Supporting information for

Reactivity Studies on $[Cp'FeI]_2$: From Iron Hydrides to P_4-Activation

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Table of Content:

1. *Representative NMR Spectra of **2**, **3** and **4***

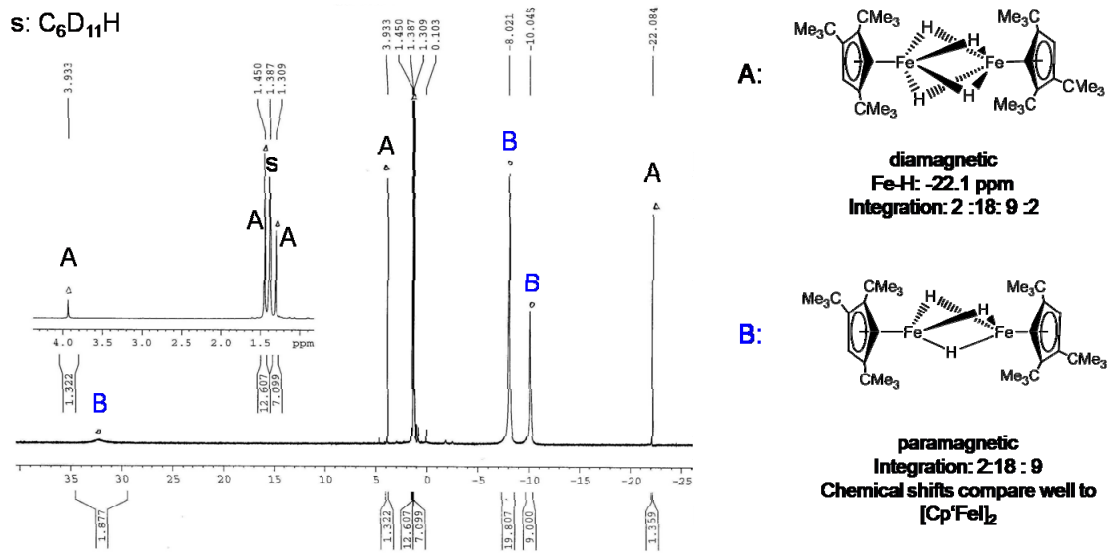


Figure S1. ^{1}H NMR spectrum of the crystallized material obtained from reaction of $[Cp'FeI]_2$ and $KHBEt_3$ in pentane under 1 atm of argon. Complexes **2** and **3** are obtained in a 40:60 ratio. ^{1}H NMR spectrum recorded in cyclohexane-d_{12} at ambient temperature.

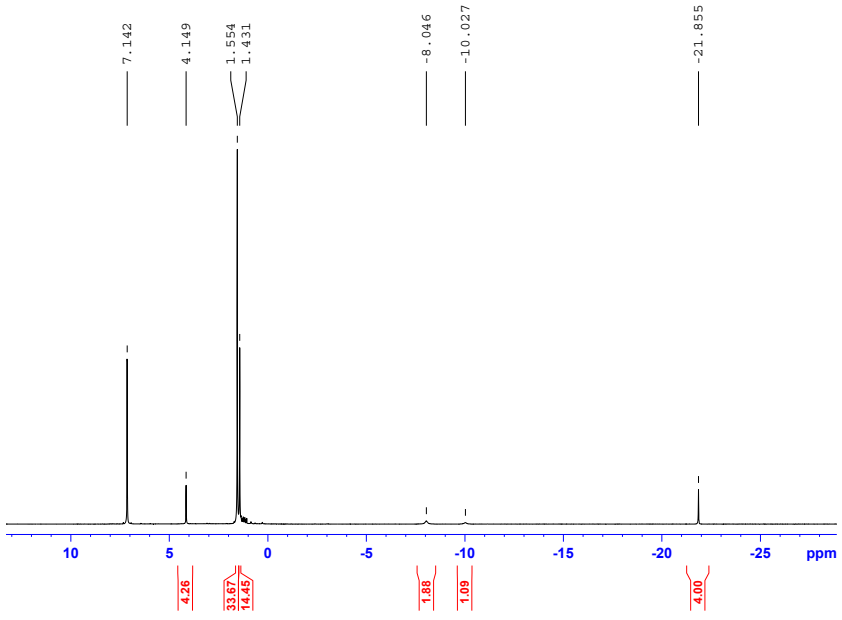


Figure S2. ^{1}H NMR spectrum of $[Cp'FeH_2]_2$ (**2**) recorded in C_6D_6 at ambient temperature. The resonances at δ -8.05 and -10.03 indicate a small amount of $[Cp'_2Fe_2H_3]$ (**3**) (~ 5 %).

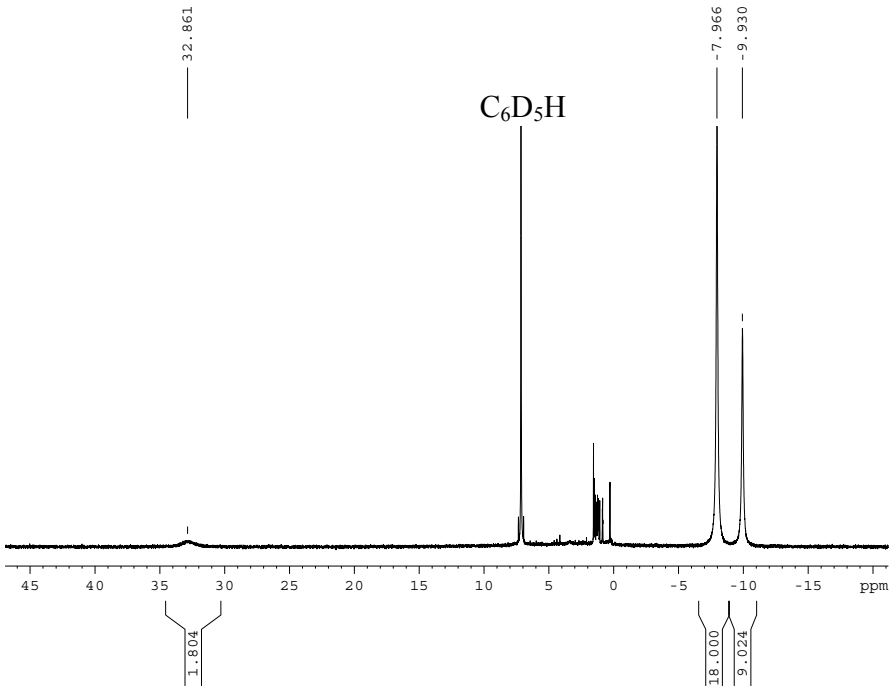


Figure S3. ^{1}H NMR spectrum of $[Cp'_2Fe_2H_3]_2$ (**3**) recorded in C_6D_6 at ambient temperature.

