Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Role of Lewis Acid/Base Anchor Atoms in Catalyst Regeneration: A Comprehensive Study on Biomimetic EP_3Fe Nitrogenases

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1. Theoretical section (sample input files ORCA 4.1.2)

Geometry optimization

```
!PAL [number of processors]
! RI BP86 ZORA ZORA-def2-SVP def2/J d3bj VerySlowConv tightscf Opt Freq
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%method Z_tol 1e-6 end
%freq Temp 195 end

* xyz [charge] [multiplicity]
[initial guess of geometry]
*
```

Single-point energy calculations (in diethyl ether solution)

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%method Z_tol 1e-6 end
%freq Temp 195 end
%cpcm smd true SMDsolvent "diethyl ether" end

* xyz [charge] [multiplicity]
[optimized geometry]
*
```

Verification of methodology

Table S1 . Comparison of bond lengths and angles calculated at BP86 and ωB97X-D3 levels of theory

Structure	BP86 geometry Bond distances (d) in Å Bond angles (α) in degrees							ωB97X-D3 geometry Bond distances (d) in Å Bond angles (α) in degrees						
	Fe-P			Fe-X	α(P-Fe-P)			Fe-P			Fe-X	α(P-Fe-P))		
PP$_3$Fe	2.21	2.20	2.21	2.09	115	113	131	2.25	2.23	2.24	2.10	116	114	128
NP$_3$Fe	2.21	2.18	2.18	2.33	115	113	129	2.25	2.18	2.20	2.29	120	117	123

2. Computation of molecular Gibbs free energies (G), bond lengths, ADCH charges, cDFT indices, and binding affinities (A)

2.1. Equations utilised

Calculation of Molecular Gibbs Free Energy:

The Gibbs free energy (G) was calculated for each molecule by adding the single-point electronic energy ($E_{\omega B97X\text{-}D3}$) to the thermal correction to Gibbs free energy resulting from vibration analysis ($(G - E)_{BP86}$):

$$G = E_{\omega B97X - D3} + (G - E)_{BP86} \quad (1)$$

Thermal corrections were computed at 195 K temperature and 1 atm pressure, corresponding to the typically applied experimental conditions.[21]

The Gibbs free energies computed in the gas phase were then corrected to account for different concentrations using the following equation:

$$G(c = x\,M) = G(c = 0.0625\,M) + RT \times ln\frac{Q(c = x\,M)}{Q(c = 0.0625\,M)} \quad (2)$$

The molar concentration is given in parenthesis; x represents the molar concentration at which the Gibbs free energy is to be calculated, and Q represents the reaction quotient. This formula gives a correction of -1.28 kcal/mol in the case of NH_3 release, and a correction of +1.28 kcal/mol in N_2 coordination steps (x = 2.3 mM was used as this is the experimental concentration of the catalyst that resulted in the highest turnover number).[24]

The highest turnover number observed was in the presence of 162 mol equiv of reductant and 322 mol equiv of acid,[24] and after replacing these values into equation 2, we get a correction of 1.97 kcal/mol to be subtracted from the Gibbs free energy of electron addition steps, and a correction of 2.24 kcal/mol to be subtracted from the Gibbs free energy of proton addition steps.

Calculation of Conceptual Density Functional Theory (cDFT) indices:

Conceptual Density Functional Theory (cDFT) offers a framework for understanding molecular behavior using electronic densities, providing insights into reactivity, allowing for predictive and interpretative analyses.[49]

The electronegativity index is defined according to the following equation:[50]

$$\chi^{-} = E(N - 1) - E(N) = I \quad (3)$$

$$\chi^{+} = E(N) - E(N+1) = A \quad (4)$$

$$\chi = \frac{\chi^{-} + \chi^{+}}{2} = \frac{I + A}{2} \quad (5)$$

Where N refers to the number of electrons carried by the chemical system at its most stable status, and I and A are the ionizing energy and the electron affinity of the neutral atom respectively. This formula is the same as proposed by Mulliken to calculate electronegativity.[49,50]

The hardness (η) is defined according to the following equation:[51]

$$\eta = I - A \quad (6)$$

Softness, S is considered as the reciprocal of the hardness:

$$S = \frac{1}{\eta} \quad (7)$$

The electrophilicity index (ω) is defined according to the following equation:[49,52]

$$\omega = \frac{\mu^{2}}{2\eta} \quad (8)$$

Where μ is the electronic chemical potential which is calculated by multiplying the electronegativity (χ) by a minus.

