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Supporting Information for

Triphos-Fe Dinitrogen and Dinitrogen-Hydride Complexes: Relevance to Catalytic N_2 Reductions.

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1. Experimental procedure

1.1. General considerations

All manipulations were performed using standard Schlenk or glovebox techniques under a nitrogen atmosphere. THF was distilled from sodium and other solvents were from a MB SPS-800 solvent purification system then degassed under vacuum at –100 °C. All solvents were tested with a standard purple solution of sodium benzophenone ketyl in THF in order to confirm moisture removal. Solution ^{1}H (300 MHz), $^{13}C\{^{1}H\}$ (75 MHz) and ^{31}P (121 MHz) spectra were recorded on a Bruker 300 MHz spectrometer. Chemical shifts (δ) are expressed with a positive sign, in parts per million. The following abbreviations are used: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; p, pseudo. Solution magnetic susceptibilities were determined by the Evans method using a capillary of the deuterated solvent[1,2]. Its chemical shift was then compared to the one of the paramagnetic containing solution allowing the determination. $[FeCl_2(THF)_{1.5}]$[3], $P^{Ph}P_2^{Cy}$,[4] $[(P^{Ph}P_2^{Cy})FeCl_2]$,[5] KC_8[6] and $HBAr^F{}_4$[7] were synthesized following literature procedures. All other chemicals were purchased from commercial vendors and used without further purification unless otherwise stated.

1.2. Synthesis of $[(P^{tBu}P_2^{Cy})FeCl_2]$ (2b):

A Schlenk flask was charged with 470 mg (2 mmol) of $FeCl_2(THF)_{1.5}$ and 10 mL of THF. 9.5 mL (2 mmol) of a solution of **1b** in THF were added to the suspension. The reaction mixture was stirred for 1 h after complete dissolution of the Fe^{II} species to give a light yellowish solution. The desired complex **2b** crystallized at – 30 °C. The crystals were washed with pentane and the volatiles were removed *in vacuo*. **2b** (1.10 g) was stored as a white crystalline powder. Y = 83 %

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 114.4(bs), 100.8 (bs), 82.3 (bs), 32.3 (bs), 9.7 (bs), 7.9 (bs), 5.1 (bs), 2.3-0.7 (bs), – 3.5 (bs) ppm. **μ_{eff}** (Evans, THF-d_8, 298K) = 5.2 $\mu_{B.}$ **^{57}Fe Mössbauer**: δ = 0.730 $mms.^{-1}$, ΔE_Q = 2.869 $mm.s^{-1}$.

EA: for $C_{32}H_{61}FeCl_2P_3$, C_4H_8O Found (calc.): C, 57.02 (58.62); H, 9.03 (9.43)

The title complex is pure as proved by ^{57}Fe Mössbauer spectroscopy. Signals in the diamagnetic region of the ^{1}H spectrum correspond to H atoms least perturbed by the paramagnetic Fe center.

1.3. Synthesis of [($P^{Ph}P_2^{Cy}$)FeCl] (3a)

A Schlenk flask was charged with 686 mg (1 mmol) of **2a** and 10 mL of THF. 2.3 g of freshly prepared sodium amalgam (1 wt% in Na, 1 mmol) was then added to the reaction mixture. The solution was vigorously stirred for 15 h and became dark yellow. The remaining mercury was separated by cannula filtration. The solvent was removed *in vacuo* and the complex **3a** was then extracted from the salt with toluene (2 x 10 mL). **3a** (598 mg, 0.92 mmol) was then isolated as a yellowish powder after removal of all volatiles. Y = 92 %

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 109.5 (bs), 63.9 (bs) 26.0 (bs), 14.8 (bs), 11.8 (bs), 9.5 (bs), 6.9 (bs), 4.6 (bs), 2.6 (bs), 1.5 – 0.5 (m), 0.4 (bs), –0.4 (bs), –1.0 (bs), –8.7 (bs), –9.9 (bs), –17.2 (bs), –62.8 (bs), –72.0 (bs) ppm. **μ_{eff}** (Evans, THF-d_8, 298K) = 4.12 μ_B. **^{57}Fe Mössbauer**: δ = 0.697 mms.$^{-1}$, ΔE_Q = 1.586 mm.s^{-1}.

EA: for $C_{34}H_{57}FeClP_3$ Found (calc.): C, 56.39 (62.82); H, 8.75 (8.84)

The title complex is pure as proved by ^{57}Fe Mössbauer spectroscopy. Signals in the diamagnetic region of the ^{1}H spectrum correspond to H atoms least perturbed by the paramagnetic Fe center.

1.4. Synthesis of [($P^{tBu}P_2^{Cy}$)FeCl] (3b)

A Schlenk flask was charged with 666 mg (1 mmol) of **2b** and 10 mL of THF. 2.3 g of freshly prepared sodium amalgam (1 wt% in Na, 1 mmol) was then added to the reaction mixture. The solution was vigorously stirred for 15 h and became yellow. The remaining mercury was separated by cannula filtration. The solvent was removed *in vacuo* and the complex **3b** was then extracted from the salt with toluene (2 x 10 mL). **3b** (599 mg, 0.85 mmol) was then isolated as a yellow powder after removal of all volatiles. Y = 85 %.

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 90.8 (bs), 61.5 (bs), 26.6 (bs), 10.7 (bs), 8.8 (bs), 6.5 (bs), 3.3 (bs), 1.35 – -0.06 (m), -7.5 (bs), -9.6 (bs), -10.6 (bs), -66.0 (bs), -86.4 (bs) ppm. **μ_{eff}** (Evans, THF-d_8, 298K) = 4.1 μ_B.

EA: for $C_{32}H_{61}FeClP_3$ Found (calc.): C, 57.02 (61.00); H, 9.55 (9.76)

Signals in the diamagnetic region of the ^{1}H spectrum correspond to H atoms least perturbed by the paramagnetic Fe center.

1.5. Synthesis of [($P^{Ph}P_2^{Cy}$)Fe(N_2)$_2$] (4a)

A Schlenk flask was charged with 343 mg (0.5 mmol) of **2a** and 10 mL of THF, the solution was stirred until complete dissolution of the Fe^{II} species. Another Schlenk flask was charged with 150 mg (1.1 mmol) of KC_8 and 10 mL of THF. Both Schlenk were cooled down to −80 °C then the solution of Fe^{II} was added to the suspension of KC_8 by cannula transfer under vigorous stirring. The reaction mixture was stirred in the bath for 3 h until it reached room temperature. The reaction mixture was centrifuged, the orange solution was filtered and taken into a vial. The remaining solid was washed with 5 mL of THF and centrifuged again. The combined solution (25 mL) were titrated by ^{31}P NMR (*vs* PPh_3). The concentration of **4a** was found to be 0.018 M. The complex was used in solution for further reactions. This reaction was done on a smaller scale in THF-d_8 for further characterization. Y (NMR) = 90 %

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 7.76 – 7.61 (m, H_{Ar}), 7.49 – 7.39 (m, H_{Ar}), 7.37 – 7.11 (m, H_{Ar}), 2.31 – 1.48 (m, H_{alk}), 1.43 – 1.10 (m, H_{alk}), 1.00 – 0.81 (m, H_{alk}). **^{13}C{^{1}H} NMR** (75.5 MHz, THF-d_8, 298 K): δ = 141.8 (dt, J_{C-P} = 12.8 and 2.3 Hz, PC_{Ar}), 131.5 (d, J_{C-P} = 10.1 Hz, P*Ph*), 128.8 (d, J_{C-P} = 1.9 Hz, P*Ph*), 127.9 (d, J_{C-P} = 7.8 Hz, P*Ph*), 38.8 (pt, J_{C-P} = 8.7 Hz, PC_{Cy}), 34.7 (pdt, J_{C-P} = 28.8 and 13.2 Hz, P*Et*P), 33.8 (pt, J_{C-P} = 5.8 Hz, PC_{Cy}), 30.3 (s, P*Cy*), 28.7 (pt, J_{C-P} = 6.1 Hz, P*Cy*), 28.5 (pt, J_{C-P} = 2.8 Hz, P*Cy*), 28.2 (pt, J_{C-P} = 3Hz, P*Cy*), 28.0-27.7 (m, P*Cy*), 27.5 (s, P*Cy*), 27.3 (s, P*Cy*), 27.1 (s, P*Cy*), 20.6 (pdt, J_{C-P} = 19.8 and 12.1 Hz, P*Et*P) ppm. **^{31}P{^{1}H} NMR** (121.5 MHz, THF-d_8, 298 K): δ = 120.1 (t, J_{P-P} = 69.2 Hz, 1P), 102.4 (d, J_{P-P} = 69.2 Hz, 2P) ppm. **IR** (THF): 2047 and 1982 cm^{-1}

1.6. Synthesis of [($P^{tBu}P_2^{Cy}$)Fe(N_2)$_2$] (4b)

A Schlenk flask was charged with 333 mg (0.5 mmol) of **2b** and 10 mL of THF, the solution was stirred until complete dissolution of the Fe^{II} species. Another Schlenk flask was charged with 150 mg (1.1 mmol) of KC_8 and 10 mL of THF. Both Schlenk were cooled down to −80 °C then the solution of Fe^{II} was added to the suspension of KC_8 by cannula transfer under vigorous stirring. The reaction mixture was stirred in the bath for 3 h until it reached room temperature. The reaction mixture was centrifuged, the orange solution was filtered and taken into a vial. The remaining solid was washed with 5 mL of THF and centrifuged again. The combined solution (25 mL) were titrated by ^{31}P NMR (*vs* PPh_3). The concentration of **4b** was found to be 0.017 M. The complex was used in solution for further reactions. This reaction was done on a smaller scale in THF-d_8 for further characterization. Y (NMR) = 85 %.

The complex readily loses coordinated N_2 under vacuum. Solvent can be slowly evaporated by

bubbling N_2 into the solution of the complex. The resulting orange solid was extracted with pentane from which crystals suitable for diffraction were subsequently obtained.

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 2.22 – 1.46 (m), 1.39 – 0.75 (m), 0.96 (d, J_{H-P} = 11.6 Hz, PC(CH_3)$_3$) ppm. **^{13}C{^{1}H} NMR** (75.5 MHz, THF-d_8, 298 K): δ = 42.3 (pt, J_{C-P} = 8.7 Hz, PC_{Cy}), 38.0 (pt, J_{C-P} = 5.1 Hz, PC_{Cy}), 34.8 (d, J_{C-P} = 12.2 Hz, PC(CH_3)$_3$), 30.0 (d, J_{C-P} = 30.1 Hz, PCy), 29.3 (d, J_{C-P} = 23.3 Hz, PCy), 28.9 – 28.1 (m), 28.0 (d, J_{C-P} = 3.7 Hz, PC(CH$_3$)$_3$), 27.4 (d, J_{C-P} = 6.4 Hz, PCy), 23.5 (dt, J_{C-P} = 16.8 and 10.9 Hz, PEtP) ppm. **^{31}P{^{1}H} NMR** (121.5 MHz, THF-d_8, 298 K): δ = 150.5 (t, J_{P-P} = 48.0 Hz, 1P), 97.0 (d, J_{P-P} = 48.0 Hz, 2P) ppm. **IR** (THF): 2048 and 1981 cm^{-1}.

1.7. Synthesis of [($P^{Ph}P_2^{Cy}$)Fe(N_2)(H)$_2$] (6a)

A Schlenk flask was charged with 308 mg (0.45 mmol) of **2-Ph** and 10 mL of THF. 3 mL (1 mmol) of $LiEt_3BH$ in solution in THF was added at room temperature to the reaction mixture under stirring. The solution was stirred for 2 h and turned orange. Volatiles were removed *in vacuo* and the resulting solid was dissolved in 10 mL of pentane. The solution was reduced and put at – 30 °C for 15 h, giving the desired compound in crystalline form. The crystals were washed with cold pentane then dried and the supernatant was reduced and put to crystallization another time giving in total 230 mg of complex. Y = 79 %.

^{1}H NMR (300 MHz, THF-d_8, 298 K): δ = 7.68 (pt,J = 8.0 Hz, 2H, H_{Ar}), 7.33 (m, 3H, H_{Ar}), 2.37-1.02 (m, 52 H), -9.83 (tdd, J_{H-P} = 51.2 and 45.0 Hz, J_{H-H} = 13.7 Hz, 1H, Fe−H_{cisN2}), -20.94 (tdd, J_{H-P} = 54.9 and 37.7 Hz, J_{H-H} = 13.6 Hz, 1H, Fe−$H_{transN2}$) ppm. **^{13}C{^{1}H} NMR** (75.5 MHz, THF-d_8, 298 K): δ = 142.2 (d, J_{C-P} = 11.3 Hz, PC_{Ar}), 132.4 (d, J_{C-P} = 11.7 Hz, PPh), 129.4 (d, J_{C-P} = 1.7 Hz, PPh), 128.3 (d, J_{C-P} = 7.9 Hz, PPh), 39.4 (pt, J_{C-P} = 3.8 Hz, PC_{Cy}), 38.4 (ptd, J_{C-P} = 14.9 and 5.8 Hz, PC_{Cy}), 33.3 (pdt, J_{C-P} = 28.5 and 10.2 Hz, PEtP), 29.9 (s, PCy), 29.4 (s, PCy), 29.3 (d, J_{C-P} = 6.8 Hz, PCy), 28.3 (m, PCy), 27.9 (pt, J_{C-P} = 5.7 Hz, PCy), 27.4 (d, J_{C-P} = 14.1 Hz, PCy), 26.4 (pdt, J_{C-P} =22.6 and 11.5 Hz, PEtP) ppm. **^{31}P{^{1}H} NMR** (121.5 MHz, THF-d_8, 298 K): δ = 120.2 (t, J_{P-P} = 6.7 Hz, 1P), 111.1 (d, J_{P-P} = 6.7 Hz, 2P) ppm. **IR** (THF) : 2051 cm^{-1}. **^{57}Fe Mössbauer**: δ = 0.063 mms.$^{-1}$, ΔE_Q = 0.673 mm.s^{-1}.

