Supporting Information

for

[FeFe] Hydrogenase Active Site Modeling: a Key Intermediate Bearing Thiolate Proton and Fe Hydride

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Experimental Section

General Methods. All reactions were carried out by using standard Schlenk and vacuum-line techniques under an atmosphere of purified nitrogen. All commercially available chemicals from Aldrich were of ACS grade and used without further purification. Solvents were of HPLC grade and purified as follows: hexane, diethyl ether and THF (tetrahydrofuran) were distilled from sodium/benzophenone under N_2. Dichloromethane was distilled from CaH_2 under N_2. Acetone was distilled over 3 Å molecular sieves under N_2. Deuterated solvents obtained from Merck were distilled over 4 Å molecular sieves under N_2 prior to use. [(μ-bdt)$Fe_2(CO)_6$] was prepared according to related literature procedures.[1]

Infrared spectra were recorded on a Perkin Elmer Spectrum One using a 0.05-mm CaF_2 cell. The ν(SH) measurement was performed with a KBr pellet. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^2D NMR spectra were recorded on a Bruker AV-500 or DRX-500 spectrometer operating at 500, 125.7, 202.49 and 76.8 MHz, respectively. UV-vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer using a 1-cm quartz cell. Mass spectral analyses were done on a Waters LCT Premier XE at Mass Spectrometry Center in the Institute of Chemistry, Academia Sinica. Elemental analyses were performed on an Elementar vario EL III elemental analyzer.

Molecular Structure Determinations. The X-ray single crystal crystallographic data collections for [PPN][**2**]·THF (CCDC 913855), and [**2HSH**][OTf]·0.5CH_2Cl_2·0.5H_2O·HOTf (CCDC 913856) were carried out at 150 K on a Bruker SMART APEX CCD four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) outfitted with a low-temperature, nitrogen-stream aperture. The structures were solved using direct methods, in conjunction with standard

difference Fourier techniques and refined by full-matrix least-squares procedures. A summary of the crystallographic data for complexes [PPN][**2**]·THF and [**2HSH**][OTf]·0.5CH_2Cl_2·0.5H_2O·HOTf is shown in Table S1. Selected metric data of each structure are listed in Table S2. An empirical absorption correction (multi-scan) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in geometrically calculated positions by the riding model. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SHELXTL97 program suites.[2] There is one THF solvent molecule co-existed in the cell for [PPN][**2**]. The C18-C23 of the phenyl substituent on the bridging phosphido group and the C63 of the co-solvated THF molecule are disordered. For [**2HSH**][OTf], there are two asymmetric cations, two OTf^- anions, two HOTf, one CH_2Cl_2 and one water molecules in each asymmetric unit.

Computational Studies. All computational calculations were carried out with Gaussian09 program.[3] The DFT calculation with basis function B3LYP[4] and basis set 6-311++G(d) are performed to obtain geometry optimization and free energy. The polarizable continuum model (PCM)[5] in CH_2Cl_2 was applied to correct the solvation effects for the species. HOTf was used as a proton source in the protonation mechanism which the estimation of $\Delta G_{solv}(H^+)$ can be obtained by the following equation:

$$\Delta G_{solv}(H^+) = G_{solv}(AH) - G_{solv}(A^-)$$

The solvation free energy of a proton in the current work is –262.1 kcal mol^{-1}, which is consistent with values in recent investigation.[6] The computed IR spectra for the species

and their optimized structures as well as the Cartesian coordinate are displayed in the supporting section.

Synthesis of [PPN][(μ,κ^2-bdt)(μ-PPh$_2$)Fe$_2$(CO)$_5$] ([PPN][2]). To a red THF solution (50 mL) of [(μ-bdt)Fe$_2$(CO)$_6$] (600 mg, 1.429 mmol) was added 0.5 M KPPh$_2$ (2.86 mL, 1.43 mmol, Aldrich) in the THF solution. The brown solution was allowed to stir overnight. The solution was filtered through Celite and was concentrated to a small volume. The product was precipitated upon addition of hexane. The dark green-brown solid was washed with 40 mL of hexane three times and then dried under vacuum. The green-brown solution was dissolved in 30 mL of acetone, followed by addition of 820 mg (1.429 mmol) of bis(triphenylphosphine)iminium chloride (PPNCl). The reaction mixture was stirred at room temperature for 3 h and the solvent was removed in vacuo. The residue was dissolved in 20 mL of THF and the solution was filtered through Celite to remove insoluble salt. The product was precipitated upon addition of hexane. The green-brown solid was washed with 50 mL of hexane three times and then dried under vacuum. The yield was 1.3 g (82 %). Crystals of [PPN][(μ,κ^2-bdt)(μ-PPh$_2$)Fe$_2$(CO)$_5$]·THF suitable for X-ray crystallographic analysis were grown from a THF/hexane solution at 20 °C. IR (THF, cm^{-1}): ν_{CO} 2003 (m), 1962 (vs), 1934 (m), 1914 (s), 1898 (m). ^{1}H NMR (500 MHz, d-THF, 298 K): 6.54 (t, 1H, $^3J_{HH}$ = 7.0 Hz, S$_2$C$_6$*H*$_4$), 6.61 (t, 1H, $^3J_{HH}$ = 7.0 Hz, S$_2$C$_6$*H*$_4$), 7.07 (m, 3H, P(C$_6$*H*$_5$)$_2$), 7.21 (m, 3H, P(C$_6$*H*$_5$)$_2$), 7.36 (d, 1H, $^3J_{HH}$ = 7.5 Hz, S$_2$C$_6$*H*$_4$), 7.48 (m, 13H, S$_2$C$_6$*H*$_4$, PPN), 7.58 (m, 14H, P(C$_6$*H*$_5$)$_2$, PPN), 7.68 (m, 6H, PPN), 7.74 (m, 2H, P(C$_6$*H*$_5$)$_2$) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, d-THF, 291 K): 117.30 (s, 1C, S$_2$*C*$_6$H$_4$), 122.66 (s, 1C, S$_2$*C*$_6$H$_4$), 126.58 (d, 2C, J_{PC} = 9.2 Hz, P(*C*$_6$H$_5$)$_2$), 126.90 (s, 1C, P(*C*$_6$H$_5$)$_2$), 127. 15 (d, 2C, J_{PC} = 9.7 Hz, P(*C*$_6$H$_5$)$_2$), 127.27

(s, 1C, P(C_6H_5)$_2$), 127.75 (s, 6C, PPN), 128.87 (s, 1C, $S_2C_6H_4$), 129.08 (s, 1C, $S_2C_6H_4$), 129.38 (m, 12C, PPN), 132.26 (m, 12C, PPN), 133.62 (s, 6C, PPN), 133.85 (m, 4C, P(C_6H_5)$_2$), 140.04 (d, 1C, J = 19.2 Hz, *ipso*-$S_2C_6H_4$), 141.68 (d, 1C, J_{PC} = 34.3 Hz, *ipso*-P(C_6H_5)$_2$), 143.78 (d, 1C, J_{PC} = 28.2 Hz, *ipso*-P(C_6H_5)$_2$), 161.20 (s, 1C, *ipso*-$S_2C_6H_4$), 217.08 (d, 3C, J_{PC} = 3.8 Hz, *C*O), 218.61 (d, 1C, J_{PC} = 9.9 Hz, *C*O), 220.81 (d, 1C, J_{PC} = 18.9 Hz, *C*O) ppm. $^{31}P\{^1H\}$ NMR (202.48 MHz, d-THF, 298 K): 144.2 (s), 21.9 (s, PPN) ppm. ESI-MS: m/z 577.0 {**2**}, 549.0 {**2** – CO}, 521.0 {**2** – 2CO}, 493.0 {**2** – 3CO}, 465.0 {**2** – 4CO}, 437.0 {**2** – 5CO}. Anal. Calcd for $C_{59}H_{44}Fe_2NO_5P_3S_2$: N, 1.26; C, 63.51; H, 3.97. Found: N, 1.25, C, 63.46; H, 4.37.

