Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Double α,α CH Bond Insertion into sp^3 CH_2 Moiety: Synthesis of a Fe Carbene bis-Hydride Dinitrogen Complex.

Julien Petit, Anthony Cavaillé, Nathalie Saffon-Merceron, Marie Fustier-Boutignon and Nicolas Mézailles*

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1. Experimental procedures

Reagents and solvents

All the reactions were carried out in the glove box or using standard schlenck techniques under N_2. The commercial compounds stored under N_2 or Ar were used directly without any further purification, while the non-stored under inert atmosphere, they were degassed before use. All solvents were taken from MBSPS-800 solvent purification system, then they were degassed and dried using molecular sieves.

NMR

^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. ^{1}H chemical shifts reported are referenced internally to residual protosolvent (^{1}H) while ^{31}P chemical shifts are referenced to an external standard of phosphoric acid.

Solid state NMR experiments were recorded on a Bruker Avance 400 III HD spectrometer operating at a magnetic field of 9.4 T. Samples were packed into 3.2 m zirconia rotors under argon inside a glove box. The rotor was spun at 14 kHz and 8 kHz at 295 K. ^{13}C CPMAS spectra were recorded with a recycle delay of 1.5 s and a contact times of 3 ms. Chemical shifts were externally referenced to liquid TMS.

Elemental analysis (C, H, N)

Elemental analysis of crystalline **3d** dimer powder were carried out by combustion analysis using vario MICRO cube apparatus from Elementar.

X-ray diffraction analysis

Crystallographic data for compounds complex **2** and **3d** were collected at 193(2) K on a Bruker-AXS Kappa APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source (**3d**) and on a Bruker-AXS D8-Venture diffractometer equipped with a CMOS detector (Photon 100) and a 30W air-cooled microfocus source (**2**) using Mo Kα radiation (λ=0.71073 Å). Phi- and omega-scans were used. Space group was determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed.[1] The structure were solved using an intrinsic phasing method (SHELXT),[2] and refined using the least-squares method on F2.[3] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp3 carbon and 1.2 times for all other carbon atoms, except for the hydrides of **3d** (located by difference Fourier map and freely refined). Several solvent molecules of THF were disordered: several restraints (SAME, SIMU, DELU, ISOR) were applied to model the disorders. Some bond lengths were restrained with DFIX to suitable target values. CCDC-2062762 (**2**) and CCDC-2062763 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

^{57}Fe Mössbauer Spectroscopy

Solid Mössbauer crystals of **3d** dimer were packed in Delron disk sample cups and loaded into the spectrometer at 80 K under reduced helium pressure. Mössbauer measurements were performed using conventional constant-acceleration-type spectrometer equipped with a 50 mCi ^{57}Co source and a liquid-N_2 cryostat. Least-square fittings of the Mössbauer spectra were performed considering line shapes using the Recoil software package.

Raman (instrument of the Equipex-Critex in the LCA, Toulouse-INP)

Resonance Raman analysis were conducted on a LabRAM HR Evolution Confocal Raman microscope with a Syncer-OE-Raman CCD detector, using a BX41 (CDRH)-OLYMPUS microscope and NUV camera (B/S UV 50/50+lens F125 D25). Resonance Raman Spectra were collected on a crystalline solid-state sample of **3d** dimer under N_2 atmosphere at -30°C with a 532nm excitation (0.1% x 50mW). The solid-state sample was located between two layers of glass. Background signal was subtracted to the **3d** dimer analysis by doing the same analysis in the same condition, without the sample.

Infra-Red

IR spectra were recorded on a Varian 640 Fourier transform infrared spectrophotometer.

Syntheses

"PCH_2P" ligand,[4] KC_8,[5] and $(THF)_{1.5}FeCl_2$[6] were prepared according to literature procedure.

$(PCH_2P)FeCl_2$, complex 2

A solution of "PCH_2P" ligand (1.182g, 2mmol, 1eq.) in THF (10mL) was added on solid $FeCl_2(THF)_{1.5}$ (470mg, 2mmol, 1eq.). A bright yellow solution was obtained. The solution was then concentrated and put at -30°C for 48h, giving yellow crystals. The crystals were filtered, washed with pentane (3*5mL) and dried under reduced pressure. The remaining solution was put under the same protocol to yield a second crop of crystals. In the end, 1.112g (1.55mmol) of the title complex is obtained as yellow crystals (ρ=78%).

^{1}H NMR (300MHz, THF-d_8, 298K) δ : 130.3(bs), 120.5 (bs), 60.1 (bs), 13.5 (bs), 6.5 (bs), 6.1 (bs), 5.4 (bs), 2.1 - -7.0 (bs), -3.5 (bs), -4.6 (bs). μ_{eff} (Evans, benzene-d_6, 298K): 5.0 μ_B. ^{57}Fe Mössbauer δ = 0.77 mm.s^{-1}, ΔE_Q = 2.71 mm.s^{-1}.

Reduction of complex 2 yielding a mixture of 3cis and 3trans complexes

A schlenk flask was charged with KC_8 (135mg, 0.1mmol, 2eq.) and $(PCH_2P)FeCl_2$ (359mg, 0.05mmol, 1eq.) and cooled to -100°C. A Schlenk flask containing THF dipped in liquid N_2 until THF starts freezing. At this moment, THF (10mL) was syringed from the Schlenk and added to the two solids at -100°C under vigorous stirring. The temperature was maintained over 10h between -100°C and -80°C. The mixture was then allowed to slowly warm to 20°C over 16h. The black suspension was filtered to remove graphite, and the solid was washed with THF (3*5mL). The obtained bright orange solution contained free "PCH_2P" ligand, ***3cis*** and ***3trans*** complexes, as shown by NMR (Figure S3-S5).

^{1}H NMR (300MHz, THF-d_8, 298K) δ : -8.1 (t, J=40.9Hz, FeH_2 3*trans*), -12.4 (t, J=50.2Hz, FeH_2 3*cis*). ^{31}P{^{1}H} NMR (121.4MHz, THF-d_8, 298K) δ: 96.6 (s, 3*trans*), 97.1 (s, 3*cis*), -16.9 (s, PCH2P).

[(PCP)Fe(H)$_2$]$_2$[μ-N$_2$], complex 3d

A schlenk flask was charged with KC_8 (135mg, 0.1mmol, 2eq.) and (PCH_2P)$FeCl_2$ (359mg, 0.05mmol, 1eq.) and cooled to -100°C. A Schlenk flask containing THF dipped in liquid N_2 until THF starts freezing. At this moment, THF (10mL) was syringed from the Schlenk and added to the two solids at -100°C under vigorous stirring. The temperature was maintained over 10h between -100°C and -80°C. The mixture was then allowed to slowly warm to 20°C over 16h. The black suspension was filtered to remove graphite, and the solid was washed with THF (3*5mL). The obtained bright orange solution was kept at RT over one month to afford orange crystals. Alternatively, crystals could be obtained upon cooling of the solution at -36°C. These crystals are washed with THF and dried under reduced pressure, giving the title compound as an orange crystalline material (144mg, ρ=44%).

^{1}H NMR (300MHz, THF-d_8, 298K) δ : 6.58-7.32 (12H, m, Ar), 1.17-2.23 (96H, m, Cy & N-CH_2-P), -8.15 (4H, t, J=40.8Hz, FeH_2).

^{31}P{^{1}H} NMR (121.4MHz, THF-d_8, 298K) δ: 94.8 (s).

CP MAS ^{13}C NMR (121.4MHz, 298K): δ: 26.0 (Cy), 66.6 (N*C*H$_2$P), 102.7, 117.0, 127.7, 134.0 (C aromatic ring), 244.5 (N*C*N).

^{57}Fe Mössbauer δ = 0.0073(35) mm.s^{-1}, ΔE_Q = 1.5843(70) mm.s^{-1}.

2. NMR, ^{57}Fe Mössbauer and Raman spectra

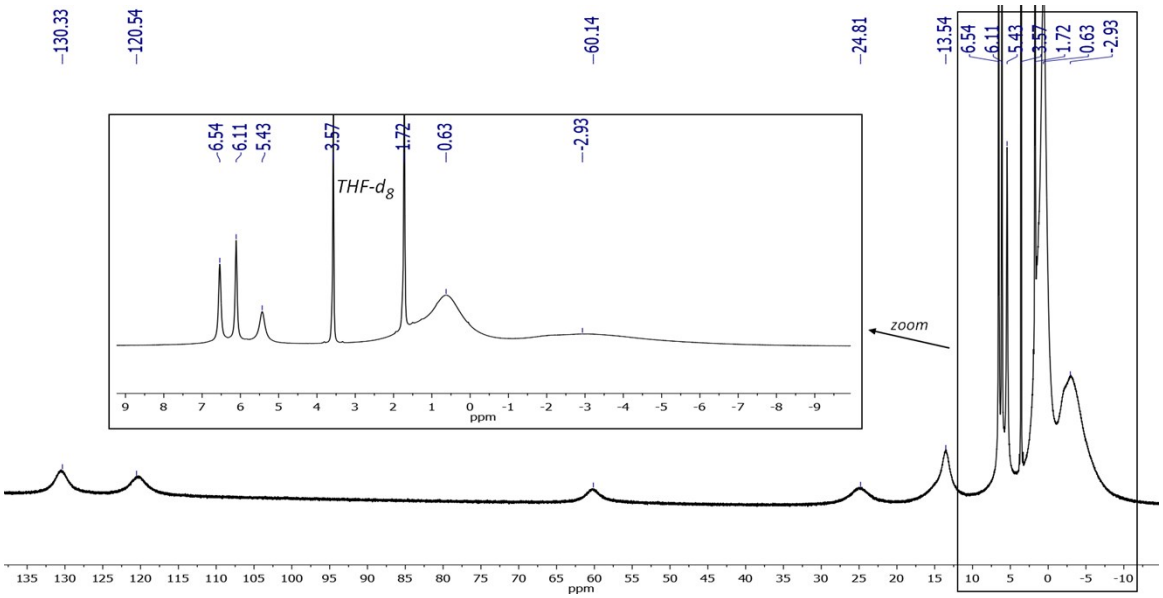


Figure S1 – ^{1}H NMR of **2** in THF-d_8 (no signal in ^{31}P{^{1}H} NMR)

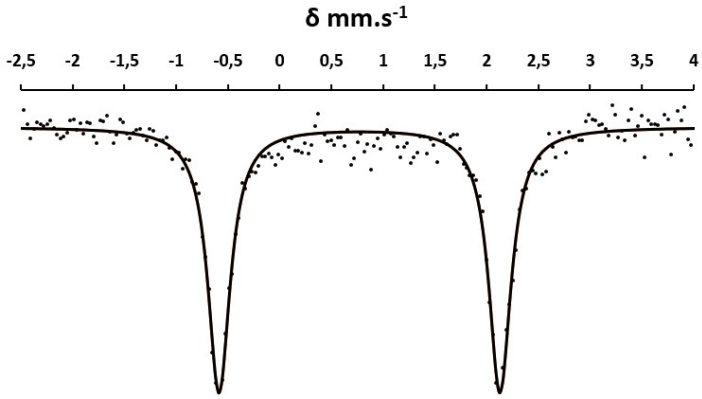


Figure S2 – Mössbauer spectrum of complex **2**.

