.598182
H	3.798875	-4.250920	2.775631
C	2.832101	-4.618658	4.686296
H	3.112753	-5.676633	4.714425
C	2.074060	-4.064898	5.732662
H	1.762006	-4.690085	6.575825
C	1.699862	-2.712280	5.696034
H	1.095017	-2.290732	6.506014
C	0.000884	0.018953	5.354640
C	-1.050297	-0.848644	4.977405
H	-0.877612	-1.652158	4.252760
C	-2.321846	-0.689703	5.546855
H	-3.134231	-1.362708	5.253658
C	-2.551964	0.326455	6.491207
H	-3.546550	0.443694	6.933965
C	-1.509002	1.187143	6.870418
H	-1.684031	1.973265	7.612275
C	-0.233871	1.037774	6.302174
H	0.582030	1.704088	6.604074
C	1.879499	1.307615	2.225746
C	1.325360	0.211238	2.778654
C	6.283025	3.834090	9.679086
C	6.159930	4.869864	8.827452
H	6.926365	3.897449	10.566749
H	6.696814	5.814237	8.990349
H	1.681919	1.611391	1.188648
H	0.658359	-0.458012	2.218650
H	6.264848	2.388929	4.923003

Table S54. Cartesian Coordinates for *unsym*-[(dppv)Ni^{II}(μ-pdtH)(μ-H)Fe^{II}(dppv)(CO)]$^{2+}$·[OEt_2] with Fe(dppv) apical-basal, Ni(dppv) dibasal, and and pdt oriented toward **Ni (*unsym*-[H1H]$^{2+}$·[OEt_2], –4930.73746062 E_h)**

atom	x	y	z
Fe	3.810793	2.583944	7.522470
H	2.931982	2.898232	6.235889
Ni	3.247542	1.332550	5.003053
S	3.295123	0.385394	7.037109
S	5.291160	2.150170	5.755101
P	4.032191	4.809727	7.914666
P	4.999621	2.258181	9.489281
P	3.251443	1.877556	2.848848
P	1.507814	0.045833	4.615148
O	1.266546	2.770838	8.915597
C	2.478752	5.791379	7.798648
C	1.731193	6.102428	8.954067
H	2.081470	5.789003	9.943354
C	0.523744	6.811945	8.845487
H	-0.045724	7.051348	9.749540
C	0.054042	7.216476	7.586652
H	-0.882801	7.777323	7.504364
C	0.792725	6.905725	6.431429
H	0.430327	7.230368	5.449795
C	1.995499	6.190856	6.532194
H	2.572557	5.964460	5.627900
C	5.331119	5.905849	7.167091
C	6.631567	5.389074	6.976830
H	6.828379	4.324496	7.141455
C	7.687861	6.238336	6.613695
H	8.695263	5.827911	6.487303
C	7.455409	7.610266	6.421095
H	8.281168	8.275267	6.146765
C	6.161271	8.128779	6.591088
H	5.973316	9.197897	6.446248
C	5.103119	7.286365	6.968349
H	4.106204	7.709408	7.122445
C	4.332613	1.142478	10.807884
C	5.002028	1.076588	12.054310
H	5.933670	1.631226	12.213525
C	4.488701	0.287884	13.092657
H	5.013660	0.247745	14.052836
C	3.306274	-0.448560	12.901532
H	2.906637	-1.063137	13.714925
C	2.641092	-0.394261	11.667766

H	1.719702	-0.965834	11.513711
C	3.148783	0.398589	10.624570
H	2.616974	0.433158	9.669912
C	6.809390	1.838387	9.504203
C	7.783562	2.848185	9.338740
H	7.480168	3.898170	9.267529
C	9.149747	2.520317	9.308838
H	9.895315	3.316100	9.205227
C	9.559801	1.183555	9.440470
H	10.625158	0.930986	9.426509
C	8.598453	0.174069	9.620569
H	8.912546	-0.866611	9.755138
C	7.232937	0.497659	9.656660
H	6.497894	-0.292186	9.848357
C	2.307190	2.704227	8.382006
C	4.753353	-0.780383	7.030198
H	5.203082	-0.705423	8.035335
H	4.300996	-1.781545	6.929339
C	5.801749	-0.570305	5.931465
H	6.571039	-1.360364	6.039632
H	5.332173	-0.710711	4.939424
C	6.527051	0.777433	5.964571
H	7.230636	0.865695	5.123279
H	7.056250	0.947358	6.916402
C	4.704368	1.198216	1.942103
C	5.958801	1.847795	2.009618
H	6.095295	2.770557	2.585210
C	7.058439	1.316232	1.318324
H	8.020730	1.837594	1.356831
C	6.928102	0.135080	0.567427
H	7.789282	-0.270297	0.026159
C	5.687293	-0.518160	0.505788
H	5.574617	-1.433518	-0.084552
C	4.579864	0.008602	1.189143
H	3.613118	-0.501113	1.118160
C	3.020860	3.600945	2.254094
C	3.456939	3.992767	0.968059
H	4.043371	3.306090	0.348787
C	3.134929	5.269114	0.481661
H	3.471567	5.568895	-0.516293
C	2.378195	6.154755	1.267419
H	2.123675	7.147195	0.881034
C	1.942370	5.765235	2.545224
H	1.344090	6.453207	3.151775

C	2.261960	4.492502	3.042537
H	1.917742	4.183926	4.036839
C	1.739312	-1.761089	4.845483
C	2.258078	-2.536529	3.784177
H	2.483402	-2.069954	2.818880
C	2.475839	-3.912197	3.956449
H	2.865467	-4.508445	3.124777
C	2.183617	-4.522750	5.187200
H	2.347408	-5.597434	5.318010
C	1.670350	-3.755512	6.247882
H	1.429648	-4.231945	7.204117
C	1.449914	-2.379310	6.084739
H	1.037576	-1.790909	6.910490
C	-0.043641	0.513227	5.475493
C	-1.124931	-0.396357	5.543608
H	-1.016895	-1.420613	5.172046
C	-2.346907	0.016677	6.094466
H	-3.181572	-0.690100	6.146951
C	-2.499659	1.328515	6.574866
H	-3.455655	1.643845	7.005665
C	-1.429204	2.234747	6.501637
H	-1.544412	3.256229	6.877708
C	-0.203162	1.832453	5.950859
H	0.632911	2.537969	5.894106
C	1.822285	1.022510	2.073006
C	1.069429	0.213725	2.839813
C	4.986745	3.893566	10.339494
C	4.529037	4.975985	9.682225
H	5.357112	3.956926	11.371536
H	4.522062	5.975288	10.138969
H	1.598558	1.218283	1.015592
H	0.184690	-0.316691	2.462296
H	6.069403	3.097302	5.122300
O	7.666711	4.245848	3.786307
C	9.074972	3.946891	3.753770
C	9.350081	2.600089	4.405980
H	9.632401	4.752047	4.279287
H	9.428035	3.947071	2.700098
H	10.432878	2.387971	4.383586
H	9.027409	2.593230	5.462320
H	8.837734	1.785123	3.864187
C	7.423548	5.524187	3.157457
C	5.951506	5.887622	3.254674
H	7.750994	5.472932	2.097149

H	8.044112	6.295958	3.658854
H	5.781946	6.866023	2.772950
H	5.315656	5.147934	2.740269
H	5.633920	5.966749	4.307745