Synthesis of [(μ,κ^2-bdt)(μ-PPh$_2$)(μ-H)Fe$_2$(CO)$_5$] (2H). A CH_2Cl_2 solution (10 mL) of [PPN][**2**] (357 mg, 0.32 mmol) was treated with HOTf (29 μL, 0.32 mmol). The solution was stirred for 10 min at room temperature. The olive-green solution was filtered and dried in vacuo. Hexane was added to extract the product. The solution was dried under reduced pressure to obtain the olive-green semi-solid. The yield was 166 mg (90%). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2080 (s), 2031 (vs), 2013 (s), 1984 (m). ^1H NMR (500 MHz, CD_2Cl_2, 243 K): –14.08 (d, 1H, $^2J_{HP}$ = 51.5 Hz, Fe*H*Fe), 6.91 (t, 1H, $^3J_{HH}$ = 7.0 Hz, $S_2C_6H_4$), 7.06 (t, 1H, $^3J_{HH}$ = 7.5 Hz, $S_2C_6H_4$), 7.20 (m, 2H, P(C_6H_5)$_2$), 7.39 (m, 4H, P(C_6H_5)$_2$), 7.53 (m, 2H, $S_2C_6H_4$, P(C_6H_5)$_2$), 7.62 (m, 2H, $S_2C_6H_4$, P(C_6H_5)$_2$), 7.72 (m, 2H, P(C_6H_5)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 243 K): 121.56 (s, 1C, $S_2C_6H_4$), 126.80 (s, 1C, $S_2C_6H_4$), 128.54 (d, 2C, J_{PC} = 11.7 Hz, P(C_6H_5)$_2$), 128.79 (d, 2C, J_{PC} = 10.3 Hz, P(C_6H_5)$_2$), 129.58 (d, 1C, J_{PC} = 34.5 Hz, *ipso*-P(C_6H_5)$_2$) 129.94 (s, 1C, P(C_6H_5)$_2$), 130.59 (d, 1C, J_{PC} = 3.2 Hz, P(C_6H_5)$_2$), 130.70 (s, 1C, $S_2C_6H_4$), 131.52 (s, 1C, $S_2C_6H_4$), 132.59 (d, 2C, J = 10.19 Hz, P(C_6H_5)$_2$), 135.31 (d, 2C, J_{PC} = 8.3 Hz, P(C_6H_5)$_2$),

136.77 (d, 1C, J_{PC} = 33.2 Hz, *ipso*-P(C_6H_5)$_2$), 137.84 (d, 1C, J_{PC} = 24.4 Hz, $S_2C_6H_4$), 158.74 (s, 1C, *ipso*-$S_2C_6H_4$), 201.31 (br, 1C, *C*O), 208.21 (br, 2C, *C*O), 211.34 (d, 1C, J_{PC} = 14.2 Hz, *C*O), 212.12 (d, 1C, J_{PC} = 14.7 Hz, *C*O) ppm. $^{31}P\{^1H\}$ NMR (202.48 MHz, CD_2Cl_2, 243 K): 130.9 (s) ppm.

Synthesis of [(μ,κ^2-bdtH)(μ-PPh$_2$)(μ-H)Fe$_2$(CO)$_5$][OTf] ([2HSH][OTf]). To a CH_2Cl_2 solution (8 mL) of [PPN][**2**] (446 mg, 0.40 mmol) was added HOTf (180 μL, 2.03 mmol). The solution was stirred for 10 min at ambient temperature, during which time the solution color changed from green-brown, orange yellow and finally orange red. The orange-red solution was filtered and was concentrated under reduced pressure. An orange-red semi-solid was appeared upon addition of hexane. The solid was washed by hexane twice and dried in vacuo. The yield was 239 mg (82%). Orange-red crystals of [(μ,κ^2-bdtH)(μ-PPh$_2$)(μ-H)Fe$_2$(CO)$_5$][OTf]·0.5CH_2Cl_2·0.5H_2O·HOTf suitable for X-ray crystallographic analysis were grown from a CH_2Cl_2/hexane solution at 20 °C. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2101 (s), 2059 (vs), 2041 (s), 2017 (m); ν_{SH} 2469 (br). ^1H NMR (500 MHz, CD_2Cl_2, 273 K): −15.62 (d, 1H, $^2J_{HP}$ = 50.0 Hz, Fe*H*Fe), 6.27 (s, 1H, S*H*), 7.24 (m, 2H, P(C_6H_5)$_2$), 7.49 (m, 3H, $S_2C_6H_4$, P(C_6H_5)$_2$), 7.56 (m, 1H, $S_2C_6H_4$), 7.66 (m, 2H, P(C_6H_5)$_2$), 7.80 (m, 6H, $S_2C_6H_4$, P(C_6H_5)$_2$) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 273 K): 127.25 (d, 1C, J_{PC} = 39.1 Hz, *ipso*-P(C_6H_5)$_2$), 128.28 (s, 1C, $S_2C_6H_4$), 129.23 (d, 2C, J_{PC} = 12.5 Hz, P(C_6H_5)$_2$), 129.49 (d, 2C, J_{PC} = 10.9 Hz, P(C_6H_5)$_2$), 130.67 (s, 1C, P(C_6H_5)$_2$), 131.28 (s, 1C, $S_2C_6H_4$), 132.07 (s, 1C, P(C_6H_5)$_2$), 132.78 (m, 4C, P(C_6H_5)$_2$, $S_2C_6H_4$), 134.09 (d, 1C, J_{PC} = 36.9 Hz, *ipso*-P(C_6H_5)$_2$), 134.47 (d, 2C, J_{PC} = 7.9 Hz, P(C_6H_5)$_2$), 135.12 (s, 1C, $S_2C_6H_4$), 141.78 (s, 1C, *ipso*-$S_2C_6H_4$), 199.0 (m, 1C, *C*O), 203.62 (m, 1C, *C*O), 204.24 (d, 1C, J_{PC} = 12.8 Hz, *C*O), 206.63 (d, 1C, J_{PC} = 15.3 Hz,

*C*O), 206.77 (d, 1C, J_{PC} = 19.7 Hz, *C*O) ppm. $^{31}P\{^{1}H\}$ NMR (202.48 MHz, CD_2Cl_2, 273 K): 145.8 (s) ppm. ESI-MS: m/z 579.0 {**2HSH**}, 551.0 {**2HSH** – CO}, 523.0 {**2HSH** – 2CO}, 495.0 {**2HSH** – 3CO}, 467.0 {**2HSH** – 4CO}, 439.0 {**2HSH** – 5CO}. Anal. Calcd for $C_{25.5}H_{19}ClF_6Fe_2O_{11.5}PS_4$: C, 32.94; H, 2.06. Found: C, 33.02; H, 2.48.