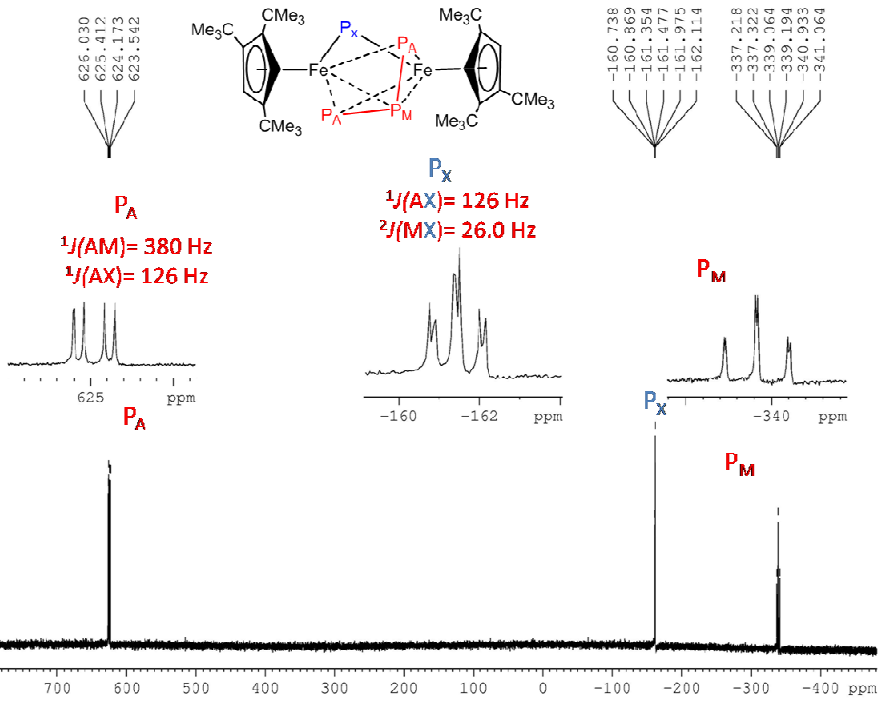


Figure S4. ^{31}P{^{1}H} NMR spectrum of $[\{Cp'_2Fe_2\}_2(\mu\text{-}P_4)]$ (**4**) recorded in C_7D_8 at ambient temperature.

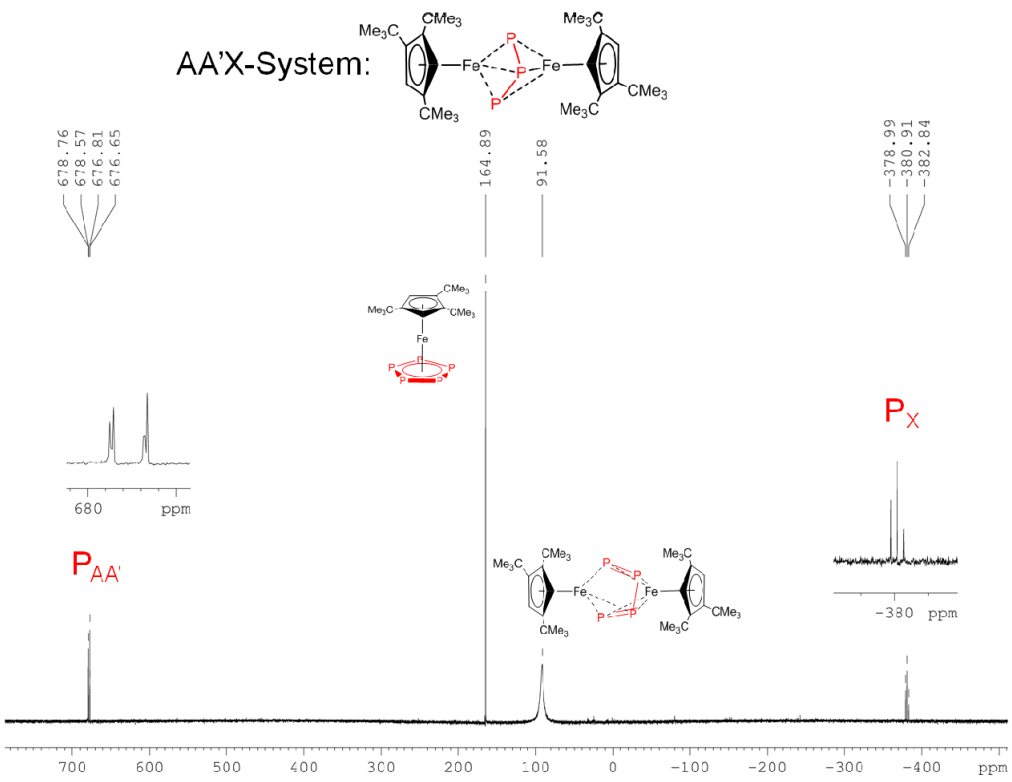


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of the thermal degradation products of [{Cp'$_2$Fe$_2$}$_2$(μ-P$_4$)] (**4**) (after 7d at 75 °C).

2. *Variable Temperature ^{1}H NMR Behavior of Complexes **2** and **3**.*

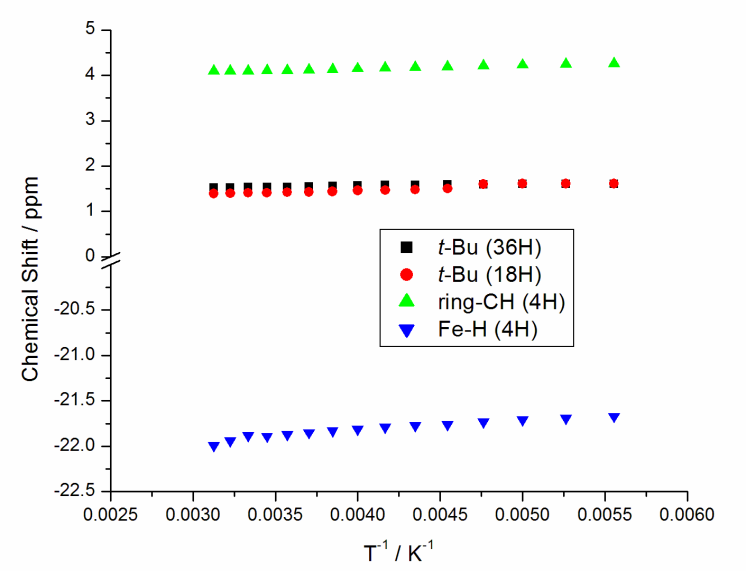


Figure S6. Chemical Shift (δ) vs. T^{-1} plot for the ^{1}H NMR resonances of $[Cp'FeH_2]_2$ (**2**) in toluene-d_8 from -83 to +47 °C.

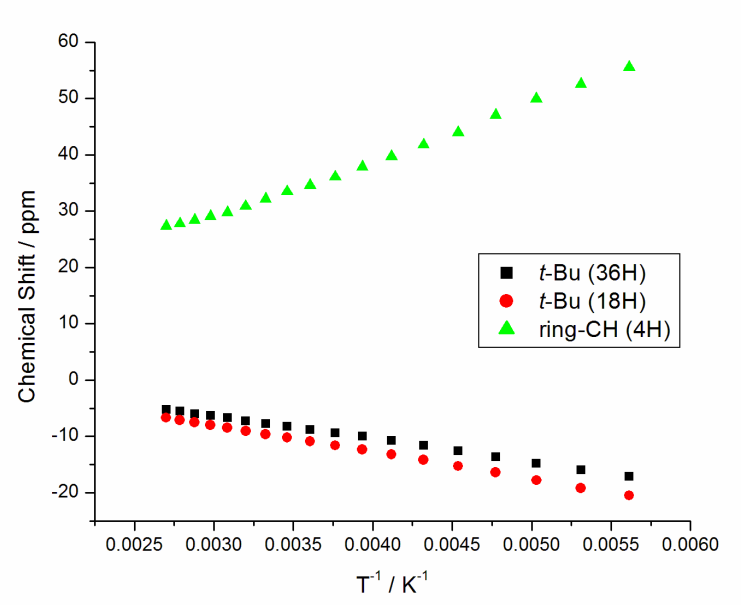


Figure S7. Chemical Shift (δ) vs. T^{-1} plot for the ^{1}H NMR resonances of $[Cp'_2Fe_2H_3]$ (**3**) in toluene-d_8 from -83 to +47 °C.