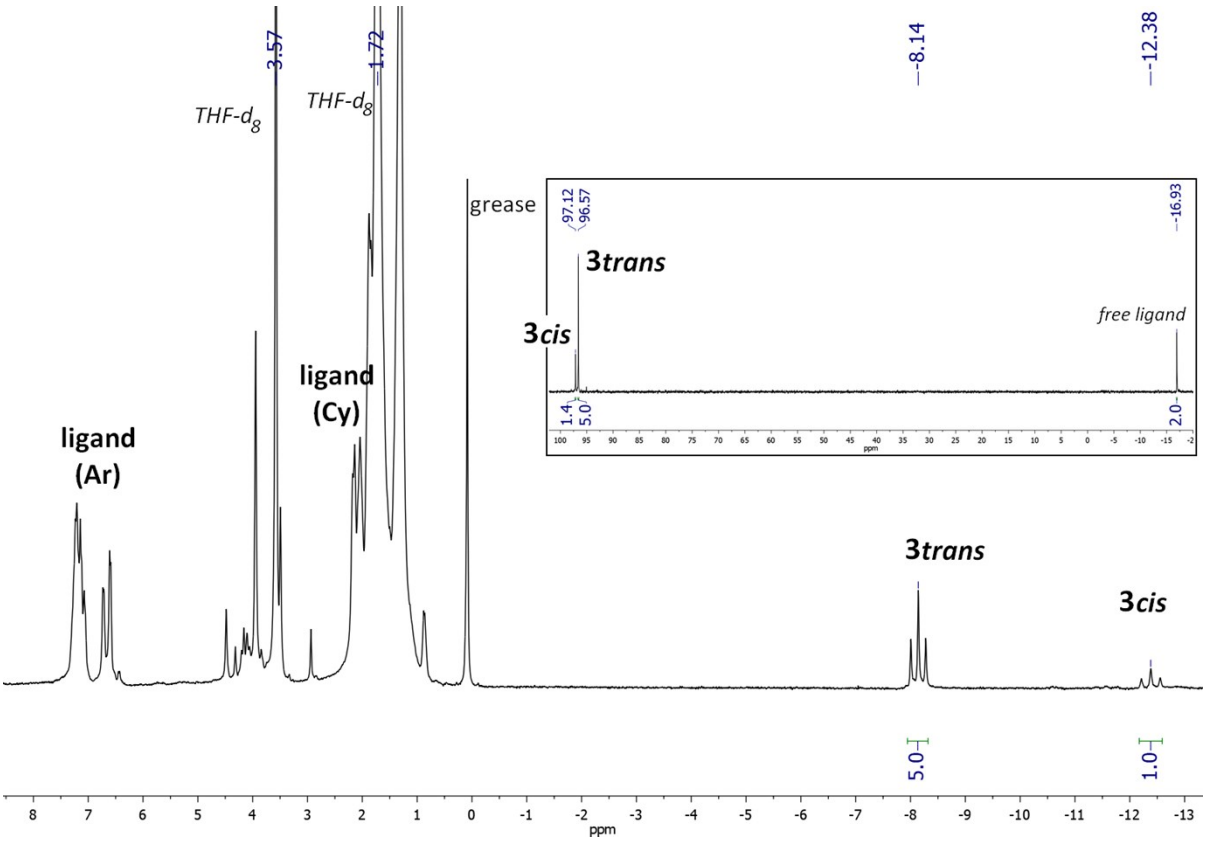


Figure S3 – ^{1}H and ^{31}P NMR in THF-d_8 of crude mixture, after the reaction of **2** with two equivalents of KC_8 at -100°C.

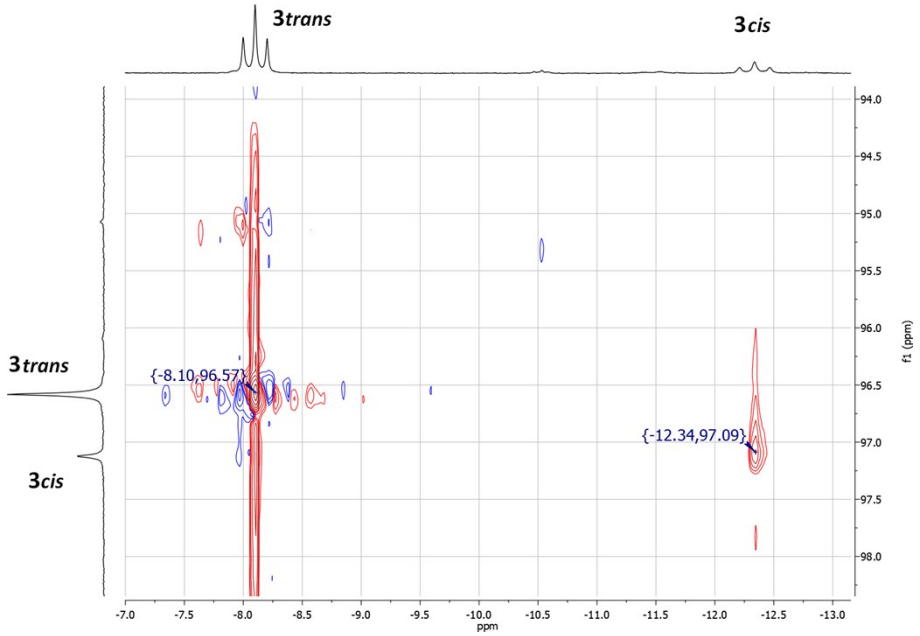


Figure S4 – hsqc ($^{1}H/^{31}P$) in THF-d_8 of crude mixture, after the reaction of **2** with two equivalents of KC_8 at -100°C.

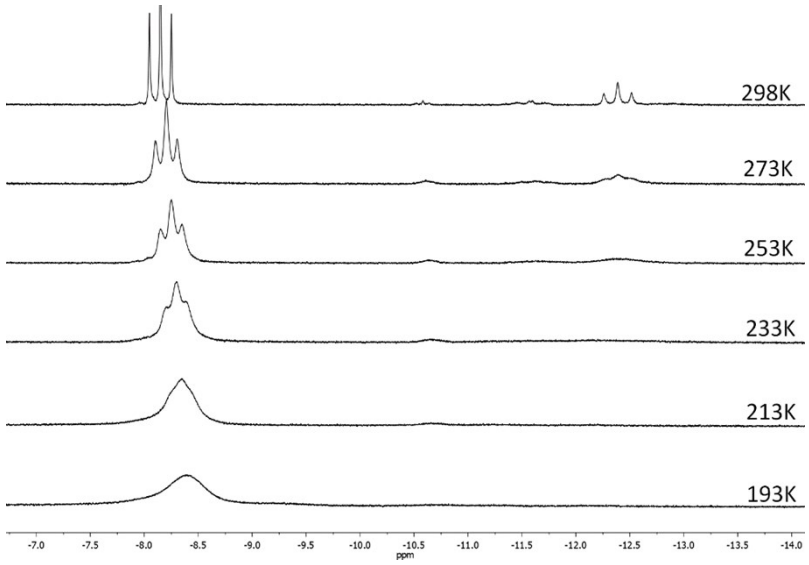


Figure S5. Variable temperature ^{1}H NMR in THF-d_8 of crude mixture, after the reaction of **2** with two equivalents of KC_8 at -100°C. Only the hydride area is shown here.

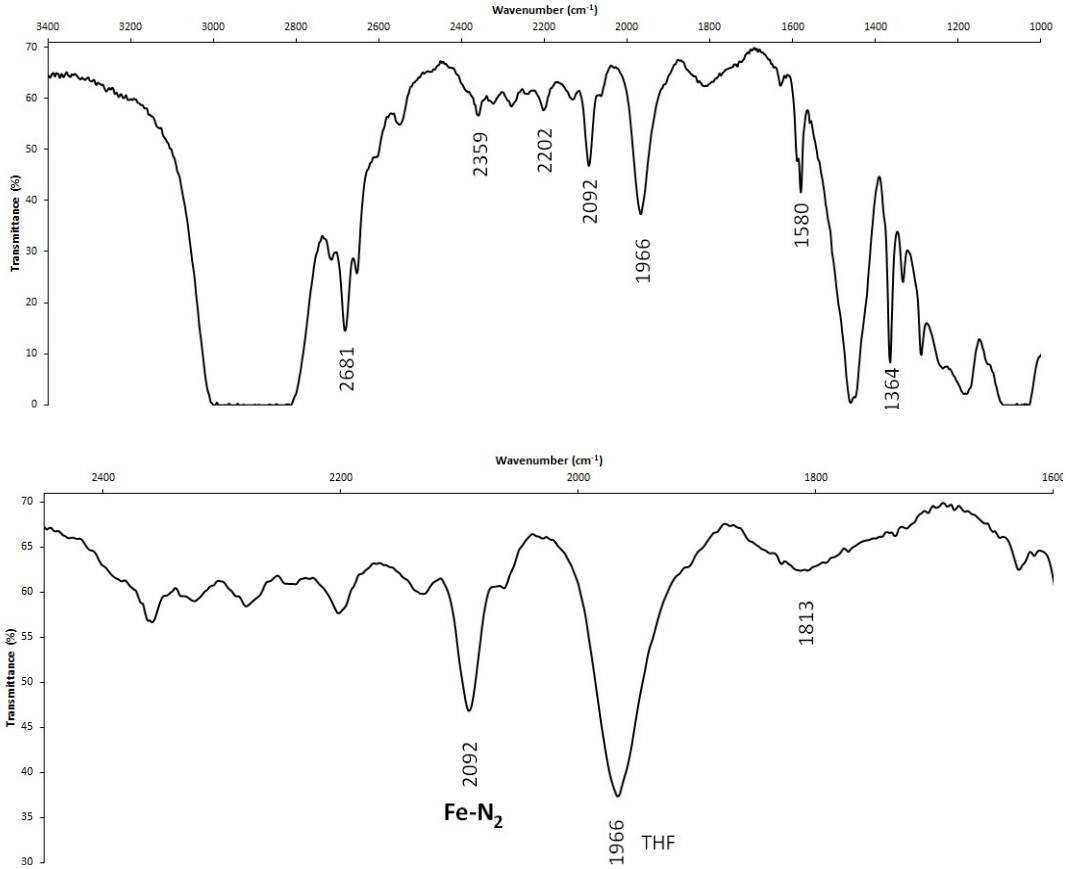


Figure S6. Infra-red spectra of crude mixture in THF (top) and zoom of the 1600-2450cm^{-1} area (below). Remaining THF is observed because of a non-optimal substraction of the background THF solution because of the very poor solubility of the complex **3d** after crystallization.

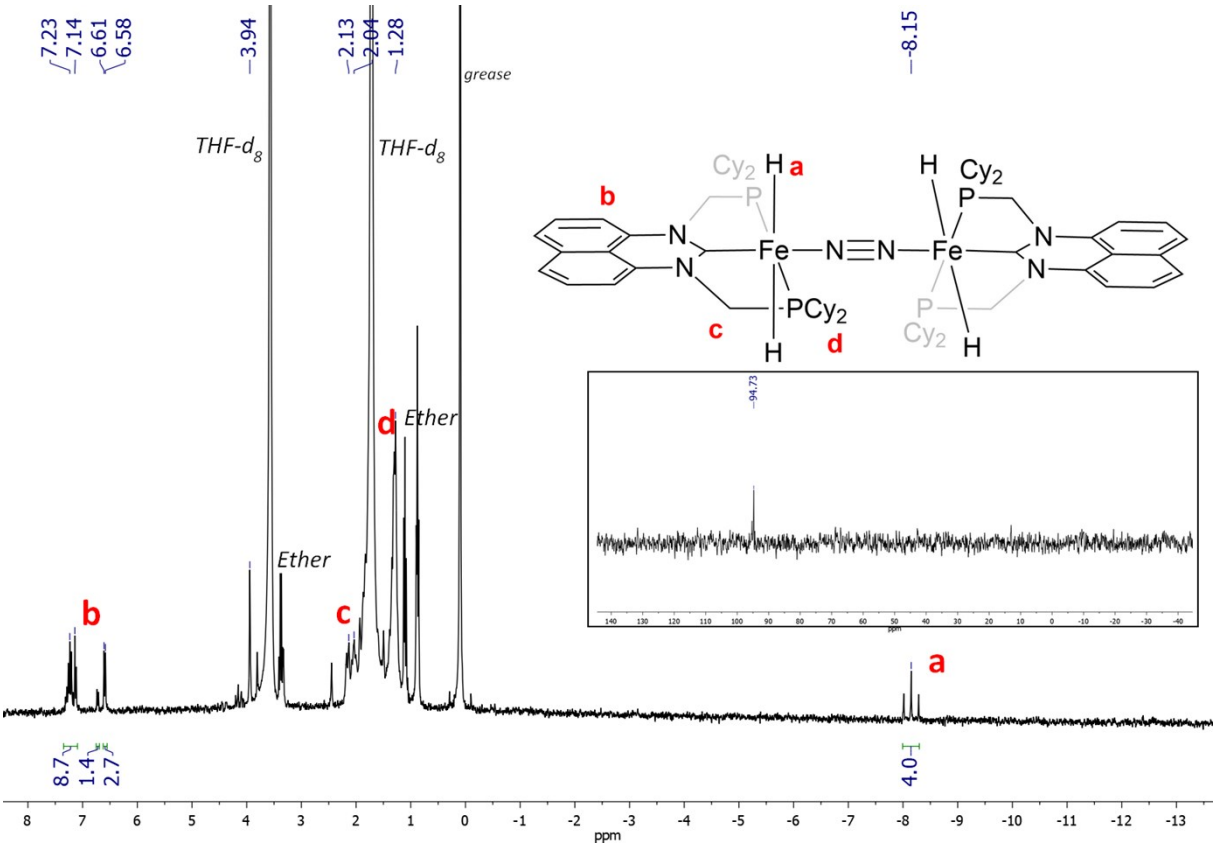
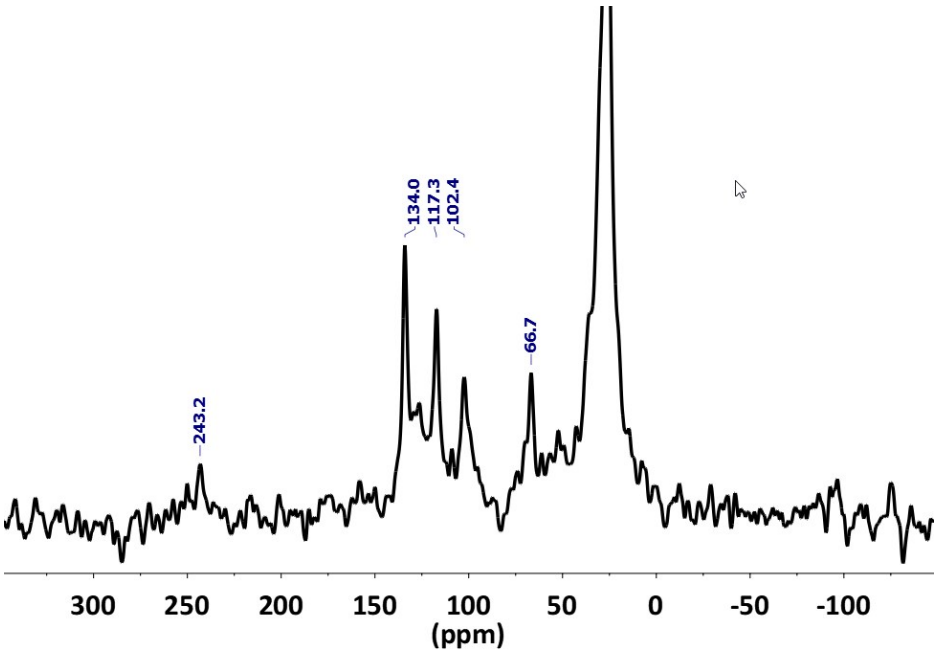


Figure S7. ^{1}H and $^{31}P\{^{1}H\}$ (inset) in THF-d_8 NMR of compound **3d**.



