Electronic Supplementary Information for Dalton Transactions

Isomerization of the Hydride Complexes $[HFe_2(SR)_2(PR_3)_x(CO)_{6-x}]^+$ (x = 2, 3, 4) Relevant to the Active Site Models for the [FeFe]-Hydrogenases

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Supporting Information

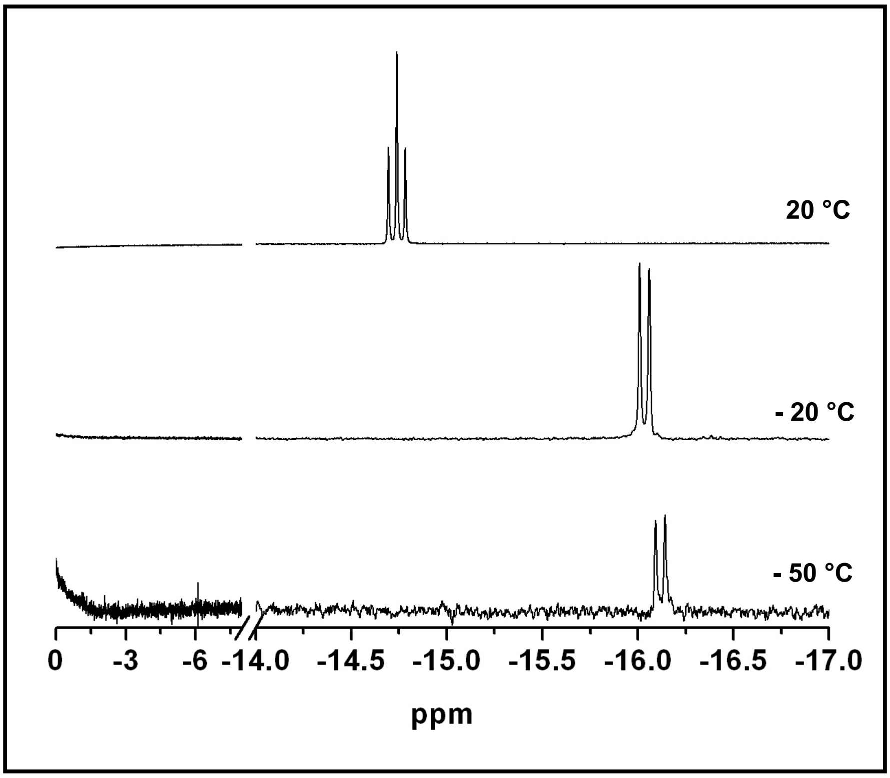

Figure S1. ^{1}H NMR (500 MHz) spectra of a CD_2Cl_2 solution of **1**, $Fe_2(edt)(CO)_4(dppv)$, after protonation with 3 equiv $HBF_4{\bullet}Et_2O$ at -80 °C, then warmed to recorded temperatures. Spectrum recorded at 20 °C is after 48 h at room temperature.