*3. Crystallographic Details of **2**, **3** and **4***

Table S1. X-Ray Crystal Structure Data for **2** (internal number: c07302; CCDC-738663)

Crystal data	
Chemical formula	$C_{34}H_{62}Fe_2$
M_r	582.54
Cell setting, space group	Tetragonal, *P*4(1)2(1)2
Temperature (K)	100 (2)
a, *c* (Å)	9.0398 (2), 40.2263 (12)
V (Å^3)	3287.21 (14)
Z	4
D_x (Mg m^{-3})	1.177
Radiation type	Cu *K*α
μ (mm^{-1})	7.19
Crystal form, colour	Block, purple
Crystal size (mm)	0.25 × 0.20 × 0.10
Data collection	
Diffractometer	CCD area detector
Data collection method	phi and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)
T_{min}	0.267
T_{max}	0.533
No. of measured, independent and observed reflections	22777, 3095, 3020
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.038
θ_{max} (°)	69.8
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.025, 0.065, 1.05
No. of relections	3095 reflections

No. of parameters	180
H-atom treatment	Mixture of independent and constrained refinement
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 1.1409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, –0.25
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	0.080 (4)

Computer programs: *Bruker SMART*; *Bruker SAINT*; *Bruker SHELXTL*.

The methodology used for the location of hydrogen atoms follows previous reports by *Ibers* and *Bau*.[1, 2] Difference Fourier techniques have been successfully applied to locate the hydride ligands in complex **2**. The structure was solved and refined without the inclusion of the hydride ligands (R_1-factor= 0.0279). Inspection of the difference Fourier map revealed three peaks of the expected height of 0.59, 0.56 and 0.50 e/Å^3, respectively, at reasonable distances from the Fe-center of *ca.* 1.5-1.6 Å. The 4th hydrogen atom is generated by a symmetry operation. The R_1-factor drops from 0.0279 to 0.0241 when the hydrogen atoms are included in the least-squares refinement cycle and refined isotropically (8 additional variables, 3095 independent reflections). The refined Fe-H distances ranging from 1.57(3)-1.63(3) Å are in good agreement with Fe-H bond distances determined by neutron and X-ray diffraction experiments.[3, 4]

Table S2. X-Ray Crystal Structure Data for **3** (internal number: c06398; CCDC-738662)

Crystal data	
Chemical formula	$C_{34}H_{61}Fe_2$
M_r	581.53
Cell setting, space group	Triclinic, *P*-1
Temperature (K)	100 (2)
a, *b*, *c* (Å)	10.2629 (2), 12.4476 (3), 14.5233 (3)
α, β, γ (°)	112.514 (2), 91.655 (2), 105.741 (2)
V (Å^3)	1631.16 (7)
Z	2
D_x (Mg m^{-3})	1.184
Radiation type	Mo *K*α

μ (mm^{-1})	0.91
Crystal form, colour	Plate, green
Crystal size (mm)	0.20 × 0.20 × 0.05

Data collection

Diffractometer	Bruker APEX
Data collection method	phi and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)
T_{min}	0.839
T_{max}	0.956
No. of measured, independent and observed reflections	12986, 6865, 4633
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.039
θ_{max} (°)	27.2

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.108, 1.00
No. of relections	6865 reflections
No. of parameters	355
H-atom treatment	Mixture of independent and constrained refinement
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.7314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.50, –0.75

Computer programs: *Bruker SMART*; *Bruker SAINT*; *SHELXS-97* (Sheldrick, 1997); *SHELXL-97* (Sheldrick, 1997).

The methodology used for the location of hydrogen atoms follows previous reports by *Ibers* and *Bau*.[1, 2] Difference Fourier techniques have been successfully applied to locate the hydride ligands in complex **3**. The structure was solved and refined without the inclusion of the hydride ligands (R_1-factor= 0.0477). Inspection of the difference Fourier map revealed three peaks of the expected height of 0.73, 0.60 and 0.52 e/$Å^3$, respectively, at reasonable distances from the Fe-center of *ca.* 1.33-1.50 Å. The R_1-factor drops from 0.0477 to 0.0459 when the hydrogens are included in the least-squares refinement cycle and refined isotropically (8 additional variables, 6865

independent reflections). The refined Fe-H distances ranging from 1.49(4)-1.66(4) Å are in good agreement with Fe-H bond distances determined by neutron and X-ray diffraction experiments.[3, 4]

Table S3. X-Ray Crystal Structure Data for **4** (internal number: c08397; CCDC-738664)

Crystal data	
Chemical formula	$C_{34}H_{58}Fe_2P_4$
M_r	702.38
Cell setting, space group	Orthorhombic, *P*2(1)2(1)2(1)
Temperature (K)	100 (2)
a, *b*, *c* (Å)	13.3878 (3), 13.7768 (3), 19.6471 (4)
V (Å^3)	3623.73 (14)
Z	4
D_x (Mg m^{-3})	1.287
Radiation type	Mo *K*α
μ (mm^{-1})	1.00
Crystal form, colour	Block, red
Crystal size (mm)	0.25 × 0.20 × 0.05
Data collection	
Diffractometer	Bruker APEX-II CCD
Data collection method	ϕ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)
T_{min}	0.788
T_{max}	0.952
No. of measured, independent and observed reflections	51726, 7410, 6562
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.045
θ_{max} (°)	26.4
Refinement	
Refinement on	F^2

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.088, 1.02
No. of relections	7410 reflections
No. of parameters	379
H-atom treatment	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 2.5753P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.95, –0.51
Absolute structure	Flack H D (1983), Acta Cryst. A39, 876-881
Flack parameter	0 (The crystal is a racemic twin)

Computer programs: *Bruker APEX2*; *Bruker SAINT*; *SHELXS-97* (Sheldrick, 2008); *SHELXL-97* (Sheldrick, 2008); *Bruker SHELXTL*.

*4. Kinetic Studies on H/D Reactions with **2***

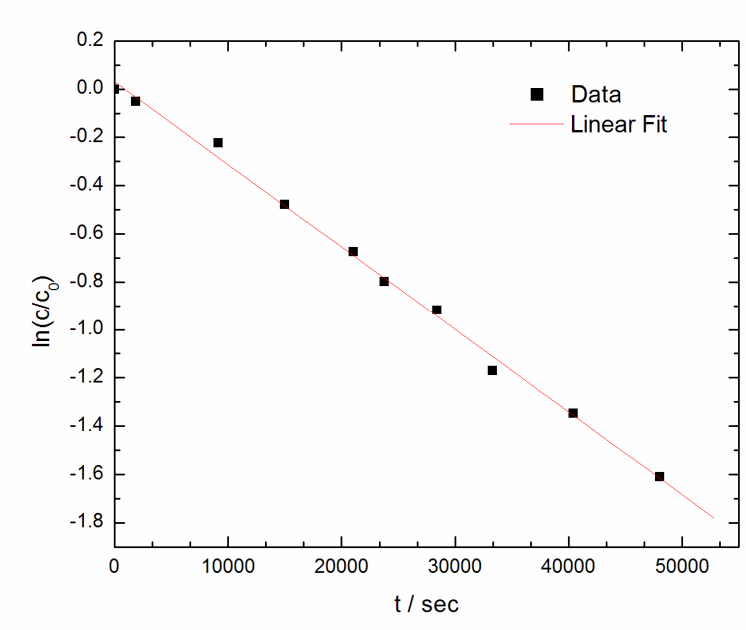


Figure S8. H/D Exchange Reaction of **2** with D_2 (1 atm) in C_6D_{12} at 298 K. The decay of the Fe-H resonance was monitored over time by ^{1}H NMR spectroscopy (R^2= 0.9964, k= 3.4(4)x10^{-5} s^{-1})