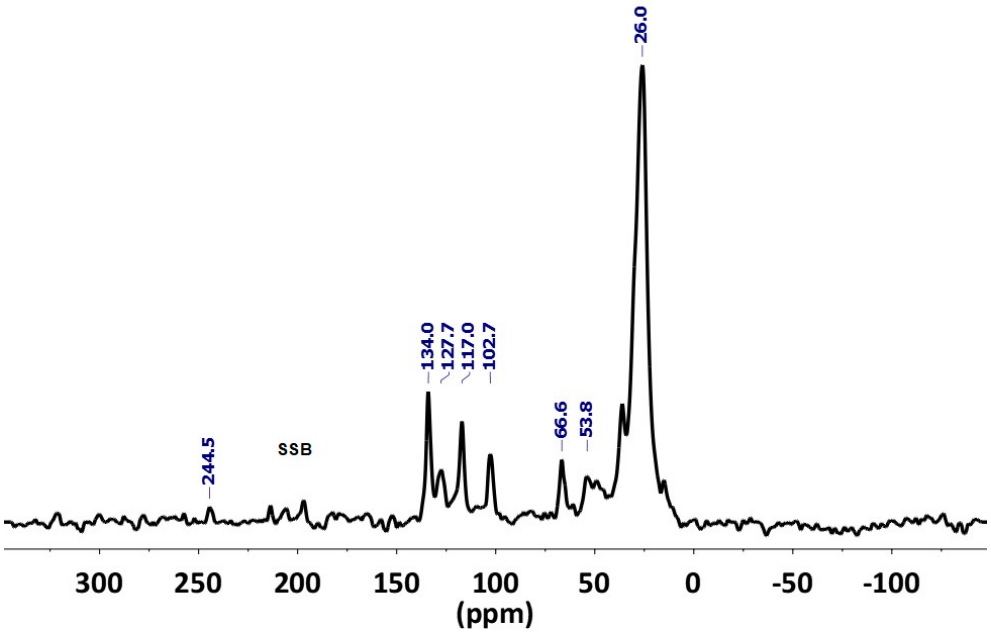


Figure S8. CPMAS ^{13}C NMR spectra of compound **3d**, probe= 3.2 mm, recorded at Vr= 14 kHz (top) and 8 kHz (bottom). Using two different rotation speeds allows to clearly identify the signal at 244 ppm as the carbene center.

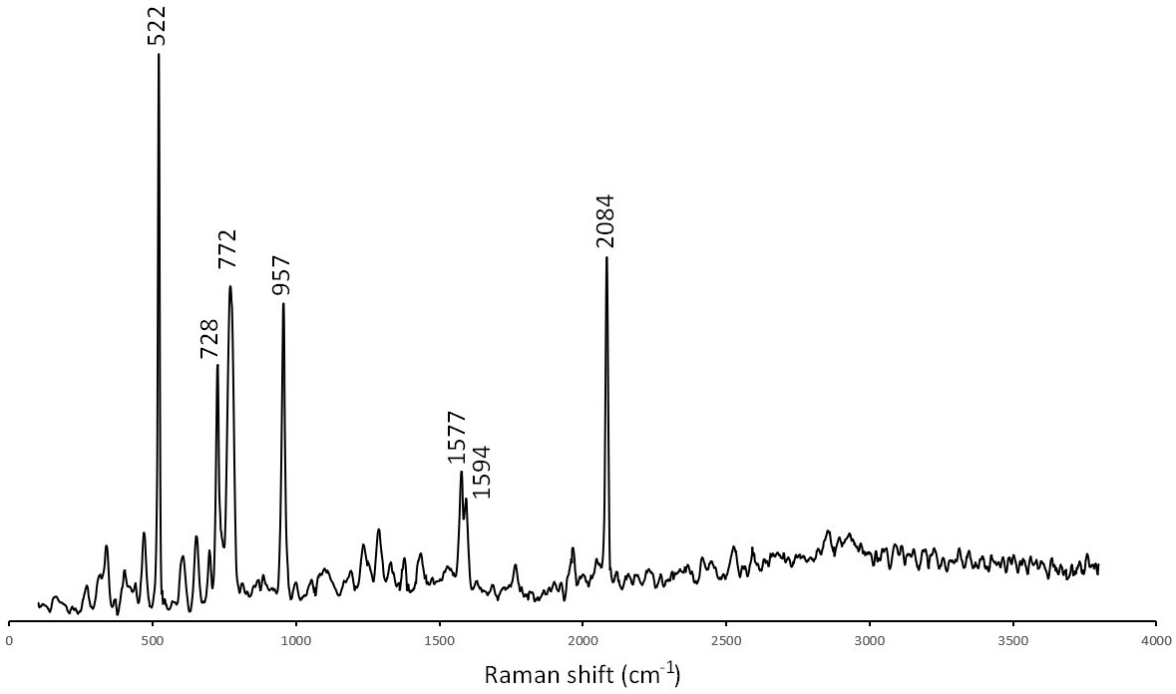


Figure S9. Raman spectrum of **3d** in the solid state (Fe-N_2-Fe stretch at 2084cm^{-1}).

3. X-Ray diffraction data

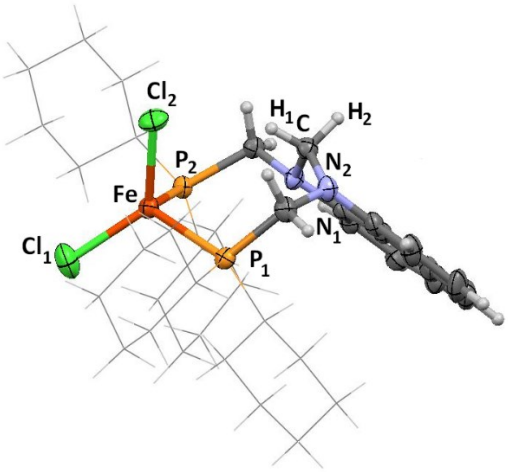


Figure S10. X-ray crystallographic structure of complex **2**.

Table S1. Crystal data and structure refinement for **2**.

Empirical formula	C37 H56 Cl2 Fe N2 P2, 1.5 (C 4 H 8 O)	
Formula weight	825.68	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0591(4) Å	α= 80.9776(13)°.
	b = 11.1758(4) Å	β= 77.2074(14)°.
	c = 18.3680(7) Å	γ = 86.6279(14)°.
Volume	2185.75(14) $Å^3$	
Z	2	
Density (calculated)	1.255 Mg/m^3	
Absorption coefficient	0.576 mm^{-1}	
F(000)	884	
Crystal size	0.200 x 0.160 x 0.150 mm^3	
Theta range for data collection	2.858 to 28.282°.	
Index ranges	-14<=h<=14, -14<=k<=14, -24<=l<=24	

Reflections collected	47842
Independent reflections	10829 [R(int) = 0.0636]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7463 and 0.6828
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10829 / 214 / 533
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1073
R indices (all data)	R1 = 0.0828, wR2 = 0.1254
Extinction coefficient	n/a
Largest diff. peak and hole	0.492 and -0.430 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [°] for **2**.

Fe(1)-Cl(2)	2.2320(8)
Fe(1)-Cl(1)	2.2565(7)
Fe(1)-P(1)	2.4717(7)
Fe(1)-P(2)	2.4819(7)
P(1)-C(14)	1.852(2)
P(1)-C(20)	1.853(2)
P(1)-C(2)	1.859(2)
P(2)-C(32)	1.844(2)
P(2)-C(26)	1.856(2)
P(2)-C(3)	1.879(3)
N(1)-C(4)	1.397(3)
N(1)-C(2)	1.459(3)
N(1)-C(1)	1.473(3)
N(2)-C(6)	1.404(3)
N(2)-C(1)	1.436(3)

N(2)-C(3)	1.455(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(13)	1.382(3)
C(4)-C(5)	1.439(3)
C(5)-C(10)	1.423(3)
C(5)-C(6)	1.427(3)
C(6)-C(7)	1.379(4)
C(7)-C(8)	1.402(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.363(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.417(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.413(4)
C(11)-C(12)	1.357(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.411(4)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(19)	1.533(4)
C(14)-C(15)	1.534(3)
C(14)-H(14)	1.0000
C(15)-C(16)	1.535(4)
C(15)-H(15A)	0.9900

C(15)-H(15B)	0.9900
C(16)-C(17)	1.517(4)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.521(4)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.531(4)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.532(3)
C(20)-C(25)	1.538(3)
C(20)-H(20)	1.0000
C(21)-C(22)	1.530(4)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.525(4)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.519(4)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.528(4)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900

C(26)-C(27)	1.529(4)
C(26)-C(31)	1.539(4)
C(26)-H(26)	1.0000
C(27)-C(28)	1.525(4)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.522(4)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.500(5)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.522(4)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-C(33)	1.528(3)
C(32)-C(37)	1.534(3)
C(32)-H(32)	1.0000
C(33)-C(34)	1.529(3)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.522(4)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.519(4)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900

C(36)-C(37)	1.524(4)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-C(41)	1.448(11)
C(38)-C(39)	1.516(12)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-O(1)	1.449(11)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
O(1)-C(40)	1.325(11)
C(40)-C(41)	1.480(11)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(38')-C(39')	1.469(17)
C(38')-C(41')	1.517(16)
C(38')-H(38C)	0.9900
C(38')-H(38D)	0.9900
C(39')-O(1')	1.585(17)
C(39')-H(39C)	0.9900
C(39')-H(39D)	0.9900
O(1')-C(40')	1.246(15)
C(40')-C(41')	1.460(16)
C(40')-H(40C)	0.9900
C(40')-H(40D)	0.9900

C(41')-H(41C)	0.9900
C(41')-H(41D)	0.9900
C(43)-C(44)	1.37(3)
C(43)-C(46)	1.54(3)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-O(2)	1.34(2)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
O(2)-C(45)	1.41(2)
C(45)-C(46)	1.35(2)
C(45)-H(45A)	0.9900
C(45)-H(45B)	0.9900
C(46)-H(46A)	0.9900
C(46)-H(46B)	0.9900

Cl(2)-Fe(1)-Cl(1)	123.30(3)
Cl(2)-Fe(1)-P(1)	108.44(3)
Cl(1)-Fe(1)-P(1)	104.60(3)
Cl(2)-Fe(1)-P(2)	110.91(3)
Cl(1)-Fe(1)-P(2)	97.69(3)
P(1)-Fe(1)-P(2)	111.35(2)
C(14)-P(1)-C(20)	106.46(11)
C(14)-P(1)-C(2)	103.01(11)
C(20)-P(1)-C(2)	101.27(11)
C(14)-P(1)-Fe(1)	115.80(8)
C(20)-P(1)-Fe(1)	119.55(8)
C(2)-P(1)-Fe(1)	108.56(8)
C(32)-P(2)-C(26)	107.22(11)