Calculation of Binding Affinities (Gibbs Free Energies of N_2 and H_2 Coordination):

The affinity (A) of a small X_2 molecule (i. e. N_2 or H_2) to the iron center can be quantified by the negative Gibbs free energy change (-ΔG) of the reaction $EP_3Fe + X_2 \rightarrow EP_3Fe\text{-}X_2$, which derives from the molecular Gibbs free energies (G) as:

$$A_{X_2} = -\Delta G_{EP_3Fe + X_2 \rightarrow Fe - X_2} = G_{EP_3Fe} + G_{X_2} - G_{EP_3Fe - X_2} \quad (9)$$

2.2. Gibbs free energy calculations

Table S2 . Calculation of Gibbs free energy required for proton, electron and hydrogen atom release from the acid, reductant and PCET reagent, respectively. All energies are in Hartree if otherwise not stated. ΔG values were calculated based on the following equations:

$\Delta G(H^+) = G(Ph_2NH) - G(Ph_2NH_2^+)$
$\Delta G(e^-) = G(Cp_2^*Co^+) – G(Cp_2^*Co)$
$\Delta G(H) = G(Cp_2^*Co^+) – G((Cp^*CoC_5Me_5H)^+)$
$\Delta G(NH_3 \rightarrow NH_4^+) = G(NH_4^+) – G(NH_3) + \Delta G(H^+)$

Molecule	E [Ha]	G-E [Ha]	G [Ha]	ΔG [kcal/mol]
$Ph_2NH_2^+$	-519.689217	0.186134	-519.503083	
Ph_2NH	-519.262565	0.172803	-519.089762	
H^+ release				**259.36**
Cp_2^*Co	-2180.525088	0.403473	-2180.121616	
$Cp_2^*Co^+$	-2180.419405	0.409662	-2180.009742	
e^- release				**70.20**
$(Cp^*CoC_5Me_5H)^+$	-2180.974838	0.418081	-2180.556757	
$Cp_2^*Co^+$	-2180.419405	0.409662	-2180.009742	
H atom release				**343.25**
NH_3	-56.643965	0.022744	-56.621221	
NH_4^+	-57.090538	0.03717650	-57.053362	
$NH_3 \rightarrow NH_4^+$				**-11.81**

Table S3 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $BP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

$G_{rel}[kcal/mol] = G – G(BP_3FeN_2^-) + n_{H+}.[\Delta G(H^+) - 2.24] + n_{e-}.[\Delta G(e^-) – 1.97] + n_{NH3}.[G(NH_3) – 1.28 + \Delta G(NH_3 \rightarrow NH_4^+) – 2.24] – n_{N2}.[G(N_2) – 1.28]$

where G, $G(BP_3FeN_2^-)$, $G(NH_3)$ and $G(N_2)$ denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($BP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; $\Delta G(H^+)$, $\Delta G(e^-)$ and $\Delta G(NH_3 \rightarrow NH_4^+)$ represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$BP_3FeN_2^-$	2	0
BP_3FeNNH	4	-29.5
$BP_3FeNNH_2^+$	4	-58.0
BP_3FeNNH_2	3	-68.7
$BP_3FeNNH_3^+$	5	-80.1
BP_3FeN^+	1	-130.5
BP_3FeN	2	-151.5
BP_3FeNH^+	6	-184.9
BP_3FeNH	5	-210.4
$BP_3FeNH_2^+$	5	-270.3
BP_3FeNH_2	4	-290.6
$BP_3FeNH_3^+$	4	-334.8
BP_3Fe^+	4	-355.8
BP_3Fe	3	-361.4

BP_3FeN_2	3	-361.9
$BP_3FeN_2^-$	2	-338.6

Table S4 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $NP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = $G - G(NP_3FeN_2^-) + n_{H+}.[\Delta G(H^+) - 2.24] + n_{e-}.[\Delta G(e^-) - 1.97] + n_{NH3}.[G(NH_3) - 1.28 + \Delta G(NH_3 \rightarrow NH_4^+) - 2.24] - n_{N2}.[G(N_2) - 1.28]$