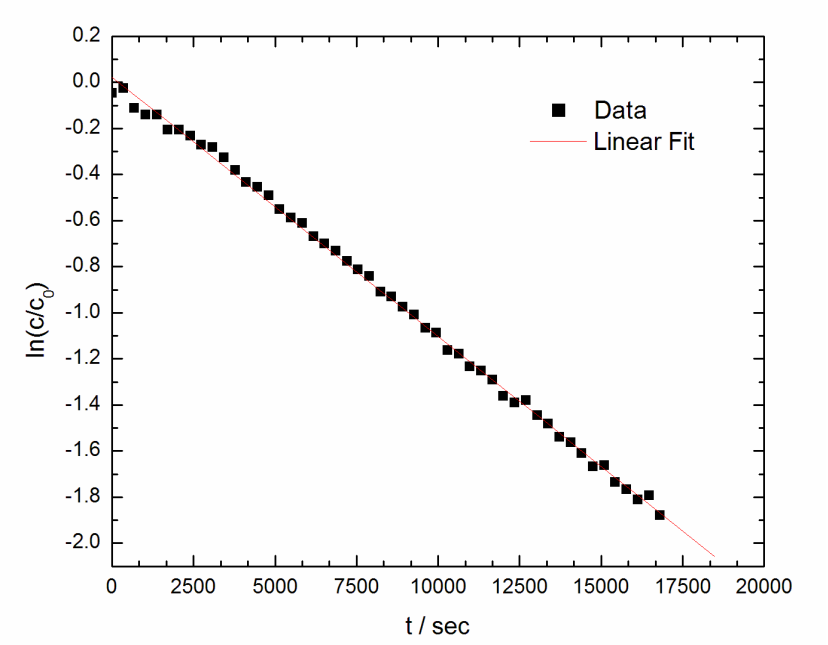
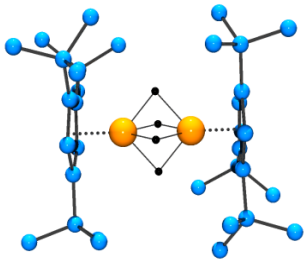


Figure S9. H/D Exchange Reaction of **2** with C_7D_8 at 346 K. The decay of the Fe-H resonance was monitored over time by ^{1}H NMR spectroscopy (R^2= 0.9978, k= 1.1(2)x10^{-4} s^{-1})

5. Cartesian Coordinates of Fully Optimized Structures

*5.1 [Cp'FeH$_2$]$_2$ (**2**) (Basis set: 6-311G(d,p))*

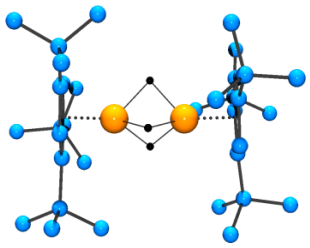


Fe	1.004500	-0.399000	-0.078400
C	2.760900	-0.250600	0.884100
C	2.918000	0.055400	-0.546600
C	2.504800	-1.124600	-1.260000
H	2.423600	-1.200000	-2.335500
C	2.057900	-2.129700	-0.358900
C	2.241500	-1.600100	0.953300
H	1.954500	-2.110400	1.862200
C	3.465600	1.262500	-1.323400
C	3.060600	0.553000	2.163900
C	1.480500	-3.480700	-0.737400

Fe	-1.004500	0.399000	-0.078000
C	-2.760600	0.250400	0.885000
C	-2.918200	-0.055300	-0.545600
C	-2.505200	1.124900	-1.259000
H	-2.424400	1.200600	-2.334400
C	-2.058000	2.129800	-0.357700
C	-2.241200	1.599900	0.954400
H	-1.953900	2.109900	1.863300
C	-3.466000	-1.262100	-1.322600
C	-3.059900	-0.553600	2.164700
C	-1.480800	3.480900	-0.736100
C	2.655400	-4.451300	-1.007300
H	3.281300	-4.559300	-0.110200
H	2.270100	-5.443200	-1.286800
H	3.286400	-4.077700	-1.826000
C	0.606500	-4.030000	0.407300
H	1.204200	-4.208800	1.311700
H	-0.185100	-3.311000	0.650000
H	0.147900	-4.981900	0.105200
C	0.612800	-3.344900	-2.007100
H	-0.170000	-2.595900	-1.840400
H	1.215900	-3.027200	-2.868500
H	0.148700	-4.310900	-2.252000
C	5.003000	1.101900	-1.438500
H	5.246800	0.156000	-1.942000
H	5.422200	1.929900	-2.029800
H	5.485100	1.096800	-0.454500
C	2.883000	1.280200	-2.762500
H	3.238900	0.429700	-3.357700
H	1.786200	1.260600	-2.735300
H	3.209100	2.197500	-3.271200
C	3.119600	2.634500	-0.714300
H	2.033400	2.734400	-0.605300
H	3.586100	2.800900	0.259000
H	3.474500	3.425200	-1.390600
C	4.530800	1.036300	2.166200
H	5.209900	0.182300	2.033400
H	4.739800	1.760700	1.375100
H	4.759000	1.513500	3.130500
C	2.899900	-0.355800	3.409100
H	1.863200	-0.703500	3.512000
H	3.564000	-1.229300	3.356700
H	3.154400	0.222100	4.308100
C	2.080900	1.733100	2.376500
H	2.043600	2.416900	1.529400
H	1.067100	1.341900	2.521100
H	2.378700	2.299100	3.272700
C	-0.613700	3.345500	-2.006200
H	0.169100	2.596300	-1.840200
H	-1.217300	3.028200	-2.867400
H	-0.149600	4.311500	-2.250900
C	-2.655900	4.451600	-1.005100
H	-3.281400	4.559200	-0.107700
H	-2.270700	5.443600	-1.284400

H	-3.287200	4.078300	-1.823600
C	-0.606200	4.029900	0.408400
H	-1.203600	4.208600	1.313000
H	0.185400	3.310700	0.650600
H	-0.147600	4.981800	0.106400
C	-2.883700	-1.279500	-2.761900
H	-3.239900	-0.428900	-3.356900
H	-1.786900	-1.259800	-2.735000
H	-3.209800	-2.196700	-3.270700
C	-5.003400	-1.101600	-1.437300
H	-5.247300	-0.155500	-1.940500
H	-5.422700	-1.929400	-2.028700
H	-5.485200	-1.096800	-0.453200
C	-3.119800	-2.634300	-0.713900
H	-2.033500	-2.734100	-0.605100
H	-3.586100	-2.800800	0.259400
H	-3.474700	-3.424800	-1.390400
C	-2.080100	-1.733700	2.376700
H	-2.043300	-2.417400	1.529600
H	-1.066200	-1.342600	2.520900
H	-2.377500	-2.299700	3.273100
C	-2.898800	0.354900	3.410200
H	-1.862100	0.702500	3.512900
H	-3.563000	1.228400	3.358100
H	-3.153100	-0.223300	4.309000
C	-4.530100	-1.037000	2.167200
H	-5.209200	-0.182900	2.034800
H	-4.739200	-1.761100	1.376000
H	-4.758000	-1.514400	3.131500
H	0.000200	-0.000200	1.162400
H	-0.481400	-1.152800	-0.090800
H	-0.000200	0.000200	-1.338500
H	0.481400	1.152800	-0.090600

*5.2 [Cp'$_2$Fe$_2$H$_3$] (**3**) (Basis set: 6-311G(d,p))*

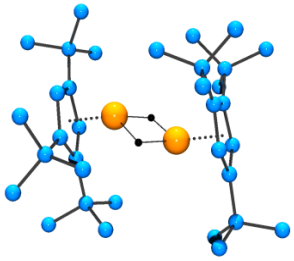


C	2.744500	-0.588000	-0.873500
C	2.770700	-0.849900	0.582400
C	2.782600	0.437200	1.222900
H	2.736700	0.588400	2.298800
C	2.773000	1.496900	0.264000
C	2.749600	0.857500	-1.012200
H	2.694200	1.386900	-1.958900
C	2.780500	-1.499000	-2.124500