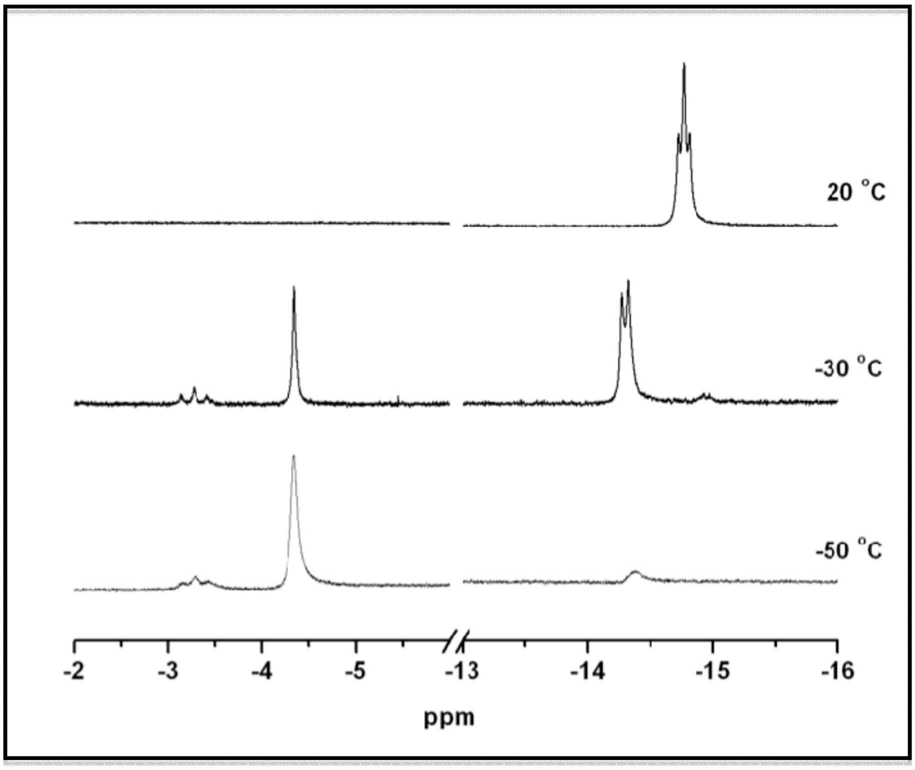

Figure S2. ^{1}H NMR (500 MHz) spectra of a CD_2Cl_2 solution of **2**, $Fe_2(pdt)(CO)_4(dppv)$, after protonation with 3 equiv HBF_4•Et_2O at -80 °C, then warmed to recorded temperatures. Spectrum recorded at 20 °C is after 16 h at room temperature.

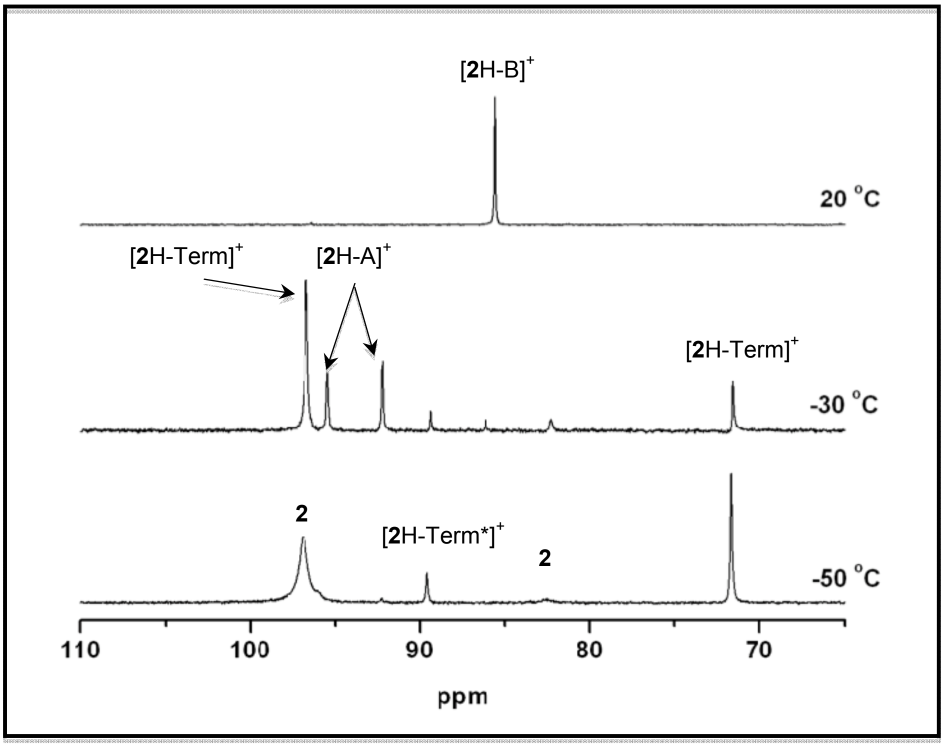

Figure S3. Protonation of **2**, $Fe_2(pdt)(CO)_4(dppv)$, with 3 equiv $HBF_4{\bullet}Et_2O$ at -80 °C, then warmed to recorded temperatures. $^{31}P\{^1H\}$ NMR (202 MHz) acquired with -50 °C ^1H NMR above shows the growth of signals at 97 and 72 ppm ([**2**H-Term]$^+$, for terminal hydride derivative wherein dppv is apical, basal) and a signal at 89 ppm ([**2**H-Term*]$^+$, terminal hydride with hydride on dibasal-dppv side). When sample is warmed to – 30 °C, new signals are observed at 92 and 95 ppm ([**2**H-A]$^+$ - is bridging hydride of apical,basal-dppv). When sample is warmed to room temperature, only one signal is observed at 86 ppm ([**2**H-B]$^+$- thermodynamic product with dppv as dibasal (triplet in high-field ^1H NMR). At low temperature, signals at 96 and 82 ppm are due to remaining starting material.