where G, $G(NP_3FeN_2^-)$, $G(NH_3)$ and $G(N_2)$ denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($NP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; $\Delta G(H^+)$, $\Delta G(e^-)$ and $\Delta G(NH_3 \rightarrow NH_4^+)$ represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$NP_3FeN_2^-$	4	0
NP_3FeNNH	4	-60.8
$NP_3FeNNH_2^+$	4	-110.5
NP_3FeNNH_2	1	-94.2
$NP_3FeNNH_3^+$	5	-130.4
NP_3FeN^+	1	-192.3
NP_3FeN	2	-179.4
NP_3FeNH^+	6	-242.1
NP_3FeNH	5	-244.9
$NP_3FeNH_2^+$	5	-326.9
NP_3FeNH_2	4	-320.6
$NP_3FeNH_3^+$	4	-379.5
NP_3Fe^+	4	-402.8
NP_3Fe	3	-378.2
NP_3FeN_2	3	-385.8
$NP_3FeN_2^-$	4	-338.6

Table S5 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $AlP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = $G - G(AlP_3FeN_2^-) + n_{H+}.[\Delta G(H^+) - 2.24] + n_{e-}.[\Delta G(e^-) - 1.97] + n_{NH3}.[G(NH_3) - 1.28 + \Delta G(NH_3 \rightarrow NH_4^+) - 2.24] - n_{N2}.[G(N_2) - 1.28]$

where G, $G(AlP_3FeN_2^-)$, $G(NH_3)$ and $G(N_2)$ denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($AlP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; $\Delta G(H^+)$, $\Delta G(e^-)$ and $\Delta G(NH_3 \rightarrow NH_4^+)$ represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$AlP_3FeN_2^-$	2	0
AlP_3FeNNH	4	-24.3

$AlP_3FeNNH_2^+$	4	-56.7
AlP_3FeNNH_2	3	-62.0
$AlP_3FeNNH_3^+$	5	-80.2
AlP_3FeN^+	1	-120.3
AlP_3FeN	2	-146.9
AlP_3FeNH^+	6	-183.5
AlP_3FeNH	5	-206.4
$AlP_3FeNH_2^+$	5	-267.0
AlP_3FeNH_2	4	-291.0
$AlP_3FeNH_3^+$	4	-333.0
AlP_3Fe^+	4	-351.7
AlP_3Fe	3	-358.8
AlP_3FeN_2	3	-361.0
$AlP_3FeN_2^-$	2	-338.6

Table S6 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $GaP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = G – G($GaP_3FeN_2^-$) + n_{H+}.[ΔG(H^+) - 2.24] + n_{e-}.[ΔG(e^-) – 1.97] + n_{NH3}.[G(NH_3) – 1.28 + ΔG(NH_3 → NH_4^+) – 2.24] – n_{N2}.[G(N_2) – 1.28]

where G, G($GaP_3FeN_2^-$), G(NH_3) and G(N_2) denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($GaP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; ΔG(H^+), ΔG(e^-) and ΔG($NH_3 \rightarrow NH_4^+$) represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$GaP_3FeN_2^-$	2	0
GaP_3FeNNH	4	-25.5
$GaP_3FeNNH_2^+$	4	-57.8
GaP_3FeNNH_2	3	-61.6
$GaP_3FeNNH_3^+$	5	-80.3
GaP_3FeN^+	1	-123.1
GaP_3FeN	2	-147.2
GaP_3FeNH^+	6	-185.2
GaP_3FeNH	5	-207.3
$GaP_3FeNH_2^+$	5	-268.1
GaP_3FeNH_2	4	-290.3
$GaP_3FeNH_3^+$	4	-332.9
GaP_3Fe^+	4	-352.1
GaP_3Fe	3	-357.3
GaP_3FeN_2	3	-358.7
$GaP_3FeN_2^-$	2	-338.6

Table S7 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $PP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = G – G($PP_3FeN_2^-$) + n_{H+}.[ΔG(H^+) - 2.24] + n_{e-}.[ΔG(e^-) – 1.97] + n_{NH3}.[G(NH_3) – 1.28 + ΔG($NH_3 \rightarrow NH_4^+$) – 2.24] – n_{N2}.[G(N_2) – 1.28]