C	2.947000	-2.124400	1.436000
C	2.914400	2.984100	0.568100
Fe	1.095200	0.247200	0.017600
Fe	-1.123500	0.285400	-0.029800
C	4.400400	3.232800	0.943400
H	4.568000	4.301000	1.162800
H	4.688800	2.650300	1.833100
H	5.068800	2.941900	0.117000
C	2.560000	3.847600	-0.660200
H	3.215900	3.625200	-1.517200
H	1.515900	3.691500	-0.972200
H	2.684100	4.915600	-0.416500
C	2.013300	3.395000	1.754000
H	2.135700	4.468800	1.973000
H	0.955500	3.198000	1.521700
H	2.266700	2.836500	2.669400
C	2.890900	-0.628700	-3.404000
H	2.011100	0.022500	-3.529900
H	3.797900	-0.002900	-3.400800
H	2.942500	-1.289100	-4.284700
C	4.028100	-2.416400	-2.108400
H	4.950900	-1.823100	-2.001000
H	4.000000	-3.152500	-1.293400
H	4.093000	-2.976500	-3.056600
C	1.489800	-2.339000	-2.283900
H	1.503500	-2.875700	-3.248000
H	1.366300	-3.080200	-1.485700
H	0.611200	-1.677800	-2.250000
C	2.182300	-3.359800	0.920100
H	1.112200	-3.130300	0.800000
H	2.570400	-3.729100	-0.038200
H	2.279100	-4.182600	1.647900
C	2.456900	-1.880600	2.888000
H	3.057600	-1.121300	3.411700
H	1.400300	-1.571800	2.911400
H	2.550300	-2.817300	3.460900
C	4.467100	-2.437300	1.511000
H	4.641100	-3.316200	2.154900
H	4.894600	-2.648800	0.520700
H	5.018000	-1.584300	1.938900
C	-2.849400	-0.704800	-0.583300
C	-2.822000	-0.434100	0.874600
C	-2.739100	1.003800	1.007600
H	-2.645700	1.530800	1.952700
C	-2.708600	1.641500	-0.269900
C	-2.778100	0.584500	-1.226900
H	-2.711900	0.732700	-2.302700
C	-3.100300	-1.970600	-1.429000
C	-2.926400	-1.332700	2.132000
C	-2.626300	3.133100	-0.574600
C	-1.673300	-2.219000	2.331200
H	-1.744000	-2.766600	3.286700
H	-1.540300	-2.952900	1.527000
H	-0.773900	-1.585100	2.343600

C	-4.208900	-2.199700	2.093900
H	-5.103400	-1.571600	1.951000
H	-4.188500	-2.950400	1.292400
H	-4.322400	-2.740100	3.048800
C	-3.034400	-0.448300	3.402400
H	-2.130400	0.163600	3.551000
H	-3.911300	0.218100	3.368200
H	-3.140900	-1.098700	4.285600
C	-2.389300	-3.235700	-0.906100
H	-1.308800	-3.054100	-0.798400
H	-2.783000	-3.573800	0.061400
H	-2.531500	-4.062600	-1.621800
C	-2.604100	-1.757200	-2.883800
H	-3.173100	-0.974600	-3.409100
H	-1.535100	-1.494800	-2.913100
H	-2.740300	-2.691800	-3.451600
C	-4.633200	-2.212100	-1.499900
H	-4.851600	-3.081000	-2.144200
H	-5.068300	-2.403900	-0.509100
H	-5.143600	-1.333300	-1.925900
C	-3.957800	3.569500	-1.238200
H	-3.937300	4.648200	-1.468300
H	-4.132900	3.023800	-2.179300
H	-4.813800	3.376800	-0.571300
C	-2.418700	3.948300	0.718800
H	-3.258500	3.815800	1.420400
H	-1.488800	3.654400	1.231800
H	-2.348300	5.021900	0.479800
C	-1.446700	3.407800	-1.536000
H	-1.358800	4.487100	-1.746300
H	-0.512100	3.039500	-1.085600
H	-1.575900	2.882000	-2.495700
H	-0.034900	-0.952500	0.164000
H	-0.024100	1.053800	0.925200
H	0.031200	0.729000	-1.132800

5.3 [Cp'FeH]$_2$ (Basis set: 6-311G(d,p))

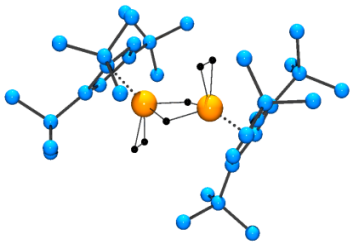


Fe	1.110600	-0.230900	-0.199800
C	2.225300	0.731300	1.113600
C	2.486200	1.202400	-0.262500
C	2.966800	0.063700	-1.003700
H	3.197800	0.054900	-2.060000
C	2.990700	-1.092000	-0.162900

C	2.576500	-0.677600	1.128800
H	2.443400	-1.343500	1.969500
C	2.385400	2.575700	-0.941200
C	1.749200	1.449500	2.391900
C	3.396900	-2.488700	-0.594900
Fe	-1.037400	0.253000	-0.018800
C	-2.616900	-0.844400	0.637100
C	-2.197000	-1.145300	-0.750600
C	-2.371300	0.089700	-1.495200
H	-2.098300	0.229700	-2.532100
C	-2.787500	1.144400	-0.634200
C	-2.946600	0.551700	0.658200
H	-3.197200	1.107300	1.552600
C	-1.725200	-2.416300	-1.471600
C	-2.789800	-1.724100	1.890600
C	-3.089600	2.580300	-1.013800
C	4.938800	-2.512300	-0.734900
H	5.416500	-2.268800	0.224300
H	5.275300	-3.510700	-1.052700
H	5.268800	-1.776700	-1.481400
C	2.962200	-3.539200	0.446300
H	3.442100	-3.353200	1.416900
H	1.873500	-3.520400	0.585100
H	3.253400	-4.543000	0.106300
C	2.751700	-2.832600	-1.954900
H	1.659300	-2.812000	-1.874700
H	3.052300	-2.114800	-2.729700
H	3.062800	-3.837400	-2.276400
C	3.707000	3.344000	-0.685900
H	4.556800	2.767200	-1.076800
H	3.678300	4.315700	-1.201500
H	3.878400	3.520400	0.381500
C	2.230200	2.401600	-2.475300
H	3.127300	1.961600	-2.929200
H	1.366200	1.762300	-2.698100
H	2.075700	3.387600	-2.934700
C	1.172500	3.412400	-0.494000
H	0.261700	2.814500	-0.624400
H	1.232700	3.739300	0.546300
H	1.097400	4.311200	-1.121900
C	2.632800	2.685800	2.683600
H	3.692500	2.394800	2.704600
H	2.513900	3.477200	1.940000
H	2.368600	3.102500	3.666700
C	1.899500	0.509000	3.614400
H	1.266000	-0.380600	3.504800
H	2.942000	0.188700	3.745500
H	1.582000	1.044300	4.520000
C	0.251600	1.831600	2.334100
H	-0.016200	2.355900	1.415200
H	-0.356900	0.918500	2.386300
H	-0.014600	2.473800	3.187600
C	-2.335900	2.978000	-2.299900
H	-1.253900	2.854400	-2.168500