EA: for $C_{34}H_{59}FeN_2P_3$ Found (calc.): C, 63.02 (63.35); H, 8.93 (9.23)

1.8. Standard procedure for NH_3 catalysis

Derived from ref [8]

A Schlenk flask was charged with 2.5 µmol of catalyst in 0.5 mL of Et_2O. This solution was put at

– 80 °C and cannula transfer to another Schlenk containing 75 mg (0,55 mmol) of KC_8 in 0.5 mL of Et_2O at – 195 °C. A third solution, containing 506 mg (0.5 mmol) of $HBAr^F_4$ in 1 mL of Et_2O at – 80 °C was then added to the Schlenk. The reaction mixture was allowed to thaw to – 80 °C and let stirring at this temperature for 1 h. The solution was then warmed up to room temperature and let stirring for 15 min. The volatiles (solvent + NH_3) were then vacuum transfer to another Schlenk containing an excess amount of sulfuric acid to form the NH_4^+ cation. This cation was then titrated using the indophenol method and a calibration curve done with a standard NH_4Cl solution in water.[9]

1.9. Standard procedure for $N(TMS)_3$ catalysis

Derived from ref [10]

A Schlenk flask was charged with 5 µmol of catalyst and 2 mL of THF. Then, 117 mg (3 mmol) of potassium and 0.38 mL (3 mmol) of TMSCl. The reaction was allowed to stir in the glovebox under dinitrogen for 48 h. The formation of $N(TMS)_3$ was monitored by ^{29}Si NMR spectroscopy (δ = 2.7 ppm). An excess amount of sulfuric acid was then added and solution was stirred at 50 °C for 15 h to ensure the full conversion of $N(TMS)_3$ to ammonium salts. The solution was then froze and an excess amount of KOH was added. The solution was warm up to room temperature and the volatiles (solvent + NH_3) were then vacuum transfer to another Schlenk containing an excess amount of sulfuric acid to form the NH_4^+ cation. This cation was then titrated using the indophenol method and a calibration curve done with a standard NH_4Cl solution in water.[9]

1.10. Elemental Analysis

Elemental analyses were done on the complexes prepared in this work. The samples for elemental analysis were prepared in a dry box, and weighed outside of the box under an Ar atmosphere, in order to limit as much as possible the oxidation/decomposition while weighing.

Despite using crystalline (and/or powdered) (PP2)FeCl Fe(I) or (PP2)FeCl2 Fe(II) complexes for the EA, more than ten attempts did not provide consistent and satisfactory results. Although the H content was almost always appropriate, the C content could vary by up to *ca* 6%. We suppose that the high sensitivity of the complexes to oxygen leads to such poor results.

We have not attempted EA for the dinitrogen complexes, because the complexes loose N_2 even in the solid state. The complex can therefore not be dried under vacuum to eliminate solvent.

The $(PP_2)Fe(N_2)(H)_2$ complex 6a being less sensitive to oxidation than the other complexes, and

the N_2 ligand more strongly bound to the Fe center, a satisfactory EA was obtained: $C_{34}H_{59}FeN_2P_3$ Found (calc.): C, 63.02 (63.35); H, 8.93 (9.23).

2. NMR Spectra:

2.1. Complex 2a

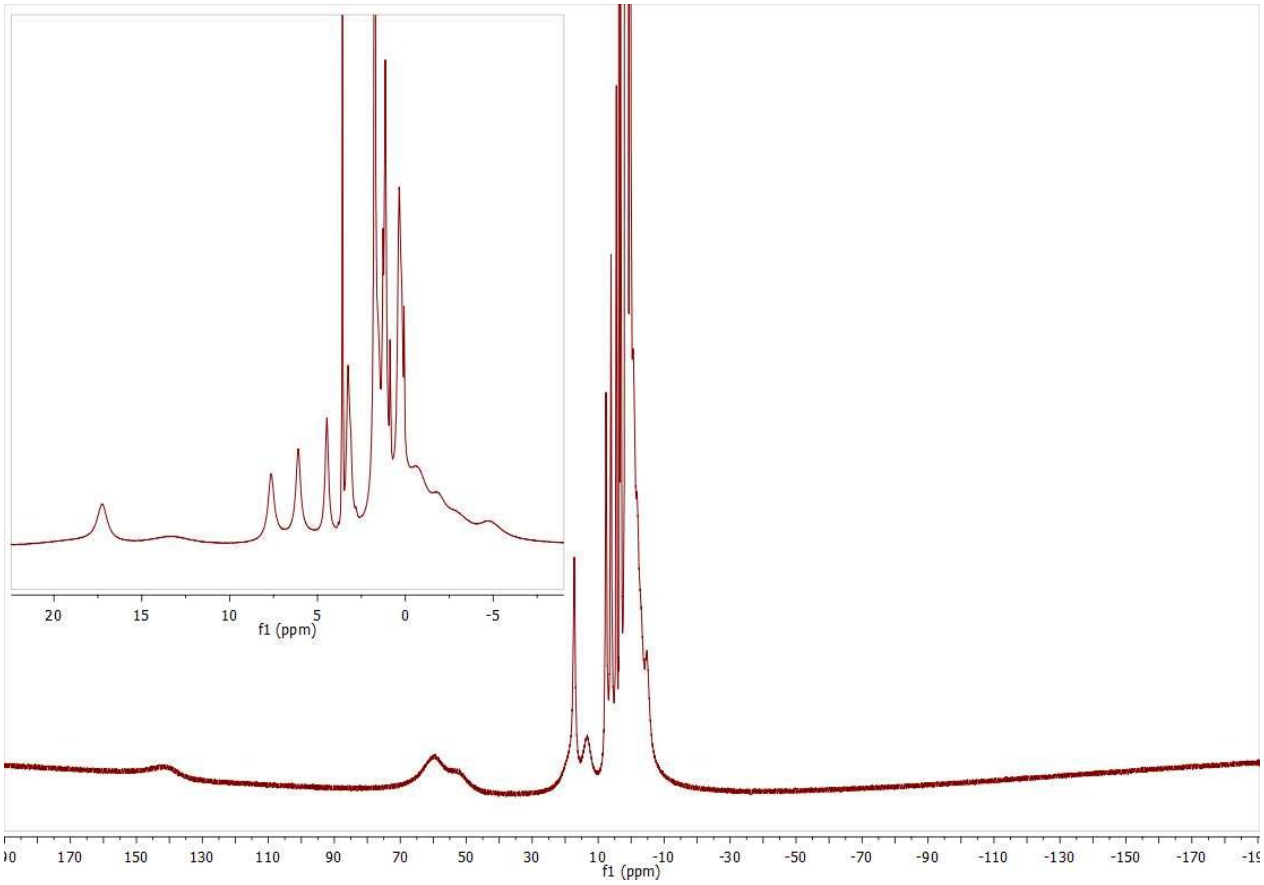


Figure S1. ^{1}H NMR spectrum of complex **2a**. (inset: diamagnetic region of the spectrum)

2.2. Complex 2b

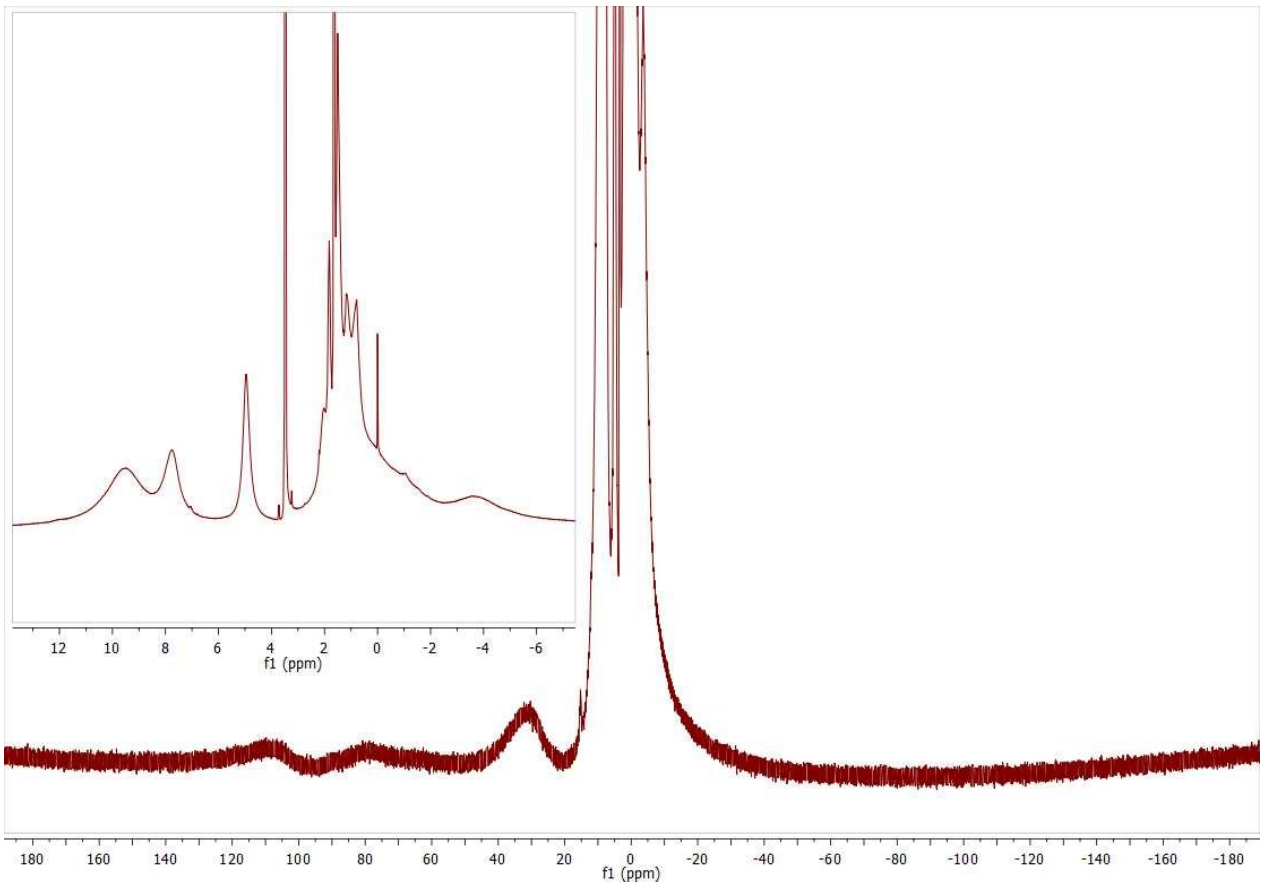


Figure S2. ^{1}H NMR spectrum of complex **2b**. (inset: diamagnetic region of the spectrum)

2.3. Complex 3a

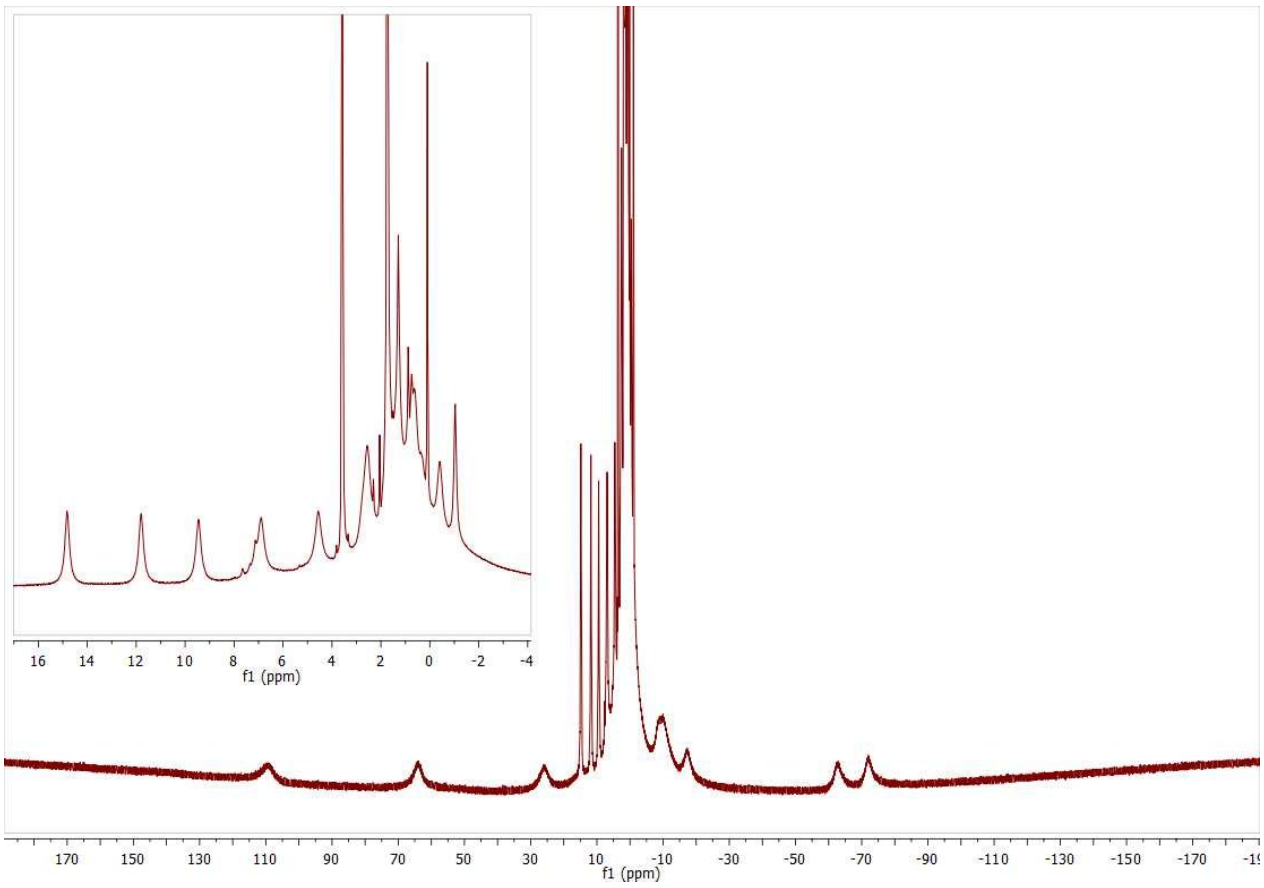


Figure S3. ^{1}H NMR spectrum of complex **3a**. (inset: diamagnetic region of the spectrum)