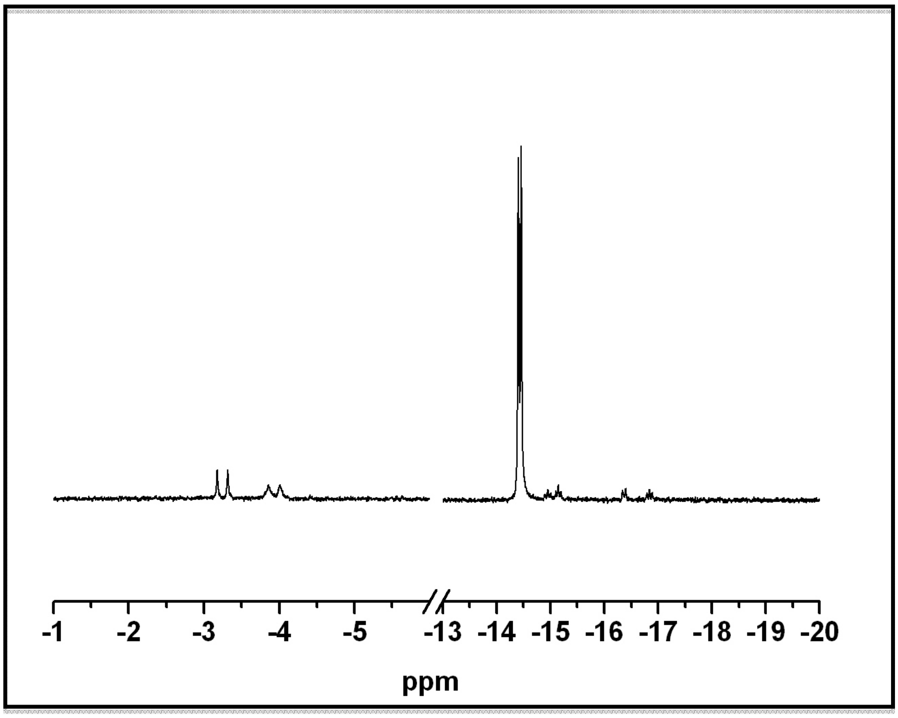

Figure S4. ^{1}H NMR (500 MHz) spectrum of a CD_2Cl_2 solution of **4**, $Fe_2(pdt)(CO)_3(PMe_3)(dppv)$, after protonation with $HBF_4•Et_2O$ at -90 °C. Signals at -3, -4 ppm are assigned to isomers of the terminal hydride and appear as doublets with J_{PH} ~ 75 Hz. The intense signal at -14.3 ppm with J_{PH} ~ 30 Hz is assigned to $[\mathbf{4}H\text{-}A]^+$. For spectra at higher temperature, see Figure S5.