C(32)-P(2)-C(3)	103.14(12)
C(26)-P(2)-C(3)	99.31(11)
C(32)-P(2)-Fe(1)	119.61(8)
C(26)-P(2)-Fe(1)	111.16(9)
C(3)-P(2)-Fe(1)	114.19(8)
C(4)-N(1)-C(2)	121.86(19)
C(4)-N(1)-C(1)	113.24(19)
C(2)-N(1)-C(1)	114.89(19)
C(6)-N(2)-C(1)	114.1(2)
C(6)-N(2)-C(3)	120.9(2)
C(1)-N(2)-C(3)	118.2(2)
N(2)-C(1)-N(1)	111.5(2)
N(2)-C(1)-H(1A)	109.3
N(1)-C(1)-H(1A)	109.3
N(2)-C(1)-H(1B)	109.3
N(1)-C(1)-H(1B)	109.3
H(1A)-C(1)-H(1B)	108.0
N(1)-C(2)-P(1)	110.58(16)
N(1)-C(2)-H(2A)	109.5
P(1)-C(2)-H(2A)	109.5
N(1)-C(2)-H(2B)	109.5
P(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	108.1
N(2)-C(3)-P(2)	117.35(16)
N(2)-C(3)-H(3A)	108.0
P(2)-C(3)-H(3A)	108.0
N(2)-C(3)-H(3B)	108.0
P(2)-C(3)-H(3B)	108.0
H(3A)-C(3)-H(3B)	107.2

C(13)-C(4)-N(1)	124.4(2)
C(13)-C(4)-C(5)	118.8(2)
N(1)-C(4)-C(5)	116.7(2)
C(10)-C(5)-C(6)	119.4(2)
C(10)-C(5)-C(4)	119.2(2)
C(6)-C(5)-C(4)	121.1(2)
C(7)-C(6)-N(2)	121.7(2)
C(7)-C(6)-C(5)	120.0(2)
N(2)-C(6)-C(5)	118.3(2)
C(6)-C(7)-C(8)	120.2(3)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	121.0(3)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(8)-C(9)-C(10)	121.0(3)
C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5
C(11)-C(10)-C(9)	122.0(3)
C(11)-C(10)-C(5)	119.6(2)
C(9)-C(10)-C(5)	118.4(3)
C(12)-C(11)-C(10)	120.2(3)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	121.3(3)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(4)-C(13)-C(12)	120.8(2)
C(4)-C(13)-H(13)	119.6

C(12)-C(13)-H(13)	119.6
C(19)-C(14)-C(15)	109.8(2)
C(19)-C(14)-P(1)	111.92(18)
C(15)-C(14)-P(1)	111.84(17)
C(19)-C(14)-H(14)	107.7
C(15)-C(14)-H(14)	107.7
P(1)-C(14)-H(14)	107.7
C(14)-C(15)-C(16)	111.2(2)
C(14)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15A)	109.4
C(14)-C(15)-H(15B)	109.4
C(16)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0
C(17)-C(16)-C(15)	111.9(3)
C(17)-C(16)-H(16A)	109.2
C(15)-C(16)-H(16A)	109.2
C(17)-C(16)-H(16B)	109.2
C(15)-C(16)-H(16B)	109.2
H(16A)-C(16)-H(16B)	107.9
C(16)-C(17)-C(18)	110.9(2)
C(16)-C(17)-H(17A)	109.5
C(18)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
C(18)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	108.0
C(17)-C(18)-C(19)	111.3(3)
C(17)-C(18)-H(18A)	109.4
C(19)-C(18)-H(18A)	109.4
C(17)-C(18)-H(18B)	109.4

C(19)-C(18)-H(18B) 109.4

H(18A)-C(18)-H(18B) 108.0

C(18)-C(19)-C(14) 110.8(2)

C(18)-C(19)-H(19A) 109.5

C(14)-C(19)-H(19A) 109.5

C(18)-C(19)-H(19B) 109.5

C(14)-C(19)-H(19B) 109.5

H(19A)-C(19)-H(19B) 108.1

C(21)-C(20)-C(25) 109.0(2)

C(21)-C(20)-P(1) 114.70(17)

C(25)-C(20)-P(1) 114.70(17)

C(21)-C(20)-H(20) 105.9

C(25)-C(20)-H(20) 105.9

P(1)-C(20)-H(20) 105.9

C(22)-C(21)-C(20) 110.1(2)

C(22)-C(21)-H(21A) 109.6

C(20)-C(21)-H(21A) 109.6

C(22)-C(21)-H(21B) 109.6

C(20)-C(21)-H(21B) 109.6

H(21A)-C(21)-H(21B) 108.2

C(23)-C(22)-C(21) 111.2(2)

C(23)-C(22)-H(22A) 109.4

C(21)-C(22)-H(22A) 109.4

C(23)-C(22)-H(22B) 109.4

C(21)-C(22)-H(22B) 109.4

H(22A)-C(22)-H(22B) 108.0

C(24)-C(23)-C(22) 111.7(2)

C(24)-C(23)-H(23A) 109.3

C(22)-C(23)-H(23A) 109.3

C(24)-C(23)-H(23B) 109.3

C(22)-C(23)-H(23B) 109.3

H(23A)-C(23)-H(23B) 107.9

C(23)-C(24)-C(25) 110.8(2)

C(23)-C(24)-H(24A) 109.5

C(25)-C(24)-H(24A) 109.5

C(23)-C(24)-H(24B) 109.5

C(25)-C(24)-H(24B) 109.5

H(24A)-C(24)-H(24B) 108.1

C(24)-C(25)-C(20) 110.1(2)

C(24)-C(25)-H(25A) 109.6

C(20)-C(25)-H(25A) 109.6

C(24)-C(25)-H(25B) 109.6

C(20)-C(25)-H(25B) 109.6

H(25A)-C(25)-H(25B) 108.2

C(27)-C(26)-C(31) 109.6(2)

C(27)-C(26)-P(2) 112.28(17)

C(31)-C(26)-P(2) 109.98(18)

C(27)-C(26)-H(26) 108.3

C(31)-C(26)-H(26) 108.3

P(2)-C(26)-H(26) 108.3

C(28)-C(27)-C(26) 112.0(2)

C(28)-C(27)-H(27A) 109.2

C(26)-C(27)-H(27A) 109.2

C(28)-C(27)-H(27B) 109.2

C(26)-C(27)-H(27B) 109.2

H(27A)-C(27)-H(27B) 107.9

C(29)-C(28)-C(27) 111.3(2)

C(29)-C(28)-H(28A) 109.4

C(27)-C(28)-H(28A) 109.4

C(29)-C(28)-H(28B) 109.4

C(27)-C(28)-H(28B) 109.4

H(28A)-C(28)-H(28B) 108.0

C(30)-C(29)-C(28) 111.2(3)

C(30)-C(29)-H(29A) 109.4

C(28)-C(29)-H(29A) 109.4

C(30)-C(29)-H(29B) 109.4

C(28)-C(29)-H(29B) 109.4

H(29A)-C(29)-H(29B) 108.0

C(29)-C(30)-C(31) 112.0(3)

C(29)-C(30)-H(30A) 109.2

C(31)-C(30)-H(30A) 109.2

C(29)-C(30)-H(30B) 109.2

C(31)-C(30)-H(30B) 109.2

H(30A)-C(30)-H(30B) 107.9

C(30)-C(31)-C(26) 111.7(3)

C(30)-C(31)-H(31A) 109.3

C(26)-C(31)-H(31A) 109.3

C(30)-C(31)-H(31B) 109.3

C(26)-C(31)-H(31B) 109.3

H(31A)-C(31)-H(31B) 107.9

C(33)-C(32)-C(37) 110.2(2)

C(33)-C(32)-P(2) 112.30(17)

C(37)-C(32)-P(2) 116.15(16)

C(33)-C(32)-H(32) 105.8

C(37)-C(32)-H(32) 105.8

P(2)-C(32)-H(32) 105.8

C(32)-C(33)-C(34) 110.6(2)

C(32)-C(33)-H(33A) 109.5

C(34)-C(33)-H(33A) 109.5

C(32)-C(33)-H(33B) 109.5

C(34)-C(33)-H(33B) 109.5

H(33A)-C(33)-H(33B) 108.1

C(35)-C(34)-C(33) 111.2(2)

C(35)-C(34)-H(34A) 109.4

C(33)-C(34)-H(34A) 109.4

C(35)-C(34)-H(34B) 109.4

C(33)-C(34)-H(34B) 109.4

H(34A)-C(34)-H(34B) 108.0

C(36)-C(35)-C(34) 111.4(2)

C(36)-C(35)-H(35A) 109.3

C(34)-C(35)-H(35A) 109.3

C(36)-C(35)-H(35B) 109.3

C(34)-C(35)-H(35B) 109.3

H(35A)-C(35)-H(35B) 108.0

C(35)-C(36)-C(37) 111.5(2)

C(35)-C(36)-H(36A) 109.3

C(37)-C(36)-H(36A) 109.3

C(35)-C(36)-H(36B) 109.3

C(37)-C(36)-H(36B) 109.3

H(36A)-C(36)-H(36B) 108.0

C(36)-C(37)-C(32) 110.2(2)

C(36)-C(37)-H(37A) 109.6

C(32)-C(37)-H(37A) 109.6

C(36)-C(37)-H(37B) 109.6

C(32)-C(37)-H(37B) 109.6

H(37A)-C(37)-H(37B) 108.1

C(41)-C(38)-C(39) 103.0(7)

C(41)-C(38)-H(38A) 111.2

C(39)-C(38)-H(38A) 111.2

C(41)-C(38)-H(38B) 111.2

C(39)-C(38)-H(38B) 111.2

H(38A)-C(38)-H(38B) 109.1

O(1)-C(39)-C(38) 110.0(7)

O(1)-C(39)-H(39A) 109.7

C(38)-C(39)-H(39A) 109.7

O(1)-C(39)-H(39B) 109.7

C(38)-C(39)-H(39B) 109.7

H(39A)-C(39)-H(39B) 108.2

C(40)-O(1)-C(39) 106.7(7)

O(1)-C(40)-C(41) 113.0(7)

O(1)-C(40)-H(40A) 109.0

C(41)-C(40)-H(40A) 109.0

O(1)-C(40)-H(40B) 109.0

C(41)-C(40)-H(40B) 109.0

H(40A)-C(40)-H(40B) 107.8

C(38)-C(41)-C(40) 107.0(8)

C(38)-C(41)-H(41A) 110.3

C(40)-C(41)-H(41A) 110.3

C(38)-C(41)-H(41B) 110.3

C(40)-C(41)-H(41B) 110.3

H(41A)-C(41)-H(41B) 108.6

C(39')-C(38')-C(41') 98.6(13)

C(39')-C(38')-H(38C) 112.0

C(41')-C(38')-H(38C) 112.0

C(39')-C(38')-H(38D) 112.0

C(41')-C(38')-H(38D)	112.0
H(38C)-C(38')-H(38D)	109.7
C(38')-C(39')-O(1')	105.4(13)
C(38')-C(39')-H(39C)	110.7
O(1')-C(39')-H(39C)	110.7
C(38')-C(39')-H(39D)	110.7
O(1')-C(39')-H(39D)	110.7
H(39C)-C(39')-H(39D)	108.8
C(40')-O(1')-C(39')	106.6(12)
O(1')-C(40')-C(41')	111.6(14)
O(1')-C(40')-H(40C)	109.3
C(41')-C(40')-H(40C)	109.3
O(1')-C(40')-H(40D)	109.3
C(41')-C(40')-H(40D)	109.3
H(40C)-C(40')-H(40D)	108.0
C(40')-C(41')-C(38')	108.9(12)
C(40')-C(41')-H(41C)	109.9
C(38')-C(41')-H(41C)	109.9
C(40')-C(41')-H(41D)	109.9
C(38')-C(41')-H(41D)	109.9
H(41C)-C(41')-H(41D)	108.3
C(44)-C(43)-C(46)	102.4(18)
C(44)-C(43)-H(43A)	111.3
C(46)-C(43)-H(43A)	111.3
C(44)-C(43)-H(43B)	111.3
C(46)-C(43)-H(43B)	111.3
H(43A)-C(43)-H(43B)	109.2
O(2)-C(44)-C(43)	109.5(15)
O(2)-C(44)-H(44A)	109.8

C(43)-C(44)-H(44A)	109.8
O(2)-C(44)-H(44B)	109.8
C(43)-C(44)-H(44B)	109.8
H(44A)-C(44)-H(44B)	108.2
C(44)-O(2)-C(45)	109.9(13)
C(46)-C(45)-O(2)	104.6(15)
C(46)-C(45)-H(45A)	110.8
O(2)-C(45)-H(45A)	110.8
C(46)-C(45)-H(45B)	110.8
O(2)-C(45)-H(45B)	110.8
H(45A)-C(45)-H(45B)	108.9
C(45)-C(46)-C(43)	104(2)
C(45)-C(46)-H(46A)	111.0
C(43)-C(46)-H(46A)	111.0
C(45)-C(46)-H(46B)	111.0
C(43)-C(46)-H(46B)	111.0
H(46A)-C(46)-H(46B)	109.0

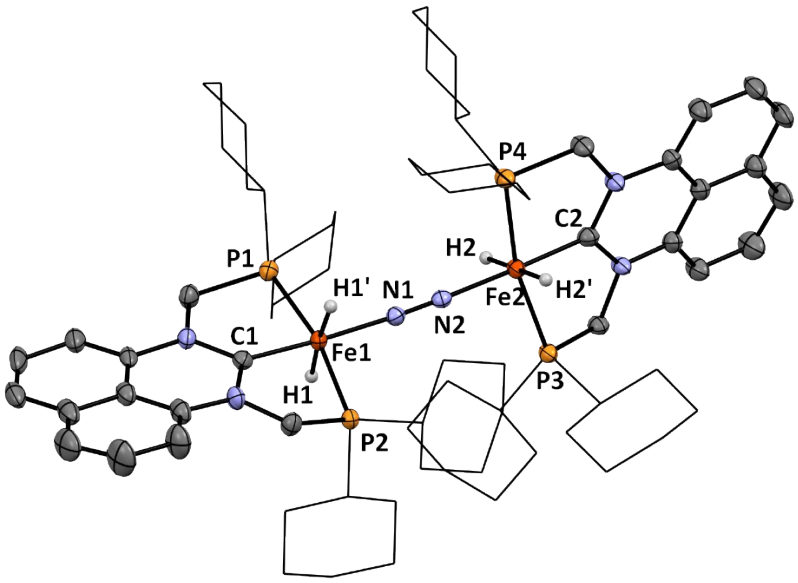


Figure S11. X-ray crystallographic structure of complex **3d**.