2.4. Complex 3b

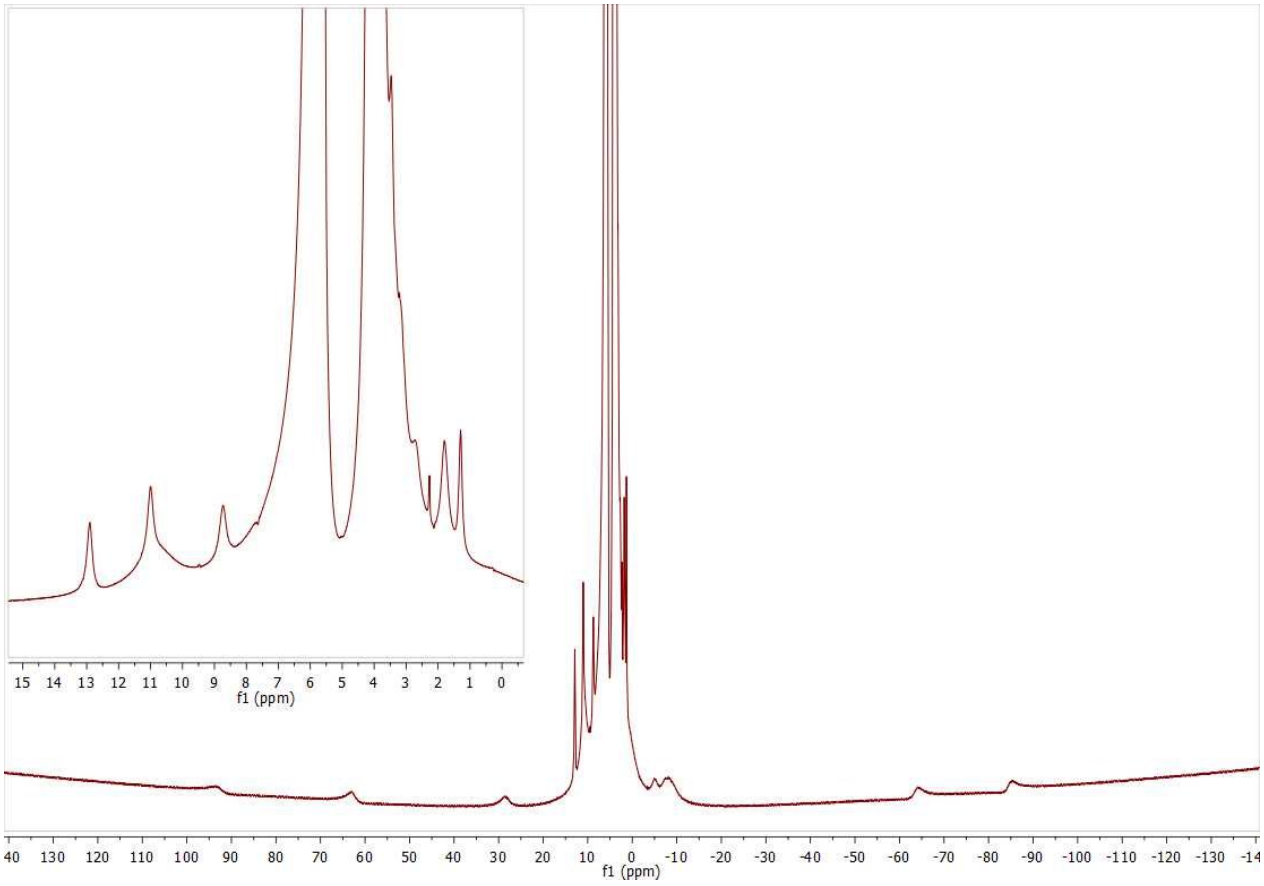


Figure S4. ^{1}H NMR spectrum of complex **3b**. (inset: diamagnetic region of the spectrum)

2.5. Complex 4a

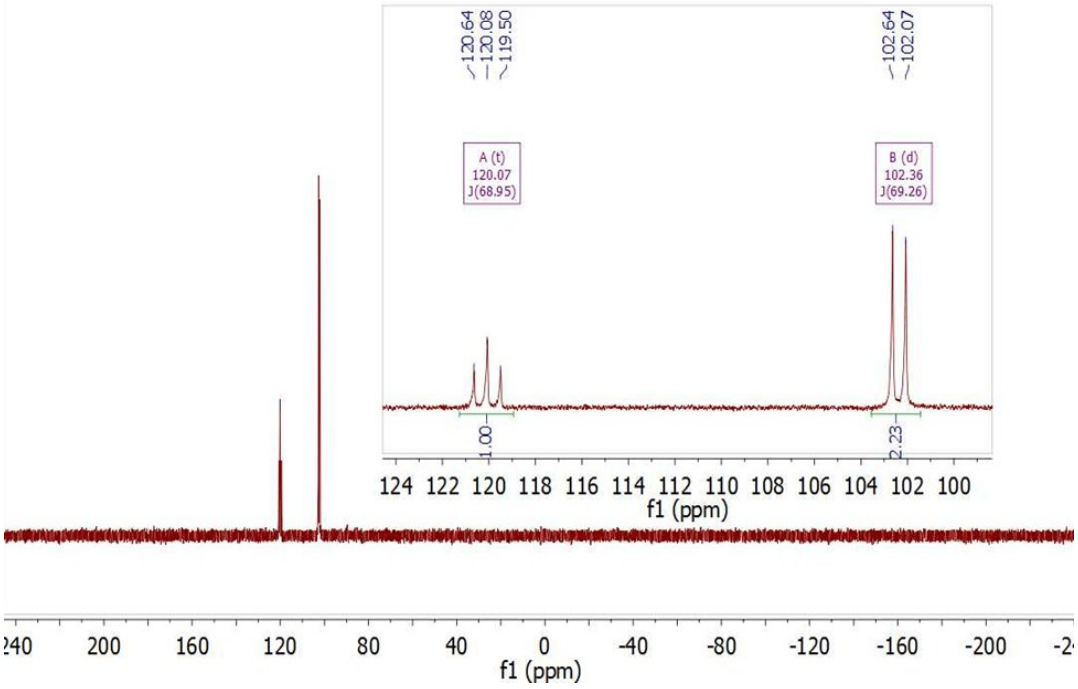


Figure S5. ^{31}P NMR spectrum of complex **4a**.

2.6. Complex 4b

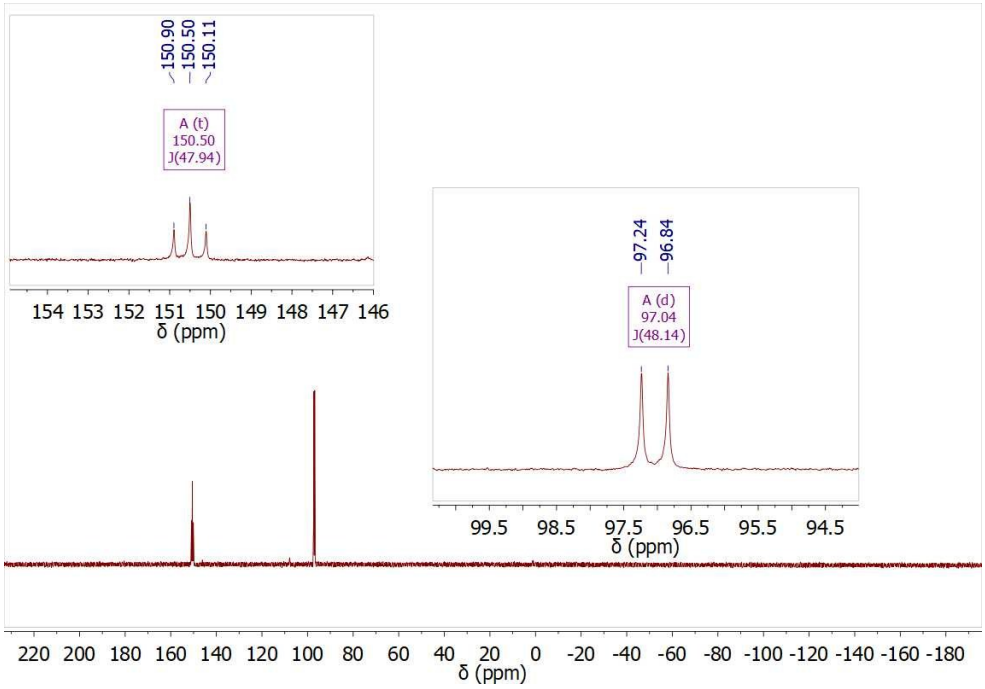


Figure S6. ^{31}P NMR spectrum of complex **4b**.

2.7. Complex 6a

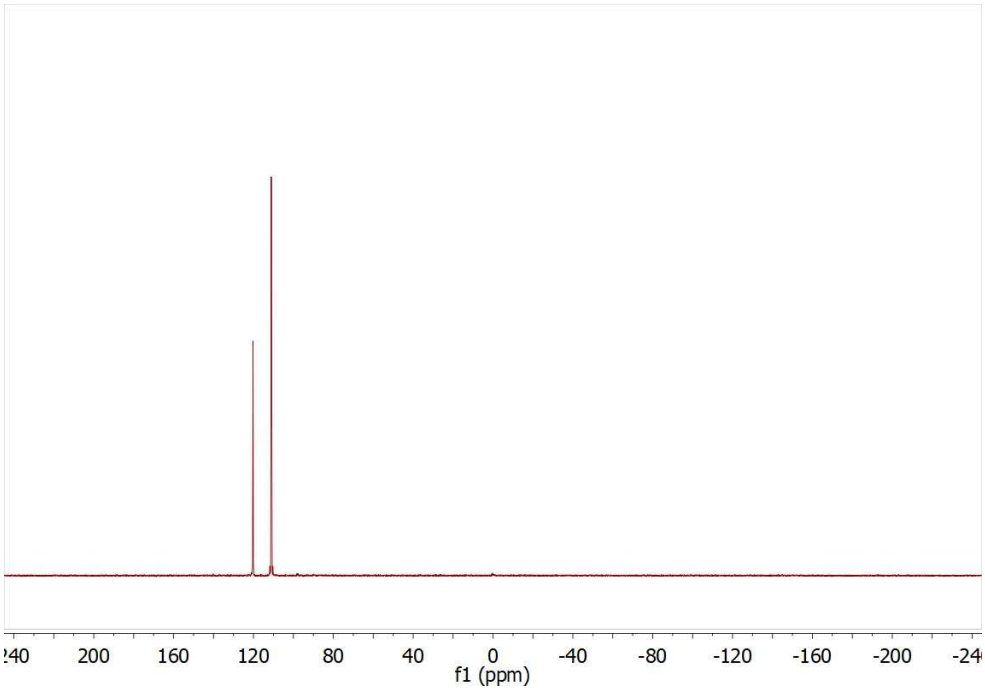


Figure S7. ^{31}P NMR spectrum of complex **6a**.

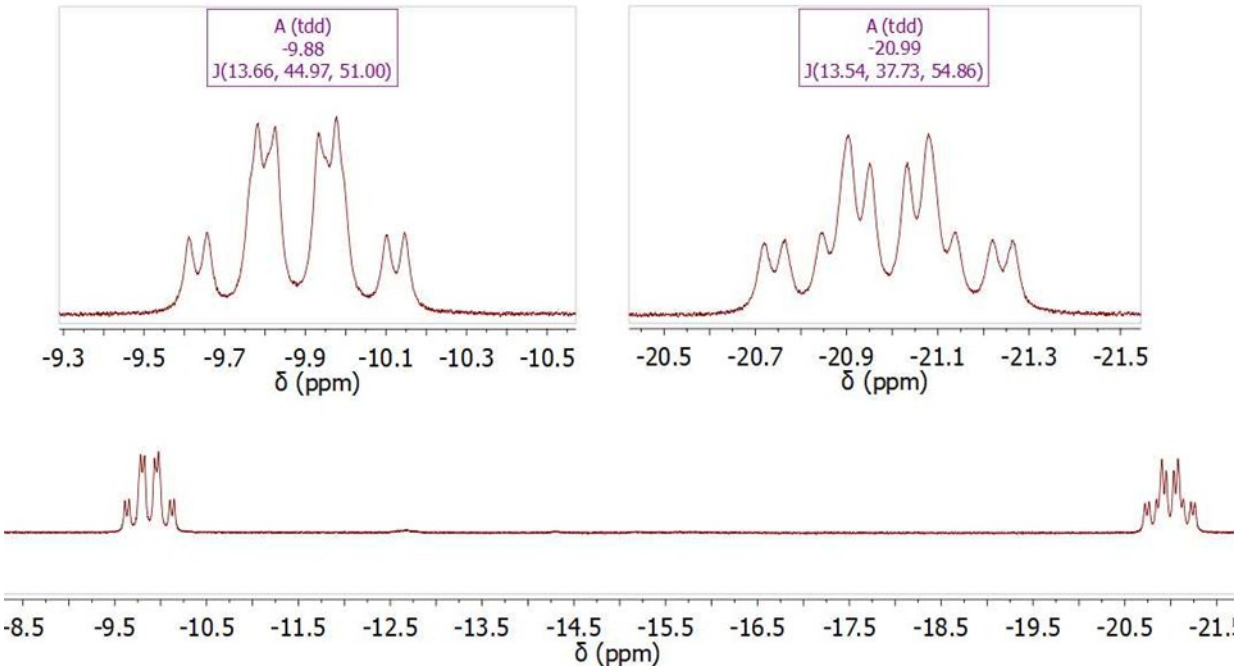


Figure S8. ^{1}H NMR spectrum (hydride region) of complex **6a**.