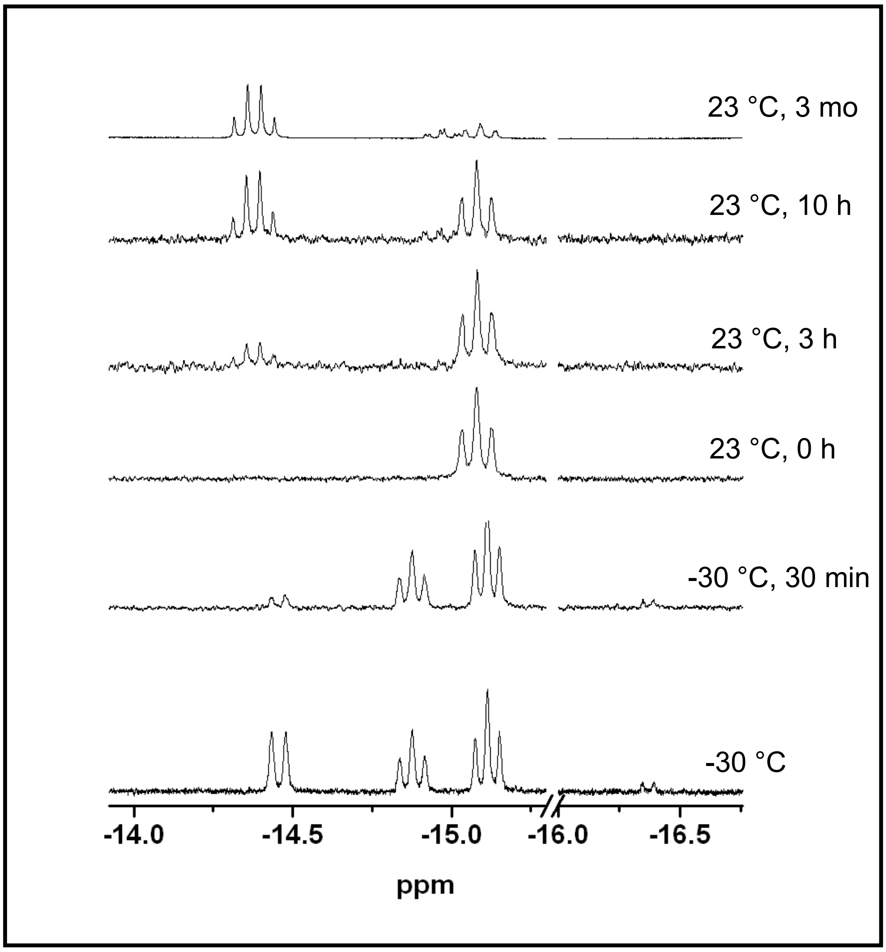

Figure S5. ^{1}H NMR (500 MHz) spectra of CD_2Cl_2 solution of **4** $Fe_2(pdt)(CO)_3(PMe_3)(dppv)$ after warming to various temperatures. Labeling is as follows (for peaks observed at -30 °C): δ -14.4 (dt) is [**4**H-A]$^+$, δ -14.7 (td) is [**4**H-B*]$^+$, δ – 15.3 (td) is [**4**H-B]$^+$ (for peaks observed at 23 °C): δ -14.3 (q) is [**4**H-C]$^+$, δ -14.8 (td) is [**4**H-D]$^+$. Peak at δ -16.4 is unknown.