H	-2.656100	2.360800	-3.150700
H	-2.545100	4.029100	-2.544100
C	-4.614600	2.700100	-1.257800
H	-5.172200	2.432200	-0.349400
H	-4.876200	3.731300	-1.539700
H	-4.927400	2.024600	-2.066200
C	-2.681400	3.537500	0.126300
H	-3.223800	3.304500	1.052600
H	-1.605500	3.462300	0.326200
H	-2.913300	4.575100	-0.153500
C	-0.860900	-2.015900	-2.695700
H	-1.456100	-1.527500	-3.477200
H	-0.068900	-1.324300	-2.373500
H	-0.402400	-2.911900	-3.134200
C	-2.958500	-3.196400	-1.988400
H	-3.547700	-2.560700	-2.664400
H	-2.633200	-4.088100	-2.544900
H	-3.610800	-3.516800	-1.168400
C	-0.828900	-3.318400	-0.603400
H	-0.004100	-2.715800	-0.196900
H	-1.362800	-3.780700	0.229400
H	-0.409600	-4.124700	-1.221000
C	-1.452000	-2.154200	2.538800
H	-0.778900	-2.650700	1.840400
H	-0.928000	-1.268700	2.920400
H	-1.656800	-2.830400	3.383200
C	-3.558600	-0.939800	2.986700
H	-2.979600	-0.074500	3.336200
H	-4.531700	-0.589300	2.617300
H	-3.727500	-1.601000	3.847800
C	-3.662600	-2.956900	1.552500
H	-4.609300	-2.636900	1.095000
H	-3.169000	-3.646500	0.863700
H	-3.891800	-3.508100	2.476200
H	-0.035800	-0.714100	0.823900
H	0.096400	0.644900	-1.128200

5.4 [Cp'FeH(H)$_2$]$_2$ (Basis set: 6-311G(d,p))

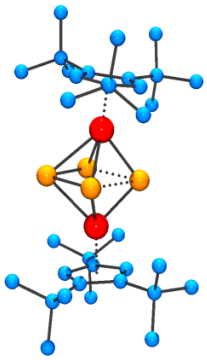


Fe	-1.042500	0.052500	0.102100
C	-2.831100	-1.002300	0.085900
C	-3.064100	0.426600	-0.157900
C	-2.527500	1.122400	0.976800
H	-2.496700	2.198600	1.081100

C	-1.965000	0.211000	1.925200
C	-2.164600	-1.084900	1.354200
H	-1.803600	-2.001900	1.799600
C	-3.831200	1.206100	-1.236900
C	-3.216600	-2.273100	-0.694400
C	-1.556800	0.522700	3.350100
Fe	1.327600	0.389800	0.305200
C	2.460700	-0.749100	-0.990300
C	3.292000	-0.215100	0.085900
C	3.180600	1.222400	0.004900
H	3.633200	1.921500	0.695100
C	2.281600	1.596900	-1.027600
C	1.857700	0.379400	-1.652400
H	1.165200	0.324900	-2.478300
C	4.265600	-0.847700	1.091000
C	2.216000	-2.182400	-1.505100
C	1.895800	3.010300	-1.420800
C	-2.850800	0.501500	4.206600
H	-3.334200	-0.483800	4.147500
H	-2.613100	0.715000	5.259900
H	-3.563200	1.257400	3.846900
C	-0.590200	-0.547000	3.898500
H	-1.076900	-1.532100	3.926200
H	0.304900	-0.627800	3.273100
H	-0.289900	-0.288900	4.924100
C	-0.922600	1.924700	3.455500
H	-0.036400	2.008600	2.817200
H	-1.639800	2.697700	3.145600
H	-0.634800	2.127500	4.497100
C	-5.331800	1.214400	-0.841300
H	-5.453600	1.673100	0.149700
H	-5.906800	1.803900	-1.571100
H	-5.751800	0.204200	-0.800600
C	-3.362900	2.684800	-1.277300
H	-3.614600	3.218200	-0.352100
H	-2.280500	2.750100	-1.438000
H	-3.873000	3.198800	-2.103500
C	-3.665700	0.670000	-2.672300
H	-2.603000	0.645700	-2.949800
H	-4.085700	-0.329000	-2.808500
H	-4.186400	1.343300	-3.368200
C	-4.743300	-2.304400	-0.948700
H	-5.289000	-2.158900	-0.006000
H	-5.068200	-1.535500	-1.653400
H	-5.024600	-3.282400	-1.365600
C	-2.895200	-3.534300	0.150200
H	-1.819100	-3.612300	0.354200
H	-3.438200	-3.523900	1.105000
H	-3.199500	-4.427300	-0.412800
C	-2.436100	-2.448400	-2.019100
H	-2.478600	-1.568400	-2.662500
H	-1.382400	-2.650400	-1.795900
H	-2.841300	-3.307700	-2.574900
C	1.709000	3.889400	-0.166200

H	0.898500	3.489100	0.455300
H	2.625400	3.921200	0.439100
H	1.462000	4.918300	-0.465900
C	3.036600	3.588300	-2.294200
H	3.189600	2.967700	-3.188300
H	2.785900	4.610100	-2.615700
H	3.978700	3.618900	-1.729100
C	0.581300	3.003100	-2.224500
H	0.702600	2.470800	-3.178500
H	-0.199300	2.499700	-1.640800
H	0.267400	4.033200	-2.443800
C	4.457500	0.079700	2.320900
H	4.932600	1.030800	2.049600
H	3.495400	0.289800	2.804800
H	5.113800	-0.420800	3.046100
C	5.649200	-0.985400	0.403200
H	6.003500	0.002400	0.077100
H	6.380600	-1.400800	1.112700
H	5.605500	-1.637400	-0.475600
C	3.811800	-2.206300	1.659200
H	2.816800	-2.112300	2.114000
H	3.776500	-2.994200	0.904300
H	4.521600	-2.525700	2.436000
C	1.376300	-3.060000	-0.545200
H	1.796900	-3.125100	0.458900
H	0.373000	-2.630100	-0.450500
H	1.297900	-4.075700	-0.962200
C	1.423200	-2.138200	-2.837100
H	0.428700	-1.699700	-2.692800
H	1.958100	-1.560000	-3.602400
H	1.288900	-3.164600	-3.204700
C	3.567600	-2.861500	-1.840600
H	4.149100	-2.230100	-2.527000
H	4.177900	-3.053600	-0.955600
H	3.376800	-3.825400	-2.334700
H	1.482300	0.163000	1.845000
H	-0.017900	1.315300	0.223500
H	-0.693300	-0.540900	-1.311500
H	1.342500	1.039600	1.726300
H	-0.940900	0.293800	-1.449600
H	0.251000	-0.805600	0.568700

*5.5 [Cp'Fe]$_2$(μ-P$_4$) (**4**) (Basis set: 6-311G(d,p))*

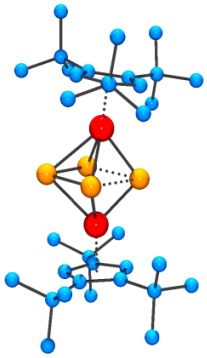


C	3.473900	-0.509900	-0.535000
C	3.339300	-0.272700	0.909900
C	3.089500	1.140500	1.067700
H	2.894300	1.633700	2.009900
C	3.076500	1.792800	-0.203800
C	3.319900	0.778300	-1.163800
H	3.304700	0.942300	-2.233000
C	-3.339100	0.273000	0.910100
C	-3.473700	0.510100	-0.534800
C	-3.320200	-0.778100	-1.163500
H	-3.305100	-0.942100	-2.232700
C	-3.077000	-1.792700	-0.203400
C	-3.089900	-1.140300	1.068100
H	-2.894900	-1.633500	2.010300
C	3.954300	-1.698500	-1.383400
C	5.497600	-1.569000	-1.498700
H	5.892600	-2.378700	-2.130300
H	5.982100	-1.624200	-0.516600
H	5.764000	-0.606300	-1.956400
C	3.599300	-3.104700	-0.861300
H	2.511300	-3.235800	-0.811800
H	4.025800	-3.319600	0.120600
H	4.001100	-3.847200	-1.565700
C	3.367800	-1.621000	-2.817700
H	2.271700	-1.616600	-2.795000
H	3.703100	-2.499600	-3.386000
H	3.710000	-0.731600	-3.360700
C	3.529000	-1.185400	2.131200
C	4.989400	-1.708200	2.141200
H	5.690400	-0.862800	2.098400
H	5.208000	-2.371800	1.300800
H	5.171600	-2.264000	3.072400
C	3.347900	-0.375900	3.440100
H	2.340500	0.056800	3.492400
H	4.089400	0.430500	3.521600
H	3.478400	-1.051600	4.296500
C	2.516300	-2.354800	2.215100
H	2.365500	-2.868300	1.267200
H	1.540400	-1.972600	2.544800