3. Mössbauer Spectra:

Spectra were collected on a constant-acceleration conventional spectrometer with a 1.85 GBq source of ^{57}Co (Rh matrix) at 80 K, using a MD306 Oxford cryostat. The thermal scanning was monitored by an Oxford ITC4 servo control device (0.1 K). The absorber was a sample of the desired complex (powder) containing 10 mg of iron, that was enclosed in a 20 mm diameter cylindrical plastic sample holder. Mössbauer's parameters and their standard deviations of statistical origin were obtained by least-squares fitting to Lorentzian lines using Recoil software.

3.1. Complex 2b

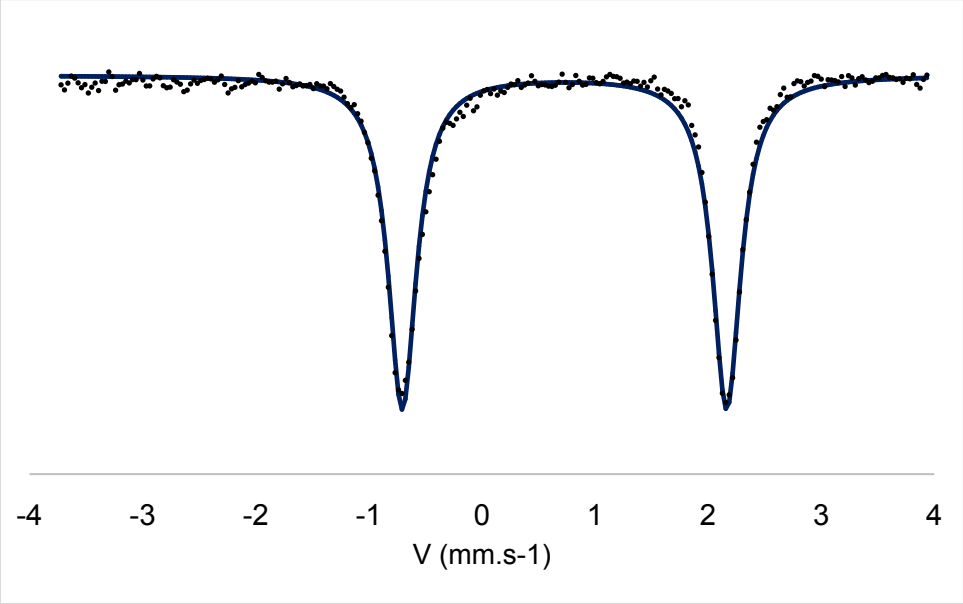


Figure S9. Mössbauer spectrum of complex **2b** (black dots: raw data, blue line, simulated curve), δ=0.730 mm.s^{-1} Δ=2.869 mm.s^{-1}.

3.2. Complex 3a

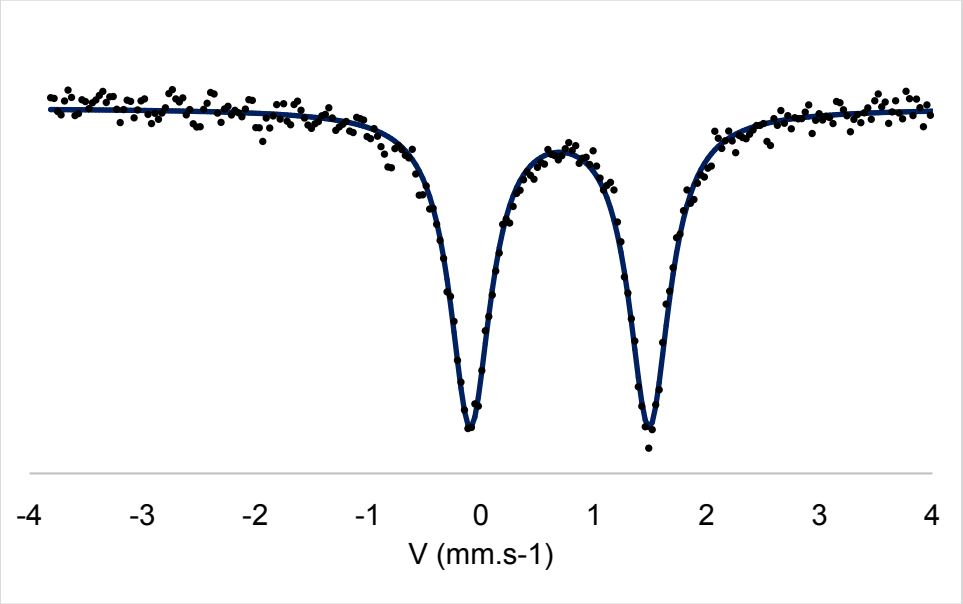


Figure S10. Mössbauer spectrum of complex **3a** (black dots: raw data, blue line, simulated curve), δ=0.697 mm.s^{-1} Δ=1.586 mm.s^{-1}.

3.3. Complex 6a

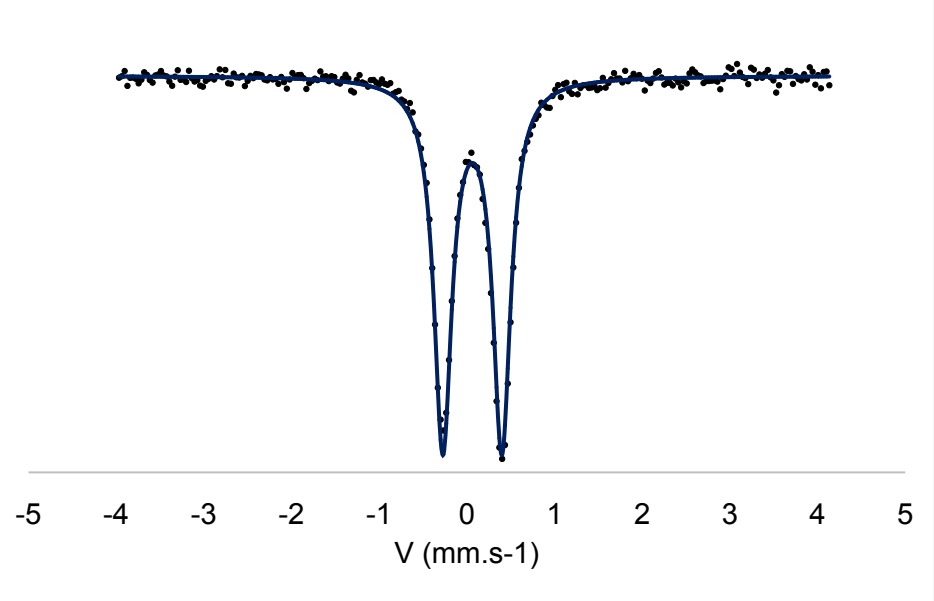


Figure S11. Mössbauer spectrum of complex **6a** (black dots: raw data, blue line, simulated curve), δ=0.063 mm.s^{-1} Δ=0.673 mm.s^{-1}.

4. DFT Calculations

4.1. Computational Details

Calculations were performed with the Gaussian09 package[11]. The M06L functional[12] was used with the all electron Def2-TZVP[13] basis set for Fe, Def2-SVP[13] basis set for P and N, 6-311+G**[14] basis set for H coordinated to Fe or N and 6-31G*[15] for all the other atoms. All geometries have been computed and optimized in the gas phase. The stationary points were characterized as minima by full vibration frequencies calculations and finding no imaginary frequency. A single point PCM[16] calculations has been performed using the same parameters to account for the inclusion of solvent effect. Thermal correction to Gibbs Free Energy were applied to the above calculated energies.

4.2. Computational data for 4a

Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-0.000029	0.120143	-0.257685
2	15	0	0.000010	-0.462007	1.824257
3	15	0	2.216920	0.277116	0.086762
4	15	0	-2.216982	0.276916	0.086776
5	7	0	0.000012	-1.162886	-1.551056
6	7	0	0.000000	-1.922737	-2.396969
7	7	0	-0.000101	1.739478	-1.080523
8	7	0	-0.000108	2.745166	-1.610412
9	6	0	-1.476531	0.155527	2.762018
10	1	0	-1.591858	-0.324528	3.743507
11	1	0	-1.318922	1.230009	2.925375
12	6	0	-2.679011	-0.088745	1.861604
13	1	0	-3.556976	0.501307	2.159427
14	1	0	-2.972782	-1.145646	1.915385
15	6	0	0.000156	-2.253076	2.318732
16	6	0	0.000314	-3.233431	1.323749
17	1	0	0.000367	-2.914958	0.280297
18	6	0	0.000409	-4.587084	1.655673
19	1	0	0.000531	-5.338698	0.867662
20	6	0	0.000354	-4.975756	2.992314
21	1	0	0.000433	-6.032474	3.254792
22	6	0	0.000200	-4.007976	3.996447
23	1	0	0.000156	-4.308024	5.043494
24	6	0	0.000102	-2.657926	3.660094
25	1	0	-0.000030	-1.909260	4.454951
26	6	0	2.934503	1.985305	-0.172766
27	1	0	2.583376	2.286687	-1.173656
28	6	0	2.337362	2.968978	0.840619
29	1	0	1.242520	2.877023	0.862873

30	1	0	2.695958	2.698274	1.849205
31	6	0	2.765935	4.399387	0.537617
32	1	0	2.362397	4.692190	-0.444406
33	1	0	2.328845	5.090159	1.271193
34	6	0	4.285300	4.520084	0.528001
35	1	0	4.667781	4.324936	1.543460
36	1	0	4.592595	5.543544	0.274827
37	6	0	4.910480	3.523407	-0.440167
38	1	0	4.616413	3.785728	-1.469122
39	1	0	6.006604	3.587025	-0.407149
40	6	0	4.461615	2.090700	-0.155890
41	1	0	4.842672	1.777116	0.831305
42	1	0	4.915841	1.413470	-0.891296
43	6	0	3.393866	-0.819275	-0.855172
44	1	0	4.408136	-0.623437	-0.462060
45	6	0	3.369639	-0.465462	-2.346295
46	1	0	2.344381	-0.592659	-2.725836
47	1	0	3.621550	0.594454	-2.496446
48	6	0	4.321535	-1.349166	-3.145415
49	1	0	5.357788	-1.145086	-2.827300
50	1	0	4.268438	-1.090730	-4.211352
51	6	0	4.012044	-2.825789	-2.933013
52	1	0	3.007535	-3.044210	-3.328913
53	1	0	4.714887	-3.452299	-3.498466
54	6	0	4.052038	-3.180282	-1.451523
55	1	0	5.077825	-3.040892	-1.071818
56	1	0	3.807656	-4.240229	-1.299921
57	6	0	3.092913	-2.307035	-0.648235
58	1	0	3.145509	-2.573405	0.417068
59	1	0	2.061704	-2.516449	-0.964198
60	6	0	-3.393831	-0.819510	-0.855240
61	1	0	-4.408126	-0.623759	-0.462146
62	6	0	-3.092787	-2.307266	-0.648386
63	1	0	-3.145388	-2.573704	0.416900
64	1	0	-2.061561	-2.516601	-0.964345
65	6	0	-4.051842	-3.180528	-1.451743
66	1	0	-3.807402	-4.240469	-1.300195
67	1	0	-5.077644	-3.041218	-1.072052
68	6	0	-4.011835	-2.825948	-2.933210
69	1	0	-3.007303	-3.044285	-3.329097
70	1	0	-4.714627	-3.452469	-3.498715
71	6	0	-4.321408	-1.349331	-3.145534
72	1	0	-5.357681	-1.145330	-2.827433
73	1	0	-4.268301	-1.090830	-4.211455
74	6	0	-3.369582	-0.465617	-2.346341
75	1	0	-3.621545	0.594294	-2.496441
76	1	0	-2.344304	-0.592737	-2.725855
77	6	0	-2.934698	1.985064	-0.172657
78	1	0	-2.583620	2.286514	-1.173544
79	6	0	-4.461817	2.090355	-0.155728
80	1	0	-4.916020	1.413127	-0.891150
81	1	0	-4.842822	1.776703	0.831465
82	6	0	-4.910787	3.523044	-0.439932
83	1	0	-4.616770	3.785426	-1.468886

84	1	0	-6.006914	3.586586	-0.406879
85	6	0	-4.285645	4.519725	0.528256
86	1	0	-4.668084	4.324514	1.543718
87	1	0	-4.593013	5.543174	0.275129
88	6	0	-2.766272	4.399124	0.537824
89	1	0	-2.329204	5.089896	1.271414
90	1	0	-2.362781	4.691993	-0.444199
91	6	0	-2.337597	2.968731	0.840755
92	1	0	-2.696150	2.697960	1.849338
93	1	0	-1.242748	2.876847	0.862975
94	6	0	1.476454	0.155775	2.762004
95	1	0	1.318700	1.230247	2.925286
96	1	0	1.591844	-0.324195	3.743527
97	6	0	2.678974	-0.088399	1.861616
98	1	0	2.972873	-1.145263	1.915456
99	1	0	3.556864	0.501774	2.159418