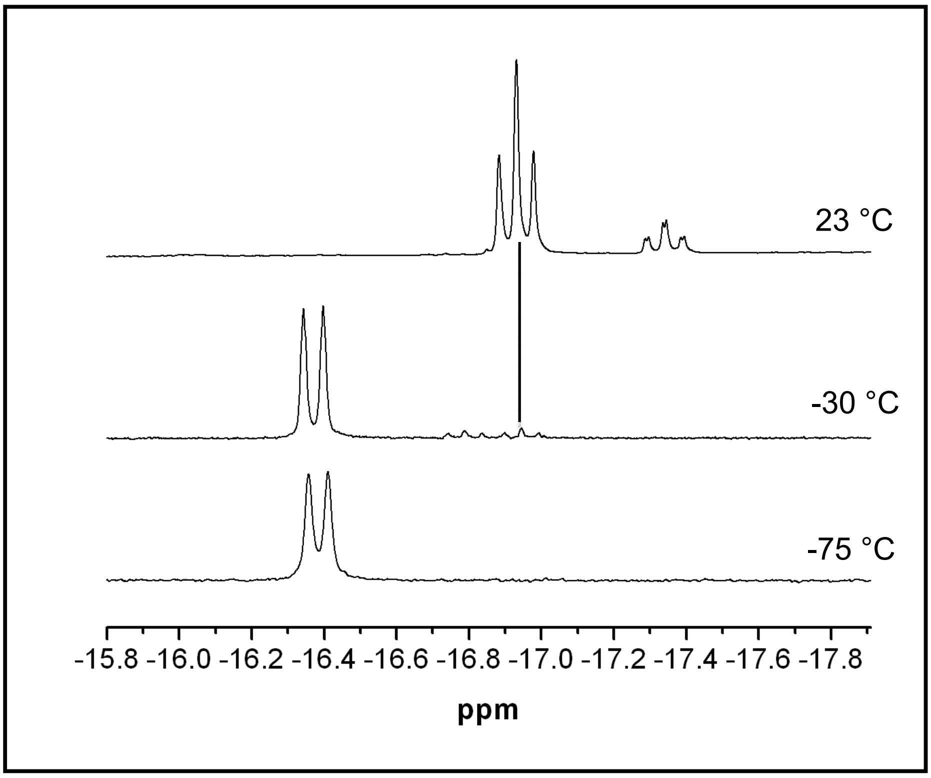

Figure S6. ^{1}H NMR (500 MHz) spectra of CD_2Cl_2 solution of **3**, $Fe_2(edt)(CO)_3(PMe_3)(dppv)$, after protonation with $[H(Et_2O)_2]BAr^F{}_4$ at -90 °C and recorded at various temperatures. At -75 °C, a doublet is the sole species present in the ^{1}H NMR spectrum, J_{PH} ~30 Hz (indicating a single P atom *cis* to the hydride). Upon warming to -30 °C, two new triplets are observed in the ^{1}H NMR, J_{PH} ~25 Hz (indicating two P atoms *cis* to the hydride). Upon equilibration of [**3**H]$^+$ at room temperature for several months, the ^{1}H NMR displays a triplet and a triplet of doublets, and possibly one more signal with unresolved coupling under the major resonance at δ -16.8. As seen for [**4**H]$^+$, the unstable rotamer [**3**H-B*]$^+$ is observed at δ -16.8.

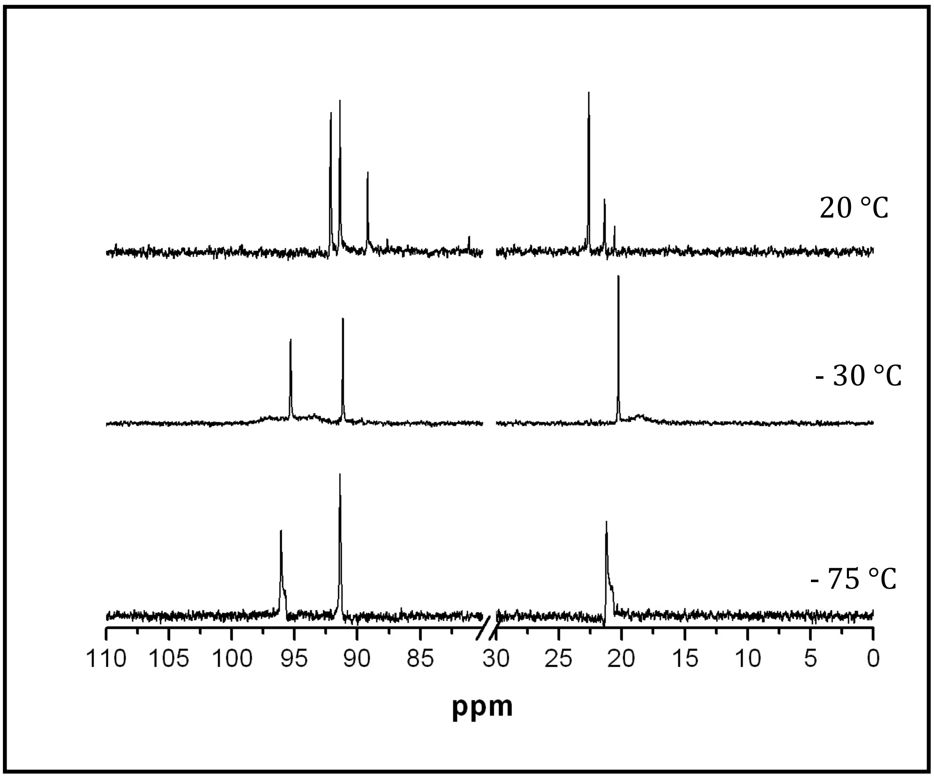

Figure S7. $^{31}P\{^1H\}$ NMR spectra of CD_2Cl_2 solution of **3,** $Fe_2(edt)(CO)_3(PMe_3)(dppv)$, after protonation with $[H(Et_2O)_2]BAr^F_4$ at -90 °C and recorded at various temperatures. At –75 °C, the $^{31}P\{^1H\}$ spectrum shows mostly one isomer, with two signals in the dppv region (apical-basal) and one signal in the PMe_3 region. At -30 °C, the same peaks remain, smaller broad peaks are due to slight remainder of starting material. Upon equilibration of [**3**H]$^+$ at room temperature for several months, the $^{31}P\{^1H\}$ NMR spectrum displays in the dppv region a set of equally intense peaks at 92, 93 ppm (apical-basal, major isomer), a single resonance at 89 ppm (dibasal, minor isomer), and in the PMe_3 region three peaks. The missing dppv signal for the third isomer wherein the dppv is possibly dibasal is not observed.