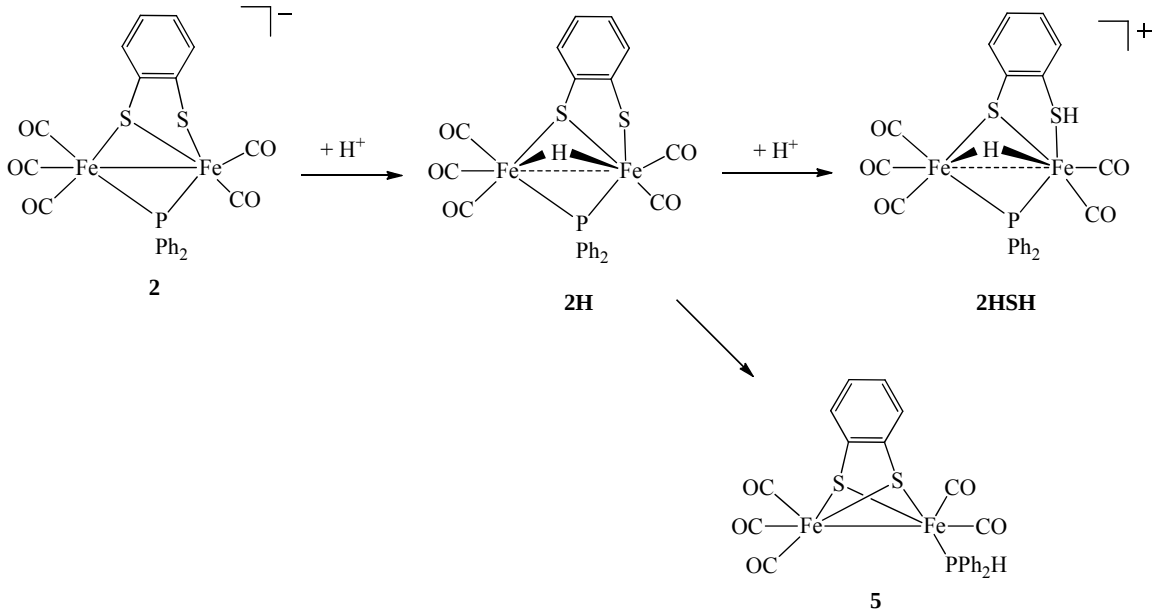
Reaction of 2 with DOTf. Complex **2** (15 mg, 13.4 μmol) was transferred in a drybox to a NMR tube and dissolved in CH_2Cl_2. The tube was frozen in a 193 K cold bath. To the NMR tube was added DOTf (1.2 μL, 13.4 μmol) by microsyringe. The sample was analyzed by low temperature NMR spectroscopy. Below 233 K, no reaction was observed due to the melting point of trifluoromethanesulfonic acid is 233 K. As temperature was increased, the signal ascribed to FeDFe appeared. No SD signal was recorded throughout the measurements. In a similar fashion, DOTf (4.8 μL, 53.6 μmol) was added to a NMR tube containing **2** (15 mg, 13.4 μmol) by microsyringe. The SD and FeDFe signals were observed at the temperature above 233 K. For **2D**, ^{2}D NMR (76.8 MHz, CH_2Cl_2, 243 K): –14.27 (d, 1D, $^{2}J_{HP}$ = 7.67 Hz, Fe*D*Fe). For **2DHD**, ^{2}D NMR (76.8 MHz, CH_2Cl_2, 243 K): –15.92 (d, 1D, $^{2}J_{HP}$ = 7.9 Hz, Fe*D*Fe), 6.18 (br, 1D, S*D*).

Conversion of 2H to 5. Complex **2H** (577 mg, 1 mmol) was dissolved in 10 mL of Ch_2Cl_2. The solution was stirred at room temperature and monitored by FTIR spectroscopy. The solution color gradually changed to orange-red from green. The conversion was completed in 4 days. The solution was dried under vacuum to yield an orange-red solid. The solid was subjected to column chromatography on silica gel. CH_2Cl_2/hexane (v/v = 1/2) was used as the eluent. The major band in orange-red was [(μ-bdt)$Fe_2(CO)_5(PPh_2H)$] (**5**). The yield was 461 mg (80%). For complex **5**: IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2052 (vs), 1994 (vs), 1982 (sh), 1940 (w). ^{1}H NMR (500 MHz, $CDCl_3$, 298

K): 6.41 (m, 2H, $S_2C_6H_4$), 6.76 (d, 1H, J_{PH} = 338.1 Hz, P*H*), 6.80 (m, 2H, $S_2C_6H_4$), 7.38 (m, 6H, $P(C_6H_5)_2$), 7.61 (m, 4H, $P(C_6H_5)_2$) ppm. $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 298 K): 125.63 (s, 2C, $S_2C_6H_4$), 128.11 (s, 2C, $S_2C_6H_4$), 128.82 (s, 2C, $P(C_6H_5)_2$), 128.90 (s, 2C, $P(C_6H_5)_2$), 130.21 (s, 2C, $P(C_6H_5)_2$), 132.22 (s, 2C, $P(C_6H_5)_2$), 132.31 (s, 2C, $P(C_6H_5)_2$), 133.12 (s, 1C, *ipso*-$S_2C_6H_4$), 133.46 (s, 1C, *ipso*-$S_2C_6H_4$), 148.52 (d, 2C, J_{PC} = 4.0 Hz, *ipso*-$P(C_6H_5)_2$), 209.15 (s, 3C, *C*O), 212.95 (d, 2C, J_{PC} = 7.5 Hz, *C*O) ppm. $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, 298 K): 37.73 (s) ppm. FAB+-MS: m/z 578.9 {**5** + H^+}, 549.9 {**5** + H^+ – CO}, 521.9 {**5** + H^+ – 2CO}, 493.9 {**5** + H^+ – 3CO}, 437.9 {**5** + H^+ – 5CO}. Anal. Calcd for $C_{23.3}H_{15.6}Cl_{0.6}Fe_2O_5PS_2$: C, 46.36; H, 2.61. Found: C, 46.34; H, 2.58.

Scheme

Scheme S1. Reaction scheme for protonation of **2** and tautomerization of **2H** to **5**.



Figures

Figure S1. Variable temperature ^{2}D- (a) and ^{31}P- (b) NMR spectra of **2D** from the in-situ reaction of complex **2** with 1 equiv of DOTf at 233 K. The CD_2Cl_2 is indicated as an asterisk.

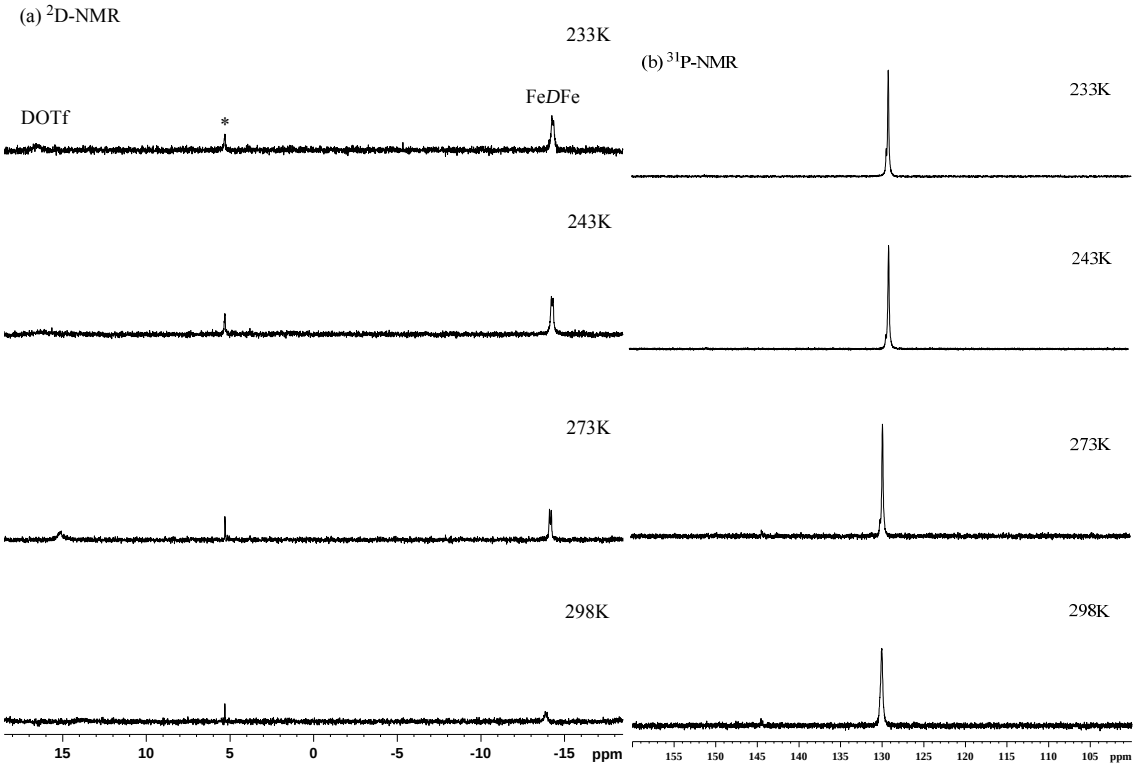


Figure S2. Variable temperature ^{2}D- (a) and ^{31}P- (b) NMR spectra of **2DSD** from the in-situ reaction of complex **2** with 4 equiv of DOTf at 233 K. The CD_2Cl_2 is indicated as an asterisk.