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	18.5883	19.3363	31.3209
Red. masses --	4.4933	5.1235	4.6021
Frc consts --	0.0009	0.0011	0.0027
IR Inten --	0.0002	0.2555	0.0642

Thermochemistry (Hartree)

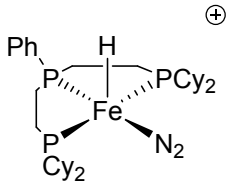
Sum of electronic and zero-point Energies= -3835.303234
Sum of electronic and thermal Energies= -3835.259597
Sum of electronic and thermal Enthalpies= -3835.258653
Sum of electronic and thermal Free Energies= -3835.378124

HF=-3836.1795956

PCM Corrections (Tetrahydrofuran)

HF=-3836.1865725

4.3. Computational data for $[(P^{Ph}P_2^{Cy})Fe(H)(N_2)]^+$



Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.000148	-0.241213	0.187401
2	15	0	-0.000276	0.292181	-2.009968
3	15	0	2.271998	-0.192458	-0.062364
4	15	0	-2.271672	-0.194528	-0.062060

5	7	0	0.001336	-1.882733	1.280917
6	7	0	0.002068	-2.712470	2.030624
7	1	0	2.842181	1.239361	-1.947804
8	1	0	3.634538	-0.323758	-2.129117
9	6	0	-1.558668	-0.279979	-2.805111
10	1	0	-1.694035	0.140947	-3.809355
11	1	0	-1.513769	-1.371911	-2.903120
12	6	0	-2.685257	0.152254	-1.857445
13	1	0	-3.634233	-0.328577	-2.128618
14	1	0	-2.844033	1.235725	-1.948097
15	6	0	-0.001538	2.092871	-2.278383
16	6	0	-0.001083	2.966226	-1.187422
17	1	0	-0.000181	2.559030	-0.176221
18	6	0	-0.001919	4.344105	-1.389474
19	1	0	-0.001558	5.015585	-0.532677
20	6	0	-0.003231	4.855749	-2.683924
21	1	0	-0.003898	5.931702	-2.844322
22	6	0	-0.003702	3.990863	-3.778721
23	1	0	-0.004731	4.390650	-4.790330
24	6	0	-0.002850	2.614713	-3.579938
25	1	0	-0.003176	1.947391	-4.442954
26	6	0	3.056263	-1.853540	0.243986
27	1	0	2.748283	-2.115792	1.270572
28	6	0	2.492168	-2.920052	-0.702438
29	1	0	1.390218	-2.899092	-0.711846
30	1	0	2.817432	-2.688626	-1.730835
31	6	0	3.005373	-4.306439	-0.327810
32	1	0	2.638005	-4.565498	0.677929
33	1	0	2.592666	-5.058337	-1.012020
34	6	0	4.529084	-4.342065	-0.344331
35	1	0	4.881183	-4.192556	-1.377383
36	1	0	4.892293	-5.330017	-0.036813
37	6	0	5.118828	-3.258434	0.549487
38	1	0	4.866535	-3.472456	1.599979
39	1	0	6.214122	-3.261539	0.490084
40	6	0	4.587201	-1.871501	0.191326
41	1	0	4.923031	-1.601086	-0.823635
42	1	0	5.016341	-1.123285	0.870226
43	6	0	3.309665	0.999813	0.901088
44	1	0	4.332389	0.936445	0.489406
45	6	0	3.337687	0.602796	2.382042
46	1	0	2.302616	0.611475	2.763036
47	1	0	3.708102	-0.424127	2.508992
48	6	0	4.197892	1.568914	3.191384
49	1	0	5.244395	1.482571	2.857742
50	1	0	4.187442	1.276856	4.248732
51	6	0	3.730576	3.009304	3.025759
52	1	0	2.724733	3.115834	3.461762
53	1	0	4.383583	3.690253	3.585103
54	6	0	3.682642	3.404447	1.555133
55	1	0	4.702564	3.404357	1.139564
56	1	0	3.303623	4.428061	1.439701
57	6	0	2.812733	2.439759	0.755640
58	1	0	2.774445	2.743783	-0.300994

59	1	0	1.777604	2.483784	1.133306
60	6	0	-3.310312	0.997392	0.900768
61	1	0	-4.333042	0.932670	0.489298
62	6	0	-2.814797	2.437715	0.754071
63	1	0	-2.776833	2.740914	-0.302810
64	1	0	-1.779684	2.483071	1.131622
65	6	0	-3.685590	3.402212	1.552817
66	1	0	-3.307588	4.426105	1.436506
67	1	0	-4.705544	3.400769	1.137330
68	6	0	-3.733017	3.008244	3.023781
69	1	0	-2.727248	3.116170	3.459610
70	1	0	-4.386674	3.688992	3.582611
71	6	0	-4.198832	1.567513	3.190660
72	1	0	-5.245277	1.479800	2.857197
73	1	0	-4.187976	1.276367	4.248255
74	6	0	-3.337693	0.601610	2.382047
75	1	0	-3.706945	-0.425610	2.509962
76	1	0	-2.302582	0.611757	2.762880
77	6	0	-3.054296	-1.856224	0.245209
78	1	0	-2.745626	-2.117837	1.271752
79	6	0	-4.585241	-1.875694	0.193174
80	1	0	-5.014837	-1.127630	0.871956
81	1	0	-4.921730	-1.605985	-0.821756
82	6	0	-5.115359	-3.263025	0.552030
83	1	0	-4.862411	-3.476450	1.602485
84	1	0	-6.210675	-3.267231	0.493088
85	6	0	-4.524931	-4.346373	-0.341684
86	1	0	-4.877651	-4.197565	-1.374626
87	1	0	-4.887021	-5.334581	-0.033669
88	6	0	-3.001244	-4.309238	-0.325876
89	1	0	-2.588114	-5.060942	-1.010043
90	1	0	-2.633154	-4.567624	0.679771
91	6	0	-2.489590	-2.922468	-0.701164
92	1	0	-2.815570	-2.691666	-1.729475
93	1	0	-1.387675	-2.900435	-0.711126
94	6	0	1.558823	-0.277762	-2.805349
95	1	0	1.515335	-1.369711	-2.903730
96	1	0	1.693545	0.143731	-3.809442
97	6	0	2.684919	0.155627	-1.857623
98	1	0	-0.000391	0.649802	1.492753

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	14.0288	20.7312	33.3458
Red. masses --	4.3040	4.8261	4.5082
Frc consts --	0.0005	0.0012	0.0030
IR Inten --	0.0034	0.0594	0.0329

Thermochemistry (Hartree)

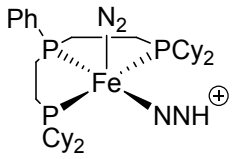
Sum of electronic and zero-point Energies= -3726.255107
Sum of electronic and thermal Energies= -3726.212362

Sum of electronic and thermal Enthalpies= -3726.211418
Sum of electronic and thermal Free Energies= -3726.330895

HF=-3727.1286585

PCM Corrections (Tetrahydrofuran)
HF=-3727.1848629

4.4. Computational data for [(P^{Ph}P2Cy)Fe(N$_2$)(N$_2$H)]



Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.026218	-0.024223	-0.165808
2	15	0	0.077274	-0.662414	2.043610
3	15	0	2.315084	0.192148	0.115687
4	15	0	-2.235769	0.263999	0.244140
5	7	0	-0.028603	-1.631098	-1.329373
6	7	0	-0.058157	-2.435276	-2.108095
7	7	0	0.003977	1.117311	-1.563559
8	7	0	0.021265	2.304921	-1.819198
9	6	0	-1.344412	0.161787	2.893653
10	1	0	-1.478043	-0.219440	3.914309
11	1	0	-1.085936	1.226560	2.972817
12	6	0	-2.598386	-0.028145	2.048115
13	1	0	-3.413085	0.627282	2.383576
14	1	0	-2.962775	-1.058913	2.147522
15	6	0	0.036586	-2.395683	2.602340
16	6	0	-0.038972	-3.433040	1.667678
17	1	0	-0.070269	-3.197981	0.605078
18	6	0	-0.075170	-4.759600	2.089690
19	1	0	-0.133862	-5.559765	1.355143
20	6	0	-0.035495	-5.058091	3.448526
21	1	0	-0.063315	-6.094044	3.779244
22	6	0	0.039938	-4.030482	4.388427
23	1	0	0.070721	-4.262779	5.450734
24	6	0	0.075611	-2.705518	3.969503
25	1	0	0.133361	-1.909602	4.713357
26	6	0	2.874277	1.931779	-0.197833
27	1	0	2.508386	2.157269	-1.212903
28	6	0	2.166242	2.893445	0.761337
29	1	0	1.080607	2.711589	0.744580
30	1	0	2.510836	2.693572	1.790662
31	6	0	2.473979	4.342991	0.407741
32	1	0	2.057981	4.558392	-0.589044
33	1	0	1.965383	5.017705	1.108375
34	6	0	3.977542	4.593760	0.411468

35	1	0	4.360289	4.476001	1.437809
36	1	0	4.195285	5.628581	0.120582
37	6	0	4.704657	3.622088	-0.510468
38	1	0	4.406756	3.816879	-1.552811
39	1	0	5.788721	3.783899	-0.465840
40	6	0	4.386131	2.165321	-0.175601
41	1	0	4.785597	1.921325	0.823047
42	1	0	4.897481	1.502277	-0.886616
43	6	0	3.470096	-0.870419	-0.870371
44	1	0	4.491362	-0.591831	-0.556118
45	6	0	3.315667	-0.558260	-2.364026
46	1	0	2.270875	-0.743408	-2.662590
47	1	0	3.503688	0.508772	-2.553882
48	6	0	4.249002	-1.416483	-3.211501
49	1	0	5.292477	-1.144372	-2.986393
50	1	0	4.094806	-1.193099	-4.274363
51	6	0	4.041736	-2.899532	-2.933309
52	1	0	3.023929	-3.189286	-3.240757
53	1	0	4.730762	-3.502490	-3.536968
54	6	0	4.226439	-3.204478	-1.452478
55	1	0	5.267655	-2.992706	-1.162720
56	1	0	4.061142	-4.269880	-1.249612
57	6	0	3.286355	-2.366237	-0.590664
58	1	0	3.457132	-2.589614	0.471647
59	1	0	2.246969	-2.656533	-0.801828
60	6	0	-3.471001	-0.788204	-0.651409
61	1	0	-4.465071	-0.486740	-0.276974
62	6	0	-3.295543	-2.283330	-0.364436
63	1	0	-3.398753	-2.491777	0.709665
64	1	0	-2.276813	-2.592920	-0.638925
65	6	0	-4.302367	-3.115019	-1.154071
66	1	0	-4.143256	-4.180705	-0.947616
67	1	0	-5.319519	-2.880741	-0.802781
68	6	0	-4.205555	-2.831839	-2.647750
69	1	0	-3.214190	-3.143859	-3.014195
70	1	0	-4.941322	-3.429754	-3.198978
71	6	0	-4.403791	-1.348906	-2.932502
72	1	0	-5.426363	-1.055038	-2.646955
73	1	0	-4.311974	-1.141555	-4.005777
74	6	0	-3.404765	-0.497673	-2.155972
75	1	0	-3.585308	0.570142	-2.348151
76	1	0	-2.383747	-0.705679	-2.515707
77	6	0	-2.774993	2.010715	-0.069188
78	1	0	-2.469202	2.209000	-1.109663
79	6	0	-4.278076	2.274972	0.044056
80	1	0	-4.845769	1.611800	-0.622678
81	1	0	-4.617817	2.053076	1.069616
82	6	0	-4.591271	3.732523	-0.291427
83	1	0	-4.356153	3.908333	-1.353024
84	1	0	-5.667395	3.914657	-0.181121
85	6	0	-3.790248	4.701624	0.569658
86	1	0	-4.107986	4.602357	1.619849
87	1	0	-4.008325	5.736825	0.280390
88	6	0	-2.294803	4.423387	0.472037

89	1	0	-1.729959	5.098135	1.128122
90	1	0	-1.941804	4.618695	-0.552803
91	6	0	-1.988247	2.973528	0.825509
92	1	0	-2.265112	2.793841	1.878785
93	1	0	-0.909583	2.774213	0.736742
94	6	0	1.587008	0.076987	2.816486
95	1	0	1.382359	1.149282	2.937453
96	1	0	1.768096	-0.335726	3.817264
97	6	0	2.776048	-0.145448	1.888818
98	1	0	3.103535	-1.191481	1.947861
99	1	0	3.636469	0.470437	2.182677
100	1	0	-0.011063	2.504279	-2.839754

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	12.1149	31.9671	33.2134
Red. masses --	4.4707	4.7520	4.5780
Frc consts --	0.0004	0.0029	0.0030
IR Inten --	0.0013	0.0816	0.0679

Thermochemistry (Hartree)

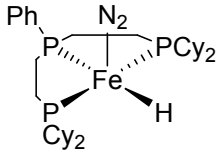
Sum of electronic and zero-point Energies= -3835.668487
Sum of electronic and thermal Energies= -3835.623204
Sum of electronic and thermal Enthalpies= -3835.622260
Sum of electronic and thermal Free Energies= -3835.747069

HF=-3836.5542084

PCM Corrections (Tetrahydrofuran)