Table S3. Crystal data and structure refinment for complex **3d**.

Empirical formula	C74 H112 Fe2 N6 P4, 4.5 (C4 H 8 O)	
Formula weight	1645.74	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.3756(11) Å	α= 104.573(2)°.
	b = 15.4294(11) Å	β= 95.791(3)°.
	c = 22.9638(19) Å	γ = 98.177(2)°.
Volume	4493.7(6) $Å^3$	
Z	2	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.447 mm^{-1}	
F(000)	1780	
Crystal size	0.200 x 0.130 x 0.130 mm^3	
Theta range for data collection	1.385 to 26.373°.	
Index ranges	-16<=h<=16, -18<=k<=19, -28<=l<=28	
Reflections collected	100492	
Independent reflections	18321 [R(int) = 0.0858]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7014	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	18321 / 888 / 1200
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1358
R indices (all data)	R1 = 0.1016, wR2 = 0.1567
Extinction coefficient	n/a
Largest diff. peak and hole	0.824 and -0.640 e.Å^{-3}

Table S4. Bond lengths [Å] and angles [°] for **3d**.

Fe(1)-N(1)	1.865(3)
Fe(1)-C(1)	1.877(3)
Fe(1)-P(1)	2.1512(9)
Fe(1)-P(2)	2.1569(9)
Fe(1)-H(1)	1.48(3)
Fe(1)-H(1')	1.53(3)
Fe(2)-C(39)	1.869(3)
Fe(2)-N(2)	1.875(3)
Fe(2)-P(3)	2.1469(9)
Fe(2)-P(4)	2.1476(9)
Fe(2)-H(2)	1.50(3)
Fe(2)-H(2')	1.51(3)
P(1)-C(2)	1.836(3)
P(1)-C(20)	1.854(3)
P(1)-C(14)	1.857(3)
P(2)-C(3)	1.839(3)
P(2)-C(26)	1.852(3)
P(2)-C(32)	1.866(4)
P(3)-C(38)	1.837(3)
P(3)-C(51)	1.848(3)
P(3)-C(57)	1.860(3)
P(4)-C(40)	1.843(3)

P(4)-C(69)	1.855(3)
P(4)-C(63)	1.861(3)
N(1)-N(2)	1.125(3)
N(3)-C(1)	1.390(4)
N(3)-C(4)	1.402(4)
N(3)-C(2)	1.459(4)
N(4)-C(1)	1.389(4)
N(4)-C(6)	1.401(4)
N(4)-C(3)	1.462(4)
N(5)-C(39)	1.396(4)
N(5)-C(41)	1.411(4)
N(5)-C(38)	1.452(4)
N(6)-C(39)	1.391(4)
N(6)-C(43)	1.404(4)
N(6)-C(40)	1.449(4)
C(2)-H(2B)	0.9900
C(2)-H(2A)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(13)	1.375(4)
C(4)-C(5)	1.413(4)
C(5)-C(6)	1.414(4)
C(5)-C(10)	1.421(4)
C(6)-C(7)	1.371(5)
C(7)-C(8)	1.399(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.360(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.406(5)

C(9)-H(9)	0.9500
C(10)-C(11)	1.411(5)
C(11)-C(12)	1.371(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.399(5)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(19)	1.526(5)
C(14)-C(15)	1.533(5)
C(14)-H(14)	1.0000
C(15)-C(16)	1.519(5)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.519(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.518(6)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.518(5)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(25)	1.521(5)
C(20)-C(21)	1.532(4)
C(20)-H(20)	1.0000
C(21)-C(22)	1.531(5)
C(21)-H(21A)	0.9900

C(21)-H(21B)	0.9900
C(22)-C(23)	1.514(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.515(5)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.519(5)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.517(5)
C(26)-C(31)	1.535(4)
C(26)-H(26)	1.0000
C(27)-C(28)	1.522(5)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.523(5)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.510(5)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.521(5)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900

C(32)-C(37)	1.522(5)
C(32)-C(33)	1.527(5)
C(32)-H(32)	1.0000
C(33)-C(34)	1.525(6)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.512(6)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(36)	1.518(6)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-C(37)	1.526(6)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(50)	1.376(5)
C(41)-C(42)	1.406(5)
C(42)-C(43)	1.409(5)
C(42)-C(47)	1.422(5)
C(43)-C(44)	1.368(5)
C(44)-C(45)	1.401(5)
C(44)-H(44)	0.9500
C(45)-C(46)	1.367(6)

C(45)-H(45)	0.9500
C(46)-C(47)	1.398(6)
C(46)-H(46)	0.9500
C(47)-C(48)	1.402(5)
C(48)-C(49)	1.357(6)
C(48)-H(48)	0.9500
C(49)-C(50)	1.408(5)
C(49)-H(49)	0.9500
C(50)-H(50)	0.9500
C(51)-C(52)	1.529(5)
C(51)-C(56)	1.530(5)
C(51)-H(51)	1.0000
C(52)-C(53)	1.535(5)
C(52)-H(52A)	0.9900
C(52)-H(52B)	0.9900
C(53)-C(54)	1.511(6)
C(53)-H(53A)	0.9900
C(53)-H(53B)	0.9900
C(54)-C(55)	1.510(6)
C(54)-H(54A)	0.9900
C(54)-H(54B)	0.9900
C(55)-C(56)	1.536(5)
C(55)-H(55A)	0.9900
C(55)-H(55B)	0.9900
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(57)-C(58)	1.528(4)
C(57)-C(62)	1.534(4)
C(57)-H(57)	1.0000

C(58)-C(59)	1.528(5)
C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(59)-C(60)	1.515(5)
C(59)-H(59A)	0.9900
C(59)-H(59B)	0.9900
C(60)-C(61)	1.528(5)
C(60)-H(60A)	0.9900
C(60)-H(60B)	0.9900
C(61)-C(62)	1.525(5)
C(61)-H(61A)	0.9900
C(61)-H(61B)	0.9900
C(62)-H(62A)	0.9900
C(62)-H(62B)	0.9900
C(63)-C(64)	1.523(5)
C(63)-C(68)	1.533(5)
C(63)-H(63)	1.0000
C(64)-C(65)	1.526(5)
C(64)-H(64A)	0.9900
C(64)-H(64B)	0.9900
C(65)-C(66)	1.516(5)
C(65)-H(65A)	0.9900
C(65)-H(65B)	0.9900
C(66)-C(67)	1.519(6)
C(66)-H(66A)	0.9900
C(66)-H(66B)	0.9900
C(67)-C(68)	1.519(5)
C(67)-H(67A)	0.9900
C(67)-H(67B)	0.9900

C(68)-H(68A)	0.9900
C(68)-H(68B)	0.9900
C(69)-C(74)	1.520(5)
C(69)-C(70)	1.527(5)
C(69)-H(69)	1.0000
C(70)-C(71)	1.528(5)
C(70)-H(70A)	0.9900
C(70)-H(70B)	0.9900
C(71)-C(72)	1.497(6)
C(71)-H(71A)	0.9900
C(71)-H(71B)	0.9900
C(72)-C(73)	1.509(6)
C(72)-H(72A)	0.9900
C(72)-H(72B)	0.9900
C(73)-C(74)	1.536(5)
C(73)-H(73A)	0.9900
C(73)-H(73B)	0.9900
C(74)-H(74A)	0.9900
C(74)-H(74B)	0.9900
O(1)-C(79)	1.424(12)
O(1)-C(76)	1.445(17)
C(76)-C(77)	1.512(16)
C(76)-H(76A)	0.9900
C(76)-H(76B)	0.9900
C(77)-C(78)	1.446(13)
C(77)-H(77A)	0.9900
C(77)-H(77B)	0.9900
C(78)-C(79)	1.452(17)
C(78)-H(78A)	0.9900

C(78)-H(78B)	0.9900
C(79)-H(79A)	0.9900
C(79)-H(79B)	0.9900
O(1')-C(79')	1.408(13)
O(1')-C(76')	1.433(16)
C(76')-C(77')	1.512(15)
C(76')-H(76C)	0.9900
C(76')-H(76D)	0.9900
C(77')-C(78')	1.438(13)
C(77')-H(77C)	0.9900
C(77')-H(77D)	0.9900
C(78')-C(79')	1.485(18)
C(78')-H(78C)	0.9900
C(78')-H(78D)	0.9900
C(79')-H(79C)	0.9900
C(79')-H(79D)	0.9900
C(80)-C(84)	1.426(12)
C(80)-C(81)	1.577(13)
C(80)-H(80A)	0.9900
C(80)-H(80B)	0.9900
C(81)-C(82)	1.434(16)
C(81)-H(81A)	0.9900
C(81)-H(81B)	0.9900
C(82)-O(2)	1.506(12)
C(82)-H(82A)	0.9900
C(82)-H(82B)	0.9900
O(2)-C(84)	1.411(11)
C(84)-H(84A)	0.9900
C(84)-H(84B)	0.9900

C(80')-C(84')	1.453(19)
C(80')-C(81')	1.54(2)
C(80')-H(80C)	0.9900
C(80')-H(80D)	0.9900
C(81')-C(82')	1.46(2)
C(81')-H(81C)	0.9900
C(81')-H(81D)	0.9900
C(82')-O(2')	1.438(18)
C(82')-H(82C)	0.9900
C(82')-H(82D)	0.9900
O(2')-C(84')	1.50(2)
C(84')-H(84C)	0.9900
C(84')-H(84D)	0.9900
C(85)-C(89)	1.41(2)
C(85)-C(86)	1.475(9)
C(85)-H(85A)	0.9900
C(85)-H(85B)	0.9900
C(86)-O(3)	1.558(16)
C(86)-H(86A)	0.9900
C(86)-H(86B)	0.9900
O(3)-C(88)	1.470(9)
C(88)-C(89)	1.458(18)
C(88)-H(88A)	0.9900
C(88)-H(88B)	0.9900
C(89)-H(89A)	0.9900
C(89)-H(89B)	0.9900
C(85')-C(89')	1.405(18)
C(85')-C(86')	1.521(16)
C(85')-H(85C)	0.9900

C(85')-H(85D)	0.9900
C(86')-O(3')	1.465(15)
C(86')-H(86C)	0.9900
C(86')-H(86D)	0.9900
O(3')-C(88')	1.517(14)
C(88')-C(89')	1.482(16)
C(88')-H(88C)	0.9900
C(88')-H(88D)	0.9900
C(89')-H(89C)	0.9900
C(89')-H(89D)	0.9900
C(90)-C(94)	1.368(18)
C(90)-C(91)	1.447(15)
C(90)-H(90A)	0.9900
C(90)-H(90B)	0.9900
C(91)-O(4)	1.430(13)
C(91)-H(91A)	0.9900
C(91)-H(91B)	0.9900
O(4)-C(93)	1.438(15)
C(93)-C(94)	1.537(16)
C(93)-H(93A)	0.9900
C(93)-H(93B)	0.9900
C(94)-H(94A)	0.9900
C(94)-H(94B)	0.9900
C(90')-C(94')	1.38(2)
C(90')-C(91')	1.514(19)
C(90')-H(90C)	0.9900
C(90')-H(90D)	0.9900
C(91')-O(4')	1.432(18)
C(91')-H(91C)	0.9900