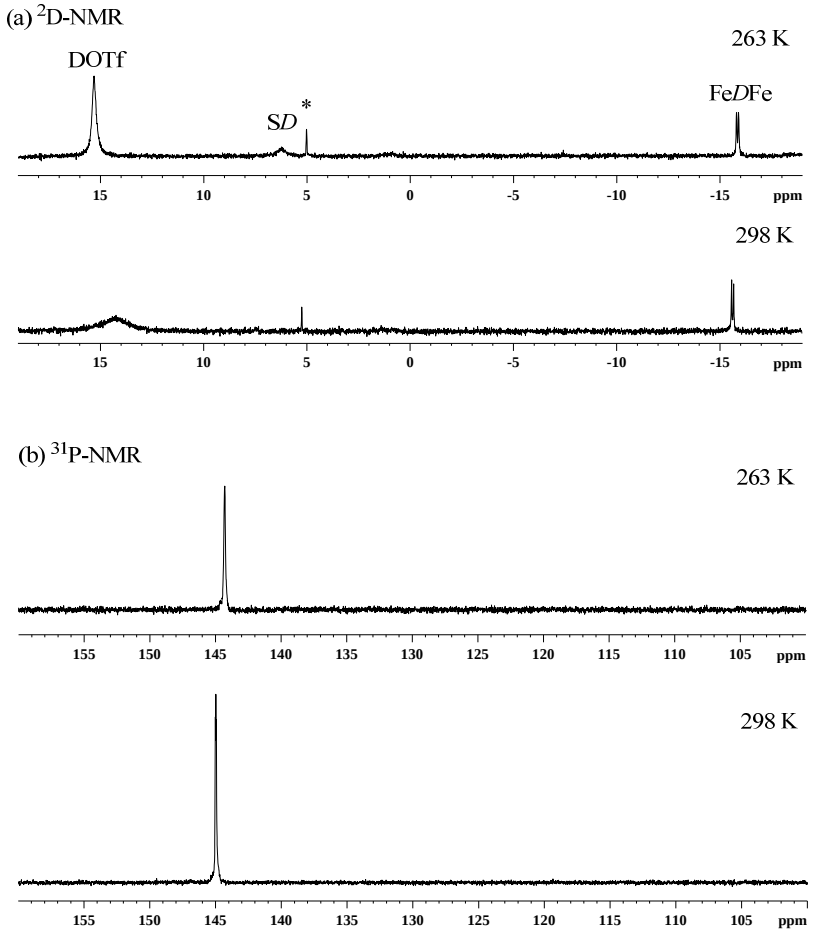
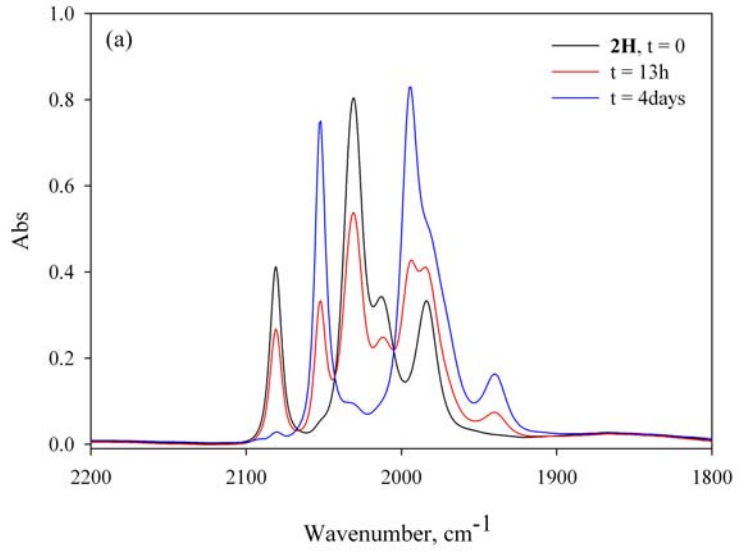


Figure S3. IR spectra changes (a) for the conversion of **2H** to **5** in CH_2Cl_2 solution at ambient temperature. The ^{31}P-NMR spectrum (b) of the reaction solution after 4 days.

(a)



(b)

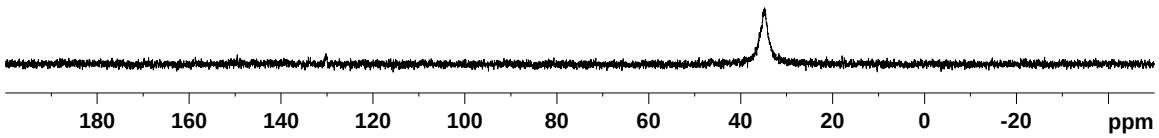


Figure S4. Experimental and computed IR spectra of **2** (a, d), **2H** (b, e) and **2HSH** (c, f). The experimental and DFT results are displayed in the left and right panels, respectively.