HF=-3836.5983056

4.5. Computational data for [(P^{Ph}P2Cy)Fe(N_2)(H)]



Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.079090	-0.083430	-0.300526
2	15	0	-0.274040	-0.759951	1.743012
3	15	0	2.226918	-0.424035	0.106832
4	15	0	-1.826956	1.043999	-0.087519
5	7	0	-0.596898	-2.138555	-2.339846
6	7	0	-0.354344	-1.410406	-1.504035
7	6	0	-1.222797	0.589058	2.612569
8	1	0	-1.573071	0.304632	3.614551
9	1	0	-0.501284	1.409114	2.743027

10	6	0	-2.370140	1.037878	1.713773
11	1	0	-2.752684	2.022815	2.014611
12	1	0	-3.210849	0.336521	1.803411
13	6	0	-1.164130	-2.299017	2.227599
14	6	0	-1.345086	-3.290685	1.257593
15	1	0	-0.963352	-3.119486	0.250985
16	6	0	-2.012630	-4.473451	1.566523
17	1	0	-2.147586	-5.234683	0.799935
18	6	0	-2.510625	-4.678080	2.850626
19	1	0	-3.038490	-5.599208	3.092070
20	6	0	-2.332006	-3.700211	3.827725
21	1	0	-2.717082	-3.857396	4.834242
22	6	0	-1.660683	-2.520949	3.518376
23	1	0	-1.519885	-1.767449	4.294682
24	6	0	3.227335	1.152581	0.235042
25	1	0	2.953521	1.701906	-0.681910
26	6	0	2.751022	1.987050	1.428213
27	1	0	1.652497	2.057209	1.430724
28	1	0	3.034660	1.469244	2.360760
29	6	0	3.391312	3.369600	1.425258
30	1	0	3.076693	3.909113	0.516850
31	1	0	3.030871	3.961337	2.278176
32	6	0	4.911384	3.255662	1.452964
33	1	0	5.218104	2.805437	2.411268
34	1	0	5.376973	4.249611	1.416925
35	6	0	5.420632	2.388722	0.307251
36	1	0	5.214383	2.897452	-0.648169
37	1	0	6.511626	2.275219	0.365557
38	6	0	4.749805	1.015614	0.280763
39	1	0	5.041532	0.444619	1.179267
40	1	0	5.120856	0.445467	-0.581707
41	6	0	3.255666	-1.493354	-1.018575
42	1	0	4.286566	-1.518174	-0.621649
43	6	0	3.279645	-0.873335	-2.420528
44	1	0	2.241979	-0.771916	-2.775553
45	1	0	3.684154	0.149085	-2.381010
46	6	0	4.081731	-1.722977	-3.399586
47	1	0	5.139618	-1.739579	-3.087603
48	1	0	4.060920	-1.265597	-4.397822
49	6	0	3.550848	-3.150008	-3.449607
50	1	0	2.519878	-3.138213	-3.838446
51	1	0	4.141790	-3.759013	-4.146890
52	6	0	3.551394	-3.774615	-2.060040
53	1	0	4.590347	-3.857535	-1.700065
54	1	0	3.153357	-4.797605	-2.094492
55	6	0	2.741397	-2.935907	-1.075681
56	1	0	2.773614	-3.399888	-0.080037
57	1	0	1.686329	-2.935894	-1.382377
58	6	0	-3.368278	0.439827	-0.946163
59	1	0	-4.217389	1.043851	-0.576670
60	6	0	-3.648834	-1.028310	-0.608135
61	1	0	-3.773476	-1.164656	0.476091
62	1	0	-2.776409	-1.634822	-0.888078
63	6	0	-4.877246	-1.548490	-1.346571

64	1	0	-5.041539	-2.605352	-1.096277
65	1	0	-5.772277	-1.004264	-1.002062
66	6	0	-4.726026	-1.367106	-2.851740
67	1	0	-3.875520	-1.972904	-3.203364
68	1	0	-5.615494	-1.738652	-3.378207
69	6	0	-4.472940	0.095444	-3.195317
70	1	0	-5.356917	0.691876	-2.913580
71	1	0	-4.346166	0.223790	-4.278618
72	6	0	-3.249791	0.635142	-2.460948
73	1	0	-3.107693	1.699261	-2.699647
74	1	0	-2.345174	0.117170	-2.816610
75	6	0	-1.785410	2.859102	-0.525043
76	1	0	-1.508242	2.862208	-1.592956
77	6	0	-3.101485	3.620156	-0.361584
78	1	0	-3.893350	3.158204	-0.968012
79	1	0	-3.439630	3.556565	0.686386
80	6	0	-2.948767	5.090952	-0.742961
81	1	0	-2.721272	5.159667	-1.819042
82	1	0	-3.900020	5.619738	-0.594319
83	6	0	-1.831060	5.759853	0.047370
84	1	0	-2.096660	5.763569	1.117450
85	1	0	-1.727145	6.812460	-0.248080
86	6	0	-0.514341	5.016513	-0.140416
87	1	0	0.285521	5.485540	0.449375
88	1	0	-0.204718	5.089128	-1.195306
89	6	0	-0.646813	3.544854	0.234757
90	1	0	-0.830864	3.465580	1.322082
91	1	0	0.289688	3.005713	0.031736
92	6	0	1.319925	-0.850831	2.725206
93	1	0	1.479349	0.146639	3.155929
94	1	0	1.234124	-1.555491	3.562605
95	6	0	2.466640	-1.220126	1.787230
96	1	0	2.470541	-2.306011	1.623763
97	1	0	3.445488	-0.962982	2.218508
98	1	0	0.514904	0.895404	-1.452111

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	11.3925	27.2679	31.8729
Red. masses --	4.3943	4.6452	4.4998
Frc consts --	0.0003	0.0020	0.0027
IR Inten --	0.0033	0.1762	0.0302

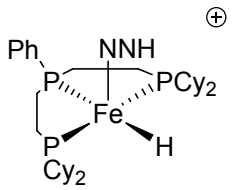
Thermochemistry (Hartree)

Sum of electronic and zero-point Energies= -3726.440947
Sum of electronic and thermal Energies= -3726.398729
Sum of electronic and thermal Enthalpies= -3726.397785
Sum of electronic and thermal Free Energies= -3726.515805

HF=-3727.3144645

PCM Corrections (Tetrahydrofuran)
HF=-3727.3223663

4.6. Computational data for $[(P^{Ph}P2Cy)Fe(N_2H)(H)]^+$



Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.114576	-0.068589	-0.281507
2	15	0	-0.202188	-0.648925	1.884100
3	15	0	2.310732	-0.471188	0.143553
4	15	0	-1.856770	1.066038	-0.025255
5	7	0	-0.454890	-1.816492	-2.520203
6	7	0	-0.230284	-1.132774	-1.552810
7	6	0	-1.155564	0.713712	2.680059
8	1	0	-1.465979	0.476552	3.705728
9	1	0	-0.465082	1.566969	2.745079
10	6	0	-2.343872	1.047380	1.783210
11	1	0	-2.794665	2.007115	2.066326
12	1	0	-3.126072	0.285802	1.901145
13	6	0	-1.144254	-2.179883	2.160071
14	6	0	-1.141217	-3.170325	1.169764
15	1	0	-0.587045	-3.004617	0.245139
16	6	0	-1.868321	-4.342789	1.349558
17	1	0	-1.864230	-5.105009	0.573401
18	6	0	-2.608394	-4.532579	2.514162
19	1	0	-3.185152	-5.444861	2.650109
20	6	0	-2.612723	-3.553817	3.506264
21	1	0	-3.188320	-3.701380	4.417447
22	6	0	-1.881127	-2.382995	3.334464
23	1	0	-1.890437	-1.628020	4.120471
24	6	0	3.308281	1.093761	0.230625
25	1	0	3.074416	1.598469	-0.721967
26	6	0	2.809580	1.997446	1.363123
27	1	0	1.711704	2.085651	1.331984
28	1	0	3.065637	1.531675	2.329604
29	6	0	3.471149	3.368631	1.293263
30	1	0	3.180701	3.858906	0.349944
31	1	0	3.100882	4.010008	2.103594
32	6	0	4.988325	3.233936	1.362580
33	1	0	5.268116	2.846208	2.354939
34	1	0	5.466179	4.216901	1.272145
35	6	0	5.514103	2.290180	0.287302
36	1	0	5.344552	2.737424	-0.704770
37	1	0	6.599173	2.161894	0.384331
38	6	0	4.826128	0.925666	0.329565
39	1	0	5.080542	0.410989	1.271247

40	1	0	5.209520	0.294977	-0.483738
41	6	0	3.257644	-1.586151	-0.991318
42	1	0	4.277144	-1.665934	-0.574389
43	6	0	3.348926	-0.956297	-2.387000
44	1	0	2.327744	-0.796553	-2.770458
45	1	0	3.811512	0.039656	-2.333695
46	6	0	4.125646	-1.848784	-3.349058
47	1	0	5.171907	-1.916807	-3.011266
48	1	0	4.153805	-1.386943	-4.343832
49	6	0	3.524888	-3.246821	-3.415406
50	1	0	2.508433	-3.187658	-3.838737
51	1	0	4.104861	-3.882079	-4.095712
52	6	0	3.454106	-3.874639	-2.029479
53	1	0	4.474743	-4.015379	-1.640400
54	1	0	3.002014	-4.873017	-2.076919
55	6	0	2.663262	-2.997711	-1.062608
56	1	0	2.644794	-3.464618	-0.068064
57	1	0	1.617754	-2.939115	-1.399213
58	6	0	-3.355162	0.363968	-0.862200
59	1	0	-4.224283	0.911024	-0.454558
60	6	0	-3.526184	-1.124634	-0.536779
61	1	0	-3.605006	-1.284290	0.549091
62	1	0	-2.625514	-1.668846	-0.857266
63	6	0	-4.743763	-1.711858	-1.242212
64	1	0	-4.822166	-2.781239	-1.007311
65	1	0	-5.658604	-1.240123	-0.850168
66	6	0	-4.664453	-1.490791	-2.747305
67	1	0	-3.795701	-2.038364	-3.147701
68	1	0	-5.549553	-1.905501	-3.244829
69	6	0	-4.517960	-0.009232	-3.070572
70	1	0	-5.422012	0.527467	-2.741694
71	1	0	-4.443953	0.149367	-4.153683
72	6	0	-3.301324	0.595282	-2.376394
73	1	0	-3.230131	1.668624	-2.602250
74	1	0	-2.383953	0.134636	-2.776150
75	6	0	-1.831305	2.867001	-0.474637
76	1	0	-1.528025	2.877056	-1.535386
77	6	0	-3.182661	3.575697	-0.344302
78	1	0	-3.947903	3.075216	-0.953233
79	1	0	-3.531168	3.517748	0.700193
80	6	0	-3.071048	5.043823	-0.750365
81	1	0	-2.826636	5.100045	-1.822767
82	1	0	-4.044411	5.535235	-0.630348
83	6	0	-1.997528	5.768064	0.051768
84	1	0	-2.291694	5.793808	1.113254
85	1	0	-1.919285	6.813446	-0.270469
86	6	0	-0.651421	5.067243	-0.080810
87	1	0	0.113628	5.570216	0.524982
88	1	0	-0.308112	5.127091	-1.125439
89	6	0	-0.748206	3.600157	0.323535
90	1	0	-0.986626	3.539514	1.400636
91	1	0	0.219110	3.096923	0.180993
92	6	0	1.407007	-0.792149	2.794661
93	1	0	1.635334	0.204984	3.191200

94	1	0	1.309728	-1.468555	3.652460
95	6	0	2.492215	-1.260079	1.825652
96	1	0	2.405148	-2.344041	1.672877
97	1	0	3.496530	-1.080703	2.233173
98	1	0	0.623233	1.140964	-1.073633
99	1	0	-0.251779	-1.401840	-3.442062

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	9.7115	24.2251	30.6621
Red. masses --	4.3396	4.4971	4.1289
Frc consts --	0.0002	0.0016	0.0023
IR Inten --	0.0364	0.0127	0.0298

Thermochemistry (Hartree)

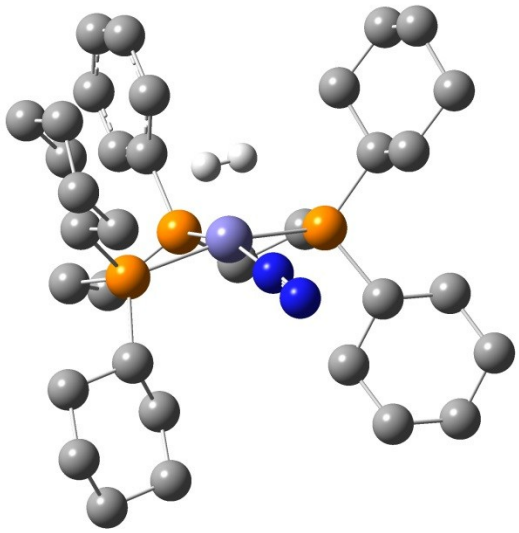
Sum of electronic and zero-point Energies=	-3726.814075
Sum of electronic and thermal Energies=	-3726.771280
Sum of electronic and thermal Enthalpies=	-3726.770336
Sum of electronic and thermal Free Energies=	-3726.890160

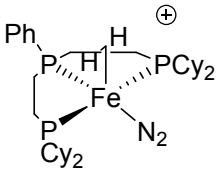
HF=-3727.6991078

PCM Corrections (Tetrahydrofuran)