H	2.860400	-3.084700	2.963000
C	3.009500	3.286300	-0.457800
C	4.476600	3.793500	-0.456100
H	4.497600	4.879200	-0.631300
H	5.057800	3.298300	-1.246600
H	4.957800	3.584700	0.509800
C	2.373500	3.600300	-1.827200
H	1.331300	3.260900	-1.860100
H	2.927400	3.114800	-2.642200
H	2.393500	4.685300	-2.002400
C	2.231600	4.017400	0.655300
H	1.191400	3.673000	0.696700
H	2.235400	5.098400	0.456600
H	2.698600	3.851500	1.635900
C	-3.528400	1.186000	2.131000
C	-2.515400	2.355300	2.214300
H	-2.363500	2.867200	1.265800
H	-1.540000	1.973200	2.545500
H	-2.860000	3.086400	2.960800
C	-4.988700	1.709200	2.140900
H	-5.689900	0.864000	2.098600
H	-5.207200	2.372500	1.300200
H	-5.170700	2.265600	3.071900
C	-3.347500	0.377000	3.440300
H	-2.340400	-0.056500	3.492300
H	-4.089600	-0.428900	3.522300
H	-3.477100	1.053100	4.296400
C	-3.953700	1.698800	-1.383400
C	-3.367100	1.621300	-2.817600
H	-2.271000	1.617000	-2.794800
H	-3.702500	2.499700	-3.386100
H	-3.709200	0.731800	-3.360600
C	-5.497000	1.569600	-1.498700
H	-5.891800	2.379200	-2.130400
H	-5.981500	1.625000	-0.516600
H	-5.763600	0.606800	-1.956300
C	-3.598600	3.105000	-0.861200
H	-4.000900	3.847500	-1.565400
H	-2.510600	3.236300	-0.812400
H	-4.024600	3.319800	0.120800
C	-3.010500	-3.286200	-0.457500
C	-2.233400	-4.017500	0.656000
H	-2.700900	-3.851700	1.636400
H	-1.193100	-3.673400	0.698100
H	-2.237200	-5.098500	0.457100
C	-4.477700	-3.792900	-0.456600
H	-5.058400	-3.297600	-1.247300
H	-4.959300	-3.583900	0.509100
H	-4.499000	-4.878600	-0.631700
C	-2.373900	-3.600400	-1.826500
H	-1.331400	-3.261600	-1.858800
H	-2.926900	-3.114400	-2.641700
H	-2.394400	-4.685300	-2.001900
P	-0.287700	1.544700	-0.379700

P	-0.000300	-0.001900	-1.899800
P	0.287900	-1.545900	-0.377100
P	-0.000100	0.000800	1.394300
Fe	1.644000	0.279600	-0.058700
Fe	-1.644000	-0.280300	-0.058300

*5.5 [Cp'Fe]$_2$(μ-P$_4$) (**4**) (Basis set: TZVP)*

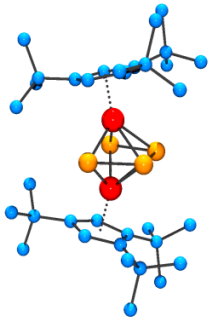


C	-3.520700	0.435800	-0.610000
C	-3.385000	0.360900	0.848200
C	-3.108400	-1.018100	1.158300
H	-2.913600	-1.400500	2.148400
C	-3.099100	-1.809700	-0.027100
C	-3.345600	-0.912800	-1.093900
H	-3.344900	-1.199400	-2.135100
C	-4.017800	1.517600	-1.580300
C	-5.561200	1.382600	-1.663900
H	-5.957400	2.112800	-2.382800
H	-6.036700	1.556100	-0.693300
H	-5.835200	0.376000	-2.003900
C	-3.653300	2.969600	-1.225400
H	-2.565700	3.095500	-1.174400
H	-4.090500	3.303200	-0.283200
H	-4.037500	3.627800	-2.016300
C	-3.457800	1.276500	-3.005300
H	-2.362700	1.284500	-3.006000
H	-3.814200	2.077700	-3.665400
H	-3.801400	0.327500	-3.430700
C	-3.596300	1.389600	1.970300
C	-5.054000	1.909900	1.909500
H	-5.758000	1.067900	1.936300
H	-5.255100	2.492200	1.009000
H	-5.247100	2.551300	2.779900
C	-3.437400	0.716200	3.355600
H	-2.429400	0.301500	3.476600
H	-4.172900	-0.085200	3.500200
H	-3.595000	1.471800	4.135600
C	-2.596300	2.567600	1.960400
H	-2.489300	3.034700	0.984600
H	-1.606800	2.213400	2.274300

H	-2.926600	3.329100	2.681000
C	-3.033400	-3.321200	-0.095100
C	-4.489000	-3.828500	0.080800
H	-4.509200	-4.926500	0.043100
H	-5.133300	-3.438100	-0.717600
H	-4.897700	-3.503800	1.046500
C	-2.500000	-3.808900	-1.454500
H	-1.471300	-3.469700	-1.617400
H	-3.124600	-3.442400	-2.278400
H	-2.515300	-4.906300	-1.480500
C	-2.170900	-3.906200	1.038900
H	-1.130600	-3.575400	0.949900
H	-2.194800	-5.002800	0.989100
H	-2.552900	-3.603500	2.022000
C	3.386500	-0.360300	0.847500
C	3.521500	-0.435200	-0.610700
C	3.345700	0.913300	-1.094700
H	3.343900	1.199800	-2.136100
C	3.099700	1.810300	-0.027800
C	3.109700	1.018500	1.157600
H	2.915500	1.401100	2.147700
C	3.597400	-1.389000	1.969900
C	2.595600	-2.565400	1.960100
H	2.480800	-3.029000	0.981900
H	1.607800	-2.210500	2.282500
H	2.930800	-3.329500	2.675600
C	5.054500	-1.912000	1.910600
H	5.760800	-1.071300	1.935700
H	5.254200	-2.496400	1.011100
H	5.246600	-2.552600	2.782400
C	3.437800	-0.715800	3.354900
H	2.429900	-0.300300	3.475200
H	4.173800	0.085000	3.500100
H	3.594300	-1.471800	4.134800
C	4.017600	-1.517700	-1.580400
C	3.460800	-1.274000	-3.006000
H	2.365700	-1.277600	-3.008700
H	3.815100	-2.076200	-3.665700
H	3.809000	-0.326100	-3.430300
C	5.561800	-1.387600	-1.661600
H	5.957500	-2.120700	-2.378500
H	6.034600	-1.560700	-0.689400
H	5.839400	-0.382100	-2.003400
C	3.647600	-2.968800	-1.225800
H	4.026900	-3.628100	-2.018300
H	2.559700	-3.090600	-1.170700
H	4.087200	-3.304800	-0.285300
C	3.032500	3.321800	-0.095300
C	2.171000	3.905600	1.040400
H	2.557800	3.606300	2.022800
H	1.131600	3.569900	0.955700
H	2.189600	5.002300	0.988500
C	4.487800	3.830400	0.078000
H	5.127700	3.452700	-0.729200

H	4.903600	3.494500	1.035900
H	4.505100	4.928100	0.054600
C	2.496900	3.809500	-1.453800
H	1.467400	3.470900	-1.615000
H	3.120200	3.442500	-2.279100
H	2.512800	4.907200	-1.479700
P	0.279000	-1.557400	-0.422800
P	0.000700	-0.005000	-1.943200
P	-0.278500	1.555600	-0.430300
P	0.000000	0.003800	1.386100
Fe	-1.633500	-0.272900	-0.073100
Fe	1.634000	0.273500	-0.073300