QuickTime™ and a
decompressor
are needed to see this picture.

Figure S8. High-field ^{1}H NMR spectra of a d^7-DMF solution of [**4**H]PF$_{6,}$ **a)** recorded at 20 °C on 500 MHz instrument and **b)** after heating to 80 °C. The spectrum recorded at 120 °C (600 MHz) was after three days at room temperature, decomposition species are labeled: $Fe_2(pdt)(CO)_2(dppv)_2$ ( ) and unknown poly-phosphine species ( ). At 80°C the peaks at –13.8 ppm [**4**H-C] and –14.5 [**4**H-D] are broadened. At 120 °C , [**4**H-B] and [**4**H-C] are labeled with ( ).

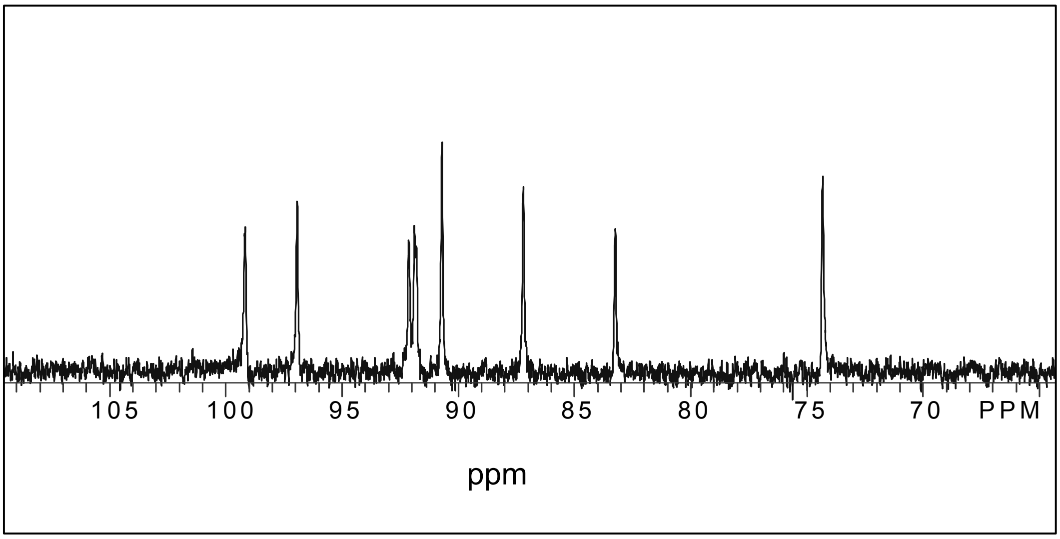

Figure S9. $^{31}P\{^1H\}$ NMR (600 MHz, CD_2Cl_2) spectrum of $[HFe_2(edt)(CO)_2(dppv)_2]^+$ recorded at –35° C. Peaks corresponding to $[\mathbf{5}H\text{-Term}]^+$ are at 99, 91, 84, 74 ppm. Remaining signals are due to $[\mathbf{5}H\text{-A}]^+$ (97, 87 ppm) and **5** (92, 93 ppm).