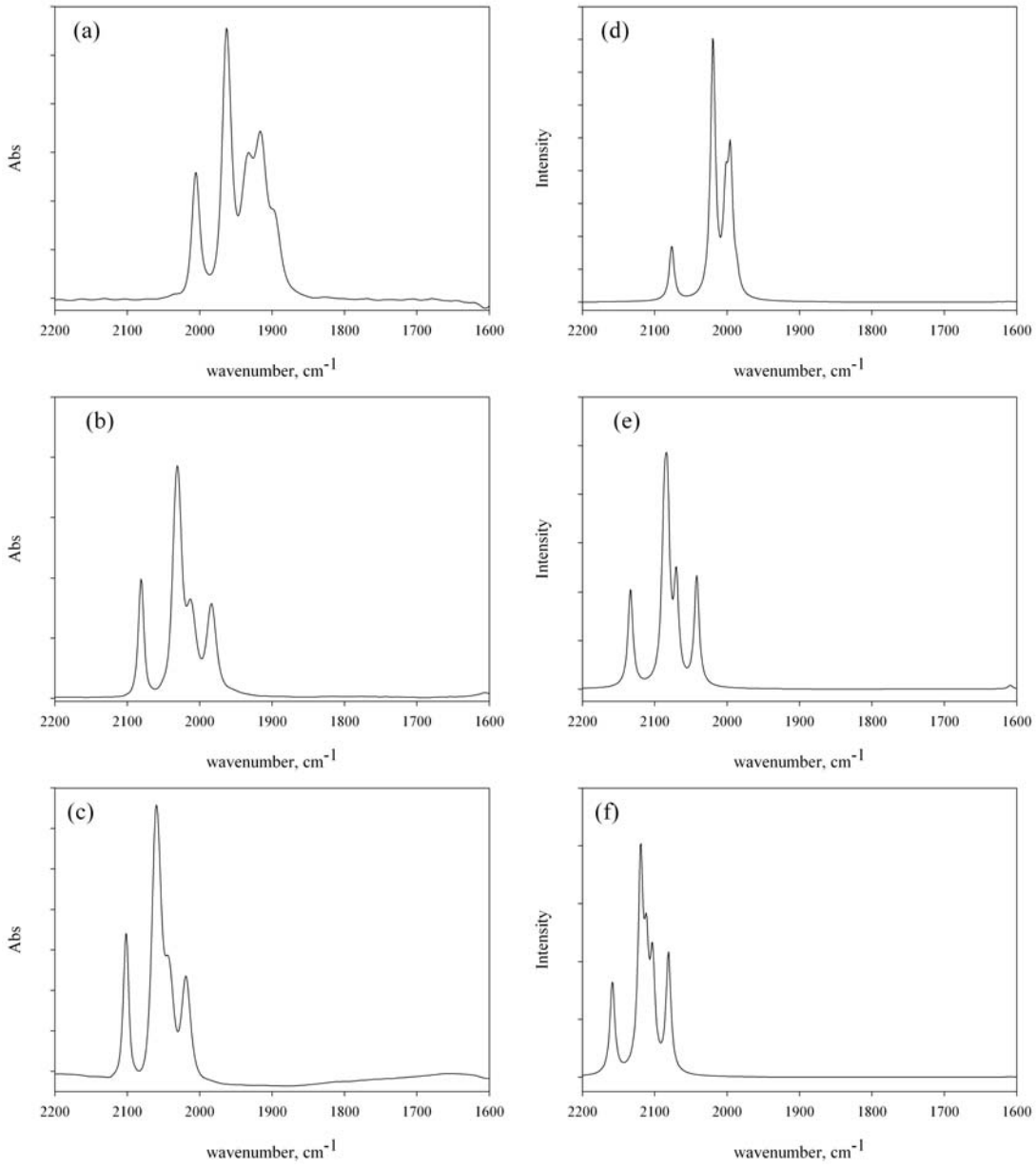


Figure S5. Computed IR spectra of the DFT geometry-optimized models: **2SH** (a), TS (b) and **2Ht** (c).

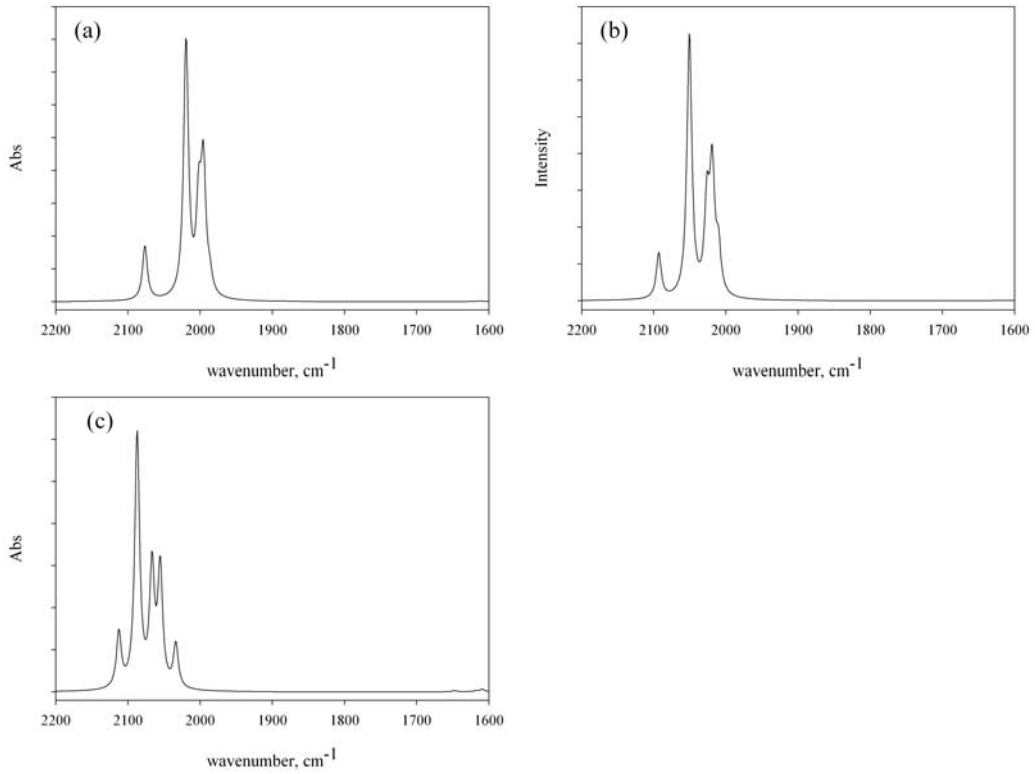
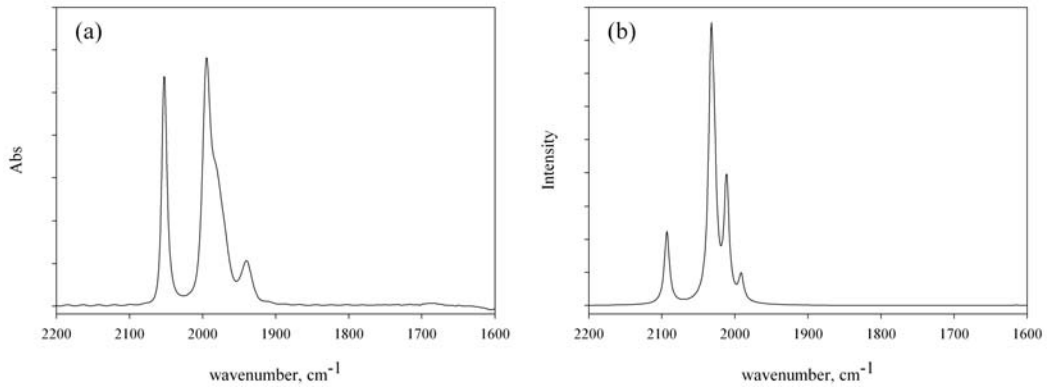


Figure S6. IR spectra of **5**: experimental (a) and the DFT geometry-optimized model (b).



A calculated ν_{CO} shift of +18 cm^{-1} for the conversion of **2H** to **5** is obtained. The data is in agreement with the observed experimental result.

Figure S7. Highest occupied molecular orbital of the DFT geometry-optimized model **2**.

Color scheme: Fe, navy blue; S, yellow; P, orange; O, red; C, grey and H, white.

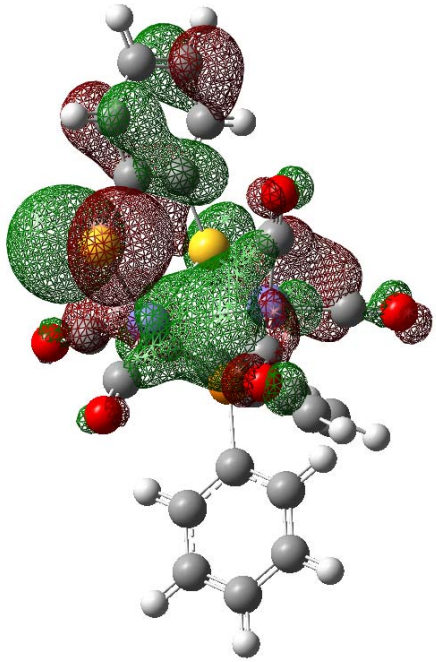
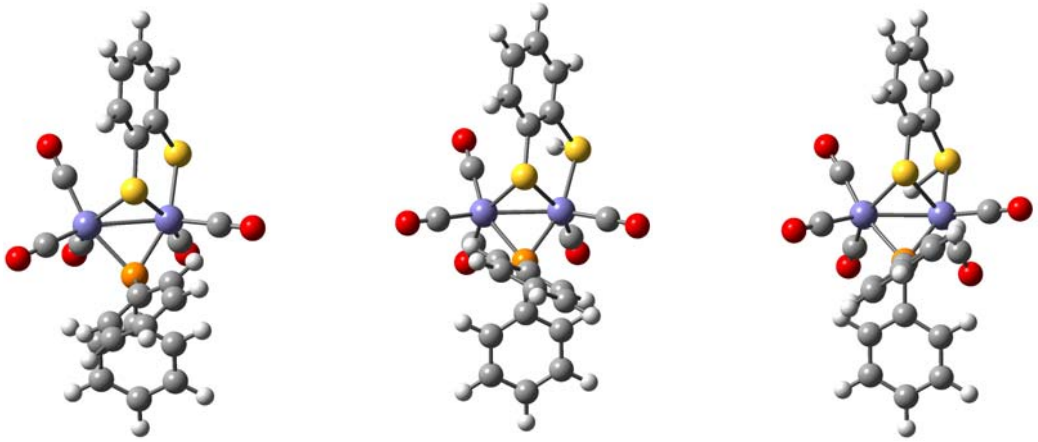
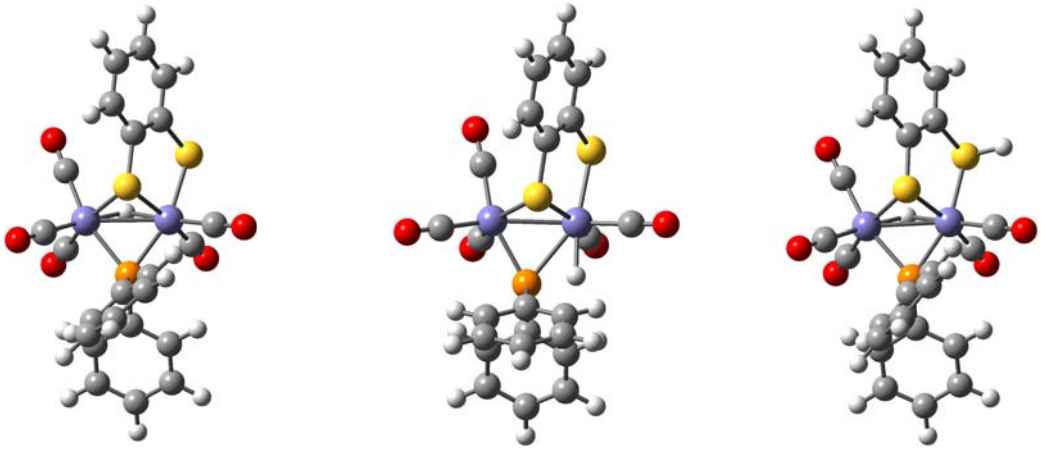