where G, G($PP_3FeN_2^-$), G(NH_3) and G(N_2) denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($PP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; ΔG(H^+), ΔG(e^-) and ΔG($NH_3 \rightarrow NH_4^+$) represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$PP_3FeN_2^-$	2	0
PP_3FeNNH	2	-45.5
$PP_3FeNNH_2^+$	2	-89.0
PP_3FeNNH_2	1	-68.7
$PP_3FeNNH_3^+$	3	-109.8
PP_3FeN^+	1	-174.6
PP_3FeN	2	-164.4
PP_3FeNH^+	2	-226.9
PP_3FeNH	3	-228.2
$PP_3FeNH_2^+$	3	-308.0
PP_3FeNH_2	2	-298.5
$PP_3FeNH_3^+$	2	-356.9
PP_3Fe^+	4	-384.7
PP_3Fe	3	-372.6
PP_3FeN_2	1	-382.6
$PP_3FeN_2^-$	2	-338.6

Table S8 . Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of (1-Cl)$NP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = G – G((1-Cl)$NP_3FeN_2^-$) + n_{H+}.[ΔG(H^+) - 2.24] + n_{e-}.[ΔG(e^-) – 1.97] + n_{NH3}.[G(NH_3) – 1.28 + ΔG($NH_3 \rightarrow NH_4^+$) – 2.24] – n_{N2}.[G(N_2) – 1.28]

where G, G((1-Cl)$NP_3FeN_2^-$), G(NH_3) and G(N_2) denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ((1-Cl)$NP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; ΔG(H^+), ΔG(e^-) and ΔG($NH_3 \rightarrow NH_4^+$) represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
(1-Cl)$NP_3FeN_2^-$	2	0.0
(1-Cl)NP_3FeNNH	4	-53.5
(1-Cl)$NP_3FeNNH_2^+$	4	-99.5
(1-Cl)NP_3FeNNH_2	1	-99.9
(1-Cl)$NP_3FeNNH_3^+$	1	-141.4
(1-Cl)NP_3FeN^+	1	-177.1
(1-Cl)NP_3FeN	2	-175.4
(1-Cl)NP_3FeNH^+	6	-229.0

(1-Cl)NP$_3$FeNH	5	-236.6
(1-Cl)NP$_3$FeNH$_2^+$	5	-315.0
(1-Cl)NP$_3$FeNH$_2$	4	-314.0
(1-Cl)NP$_3$FeNH$_3^+$	4	-369.0
(1-Cl)NP$_3$Fe$^+$	4	-386.5
(1-Cl)NP$_3$Fe	3	-369.7
(1-Cl)NP$_3$FeN$_2$	3	-378.7
(1-Cl)NP$_3$FeN$_2^-$	2	-338.6

Table S9. Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of (2-Cl)NP$_3$FeN$_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = G – G((2-Cl)NP$_3$FeN$_2^-$) + n_{H+}.[ΔG(H$^+$) - 2.24] + n_{e-}.[ΔG(e$^-$) – 1.97] + n_{NH3}.[G(NH$_3$) – 1.28 + ΔG(NH$_3$ $\rightarrow$ NH$_4^+$) – 2.24] – n_{N2}.[G(N$_2$) – 1.28]

where G, G((2-Cl)NP$_3$FeN$_2^-$), G(NH$_3$) and G(N$_2$) denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ((2-Cl)NP$_3$FeN$_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; ΔG(H$^+$), ΔG(e$^-$) and ΔG(NH$_3$ → NH$_4^+$) represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H$^+$, e$^-$, N$_2$) or released from (NH$_3$) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
(2-Cl)NP$_3$FeN$_2^-$	4	0.0
(2-Cl)NP$_3$FeNNH	4	-54.8
(2-Cl)NP$_3$FeNNH$_2^+$	4	-102.0
(2-Cl)NP$_3$FeNNH$_2$	1	-88.3
(2-Cl)NP$_3$FeNNH$_3^+$	1	-146.8
(2-Cl)NP$_3$FeN$^+$	1	-182.3
(2-Cl)NP$_3$FeN	2	-172.2
(2-Cl)NP$_3$FeNH$^+$	6	-232.8
(2-Cl)NP$_3$FeNH	5	-238.9
(2-Cl)NP$_3$FeNH$_2^+$	5	-318.1