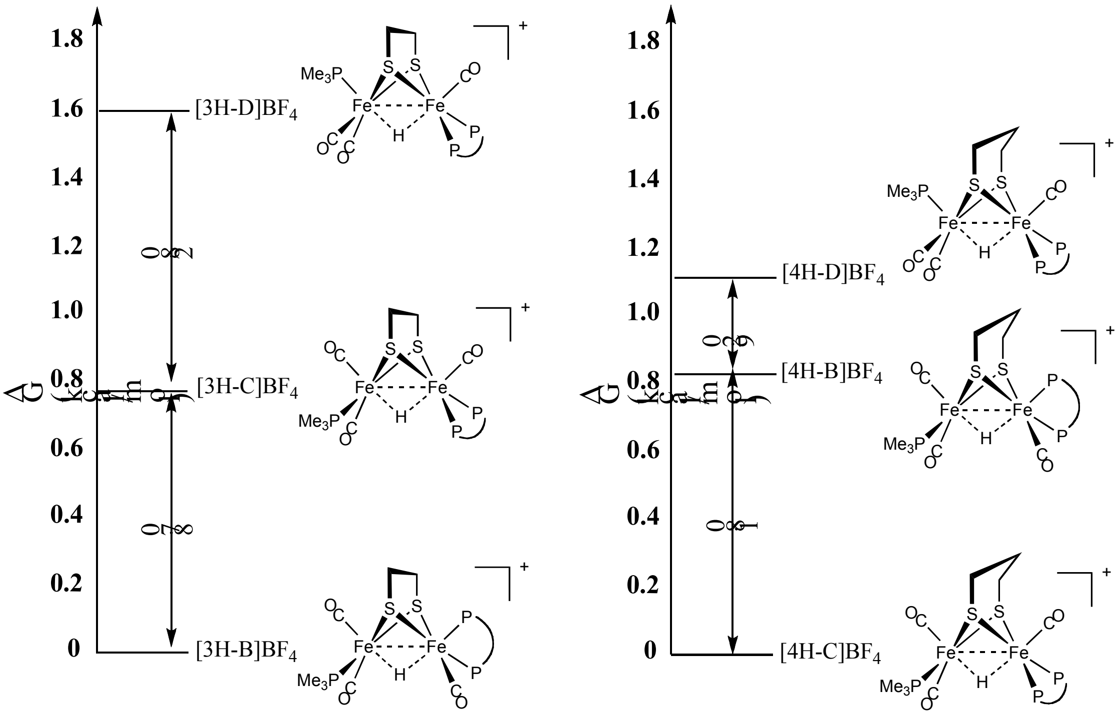

Figure S10. Difference in energy for isomers for $[\mathbf{3}H]^+$ and $[\mathbf{4}H]^+$, $[HFe_2(xdt)(CO)_3(PMe_3)(dppv)]BF_4$, as calculated experimentally.

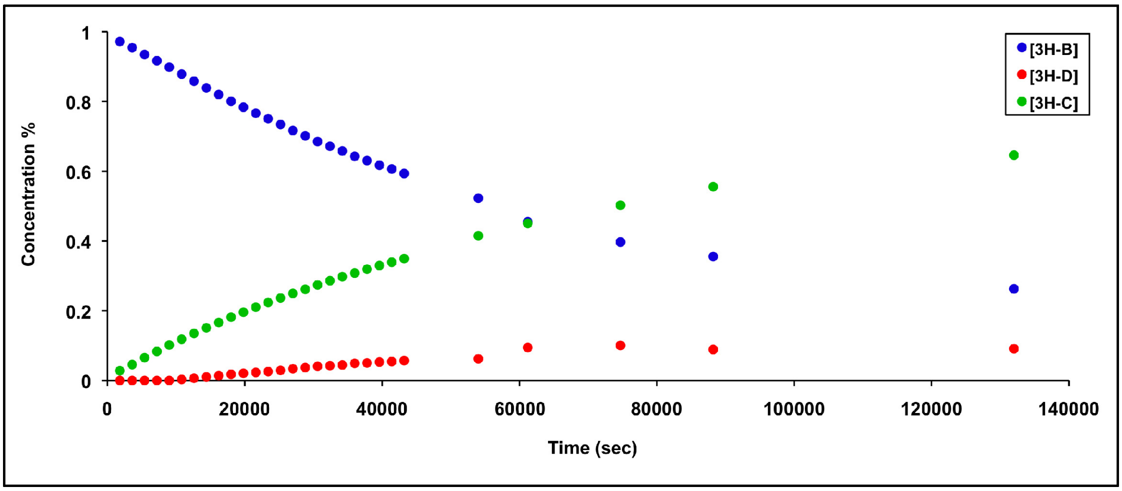

Figure S11. Plot monitoring the concentration of [**4**H-B]$^+$, [**4**H-C]$^+$ and [**4**H-D]$^+$ as a function of time. Data was collected using ^{1}H NMR spectroscopy.