Figure S8. The DFT geometry-optimized structures of **2** (a), **2SH** (b), TS (c), **2H** (d), **2Ht** (e), **2HSH** (f) and **5** (g). Color scheme: Fe, navy blue; S, yellow; P, orange; O, red; C, grey and H, white.

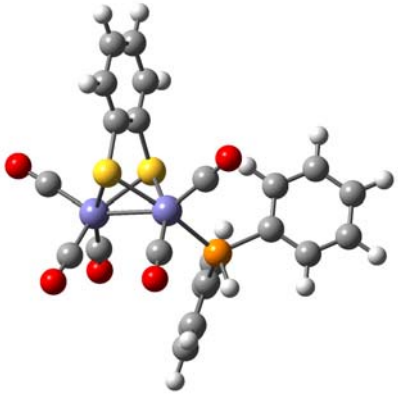
(a) (b) (c)



(d) (e) (f)



(g)



Tables

Table S1. X-ray crystallographic data.

	[PPN][**2**]·THF	[**2HSH**][OTf]·0.5CH_2Cl_2·0.5H_2O·HOTf
Empirical formula	$C_{63}H_{52}Fe_2NO_6P_3S_2$	$C_{25.5}H_{19}ClF_6Fe_2O_{11.5}PS_4$
Formula weight	1187.79	929.77
T, K	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	*P*-1
a, Å	10.5359(8)	12.5435(14)
b, Å	34.925(3)	15.0788(16)
c, Å	15.6065(12)	19.863(2)
α, °	90	92.733(2)
β, °	104.078(2)	99.228(2)
γ, °	90	109.202(2)
V, $Å^3$	5570.1(7)	3481.6(7)
Z	4	4
ρ_{calcd}, Mg m^{-3}	1.416	1.774
μ, mm^{-1}	0.736	1.285
F (000)	2456	1864
Reflections collected	32247	39835
Independent reflections	9804	15930
R_{int}	0.0749	0.0473
Goodness-of-fit on F^2	1.293	1.018
R1 [$I > 2\sigma(I)$] (all data)[a]	0.1066 (0.1255)	0.0480 (0.0706)
wR2 [$I > 2\sigma(I)$] (all data)[b]	0.1956 (0.2032)	0.1069 (0.1203)

[a] $R1 = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$. [b] $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) of the crystallographic data and the DFT geometry-optimized models for **2** and **2HSH**.

	2		**2HSH**	
	calc.	cryst.	calc.	cryst.
Fe(1)-Fe(2)	2.669	2.6163(14)	2.655	2.6134(7)
Fe(1)-S(1)	2.278	2.246(2)	2.310	2.2888(9)
Fe(1)-S(2)	2.336	2.302(2)	2.351	3.880
Fe(2)-S(1)	2.393	2.319(2)	2.363	2.2453(9)
Fe(2)-S(2)	3.912	3.836	3.978	2.3038(10)
Fe(1)-P	2.244	2.183(2)	2.264	2.2395(10)
Fe(2)-P	2.286	2.213(2)	2.323	2.2160(10)
Fe(1)-H(μ)	-	-	1.706	1.60(3)
Fe(2)-H(μ)	-	-	1.642	1.70(3)
S(2)-H	-	-	1.355	1.26(4)

Table S3. Cartesian coordinates with solvent corrected free energy (in hartree) for DFT geometry-optimized species. The imaginary frequency is reported for the transition state.

The species **2**

Fe	-0.50196000	-0.64752100	-1.12329300
Fe	-0.30863500	-0.26262600	1.51133000
S	-1.45853500	1.12725900	-0.06233200
S	-2.62390700	-1.60037500	-1.34417100
P	1.30788600	0.13985000	-0.05454200
C	-0.36520600	-0.06968500	-2.77449200
C	0.21434200	-2.25344500	-1.40254800
C	-1.86458100	-0.71252800	2.27302400
C	0.30766400	0.80567900	2.79132500
C	0.31333900	-1.89685100	1.77995300
C	-3.21636300	0.80691900	-0.10836700
C	-4.09720500	1.77251200	0.39790200
H	-3.69537100	2.68945800	0.81833000
C	-5.47102900	1.56043000	0.36877100
H	-6.14648000	2.31151600	0.76521600
C	-5.97034900	0.37147400	-0.17773100
H	-7.04114200	0.19326800	-0.20618000
C	-5.10335100	-0.58419400	-0.69073700
H	-5.49908400	-1.50046800	-1.11811500
C	-3.70726300	-0.38601000	-0.67161900
C	1.91226300	1.87794400	-0.28233100
C	2.82440100	2.42447700	0.63470000
H	3.17351500	1.83054600	1.47309700
C	3.29418000	3.72673200	0.48467900
H	3.99856400	4.13066800	1.20531400
C	2.85879600	4.51102100	-0.58559000
H	3.22407700	5.52637200	-0.70243800
C	1.95334000	3.98060200	-1.50178700
H	1.60939700	4.58071200	-2.33850400
C	1.48430100	2.67386200	-1.35157400
H	0.78306700	2.27647200	-2.07457400
C	2.91166000	-0.77645500	-0.06268600
C	3.52068200	-1.20512700	1.12305100
H	3.03457000	-1.02646800	2.07566400
C	4.75091300	-1.86395000	1.09339100
H	5.20799200	-2.19102300	2.02202700
C	5.38860100	-2.10203500	-0.12283700
H	6.34386200	-2.61667800	-0.14656100
C	4.79097100	-1.67886800	-1.31120600
H	5.27949400	-1.86403800	-2.26274000
C	3.56287900	-1.02140800	-1.28100300
H	3.10735600	-0.69945800	-2.21221700
O	-0.27743400	0.29688800	-3.86477500
O	0.65404500	-3.29894600	-1.59635100
O	-2.85508400	-0.99573800	2.78474500
O	0.74601100	1.42577600	3.66323000
O	0.68727700	-2.96191900	2.03829700