(2-Cl)NP$_3$FeNH$_2$	4	-314.0
(2-Cl)NP$_3$FeNH$_3^+$	4	-371.8
(2-Cl)NP$_3$Fe$^+$	4	-391.8
(2-Cl)NP$_3$Fe	3	-372.4
(2-Cl)NP$_3$FeN$_2$	3	-379.6
(2-Cl)NP$_3$FeN$_2^-$	4	-338.6

Table S10. Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of (3-Cl)NP$_3$FeN$_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = G – G((3-Cl)NP$_3$FeN$_2^-$) + n_{H+}.[ΔG(H$^+$) - 2.24] + n_{e-}.[ΔG(e$^-$) – 1.97] + n_{NH3}.[G(NH$_3$) – 1.28 + ΔG(NH$_3$ $\rightarrow$ NH$_4^+$) – 2.24] – n_{N2}.[G(N$_2$) – 1.28]

where G, G((3-Cl)NP$_3$FeN$_2^-$), G(NH$_3$) and G(N$_2$) denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ((3-Cl)NP$_3$FeN$_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; ΔG(H$^+$), ΔG(e$^-$) and ΔG(NH$_3$ → NH$_4^+$) represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H$^+$, e$^-$, N$_2$) or released from (NH$_3$) the initial catalyst complex until the given

intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$(3\text{-Cl})NP_3FeN_2^-$	4	0.0
$(3\text{-Cl})NP_3FeNNH$	4	-50.4
$(3\text{-Cl})NP_3FeNNH_2^+$	4	-99.8
$(3\text{-Cl})NP_3FeNNH_2$	3	-88.1
$(3\text{-Cl})NP_3FeNNH_3^+$	1	-145.2
$(3\text{-Cl})NP_3FeN^+$	1	-180.7
$(3\text{-Cl})NP_3FeN$	2	-171.1
$(3\text{-Cl})NP_3FeNH^+$	4	-227.0
$(3\text{-Cl})NP_3FeNH$	5	-236.9
$(3\text{-Cl})NP_3FeNH_2^+$	5	-315.9
$(3\text{-Cl})NP_3FeNH_2$	4	-313.5
$(3\text{-Cl})NP_3FeNH_3^+$	4	-370.0
$(3\text{-Cl})NP_3Fe^+$	4	-391.6
$(3\text{-Cl})NP_3Fe$	3	-371.9
$(3\text{-Cl})NP_3FeN_2$	3	-378.5
$(3\text{-Cl})NP_3FeN_2^-$	4	-338.6

Table S11. Gibbs free energies and relative Gibbs free energy data of the intermediates in the catalytic cycle of $(4\text{-Cl})NP_3FeN_2^-$. Relative Gibbs free energies G_{rel} were calculated based on the following equation:

G_{rel}[kcal/mol] = $G - G((4\text{-Cl})NP_3FeN_2^-) + n_{H+}.[\Delta G(H^+) - 2.24] + n_{e-}.[\Delta G(e^-) - 1.97] + n_{NH3}.[G(NH_3) - 1.28 + \Delta G(NH_3 \rightarrow NH_4^+) - 2.24] - n_{N2}.[G(N_2) - 1.28]$

where G, $G((4\text{-Cl})NP_3FeN_2^-)$, $G(NH_3)$ and $G(N_2)$ denote the Gibbs free energy of a given intermediate (in the most stable spin state), the catalyst ($(4\text{-Cl})NP_3FeN_2^-$), the ammonia molecule and the dinitrogen molecule, respectively; $\Delta G(H^+)$, $\Delta G(e^-)$ and $\Delta G(NH_3 \rightarrow NH_4^+)$ represent the Gibbs free energy of proton release, electron release and ammonia protonation, respectively, the calculation of which is presented in Table S; n_{H+}, n_{e-}, n_{NH3} and n_{N2} stand for the number of particles added to (H^+, e^-, N_2) or released from (NH_3) the initial catalyst complex until the given intermediate is formed. Numerical corrections account for the liquid-phase concentrations and the excess amount of acid and reductant.