C(91')-H(91D)	0.9900
O(4')-C(93')	1.42(2)
C(93')-C(94')	1.510(19)
C(93')-H(93C)	0.9900
C(93')-H(93D)	0.9900
C(94')-H(94C)	0.9900
C(94')-H(94D)	0.9900
C(95)-C(99)	1.35(3)
C(95)-C(96)	1.43(2)
C(95)-H(95A)	0.9900
C(95)-H(95B)	0.9900
C(96)-O(6)	1.34(2)
C(96)-H(96A)	0.9900
C(96)-H(96B)	0.9900
O(6)-C(98)	1.36(2)
C(98)-C(99)	1.44(2)
C(98)-H(98A)	0.9900
C(98)-H(98B)	0.9900
C(99)-H(99A)	0.9900
C(99)-H(99B)	0.9900

N(1)-Fe(1)-C(1)	175.92(13)
N(1)-Fe(1)-P(1)	96.45(8)
C(1)-Fe(1)-P(1)	83.54(10)
N(1)-Fe(1)-P(2)	95.53(8)
C(1)-Fe(1)-P(2)	84.82(10)
P(1)-Fe(1)-P(2)	167.32(4)
N(1)-Fe(1)-H(1)	88.0(12)
C(1)-Fe(1)-H(1)	87.9(12)

P(1)-Fe(1)-H(1)	86.0(12)
P(2)-Fe(1)-H(1)	98.5(13)
N(1)-Fe(1)-H(1')	90.9(11)
C(1)-Fe(1)-H(1')	93.2(11)
P(1)-Fe(1)-H(1')	94.5(12)
P(2)-Fe(1)-H(1')	81.1(12)
H(1)-Fe(1)-H(1')	178.8(17)
C(39)-Fe(2)-N(2)	175.34(13)
C(39)-Fe(2)-P(3)	84.75(10)
N(2)-Fe(2)-P(3)	95.05(8)
C(39)-Fe(2)-P(4)	84.26(10)
N(2)-Fe(2)-P(4)	96.27(8)
P(3)-Fe(2)-P(4)	168.13(4)
C(39)-Fe(2)-H(2)	97.4(12)
N(2)-Fe(2)-H(2)	87.2(12)
P(3)-Fe(2)-H(2)	84.4(12)
P(4)-Fe(2)-H(2)	92.6(12)
C(39)-Fe(2)-H(2')	85.8(10)
N(2)-Fe(2)-H(2')	89.7(10)
P(3)-Fe(2)-H(2')	99.1(10)
P(4)-Fe(2)-H(2')	84.5(11)
H(2)-Fe(2)-H(2')	175.5(16)
C(2)-P(1)-C(20)	102.32(15)
C(2)-P(1)-C(14)	102.13(15)
C(20)-P(1)-C(14)	101.62(15)
C(2)-P(1)-Fe(1)	101.42(10)
C(20)-P(1)-Fe(1)	125.56(11)
C(14)-P(1)-Fe(1)	120.00(11)
C(3)-P(2)-C(26)	101.49(15)

C(3)-P(2)-C(32)	102.97(16)
C(26)-P(2)-C(32)	101.12(15)
C(3)-P(2)-Fe(1)	102.04(11)
C(26)-P(2)-Fe(1)	123.48(12)
C(32)-P(2)-Fe(1)	122.11(12)
C(38)-P(3)-C(51)	101.93(15)
C(38)-P(3)-C(57)	101.88(15)
C(51)-P(3)-C(57)	101.93(15)
C(38)-P(3)-Fe(2)	102.19(11)
C(51)-P(3)-Fe(2)	122.93(11)
C(57)-P(3)-Fe(2)	122.17(11)
C(40)-P(4)-C(69)	102.70(15)
C(40)-P(4)-C(63)	102.51(15)
C(69)-P(4)-C(63)	101.34(15)
C(40)-P(4)-Fe(2)	100.63(11)
C(69)-P(4)-Fe(2)	121.03(12)
C(63)-P(4)-Fe(2)	124.95(11)
N(2)-N(1)-Fe(1)	177.5(2)
N(1)-N(2)-Fe(2)	176.4(2)
C(1)-N(3)-C(4)	126.3(3)
C(1)-N(3)-C(2)	116.6(2)
C(4)-N(3)-C(2)	117.1(2)
C(1)-N(4)-C(6)	125.8(3)
C(1)-N(4)-C(3)	116.9(2)
C(6)-N(4)-C(3)	117.1(3)
C(39)-N(5)-C(41)	125.5(3)
C(39)-N(5)-C(38)	116.7(3)
C(41)-N(5)-C(38)	117.6(3)
C(39)-N(6)-C(43)	126.1(3)

C(39)-N(6)-C(40)	116.5(2)
C(43)-N(6)-C(40)	117.3(3)
N(4)-C(1)-N(3)	112.4(3)
N(4)-C(1)-Fe(1)	124.1(2)
N(3)-C(1)-Fe(1)	123.6(2)
N(3)-C(2)-P(1)	106.2(2)
N(3)-C(2)-H(2B)	110.5
P(1)-C(2)-H(2B)	110.5
N(3)-C(2)-H(2A)	110.5
P(1)-C(2)-H(2A)	110.5
H(2B)-C(2)-H(2A)	108.7
N(4)-C(3)-P(2)	108.0(2)
N(4)-C(3)-H(3A)	110.1
P(2)-C(3)-H(3A)	110.1
N(4)-C(3)-H(3B)	110.1
P(2)-C(3)-H(3B)	110.1
H(3A)-C(3)-H(3B)	108.4
C(13)-C(4)-N(3)	123.3(3)
C(13)-C(4)-C(5)	119.6(3)
N(3)-C(4)-C(5)	117.1(3)
C(4)-C(5)-C(6)	119.3(3)
C(4)-C(5)-C(10)	120.4(3)
C(6)-C(5)-C(10)	120.3(3)
C(7)-C(6)-N(4)	123.4(3)
C(7)-C(6)-C(5)	119.1(3)
N(4)-C(6)-C(5)	117.5(3)
C(6)-C(7)-C(8)	120.5(3)
C(6)-C(7)-H(7)	119.7
C(8)-C(7)-H(7)	119.7

C(9)-C(8)-C(7)	121.2(3)
C(9)-C(8)-H(8)	119.4
C(7)-C(8)-H(8)	119.4
C(8)-C(9)-C(10)	120.4(3)
C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	123.3(3)
C(9)-C(10)-C(5)	118.3(3)
C(11)-C(10)-C(5)	118.4(3)
C(12)-C(11)-C(10)	119.9(3)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	121.8(3)
C(11)-C(12)-H(12)	119.1
C(13)-C(12)-H(12)	119.1
C(4)-C(13)-C(12)	119.8(3)
C(4)-C(13)-H(13)	120.1
C(12)-C(13)-H(13)	120.1
C(19)-C(14)-C(15)	109.7(3)
C(19)-C(14)-P(1)	110.1(2)
C(15)-C(14)-P(1)	112.6(2)
C(19)-C(14)-H(14)	108.1
C(15)-C(14)-H(14)	108.1
P(1)-C(14)-H(14)	108.1
C(16)-C(15)-C(14)	111.5(3)
C(16)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3
C(14)-C(15)-H(15B)	109.3

H(15A)-C(15)-H(15B) 108.0

C(17)-C(16)-C(15) 111.5(3)

C(17)-C(16)-H(16A) 109.3

C(15)-C(16)-H(16A) 109.3

C(17)-C(16)-H(16B) 109.3

C(15)-C(16)-H(16B) 109.3

H(16A)-C(16)-H(16B) 108.0

C(18)-C(17)-C(16) 110.7(3)

C(18)-C(17)-H(17A) 109.5

C(16)-C(17)-H(17A) 109.5

C(18)-C(17)-H(17B) 109.5

C(16)-C(17)-H(17B) 109.5

H(17A)-C(17)-H(17B) 108.1

C(17)-C(18)-C(19) 111.7(3)

C(17)-C(18)-H(18A) 109.3

C(19)-C(18)-H(18A) 109.3

C(17)-C(18)-H(18B) 109.3

C(19)-C(18)-H(18B) 109.3

H(18A)-C(18)-H(18B) 107.9

C(18)-C(19)-C(14) 113.5(3)

C(18)-C(19)-H(19A) 108.9

C(14)-C(19)-H(19A) 108.9

C(18)-C(19)-H(19B) 108.9

C(14)-C(19)-H(19B) 108.9

H(19A)-C(19)-H(19B) 107.7

C(25)-C(20)-C(21) 110.2(3)

C(25)-C(20)-P(1) 112.5(2)

C(21)-C(20)-P(1) 113.6(2)

C(25)-C(20)-H(20) 106.7

C(21)-C(20)-H(20) 106.7

P(1)-C(20)-H(20) 106.7

C(22)-C(21)-C(20) 112.1(3)

C(22)-C(21)-H(21A) 109.2

C(20)-C(21)-H(21A) 109.2

C(22)-C(21)-H(21B) 109.2

C(20)-C(21)-H(21B) 109.2

H(21A)-C(21)-H(21B) 107.9

C(23)-C(22)-C(21) 110.9(3)

C(23)-C(22)-H(22A) 109.5

C(21)-C(22)-H(22A) 109.5

C(23)-C(22)-H(22B) 109.5

C(21)-C(22)-H(22B) 109.5

H(22A)-C(22)-H(22B) 108.0

C(22)-C(23)-C(24) 110.7(3)

C(22)-C(23)-H(23A) 109.5

C(24)-C(23)-H(23A) 109.5

C(22)-C(23)-H(23B) 109.5

C(24)-C(23)-H(23B) 109.5

H(23A)-C(23)-H(23B) 108.1

C(23)-C(24)-C(25) 111.9(3)

C(23)-C(24)-H(24A) 109.2

C(25)-C(24)-H(24A) 109.2

C(23)-C(24)-H(24B) 109.2

C(25)-C(24)-H(24B) 109.2

H(24A)-C(24)-H(24B) 107.9

C(24)-C(25)-C(20) 111.9(3)

C(24)-C(25)-H(25A) 109.2

C(20)-C(25)-H(25A) 109.2

C(24)-C(25)-H(25B) 109.2

C(20)-C(25)-H(25B) 109.2

H(25A)-C(25)-H(25B) 107.9

C(27)-C(26)-C(31) 110.0(3)

C(27)-C(26)-P(2) 114.5(2)

C(31)-C(26)-P(2) 111.6(2)

C(27)-C(26)-H(26) 106.8

C(31)-C(26)-H(26) 106.8

P(2)-C(26)-H(26) 106.8

C(26)-C(27)-C(28) 111.2(3)

C(26)-C(27)-H(27A) 109.4

C(28)-C(27)-H(27A) 109.4

C(26)-C(27)-H(27B) 109.4

C(28)-C(27)-H(27B) 109.4

H(27A)-C(27)-H(27B) 108.0

C(27)-C(28)-C(29) 111.6(3)

C(27)-C(28)-H(28A) 109.3

C(29)-C(28)-H(28A) 109.3

C(27)-C(28)-H(28B) 109.3

C(29)-C(28)-H(28B) 109.3

H(28A)-C(28)-H(28B) 108.0

C(30)-C(29)-C(28) 111.2(3)

C(30)-C(29)-H(29A) 109.4

C(28)-C(29)-H(29A) 109.4

C(30)-C(29)-H(29B) 109.4

C(28)-C(29)-H(29B) 109.4

H(29A)-C(29)-H(29B) 108.0

C(29)-C(30)-C(31) 111.7(3)

C(29)-C(30)-H(30A) 109.3

C(31)-C(30)-H(30A) 109.3

C(29)-C(30)-H(30B) 109.3

C(31)-C(30)-H(30B) 109.3

H(30A)-C(30)-H(30B) 107.9

C(30)-C(31)-C(26) 111.3(3)

C(30)-C(31)-H(31A) 109.4

C(26)-C(31)-H(31A) 109.4

C(30)-C(31)-H(31B) 109.4

C(26)-C(31)-H(31B) 109.4

H(31A)-C(31)-H(31B) 108.0

C(37)-C(32)-C(33) 109.9(3)

C(37)-C(32)-P(2) 110.8(2)

C(33)-C(32)-P(2) 116.5(3)

C(37)-C(32)-H(32) 106.4

C(33)-C(32)-H(32) 106.4

P(2)-C(32)-H(32) 106.4

C(34)-C(33)-C(32) 111.9(3)

C(34)-C(33)-H(33A) 109.2

C(32)-C(33)-H(33A) 109.2

C(34)-C(33)-H(33B) 109.2

C(32)-C(33)-H(33B) 109.2

H(33A)-C(33)-H(33B) 107.9

C(35)-C(34)-C(33) 111.3(4)

C(35)-C(34)-H(34A) 109.4

C(33)-C(34)-H(34A) 109.4

C(35)-C(34)-H(34B) 109.4

C(33)-C(34)-H(34B) 109.4

H(34A)-C(34)-H(34B) 108.0

C(34)-C(35)-C(36) 110.4(4)