*5.6 [{Cp'Fe}$_2$(μ-η^4:η^4-P$_4$)] (**5**) (Basis set: 6-311G(d,p))*

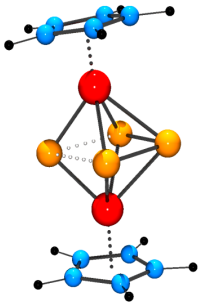


Fe	-1.284200	0.058100	0.009000
Fe	1.284100	0.058200	-0.009500
P	0.015000	0.556300	1.785300
P	-0.009800	-1.471300	1.193700
P	-0.015100	0.559300	-1.784900
P	0.009600	-1.469300	-1.196900
C	-3.185600	-0.570900	0.713100
C	-2.869900	0.761300	1.159000
C	-2.674700	1.641600	0.058400
C	-3.680100	-1.600500	1.740900
C	-3.458500	-3.074400	1.356900
C	-5.197000	-1.325300	1.946500
C	-3.006200	-1.400400	3.124400
C	-2.609600	3.153100	0.095900
C	-2.173900	3.653800	1.486800
C	-4.042500	3.674800	-0.194000
H	-2.806500	1.063200	2.193700
H	-3.787400	-3.711300	2.190300
H	-2.392000	-3.263500	1.179300
H	-4.025000	-3.371400	0.471100
H	-5.769000	-1.439800	1.020700
H	-5.347100	-0.300800	2.314400
H	-5.596700	-2.025100	2.695100
H	-3.413000	-2.149100	3.818100
H	-3.217000	-0.412400	3.550700
H	-1.921200	-1.535900	3.068500

H	-1.217300	3.208900	1.782400
H	-2.922700	3.391600	2.247200
H	-2.069300	4.747400	1.473600
H	-4.055300	4.774400	-0.160500
H	-4.752000	3.293300	0.553700
H	-4.380100	3.351600	-1.188700
C	-3.184300	-0.524500	-0.743900
C	-2.860600	0.834900	-1.100200
C	-3.663500	-1.518500	-1.822600
C	-2.887200	-2.858500	-1.916900
H	-3.534500	-3.622600	-2.372700
H	-2.007100	-2.740900	-2.559100
H	-2.532200	-3.223400	-0.954800
C	-5.171800	-1.794400	-1.579300
H	-5.338000	-2.429400	-0.705100
H	-5.721400	-0.853500	-1.436700
H	-5.588400	-2.313600	-2.454600
C	-3.561600	-0.870200	-3.228000
H	-3.878300	-1.607300	-3.978200
H	-4.212200	0.010600	-3.318300
H	-2.527100	-0.576300	-3.450800
C	-1.655200	3.689500	-0.985800
H	-0.645000	3.306300	-0.823700
H	-1.978800	3.377100	-1.987700
H	-1.631100	4.788400	-0.957500
H	-2.796200	1.206700	-2.111700
C	3.184100	-0.524600	0.744000
C	2.860300	0.834800	1.100300
C	2.674700	1.641600	-0.058100
C	3.663100	-1.518600	1.822800
C	5.171400	-1.794600	1.580000
C	3.560600	-0.870500	3.228100
C	2.886600	-2.858700	1.916500
C	2.609600	3.153100	-0.095200
C	1.654400	3.688900	0.986300
C	4.042200	3.674900	0.195800
H	2.795700	1.206500	2.111900
H	5.587700	-2.313600	2.455500
H	5.721200	-0.853800	1.437400
H	5.337800	-2.429700	0.706000
H	3.877100	-1.607700	3.978400
H	2.526000	-0.576800	3.450700
H	4.211000	0.010400	3.318800
H	2.531000	-3.222800	0.954300
H	2.006900	-2.741300	2.559300
H	3.534100	-3.623200	2.371500
H	1.977800	3.376300	1.988300
H	0.644500	3.305200	0.823700
H	1.629800	4.787700	0.958300
H	4.054800	4.774500	0.162800
H	4.752200	3.294000	-0.551800
H	4.379300	3.351300	1.190500
C	3.185800	-0.570800	-0.713000
C	2.870200	0.761400	-1.158900

C	3.680800	-1.600200	-1.740700
C	5.197800	-1.325000	-1.945400
H	5.597900	-2.024700	-2.694000
H	5.348000	-0.300500	-2.313200
H	5.769400	-1.439600	-1.019400
C	3.007700	-1.399900	-3.124500
H	3.414800	-2.148400	-3.818200
H	1.922700	-1.535300	-3.069200
H	3.218900	-0.411700	-3.550500
C	3.458800	-3.074200	-1.357000
H	4.024600	-3.371300	-0.470700
H	2.392200	-3.263300	-1.180300
H	3.788500	-3.710900	-2.190200
C	2.174500	3.654400	-1.486000
H	2.923300	3.392000	-2.246300
H	1.217700	3.210400	-1.782000
H	2.070700	4.748200	-1.472500
H	2.807000	1.063400	-2.193500

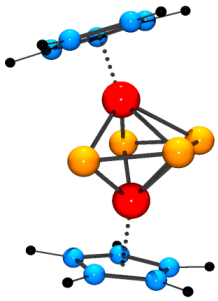
*5.7 [Cp'Fe]$_2$(μ-P$_4$) (**4a**) (Basis set: 6-311G(d,p))*



P	0.000000	0.000000	1.781600
P	1.595100	0.000000	0.278800
P	-1.595100	0.000000	0.278800
P	0.000000	0.000000	-1.524200
C	0.000000	3.376900	1.085600
C	-1.158700	3.305000	0.254000
C	1.158700	3.305000	0.254000
C	-0.718300	3.208900	-1.111500
C	0.718300	3.208900	-1.111500
C	0.000000	-3.376900	1.085600
C	1.158700	-3.305000	0.254000
C	-1.158700	-3.305000	0.254000
C	0.718300	-3.208900	-1.111500
C	-0.718300	-3.208900	-1.111500
H	-2.187300	3.287900	0.596000
H	2.187300	3.287900	0.596000
H	-2.187300	-3.287900	0.596000
H	-1.356800	3.124400	-1.984100
H	2.187300	-3.287900	0.596000
H	1.356800	-3.124400	-1.984100

H	0.000000	3.394900	2.170400
H	1.356800	3.124400	-1.984100
H	0.000000	-3.394900	2.170400
H	-1.356800	-3.124400	-1.984100
Fe	0.000000	1.635400	-0.066600
Fe	0.000000	-1.635400	-0.066600

*5.8 [{CpFe}$_2$(μ-η^4:η^4-P$_4$)] (**5a**) (Basis set: 6-311G(d,p))*



P	1.239800	0.000000	1.495200
P	1.791300	0.000000	-0.542000
P	-1.239800	0.000000	1.495200
P	-1.791300	0.000000	-0.542000
Fe	0.000000	1.256900	-0.019300
Fe	0.000000	-1.256900	-0.019300
C	0.712300	3.124500	0.569800
C	1.152200	2.829000	-0.761800
C	-0.712300	3.124500	0.569800
C	0.000000	2.627000	-1.589400
C	-1.152200	2.829000	-0.761800
H	-1.348400	3.283600	1.432100
H	0.000000	2.392800	-2.647200
H	1.348400	3.283600	1.432100
H	2.184000	2.776500	-1.087000
H	-2.184000	2.776500	-1.087000
C	0.712300	-3.124500	0.569800
C	1.152200	-2.829000	-0.761800
C	-0.712300	-3.124500	0.569800
C	0.000000	-2.627000	-1.589400
C	-1.152200	-2.829000	-0.761800
H	1.348400	-3.283600	1.432100
H	-1.348400	-3.283600	1.432100
H	0.000000	-2.392800	-2.647200
H	2.184000	-2.776500	-1.087000
H	-2.184000	-2.776500	-1.087000

6. References

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