HF=-3727.743745

4.7. Computational data for $[(P^{Ph}P2Cy)Fe(N_2)(H_2)]^+$





Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	-0.000443	0.236896	-0.264692
2	15	0	0.000267	-0.052255	1.933303
3	15	0	2.284214	0.343844	0.029711
4	15	0	-2.285039	0.341147	0.030692
5	7	0	-0.000231	-0.505330	-1.960633
6	7	0	-0.000010	-1.069830	-2.934306
7	1	0	2.848849	-0.938776	2.019207
8	1	0	3.618035	0.645753	2.093061
9	6	0	-1.524173	0.614303	2.719032
10	1	0	-1.633306	0.285643	3.760150
11	1	0	-1.454449	1.709745	2.717994
12	6	0	-2.679768	0.127346	1.845698
13	1	0	-3.619088	0.637811	2.094634
14	1	0	-2.846458	-0.944973	2.018843
15	6	0	0.002452	-1.809305	2.438225
16	6	0	0.000167	-2.820799	1.473528
17	1	0	-0.002420	-2.549944	0.417073
18	6	0	0.001257	-4.161107	1.851105
19	1	0	-0.000534	-4.938523	1.089396
20	6	0	0.004697	-4.500217	3.201247
21	1	0	0.005601	-5.546178	3.500152
22	6	0	0.006994	-3.499632	4.172911
23	1	0	0.009663	-3.763665	5.228220
24	6	0	0.005833	-2.161119	3.795345

25	1	0	0.007505	-1.387639	4.564857
26	6	0	3.103267	1.974270	-0.379403
27	1	0	2.811759	2.181550	-1.423665
28	6	0	2.585240	3.120823	0.498482
29	1	0	1.486845	3.162798	0.499635
30	1	0	2.891941	2.932065	1.541135
31	6	0	3.164682	4.460801	0.054302
32	1	0	2.817248	4.680965	-0.967168
33	1	0	2.777014	5.264292	0.693049
34	6	0	4.687176	4.436621	0.083082
35	1	0	5.027238	4.332783	1.125641
36	1	0	5.093304	5.388829	-0.278853
37	6	0	5.231688	3.277522	-0.740121
38	1	0	4.995014	3.437858	-1.803813
39	1	0	6.325657	3.233240	-0.672139
40	6	0	4.636547	1.941631	-0.299606
41	1	0	4.940359	1.735913	0.740190
42	1	0	5.056257	1.132339	-0.908635
43	6	0	3.354571	-0.929477	-0.795487
44	1	0	4.346588	-0.862369	-0.314516
45	6	0	3.519251	-0.659269	-2.296791
46	1	0	2.532414	-0.684224	-2.780978
47	1	0	3.922425	0.345911	-2.477785
48	6	0	4.419457	-1.709708	-2.940940
49	1	0	5.432712	-1.625165	-2.516444
50	1	0	4.516638	-1.506081	-4.014357
51	6	0	3.885153	-3.116765	-2.705288
52	1	0	2.912564	-3.223124	-3.212569
53	1	0	4.552212	-3.861503	-3.156030
54	6	0	3.707260	-3.391864	-1.217361
55	1	0	4.690331	-3.383887	-0.721110
56	1	0	3.287414	-4.392517	-1.052998
57	6	0	2.810031	-2.343350	-0.568142
58	1	0	2.688349	-2.552828	0.504917
59	1	0	1.801620	-2.408500	-1.010159
60	6	0	-3.354900	-0.931350	-0.796413
61	1	0	-4.346935	-0.865383	-0.315327
62	6	0	-2.809962	-2.345432	-0.571363
63	1	0	-2.688279	-2.556567	0.501372
64	1	0	-1.801559	-2.409655	-1.013525
65	6	0	-3.706930	-3.393116	-1.222288
66	1	0	-3.286862	-4.393934	-1.059531
67	1	0	-4.690023	-3.386157	-0.726068
68	6	0	-3.884813	-3.115651	-2.709779
69	1	0	-2.912157	-3.220894	-3.217164
70	1	0	-4.551615	-3.859858	-3.161775
71	6	0	-4.419525	-1.708374	-2.943178
72	1	0	-5.432833	-1.624832	-2.518611
73	1	0	-4.516701	-1.503024	-4.016268
74	6	0	-3.519687	-0.658702	-2.297270
75	1	0	-3.923250	0.346631	-2.476549
76	1	0	-2.532844	-0.682462	-2.781512
77	6	0	-3.105139	1.971747	-0.375750
78	1	0	-2.813764	2.180815	-1.419694

79	6	0	-4.638408	1.938247	-0.296027
80	1	0	-5.057744	1.129581	-0.906138
81	1	0	-4.942139	1.731015	0.743493
82	6	0	-5.234145	3.274434	-0.734847
83	1	0	-4.997544	3.436183	-1.798342
84	1	0	-6.328096	3.229601	-0.666921
85	6	0	-4.690158	4.432773	0.089777
86	1	0	-5.030258	4.327548	1.132183
87	1	0	-5.096662	5.385240	-0.271053
88	6	0	-3.167666	4.457635	0.061190
89	1	0	-2.780431	5.260498	0.700989
90	1	0	-2.820180	4.679200	-0.959960
91	6	0	-2.587808	3.117330	0.503814
92	1	0	-2.894878	2.927088	1.546079
93	1	0	-1.489415	3.159649	0.505471
94	6	0	1.523380	0.618357	2.718059
95	1	0	1.451192	1.713654	2.715755
96	1	0	1.633633	0.291228	3.759541
97	6	0	2.679769	0.132980	1.844925
98	1	0	-0.002510	1.779457	-0.970213
99	1	0	-0.000620	1.914076	-0.146180

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	13.1881	18.2787	35.5133
Red. masses --	4.1833	5.1931	4.3697
Frc consts --	0.0004	0.0010	0.0032
IR Inten --	0.0026	0.1473	0.0172

Thermochemistry (Hartree)

Sum of electronic and zero-point Energies= -3726.862763
Sum of electronic and thermal Energies= -3726.819998
Sum of electronic and thermal Enthalpies= -3726.819054
Sum of electronic and thermal Free Energies= -3726.938005

HF=-3727.7474604

PCM Corrections (Tetrahydrofuran)

HF=-3727.7907931

4.8. Computational data for $H(OEt_2)_2^+$

Cartesian Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.249545	-0.604245	-0.415065
2	8	0	-1.024239	0.091330	-0.215622
3	1	0	0.118196	-0.228920	-0.309953
4	1	0	2.845342	-0.586765	-1.704621

5	6	0	1.829292	-1.276315	0.742367
6	1	0	1.426242	-2.293765	0.722777
7	1	0	2.906555	-1.338010	0.556307
8	6	0	2.814689	1.298510	-0.623990
9	1	0	3.470976	0.972603	0.190218
10	1	0	3.441389	1.822222	-1.352550
11	1	0	2.096216	2.022527	-0.223906
12	6	0	1.501951	-0.557173	2.024394
13	1	0	1.907146	0.460379	2.038505
14	1	0	0.419407	-0.507753	2.189994
15	1	0	1.934739	-1.100573	2.870055
16	1	0	1.479434	0.459700	-2.118342
17	6	0	2.131859	0.138859	-1.298970
18	6	0	-1.956624	-0.631976	-1.077904
19	1	0	-2.644978	0.110068	-1.497151
20	1	0	-1.355160	-1.036250	-1.900493
21	6	0	-1.300507	1.489151	0.070048
22	1	0	-0.399732	1.841017	0.585068
23	1	0	-1.382897	2.021603	-0.887351
24	6	0	-2.659936	-1.708494	-0.299946
25	1	0	-3.258057	-1.290063	0.515348
26	1	0	-3.329660	-2.265958	-0.962202
27	1	0	-1.945000	-2.420305	0.126366
28	6	0	-2.527395	1.642896	0.925163
29	1	0	-3.430063	1.291352	0.413849
30	1	0	-2.423687	1.096371	1.867926
31	1	0	-2.678834	2.701086	1.158677

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	15.2254	29.6921	44.2562
Red. masses --	2.7080	2.6436	2.6008
Frc consts --	0.0004	0.0014	0.0030
IR Inten --	0.1500	0.0039	2.2716

Thermochemistry (Hartree)

Sum of electronic and zero-point Energies= -467.201757
Sum of electronic and thermal Energies= -467.186693
Sum of electronic and thermal Enthalpies= -467.185749
Sum of electronic and thermal Free Energies= -467.246371

HF=-467.4890889

PCM Corrections (Tetrahydrofuran)

HF=-467.5481699

4.9. Computational data for Et_2O

Cartesian Coordinates

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	8	0	0.000000	0.265052	-0.000005
2	6	0	1.167332	-0.511984	-0.000047
3	1	0	1.180633	-1.177361	-0.885837
4	1	0	1.180746	-1.177287	0.885798
5	6	0	2.363422	0.405731	-0.000161
6	1	0	2.354327	1.050171	0.885205
7	1	0	3.296018	-0.168305	-0.000191
8	1	0	2.354220	1.050092	-0.885582
9	6	0	-1.167332	-0.511984	0.000080
10	1	0	-1.180637	-1.177306	0.885912
11	1	0	-1.180742	-1.177343	-0.885723
12	6	0	-2.363422	0.405731	0.000131
13	1	0	-2.354323	1.050116	-0.885274
14	1	0	-3.296018	-0.168305	0.000193
15	1	0	-2.354224	1.050147	0.885512

Harmonic Frequencies

	1	2	3
	A	A	A
Frequencies --	101.1113	109.1558	193.7555
Red. masses --	1.5544	3.1864	2.6386
Frc consts --	0.0094	0.0224	0.0584
IR Inten --	0.0000	3.3658	0.5820

Thermochemistry (Hartree)

Sum of electronic and zero-point Energies= -233.419408
Sum of electronic and thermal Energies= -233.412622
Sum of electronic and thermal Enthalpies= -233.411677
Sum of electronic and thermal Free Energies= -233.449479

HF=-233.5567634

PCM Corrections (Tetrahydrofuran)

HF=-233.5586374

4.10. Summary

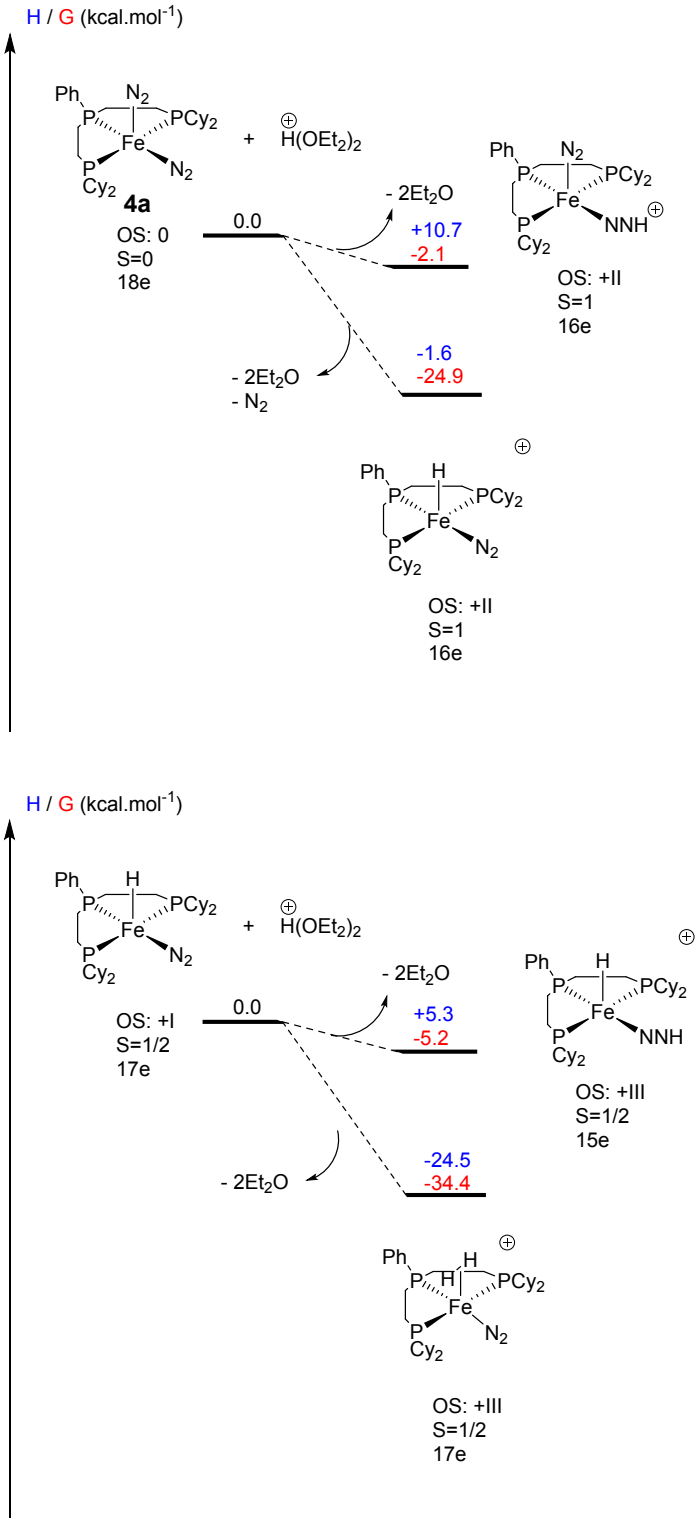


Figure S16: (Free) Enthalpy diagram for the protonation of Fe^{O} or Fe^{I}

5. Crystallographic data

The data for compounds **2b, 3a**, **4b** and **6a** were collected at low temperature (193 K) on a Bruker-AXS kappa APEX II CCD Quazar diffractometer (**6a**) equipped with a 30 W air-cooled microfocus source, or on a Bruker-AXS D8-Venture equipped with a CMOS Area detector (**2b**, **3a** and **4b**), using MoKα radiation (λ = 0.71073Å). Phi- and omega- scans were used. The data were integrated with SAINT[17] and an empirical absorption correction with SADABS was applied.[18] The structures were solved using an intrinsic phasing method (SHELXT)[19] and refined using a least-squares method on *F*2 (SHELXL-2014).[20] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined as riding models with isotropic atomic displacement parameters (*Uiso*) were fixed to be 1.2 and 1.5 times of the equivalent isotropic atomic displacement factor of each parent carbon atom, for aromatic, methyne and methylene, and methyl group, respectively. Metallic hydrides (**6a**) were located by difference Fourier map and were freely refined.