C(34)-C(35)-H(35A) 109.6

C(36)-C(35)-H(35A) 109.6

C(34)-C(35)-H(35B) 109.6

C(36)-C(35)-H(35B) 109.6

H(35A)-C(35)-H(35B) 108.1

C(35)-C(36)-C(37) 111.1(4)

C(35)-C(36)-H(36A) 109.4

C(37)-C(36)-H(36A) 109.4

C(35)-C(36)-H(36B) 109.4

C(37)-C(36)-H(36B) 109.4

H(36A)-C(36)-H(36B) 108.0

C(32)-C(37)-C(36) 111.9(3)

C(32)-C(37)-H(37A) 109.2

C(36)-C(37)-H(37A) 109.2

C(32)-C(37)-H(37B) 109.2

C(36)-C(37)-H(37B) 109.2

H(37A)-C(37)-H(37B) 107.9

N(5)-C(38)-P(3) 108.0(2)

N(5)-C(38)-H(38A) 110.1

P(3)-C(38)-H(38A) 110.1

N(5)-C(38)-H(38B) 110.1

P(3)-C(38)-H(38B) 110.1

H(38A)-C(38)-H(38B) 108.4

N(6)-C(39)-N(5) 112.5(3)

N(6)-C(39)-Fe(2) 123.4(2)

N(5)-C(39)-Fe(2) 124.1(2)

N(6)-C(40)-P(4) 106.8(2)

N(6)-C(40)-H(40A) 110.4

P(4)-C(40)-H(40A) 110.4

N(6)-C(40)-H(40B)	110.4
P(4)-C(40)-H(40B)	110.4
H(40A)-C(40)-H(40B)	108.6
C(50)-C(41)-C(42)	120.0(3)
C(50)-C(41)-N(5)	122.4(3)
C(42)-C(41)-N(5)	117.6(3)
C(41)-C(42)-C(43)	119.7(3)
C(41)-C(42)-C(47)	120.4(3)
C(43)-C(42)-C(47)	119.9(3)
C(44)-C(43)-N(6)	122.9(3)
C(44)-C(43)-C(42)	119.9(3)
N(6)-C(43)-C(42)	117.2(3)
C(43)-C(44)-C(45)	119.7(4)
C(43)-C(44)-H(44)	120.1
C(45)-C(44)-H(44)	120.1
C(46)-C(45)-C(44)	121.5(4)
C(46)-C(45)-H(45)	119.2
C(44)-C(45)-H(45)	119.2
C(45)-C(46)-C(47)	120.1(4)
C(45)-C(46)-H(46)	119.9
C(47)-C(46)-H(46)	119.9
C(46)-C(47)-C(48)	123.7(3)
C(46)-C(47)-C(42)	118.6(4)
C(48)-C(47)-C(42)	117.7(4)
C(49)-C(48)-C(47)	121.3(3)
C(49)-C(48)-H(48)	119.4
C(47)-C(48)-H(48)	119.4
C(48)-C(49)-C(50)	121.2(4)
C(48)-C(49)-H(49)	119.4

C(50)-C(49)-H(49)	119.4
C(41)-C(50)-C(49)	119.3(4)
C(41)-C(50)-H(50)	120.4
C(49)-C(50)-H(50)	120.4
C(52)-C(51)-C(56)	109.3(3)
C(52)-C(51)-P(3)	114.3(2)
C(56)-C(51)-P(3)	111.3(2)
C(52)-C(51)-H(51)	107.2
C(56)-C(51)-H(51)	107.2
P(3)-C(51)-H(51)	107.2
C(51)-C(52)-C(53)	110.7(3)
C(51)-C(52)-H(52A)	109.5
C(53)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
C(53)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	108.1
C(54)-C(53)-C(52)	111.4(3)
C(54)-C(53)-H(53A)	109.4
C(52)-C(53)-H(53A)	109.4
C(54)-C(53)-H(53B)	109.4
C(52)-C(53)-H(53B)	109.4
H(53A)-C(53)-H(53B)	108.0
C(55)-C(54)-C(53)	112.2(3)
C(55)-C(54)-H(54A)	109.2
C(53)-C(54)-H(54A)	109.2
C(55)-C(54)-H(54B)	109.2
C(53)-C(54)-H(54B)	109.2
H(54A)-C(54)-H(54B)	107.9
C(54)-C(55)-C(56)	111.6(3)

C(54)-C(55)-H(55A) 109.3

C(56)-C(55)-H(55A) 109.3

C(54)-C(55)-H(55B) 109.3

C(56)-C(55)-H(55B) 109.3

H(55A)-C(55)-H(55B) 108.0

C(51)-C(56)-C(55) 111.8(3)

C(51)-C(56)-H(56A) 109.3

C(55)-C(56)-H(56A) 109.3

C(51)-C(56)-H(56B) 109.3

C(55)-C(56)-H(56B) 109.3

H(56A)-C(56)-H(56B) 107.9

C(58)-C(57)-C(62) 110.3(3)

C(58)-C(57)-P(3) 110.7(2)

C(62)-C(57)-P(3) 115.4(2)

C(58)-C(57)-H(57) 106.6

C(62)-C(57)-H(57) 106.6

P(3)-C(57)-H(57) 106.6

C(57)-C(58)-C(59) 112.6(3)

C(57)-C(58)-H(58A) 109.1

C(59)-C(58)-H(58A) 109.1

C(57)-C(58)-H(58B) 109.1

C(59)-C(58)-H(58B) 109.1

H(58A)-C(58)-H(58B) 107.8

C(60)-C(59)-C(58) 111.1(3)

C(60)-C(59)-H(59A) 109.4

C(58)-C(59)-H(59A) 109.4

C(60)-C(59)-H(59B) 109.4

C(58)-C(59)-H(59B) 109.4

H(59A)-C(59)-H(59B) 108.0

C(59)-C(60)-C(61)	110.8(3)
C(59)-C(60)-H(60A)	109.5
C(61)-C(60)-H(60A)	109.5
C(59)-C(60)-H(60B)	109.5
C(61)-C(60)-H(60B)	109.5
H(60A)-C(60)-H(60B)	108.1
C(62)-C(61)-C(60)	111.3(3)
C(62)-C(61)-H(61A)	109.4
C(60)-C(61)-H(61A)	109.4
C(62)-C(61)-H(61B)	109.4
C(60)-C(61)-H(61B)	109.4
H(61A)-C(61)-H(61B)	108.0
C(61)-C(62)-C(57)	112.2(3)
C(61)-C(62)-H(62A)	109.2
C(57)-C(62)-H(62A)	109.2
C(61)-C(62)-H(62B)	109.2
C(57)-C(62)-H(62B)	109.2
H(62A)-C(62)-H(62B)	107.9
C(64)-C(63)-C(68)	110.3(3)
C(64)-C(63)-P(4)	112.7(2)
C(68)-C(63)-P(4)	113.5(2)
C(64)-C(63)-H(63)	106.6
C(68)-C(63)-H(63)	106.6
P(4)-C(63)-H(63)	106.6
C(63)-C(64)-C(65)	111.7(3)
C(63)-C(64)-H(64A)	109.3
C(65)-C(64)-H(64A)	109.3
C(63)-C(64)-H(64B)	109.3
C(65)-C(64)-H(64B)	109.3

H(64A)-C(64)-H(64B) 107.9

C(66)-C(65)-C(64) 111.9(3)

C(66)-C(65)-H(65A) 109.2

C(64)-C(65)-H(65A) 109.2

C(66)-C(65)-H(65B) 109.2

C(64)-C(65)-H(65B) 109.2

H(65A)-C(65)-H(65B) 107.9

C(65)-C(66)-C(67) 111.3(3)

C(65)-C(66)-H(66A) 109.4

C(67)-C(66)-H(66A) 109.4

C(65)-C(66)-H(66B) 109.4

C(67)-C(66)-H(66B) 109.4

H(66A)-C(66)-H(66B) 108.0

C(68)-C(67)-C(66) 111.7(3)

C(68)-C(67)-H(67A) 109.3

C(66)-C(67)-H(67A) 109.3

C(68)-C(67)-H(67B) 109.3

C(66)-C(67)-H(67B) 109.3

H(67A)-C(67)-H(67B) 108.0

C(67)-C(68)-C(63) 111.6(3)

C(67)-C(68)-H(68A) 109.3

C(63)-C(68)-H(68A) 109.3

C(67)-C(68)-H(68B) 109.3

C(63)-C(68)-H(68B) 109.3

H(68A)-C(68)-H(68B) 108.0

C(74)-C(69)-C(70) 109.3(3)

C(74)-C(69)-P(4) 111.4(2)

C(70)-C(69)-P(4) 110.0(2)

C(74)-C(69)-H(69) 108.7

C(70)-C(69)-H(69) 108.7

P(4)-C(69)-H(69) 108.7

C(69)-C(70)-C(71) 112.2(3)

C(69)-C(70)-H(70A) 109.2

C(71)-C(70)-H(70A) 109.2

C(69)-C(70)-H(70B) 109.2

C(71)-C(70)-H(70B) 109.2

H(70A)-C(70)-H(70B) 107.9

C(72)-C(71)-C(70) 111.1(3)

C(72)-C(71)-H(71A) 109.4

C(70)-C(71)-H(71A) 109.4

C(72)-C(71)-H(71B) 109.4

C(70)-C(71)-H(71B) 109.4

H(71A)-C(71)-H(71B) 108.0

C(71)-C(72)-C(73) 111.3(4)

C(71)-C(72)-H(72A) 109.4

C(73)-C(72)-H(72A) 109.4

C(71)-C(72)-H(72B) 109.4

C(73)-C(72)-H(72B) 109.4

H(72A)-C(72)-H(72B) 108.0

C(72)-C(73)-C(74) 110.7(3)

C(72)-C(73)-H(73A) 109.5

C(74)-C(73)-H(73A) 109.5

C(72)-C(73)-H(73B) 109.5

C(74)-C(73)-H(73B) 109.5

H(73A)-C(73)-H(73B) 108.1

C(69)-C(74)-C(73) 111.9(3)

C(69)-C(74)-H(74A) 109.2

C(73)-C(74)-H(74A) 109.2

C(69)-C(74)-H(74B) 109.2

C(73)-C(74)-H(74B) 109.2

H(74A)-C(74)-H(74B) 107.9

C(79)-O(1)-C(76) 105.1(12)

O(1)-C(76)-C(77) 101.8(18)

O(1)-C(76)-H(76A) 111.4

C(77)-C(76)-H(76A) 111.4

O(1)-C(76)-H(76B) 111.4

C(77)-C(76)-H(76B) 111.4

H(76A)-C(76)-H(76B) 109.3

C(78)-C(77)-C(76) 108.5(11)

C(78)-C(77)-H(77A) 110.0

C(76)-C(77)-H(77A) 110.0

C(78)-C(77)-H(77B) 110.0

C(76)-C(77)-H(77B) 110.0

H(77A)-C(77)-H(77B) 108.4

C(77)-C(78)-C(79) 103.9(11)

C(77)-C(78)-H(78A) 111.0

C(79)-C(78)-H(78A) 111.0

C(77)-C(78)-H(78B) 111.0

C(79)-C(78)-H(78B) 111.0

H(78A)-C(78)-H(78B) 109.0

O(1)-C(79)-C(78) 108.7(14)

O(1)-C(79)-H(79A) 110.0

C(78)-C(79)-H(79A) 110.0

O(1)-C(79)-H(79B) 110.0

C(78)-C(79)-H(79B) 110.0

H(79A)-C(79)-H(79B) 108.3

C(79')-O(1')-C(76') 107.1(12)

O(1')-C(76')-C(77') 106.1(16)

O(1')-C(76')-H(76C) 110.5

C(77')-C(76')-H(76C) 110.5

O(1')-C(76')-H(76D) 110.5

C(77')-C(76')-H(76D) 110.5

H(76C)-C(76')-H(76D) 108.7

C(78')-C(77')-C(76') 105.6(10)

C(78')-C(77')-H(77C) 110.6

C(76')-C(77')-H(77C) 110.6

C(78')-C(77')-H(77D) 110.6

C(76')-C(77')-H(77D) 110.6

H(77C)-C(77')-H(77D) 108.7

C(77')-C(78')-C(79') 107.1(11)

C(77')-C(78')-H(78C) 110.3

C(79')-C(78')-H(78C) 110.3

C(77')-C(78')-H(78D) 110.3

C(79')-C(78')-H(78D) 110.3

H(78C)-C(78')-H(78D) 108.6

O(1')-C(79')-C(78') 107.9(12)

O(1')-C(79')-H(79C) 110.1

C(78')-C(79')-H(79C) 110.1

O(1')-C(79')-H(79D) 110.1

C(78')-C(79')-H(79D) 110.1

H(79C)-C(79')-H(79D) 108.4

C(84)-C(80)-C(81) 105.6(8)