G_{solv}= -4926.649031

The species **2SH**

Fe	-0.43359700	-0.55579100	-1.15832200
Fe	-0.35193500	-0.46193200	1.44566400
S	-1.42058800	1.12160700	0.05317800
S	-2.57853000	-1.34706100	-1.67192900
P	1.32184600	0.15720200	0.03085100
C	0.27002400	-2.16766200	-1.46129100
C	-0.11300900	0.20396700	-2.73467400
C	-1.90998300	-1.25466600	1.86476400
C	-0.04685100	0.46406900	2.95188500
C	0.52408100	-1.96826600	1.79856100
C	-3.18643200	0.82359000	-0.06538800
C	-4.06985400	1.70687400	0.56723300
H	-3.67458600	2.53898800	1.13945700
C	-5.44470500	1.51641700	0.46608800
H	-6.11841200	2.20442500	0.96538500
C	-5.95657200	0.45473700	-0.28178700
H	-7.02788000	0.31181800	-0.36904100
C	-5.08811800	-0.41879500	-0.93052100
H	-5.47739900	-1.23547100	-1.52844700
C	-3.70973800	-0.23698500	-0.80829900
C	2.95382100	-0.69880400	-0.00010900
C	3.46998200	-1.25578000	-1.17647900
H	2.89576600	-1.22110400	-2.09546600
C	4.72823500	-1.85863500	-1.18174300
H	5.11444400	-2.28687800	-2.10105600
C	5.48480200	-1.91105500	-0.01239500
H	6.46217500	-2.38239600	-0.01643300
C	4.98023600	-1.35597100	1.16428100
H	5.56303400	-1.39421800	2.07893100
C	3.72446200	-0.75283400	1.17067700
H	3.34404300	-0.32426000	2.09233500
C	1.84140400	1.92738300	-0.12551300
C	1.57580300	2.86928000	0.87456300
H	1.04806400	2.57504600	1.77302300
C	1.99025200	4.19452600	0.73118700
H	1.77734100	4.91087100	1.51821400
C	2.67509000	4.59511400	-0.41378700
H	2.99788600	5.62518900	-0.52475600
C	2.94509000	3.66362800	-1.41800000
H	3.47726200	3.96658200	-2.31408000
C	2.53146100	2.34177400	-1.27560700
H	2.75203600	1.63216600	-2.06611800
O	0.68169500	-3.22232500	-1.65881900
O	0.14845500	0.69658900	-3.73971400
O	-2.89102500	-1.77818400	2.14923200
O	0.14418500	0.99376200	3.95334600
O	1.06717000	-2.94818000	2.05594900
H	-2.77247200	-2.43542300	-0.88742600

G_{solv}= -4927.075922

The transition state

Fe	-0.45616500	-0.59589500	-1.18266500
Fe	-0.36209300	-0.36233200	1.41453200

S	-1.43744300	1.15958600	-0.04761200
S	-2.58269000	-1.68191200	-1.19798900
P	1.32483900	0.13362300	-0.06262200
C	0.37596600	-2.10593200	-1.67426800
C	-0.43508500	0.11945900	-2.81738400
C	-1.91125100	-0.80306700	2.23360000
C	0.24936800	0.71032600	2.71774000
C	0.33484800	-1.96258500	1.79924100
C	-3.19066100	0.79893700	-0.09787100
C	-4.08803100	1.76771200	0.37028800
H	-3.70524100	2.70705300	0.75485300
C	-5.45813000	1.53319900	0.33144900
H	-6.14475000	2.29445500	0.68559700
C	-5.94480300	0.32205900	-0.16690400
H	-7.01260800	0.13419100	-0.19903600
C	-5.06205800	-0.65152700	-0.62099600
H	-5.43893400	-1.59587900	-0.99919200
C	-3.68145900	-0.41590800	-0.59598600
C	2.92892000	-0.77019900	-0.05974900
C	3.61887300	-0.94141300	-1.26962500
H	3.19385800	-0.57215200	-2.19752200
C	4.85332400	-1.58564000	-1.29362200
H	5.37341300	-1.71539100	-2.23709500
C	5.41766500	-2.06388700	-0.11015300
H	6.37874000	-2.56706500	-0.13035000
C	4.74311800	-1.89230300	1.09690900
H	5.17727600	-2.25773400	2.02176000
C	3.50546300	-1.24845600	1.12300100
H	2.99810000	-1.11664900	2.07174200
C	1.89098100	1.88777900	-0.19276700
C	2.81401700	2.38594000	0.74085800
H	3.19448500	1.74618400	1.52995900
C	3.25985200	3.70239800	0.66403200
H	3.97211300	4.07115700	1.39504300
C	2.79391400	4.54359000	-0.34810300
H	3.14324400	5.56912000	-0.40815100
C	1.88292800	4.05753700	-1.28281900
H	1.52032700	4.70111200	-2.07775500
C	1.43390900	2.73830700	-1.20657900
H	0.73183200	2.37730700	-1.94678900
O	0.89404200	-3.07257400	-2.00257000
O	-0.42981000	0.57385300	-3.86985700
O	-2.86470100	-1.07056600	2.80691500
O	0.65527800	1.36017300	3.56990300
O	0.73343100	-3.00415100	2.07040300
H	-1.55349700	-1.56078100	-0.06277200

Imagery frequency: -553.8494 cm^{-1}
G_{solv}= -4927.065667

The species **2H**

Fe	-0.50636000	-0.85511900	-1.03530100
Fe	-0.29821100	-0.09203300	1.52386500
S	-1.46740800	1.05982000	-0.19957200
S	-2.63017400	-1.79478900	-1.24971200

P	1.33551800	0.09333400	-0.12332600
C	0.21505800	-2.47692900	-1.31370000
C	-0.44820500	-0.38368800	-2.74884600
C	-1.85534300	-0.43282200	2.42089900
C	0.16425800	1.43006400	2.40243800
C	0.63132400	-1.26160400	2.52911600
C	-3.21440100	0.69455400	-0.15407700
C	-4.09422900	1.68655400	0.30232200
H	-3.69661000	2.63786400	0.64127000
C	-5.46264200	1.45140300	0.32475700
H	-6.14045200	2.21899000	0.68204700
C	-5.95530600	0.21762700	-0.11884800
H	-7.02303500	0.02307800	-0.10548900
C	-5.08936800	-0.76166200	-0.58410600
H	-5.48183600	-1.71110900	-0.93371200
C	-3.69720300	-0.54255100	-0.61734800
C	2.92481800	-0.82680800	0.01805900
C	3.46402700	-1.41877900	-1.13368500
H	2.93110400	-1.36155700	-2.07672200
C	4.68991700	-2.07902400	-1.08330100
H	5.09169900	-2.53398400	-1.98264500
C	5.39496600	-2.15654700	0.11760500
H	6.34753600	-2.67433800	0.15751300
C	4.87171700	-1.56514300	1.26611300
H	5.41588600	-1.61726200	2.20335700
C	3.64548200	-0.90277700	1.21728800
H	3.26303100	-0.44089800	2.12003900
C	1.90338300	1.79679500	-0.55513800
C	2.90343600	2.41805800	0.21059800
H	3.34882700	1.90192600	1.05389500
C	3.34277200	3.70109400	-0.10341300
H	4.11606100	4.16559900	0.49972100
C	2.79222100	4.38646000	-1.18763500
H	3.13679000	5.38572800	-1.43248900
C	1.80219400	3.77856700	-1.95574400
H	1.37209600	4.29978200	-2.80468500
C	1.36004600	2.49280100	-1.64263600
H	0.59424100	2.03785600	-2.25628700
O	0.63703900	-3.52533100	-1.47868500
O	-0.43659100	-0.09254400	-3.85478800
O	-2.81178100	-0.65917000	2.99243200
O	0.46367300	2.38439700	2.94815800
O	1.15894000	-2.03644600	3.17833900
H	-0.65173800	-1.38734400	0.62198900