CCDC-1821405 (**2b**), CCDC-1821406 (**3a**), CCDC-1812143 (**4b**) and CCDC-1812144 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccddc.cam.ac.uk/data_request/cif.

5.1. Molecular Structure of 2b

$C_{32}H_{61}Cl_2FeP_3$, C_4H_8O *M*=737.57, Monoclinic, space group *C*2/c, a=24.9372(11)Å, b=14.9752(6)Å, c=23.2922(16)Å, β=116.2752(18)°, *V*=7799.5(7) Å^3, *Z*=8, crystal size 0.70 x 0.25 x 0.18 mm^3, 181894 reflections collected (9735 independent, R_{int}=0.0673), 788 parameters, 645 restraints, *R*1 [I>2σ(I)]= 0.0527, *wR*2 [all data]= 0.1491, largest diff. peak and hole: 0.982 and -0.450 e.Å^{-3}.

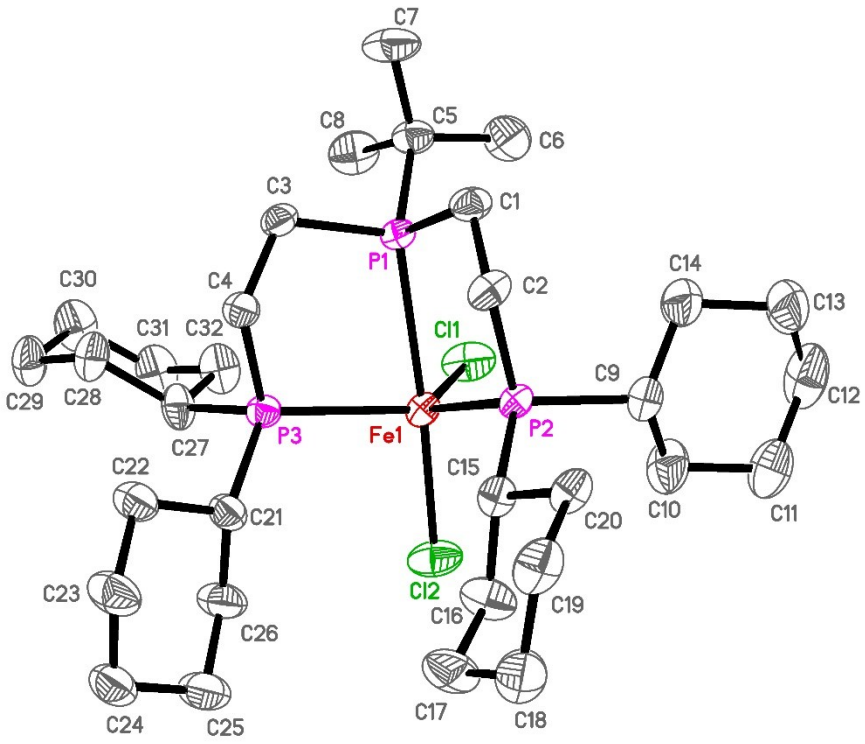


Figure 12: Molecular structure of **2b**. Hydrogen atoms and solvent molecule (THF) are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°):Fe1-Cl1 2.3042(8), Fe1-Cl2 2.3321 (8), Fe1-P1 2.7121(8), Fe1-P2 2.5074(7), Fe1-P3 2.5040(8), Cl1-Fe1-Cl2 95.17(3), Cl1-Fe1-P3 128.04(3), Cl2-Fe1-P3 98.41(3), Cl1-Fe1-P2 125.17(3), Cl2-Fe1-P2 101.59(3), P3-Fe1-P2 100.66(3), Cl1-Fe1-P1 88.61(3), Cl2-Fe1-P1 175.60(3), P3-Fe1-P1 77.45(2), P2-Fe1-P1 77.93(2).

5.2. Molecular Structure of 3a

$C_{34}H_{57}ClFeP_3$, ½ C_5H_{12} M=686.08, Monoclinic, space group $P2_1/n$, a=11.2863(4)Å, b=28.1832(10)Å, c=23.9028(8)Å, β=102.2920(10)°, V=7428.8(4) Å^3, Z=8, crystal size 0.20 x 0.20 x 0.16 mm^3, 235652 reflections collected (15070 independent, R_{int}=0.0918), 959 parameters, 798 restraints, $R1$ [I>2σ(I)]= 0.0495, $wR2$ [all data]= 0.1151, largest diff. peak and hole: 0.643 and -0.376 e.Å^{-3}.

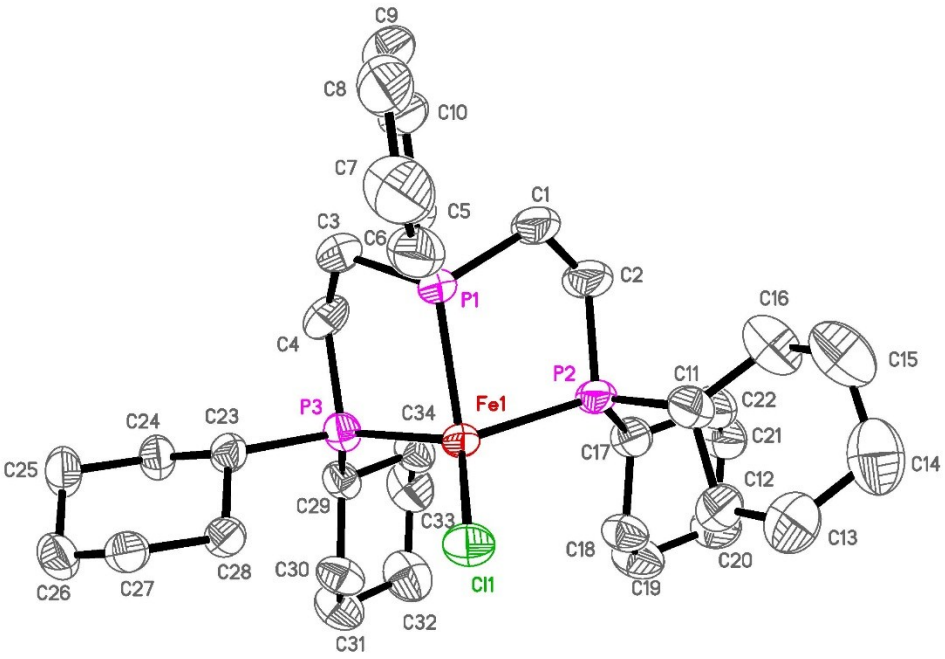


Figure S13: Molecular structure of **3a**. Only one of the two independent molecule in the asymmetric unit is shown and described. Hydrogen atoms and solvent molecule (pentane) are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°):Fe1-Cl1 2.2459(9), Fe1-P1 2.3083(9), Fe1-P2 2.3397(9), Fe1-P3 2.3358(9), Cl1-Fe1-P1 123.76(4), Cl1-Fe1-P3 123.18(3), Cl1-Fe1-P2 115.78(4), P3-Fe1-P2 115.38(3), P3-Fe1-P1 84.27(3), P2-Fe1-P1 84.13(3).

5.3. Molecular Structure of 4b

$C_{32}H_{61}FeN_4P_3,C_5H_{12}$, *M*=722.75, Orthorhombic, space group *Pbcm*, a=8.8347(6)Å, b=21.8280(15)Å, c=20.7072(14)Å, *V*=3993.3(5) Å^3, *Z*=4, crystal size 0.30 x 0.20 x 0.08 mm^3, 120568 reflections collected (6265 independent, R_{int}=0.0695), 290 parameters, 153 restraints, *R*1 [I>2σ(I)]= 0.0373, *wR*2 [all data]= 0.0963, largest diff. peak and hole: 0.543 and -0.513 e.Å^{-3}.

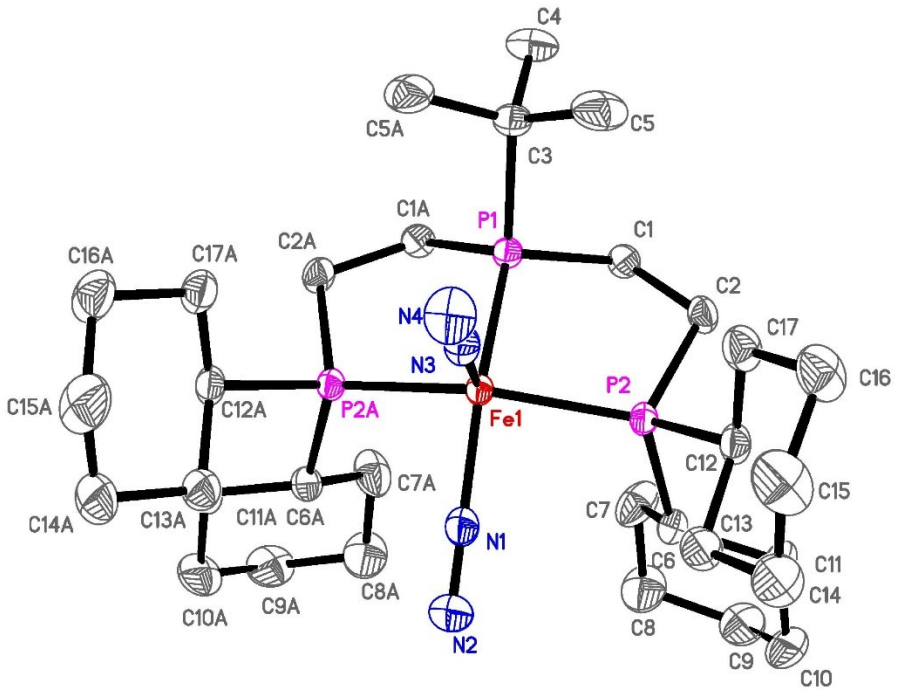


Figure S14: Molecular structure of **4b**. Hydrogen and solvent molecules are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°):Fe1-N1 1.808(8), Fe1-N3 1.834(2), Fe1-P1 2.193(1), Fe1-P2 2.220(1), N1-N2 1.128(3), N3-N4 1.118(3), N1-Fe1-N3 100.0(1), N1-Fe1-P1 155.9(1), N3-Fe1-P1 104.1(1), N1-Fe1-P2 88.0(1), N3-Fe1-P2 106.7(1), P1-Fe1-P2 85.1(1), N2-N1-Fe1 179.8(2), N4-N3-Fe1 179.7(2), P2A-Fe1-P2 146.5(1).

5.4. Molecular Structure of 6a

$C_{34}H_{59}FeN_2P_3$, *M*=644.59, Triclinic, space group *P* $\bar{1}$, a=9.9709(6)Å, b=18.7613(10)Å, c=19.3003(11)Å, α=104.771(3)°, β=90.189(3)°, γ=99.733(4)°, *V*=3436.8(3) Å^3, *Z*=4, crystal size 0.14 x 0.08 x 0.02 mm^3, 56144 reflections collected (11936 independent, R_{int}=0.1242), 834 parameters, 447 restraints, *R*1 [I>2σ(I)]= 0.0825, *wR*2 [all data]= 0.2077, largest diff. peak and hole: 0.881 and -0.514 e.Å^{-3}.

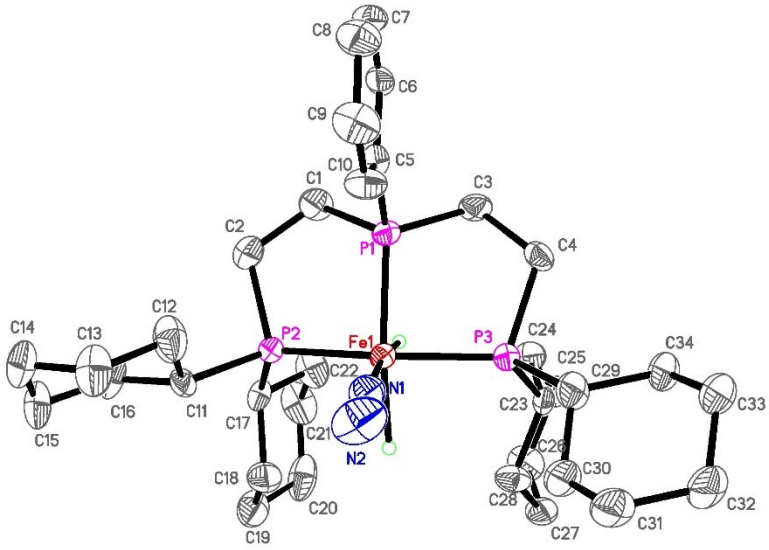


Figure S15: Molecular structure of **6a**. Only one of the two independent molecule in the asymmetric unit is shown and described. Hydrogen atoms and disordered atoms are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°):Fe1-N1 1.816(7), Fe1-P1 2.154(2), Fe1-P2 2.169(2), Fe1-P3 2.170(2), Fe1-H1C 1.52(6), Fe1-H1D 1.72(6), N1-N2 1.085(8), N1-Fe1-P1 110.3(2), N1-Fe1-P2 103.4(2), N1-Fe1-P3 100.8(2), P1-Fe1-P3 88.8(1), P1-Fe1-P2 88.4(1), P2-Fe1-P3 155.0(1), N2-N1-Fe1 175.3(7), N1-Fe1-H1C 170(2), N1-Fe1-H1D 90(2).

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