C(84)-C(80)-H(80A) 110.6

C(81)-C(80)-H(80A) 110.6

C(84)-C(80)-H(80B) 110.6

C(81)-C(80)-H(80B) 110.6

H(80A)-C(80)-H(80B) 108.8

C(82)-C(81)-C(80) 101.7(9)

C(82)-C(81)-H(81A) 111.4

C(80)-C(81)-H(81A) 111.4

C(82)-C(81)-H(81B) 111.4

C(80)-C(81)-H(81B) 111.4

H(81A)-C(81)-H(81B) 109.3

C(81)-C(82)-O(2) 106.0(10)

C(81)-C(82)-H(82A) 110.5

O(2)-C(82)-H(82A) 110.5

C(81)-C(82)-H(82B) 110.5

O(2)-C(82)-H(82B) 110.5

H(82A)-C(82)-H(82B) 108.7

C(84)-O(2)-C(82) 107.4(9)

O(2)-C(84)-C(80) 109.2(9)

O(2)-C(84)-H(84A) 109.8

C(80)-C(84)-H(84A) 109.8

O(2)-C(84)-H(84B) 109.8

C(80)-C(84)-H(84B) 109.8

H(84A)-C(84)-H(84B) 108.3

C(84')-C(80')-C(81') 101.7(16)

C(84')-C(80')-H(80C) 111.4

C(81')-C(80')-H(80C) 111.4

C(84')-C(80')-H(80D) 111.4

C(81')-C(80')-H(80D) 111.4

H(80C)-C(80')-H(80D) 109.3

C(82')-C(81')-C(80') 104.1(16)

C(82')-C(81')-H(81C) 110.9

C(80')-C(81')-H(81C) 110.9

C(82')-C(81')-H(81D) 110.9

C(80')-C(81')-H(81D) 110.9

H(81C)-C(81')-H(81D)109.0

O(2')-C(82')-C(81') 105.6(16)

O(2')-C(82')-H(82C) 110.6

C(81')-C(82')-H(82C) 110.6

O(2')-C(82')-H(82D) 110.6

C(81')-C(82')-H(82D) 110.6

H(82C)-C(82')-H(82D)108.8

C(82')-O(2')-C(84') 108.1(17)

C(80')-C(84')-O(2') 99.4(16)

C(80')-C(84')-H(84C) 111.9

O(2')-C(84')-H(84C) 111.9

C(80')-C(84')-H(84D) 111.9

O(2')-C(84')-H(84D) 111.9

H(84C)-C(84')-H(84D)109.6

C(89)-C(85)-C(86) 100.1(16)

C(89)-C(85)-H(85A) 111.8

C(86)-C(85)-H(85A) 111.8

C(89)-C(85)-H(85B) 111.8

C(86)-C(85)-H(85B) 111.7

H(85A)-C(85)-H(85B) 109.5

C(85)-C(86)-O(3) 110.0(16)

C(85)-C(86)-H(86A) 109.7

O(3)-C(86)-H(86A) 109.7

C(85)-C(86)-H(86B) 109.7

O(3)-C(86)-H(86B) 109.7

H(86A)-C(86)-H(86B) 108.2

C(88)-O(3)-C(86) 95.2(15)

C(89)-C(88)-O(3) 111.1(18)

C(89)-C(88)-H(88A) 109.4

O(3)-C(88)-H(88A) 109.4

C(89)-C(88)-H(88B) 109.4

O(3)-C(88)-H(88B) 109.4

H(88A)-C(88)-H(88B) 108.0

C(85)-C(89)-C(88) 100.8(17)

C(85)-C(89)-H(89A) 111.6

C(88)-C(89)-H(89A) 111.6

C(85)-C(89)-H(89B) 111.6

C(88)-C(89)-H(89B) 111.6

H(89A)-C(89)-H(89B) 109.4

C(89')-C(85')-C(86') 98.4(12)

C(89')-C(85')-H(85C) 112.1

C(86')-C(85')-H(85C) 112.1

C(89')-C(85')-H(85D) 112.1

C(86')-C(85')-H(85D) 112.1

H(85C)-C(85')-H(85D) 109.7

O(3')-C(86')-C(85') 106.4(15)

O(3')-C(86')-H(86C) 110.4

C(85')-C(86')-H(86C) 110.4

O(3')-C(86')-H(86D) 110.4

C(85')-C(86')-H(86D) 110.4

H(86C)-C(86')-H(86D) 108.6

C(86')-O(3')-C(88') 91.7(13)

C(89')-C(88')-O(3') 111.4(13)

C(89')-C(88')-H(88C) 109.3

O(3')-C(88')-H(88C) 109.3

C(89')-C(88')-H(88D) 109.3

O(3')-C(88')-H(88D) 109.3

H(88C)-C(88')-H(88D) 108.0

C(85')-C(89')-C(88') 104.7(12)

C(85')-C(89')-H(89C) 110.8

C(88')-C(89')-H(89C) 110.8

C(85')-C(89')-H(89D) 110.8

C(88')-C(89')-H(89D) 110.8

H(89C)-C(89')-H(89D) 108.9

C(94)-C(90)-C(91) 107.2(11)

C(94)-C(90)-H(90A) 110.3

C(91)-C(90)-H(90A) 110.3

C(94)-C(90)-H(90B) 110.3

C(91)-C(90)-H(90B) 110.3

H(90A)-C(90)-H(90B) 108.5

O(4)-C(91)-C(90) 104.6(12)

O(4)-C(91)-H(91A) 110.8

C(90)-C(91)-H(91A) 110.8

O(4)-C(91)-H(91B) 110.8

C(90)-C(91)-H(91B) 110.8

H(91A)-C(91)-H(91B) 108.9

C(91)-O(4)-C(93) 110.9(11)

O(4)-C(93)-C(94) 100.3(11)

O(4)-C(93)-H(93A) 111.7

C(94)-C(93)-H(93A) 111.7

O(4)-C(93)-H(93B) 111.7

C(94)-C(93)-H(93B) 111.7

H(93A)-C(93)-H(93B) 109.5

C(90)-C(94)-C(93) 110.5(11)

C(90)-C(94)-H(94A) 109.5

C(93)-C(94)-H(94A) 109.5

C(90)-C(94)-H(94B) 109.5

C(93)-C(94)-H(94B) 109.5

H(94A)-C(94)-H(94B) 108.1

C(94')-C(90')-C(91') 106.5(14)

C(94')-C(90')-H(90C) 110.4

C(91')-C(90')-H(90C) 110.4

C(94')-C(90')-H(90D) 110.4

C(91')-C(90')-H(90D) 110.4

H(90C)-C(90')-H(90D) 108.6

O(4')-C(91')-C(90') 102.4(15)

O(4')-C(91')-H(91C) 111.3

C(90')-C(91')-H(91C) 111.3

O(4')-C(91')-H(91D) 111.3

C(90')-C(91')-H(91D) 111.3

H(91C)-C(91')-H(91D) 109.2

C(93')-O(4')-C(91') 109.4(18)

O(4')-C(93')-C(94') 98.4(17)

O(4')-C(93')-H(93C) 112.1

C(94')-C(93')-H(93C) 112.1

O(4')-C(93')-H(93D) 112.1

C(94')-C(93')-H(93D) 112.1

H(93C)-C(93')-H(93D) 109.7

C(90')-C(94')-C(93') 105.2(16)

C(90')-C(94')-H(94C) 110.7

C(93')-C(94')-H(94C) 110.7

C(90')-C(94')-H(94D) 110.7

C(93')-C(94')-H(94D) 110.7

H(94C)-C(94')-H(94D) 108.8

C(99)-C(95)-C(96)	106.5(18)
C(99)-C(95)-H(95A)	110.4
C(96)-C(95)-H(95A)	110.4
C(99)-C(95)-H(95B)	110.4
C(96)-C(95)-H(95B)	110.4
H(95A)-C(95)-H(95B)	108.6
O(6)-C(96)-C(95)	110(2)
O(6)-C(96)-H(96A)	109.6
C(95)-C(96)-H(96A)	109.6
O(6)-C(96)-H(96B)	109.6
C(95)-C(96)-H(96B)	109.6
H(96A)-C(96)-H(96B)	108.1
C(96)-O(6)-C(98)	104(3)
O(6)-C(98)-C(99)	109(2)
O(6)-C(98)-H(98A)	109.8
C(99)-C(98)-H(98A)	109.8
O(6)-C(98)-H(98B)	109.8
C(99)-C(98)-H(98B)	109.8
H(98A)-C(98)-H(98B)	108.2
C(95)-C(99)-C(98)	103.7(17)
C(95)-C(99)-H(99A)	111.0
C(98)-C(99)-H(99A)	111.0
C(95)-C(99)-H(99B)	111.0
C(98)-C(99)-H(99B)	111.0
H(99A)-C(99)-H(99B)	109.0

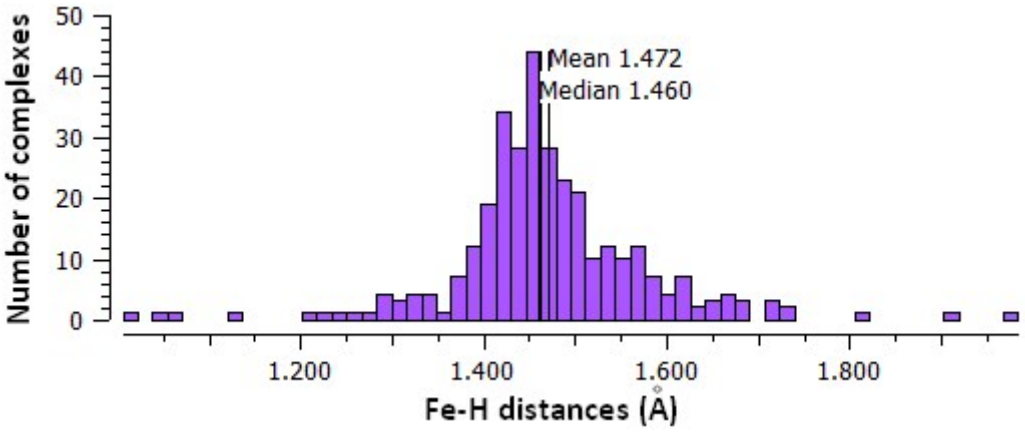


Figure S12 – Frequency distance histogram for non-bridging Fe-H in octahedral Fe complexes. Distance bonds were taken from Cambridge Structure Database (251 structures). Histogram is obtained from Mercury software.

4. Computational details

Geometry optimization were performed using Gaussian 09 (Revision D01)[7] at the OPBE level of hybrid density functional theory. The geometries of all optimized structures are given in the .xyz file attached to the publication. The atoms Fe and P were represented by a def2tzvpp basis set[8] as well as the two N next to the carbene, the C of the carbene and the two hydrides. For the dinitrogen molecule, the N atoms are represented by a 6-311+g** basis set.[9,10] All other atoms (C & H) are represented by a 6-31G(d) basis set.[11–13] The solvent (THF) influence was taken into consideration through single-point calculations on the gas-phase optimized geometries with SCRF calculations. Inclusion of a D3(BJ) correction term was taken into account through single-point calculations on the gas-phase optimized geometries at the PBE1PBE level, keeping the same basis set. All reported energies are Gibbs free energies obtained by summing the SCRF energy of single-point geometries calculated with solvent influence. The D3(BJ) correction obtained with the single-point geometries calculated at the PBE1PBE level.

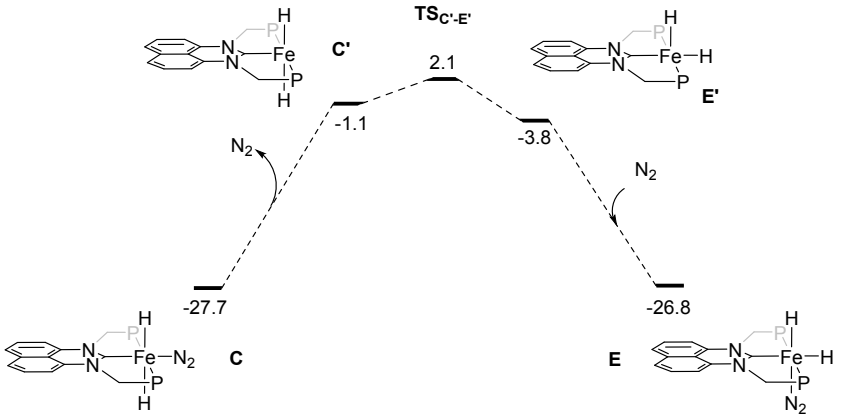


Figure S13. Computed pathway for cis-trans isomerization considering N_2 decoordination. The overall barrier of 29.8 kcal/mol is not compatible with a possible isomerization under experimental conditions.

5. References

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