G_{solv}= -4927.092492

The species **2Ht**

Fe	-0.52089300	-0.71069900	-1.12801300
Fe	-0.22555900	-0.27768900	1.43651800
S	-1.37176000	1.13001800	-0.08680800
S	-2.63880000	-1.66121600	-1.11232900
P	1.44550000	0.22038600	0.02107800
C	0.11353400	-2.39858800	-1.27030600
C	-0.80918500	-0.33599200	-2.85824600

C	-1.78002900	-0.95579800	2.05780200
C	0.08391400	0.84464700	2.80925400
C	0.58173600	-1.79531800	1.93523700
C	-3.13669400	0.85803600	-0.07056500
C	-3.97404100	1.88362900	0.38783500
H	-3.53809500	2.81395800	0.73731900
C	-5.35247200	1.70824200	0.39460800
H	-5.99890400	2.50335000	0.74999400
C	-5.89657500	0.50339400	-0.06634900
H	-6.97223700	0.35898200	-0.06841400
C	-5.07077200	-0.51213000	-0.52959800
H	-5.50123000	-1.44045800	-0.89106300
C	-3.67236400	-0.35207800	-0.53926400
C	3.02264900	-0.70999900	-0.05773900
C	3.53749700	-1.17168800	-1.27609200
H	2.99232600	-1.01933900	-2.20137300
C	4.76191200	-1.83521900	-1.30958200
H	5.15026000	-2.19597300	-2.25597800
C	5.48384900	-2.03379400	-0.13292800
H	6.43731200	-2.55030500	-0.16201100
C	4.97793800	-1.57043600	1.08072300
H	5.53454000	-1.72437300	1.99885600
C	3.74960300	-0.91365700	1.12217100
H	3.36592300	-0.56426900	2.07487800
C	1.90722200	1.96845900	-0.33059500
C	2.30101300	2.78384000	0.73793100
H	2.29912100	2.40274200	1.75309100
C	2.70334600	4.09720900	0.50552700
H	3.00774200	4.72043400	1.33956600
C	2.70542300	4.60945000	-0.79154500
H	3.01206500	5.63456800	-0.97031700
C	2.30794800	3.80366400	-1.85776000
H	2.30245500	4.19854700	-2.86811600
C	1.91271100	2.48671500	-1.63117400
H	1.60554300	1.87498300	-2.47257800
O	0.45816500	-3.48494300	-1.35807000
O	-1.00270400	-0.10179300	-3.96015000
O	-2.74088000	-1.38265900	2.50441200
O	0.28067300	1.51105000	3.72129500
O	1.06101800	-2.77276100	2.29827800
H	0.99824400	-0.04804500	-1.41713900

G_{solv}= -4927.050789

The species **5**

Fe	-1.63898900	-1.49642100	-0.05725800
Fe	-0.26511300	0.32270800	1.07837500
S	-0.76241800	0.34312200	-1.18259200
S	-2.57939700	0.22879000	1.20302300
P	1.99156000	0.05299400	0.75140200
O	-1.92564800	-3.35482100	2.20448000
O	0.14521700	-3.36833900	-1.45573900
O	0.03489000	-0.84782100	3.75354100
O	-0.09873900	3.13957300	1.86064600
C	-1.80034000	-2.62226900	1.33023500

C	-0.51292100	-2.62049400	-0.89233500
C	-0.08695400	-0.40362600	2.70079600
C	-0.12322100	2.04097400	1.52973000
C	-2.20460400	1.42395100	-1.21831700
C	-3.04970400	1.37038700	-0.10696100
C	-4.18443800	2.16950400	-0.04493400
C	-4.47343200	3.03148500	-1.11099700
C	-3.63181700	3.08561200	-2.21769300
C	-2.48877200	2.27729200	-2.27689100
C	2.69132500	-1.28176900	-0.30629100
C	2.85481300	-1.10250100	-1.68508700
C	3.40021500	-2.12121900	-2.46422600
C	3.78534500	-3.32550600	-1.87600300
C	3.62091200	-3.51051300	-0.50365100
C	3.07522000	-2.49493900	0.27919300
C	2.95561600	1.54321700	0.26601500
C	4.22753900	1.75916200	0.81515500
C	4.97539000	2.87304600	0.43994500
C	4.46524800	3.77726100	-0.49229900
C	3.20210200	3.56766400	-1.04320400
C	2.44624100	2.45951500	-0.66144800
H	-5.35846500	3.65730700	-1.06818000
H	-3.85831400	3.75329300	-3.04215700
H	2.57433600	-0.16642200	-2.15584900
H	3.52835700	-1.97033600	-3.53109100
H	4.21406300	-4.11537800	-2.48385400
H	3.92180600	-4.44363900	-0.03871400
H	2.95898600	-2.65049800	1.34732400
H	4.63777400	1.06029100	1.53707300
H	5.95542600	3.03441800	0.87672300
H	5.04897100	4.64403700	-0.78422300
H	2.79865900	4.26999000	-1.76507900
H	1.45910900	2.31541800	-1.08617500
C	-3.10041900	-1.90492300	-1.03195200
O	-4.03365000	-2.18622800	-1.63258900
H	2.65790700	-0.26541500	1.95378400
H	-4.83933800	2.12532900	0.81879800
H	-1.83360700	2.31585700	-3.14072000

G_{solv}= -4927.097014

The species **2HSH**

Fe	-0.47702600	-0.81320000	-1.06982700
Fe	-0.33438600	-0.14304700	1.49563100
S	-1.46050400	1.08030700	-0.18430000
S	-2.62279100	-1.73467400	-1.34290400
P	1.34248500	0.11394500	-0.09159200
C	0.30864100	-2.41710900	-1.38323500
C	-0.27765000	-0.23167500	-2.76088800
C	-1.89807300	-0.50869100	2.39806800
C	0.14385400	1.32045200	2.46911400
C	0.57604900	-1.36467300	2.47930800
C	-3.21406800	0.70430000	-0.14227300
C	-4.09083600	1.65805600	0.38696800
H	-3.69785000	2.58687700	0.78498500

C	-5.46082500	1.41325100	0.40132000
H	-6.13208400	2.15751500	0.81477800
C	-5.96875600	0.21904200	-0.10997800
H	-7.03542600	0.02680300	-0.09522600
C	-5.10465200	-0.73644900	-0.63856800
H	-5.49357700	-1.66901600	-1.03149600
C	-3.73320200	-0.48278100	-0.66525500
C	2.91507300	-0.82776000	0.03201600
C	3.48547500	-1.34833600	-1.13941700
H	2.98706700	-1.22799100	-2.09524200
C	4.70519400	-2.01864000	-1.09127800
H	5.13274200	-2.41935400	-2.00409000
C	5.37283200	-2.17279100	0.12361500
H	6.32177200	-2.69697200	0.15996000
C	4.81967900	-1.64794000	1.28979500
H	5.33694000	-1.75644100	2.23702800
C	3.59783900	-0.97763800	1.24610100
H	3.19591900	-0.56330700	2.16283100
C	1.90878300	1.82174800	-0.48736000
C	2.98452200	2.36495700	0.23513400
H	3.48440500	1.78230500	1.00034300
C	3.43134100	3.65644500	-0.02768100
H	4.26279000	4.06051400	0.53991800
C	2.81705700	4.42507700	-1.01708400
H	3.16991800	5.42980600	-1.22367300
C	1.75410600	3.89324100	-1.74289100
H	1.27616400	4.47880900	-2.52093600
C	1.30069000	2.60092300	-1.48073300
H	0.47858900	2.21111100	-2.06424100
O	0.76607800	-3.44287400	-1.56200900
O	-0.15311800	0.12569800	-3.83530800
O	-2.84499700	-0.74026500	2.97807200
O	0.44662800	2.24092900	3.06157900
O	1.08037400	-2.16946900	3.10306000
H	-0.68608300	-1.41082400	0.51395500
H	-2.90729900	-1.53691900	-2.65259000

G_{solv}= -4927.495155

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