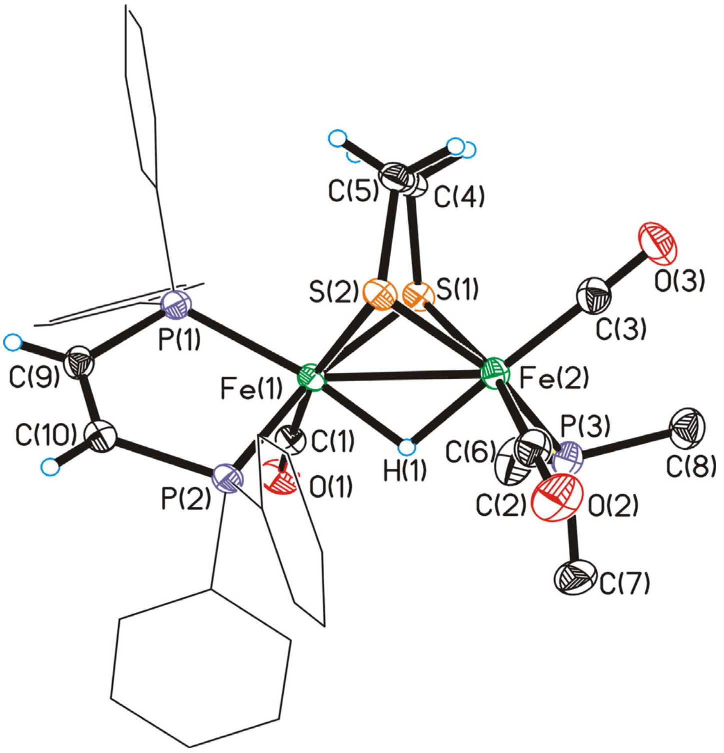

Table S1. Crystallographic data for $[\mathbf{3}\text{H-B}]^+$, $[HFe_2(edt)(CO)_3(dppv)(PMe_3)]PF_6$, including selected lengths (Å) and angles (°).

Fe(1) – Fe(2)	2.5744 (5)	Fe(1) – S(1) – Fe(2)	69.355 (17)
Fe(1) – S(1)	2.2581 (7)	Fe(1) – Fe(2) – S(1)	55.164 (17)
Fe(1) – S(2)	2.2794 (6)	Fe(2) – Fe(1) – P(1)	148.911 (18)
Fe(2) – S(1)	2.2668 (7)	Fe(2) – Fe(1) – P(2)	113.20 (2)
Fe(2) – S(2)	2.2760 (6)	Fe(2) – Fe(1) – C(1)	111.37 (6)
Fe(1) – P(1)	2.2137 (6)	P(1) – Fe(1) – P(2)	86.80 (2)
Fe(1) – P(2)	2.2282 (6)	P(1) – Fe(1) – C(1)	90.78 (6)
Fe(1) – C(1)	1.765 (2)	P(2) – Fe(1) – C(1)	91.10 (6)
Fe(2) – P(3)	2.2549 (7)	Fe(1) – Fe(2) – C(2)	112.44 (7)
Fe(2) – C(2)	1.790 (2)	Fe(1) – Fe(2) – C(3)	141.78 (7)
Fe(2) – C(3)	1.771 (2)	Fe(1) – Fe(2) –	109.54 (2)

		P(3)	
Fe(1) – H(1)	1.69 (2)	C(3) – Fe(2) – C(2)	95.45 (10)
Fe(2) – H(1)	1.64 (2)	C(3) – Fe(2) – P(3)	94.15 (7)
C(1) – O(1)	1.142 (2)	C(2) – Fe(2) – P(3)	92.44 (7)
C(2) – O(2)	1.140 (3)	Fe(1) – H(1) – Fe(2)	99.99
C(3) – O(3)	1.148 (3)		

Complex	$[Fe_2(edt)(\mu\text{-}H)(CO)_3(PMe_3)(dppv)]PF_6$
Chemical formula	$C_{34}H_{36}F_6Fe_2O_3P_4S_2$
Temperature (K)	193 (2)
Crystal size (mm^3)	0.40 x 0.24 x 0.16
Crystal system	Triclinic
Space group	P-1
a (Å)	10.818 (2)
b (Å)	11.253 (2)
c (Å)	16.208 (3)
α (°)	78.473 (3)
β (°)	86.415 (3)
γ (°)	81.525 (3)
V (Å^3)	1911.1 (6)
Z	2
Density calcd (Mg m^{-3})	1.575
μ (Mo Kα, mm^{-1})	0.71073
max./min. trans’n	0.8572 / 0.6869
reflections meas’d/Indep.	23821 / 9184
data/restraints/parameters	9184 / 0 / 467
GOF on F^2	1.024
Rint	0.0286
R1 [I > 2σ] (all data)[a]	0.0322 (0.0485)
wR2 [I > 2σ] (all data)[b]	0.0786 (0.0850)
max. peak/hole (e$^-$/Å^3)	0.392 / -0.374