Complex	Spin State	ΔG_{rel} [kcal/mol]
$(4\text{-Cl})NP_3FeN_2^-$	4	0.0
$(4\text{-Cl})NP_3FeNNH$	4	-49.3
$(4\text{-Cl})NP_3FeNNH_2^+$	4	-101.6
$(4\text{-Cl})NP_3FeNNH_2$	3	-89.4
$(4\text{-Cl})NP_3FeNNH_3^+$	1	-153.9
$(4\text{-Cl})NP_3FeN^+$	1	-188.0
$(4\text{-Cl})NP_3FeN$	2	-174.4
$(4\text{-Cl})NP_3FeNH^+$	6	-236.0
$(4\text{-Cl})NP_3FeNH$	3	-233.6
$(4\text{-Cl})NP_3FeNH_2^+$	5	-319.3
$(4\text{-Cl})NP_3FeNH_2$	4	-313.1
$(4\text{-Cl})NP_3FeNH_3^+$	4	-371.0
$(4\text{-Cl})NP_3Fe^+$	4	-398.9
$(4\text{-Cl})NP_3Fe$	3	-378.2

(4-Cl)NP_3FeN_2	1	-378.9
(4-Cl)$NP_3FeN_2^-$	4	-338.6

2.3. Bond lengths

Table S12. Bond lengths in Å for the different intermediates involved in the catalytic cycle of BP_3Fe

	Fe-N	N-N	Fe-B	Fe-P	Fe-P	Fe-P	AVG Fe-P
$BP_3FeN_2^-$	1.751	1.159	2.286	2.195	2.201	2.236	2.211
BP_3FeNNH	1.786	1.237	2.244	2.319	2.346	2.321	2.329
$BP_3FeNNH_2^+$	1.747	1.272	2.463	2.337	2.374	2.392	2.368
BP_3FeNNH_2	1.721	1.292	2.341	2.230	2.230	2.347	2.269
$BP_3FeNNH_3^+$	1.804	1.416	2.442	2.360	2.416	2.389	2.388
BP_3FeN^+	1.506	-	2.925	2.243	2.246	2.247	2.245
BP_3FeN	1.539	-	2.679	2.214	2.216	2.217	2.216
BP_3FeNH^+	1.747	-	2.551	2.385	2.389	2.391	2.388
BP_3FeNH	1.779	-	2.289	2.354	2.356	2.354	2.355
$BP_3FeNH_2^+$	1.864	-	2.661	2.377	2.389	2.389	2.385
BP_3FeNH_2	1.910	-	2.409	2.316	2.326	2.348	2.330
$BP_3FeNH_3^+$	2.133	-	2.444	2.338	2.388	2.348	2.358
BP_3Fe^+	-	-	2.132	2.298	2.360	2.349	2.336
BP_3Fe	-	-	2.376	2.253	2.255	2.258	2.255
BP_3FeN_2	1.784	1.148	2.270	2.303	2.304	2.304	2.304

Table S13. Bond lengths in Å for the different intermediates involved in the catalytic cycle of GaP_3Fe

	Fe-N	N-N	Fe-Ga	Fe-P	Fe-P	Fe-P	AVG Fe-P
$GaP_3FeN_2^-$	1.740	1.161	2.480	2.216	2.235	2.250	2.234
GaP_3FeNNH	1.775	1.239	2.572	2.334	2.344	2.352	2.343
$GaP_3FeNNH_2^+$	1.739	1.273	2.688	2.367	2.412	2.415	2.398
GaP_3FeNNH_2	1.715	1.289	2.572	2.238	2.272	2.328	2.279
$GaP_3FeNNH_3^+$	1.794	1.414	2.651	2.396	2.463	2.417	2.425
GaP_3FeN^+	1.504	-	2.955	2.262	2.271	2.269	2.267
GaP_3FeN	1.546	-	2.751	2.229	2.234	2.233	2.232
GaP_3FeNH^+	1.747	-	2.740	2.427	2.434	2.431	2.431
GaP_3FeNH	1.763	-	2.576	2.354	2.413	2.372	2.380
$GaP_3FeNH_2^+$	1.865	-	2.731	2.417	2.432	2.421	2.423
GaP_3FeNH_2	1.902	-	2.591	2.365	2.371	2.338	2.358
$GaP_3FeNH_3^+$	2.104	-	2.606	2.350	2.406	2.386	2.381
GaP_3Fe^+	-	-	2.576	2.330	2.362	2.362	2.351
GaP_3Fe	-	-	2.498	2.255	2.255	2.256	2.255
GaP_3FeN_2	1.781	1.148	2.524	2.310	2.316	2.314	2.313

Table S14. Bond lengths in Å for the different intermediates involved in the catalytic cycle of AlP_3Fe

	Fe-N	N-N	Fe-Al	Fe-P	Fe-P	Fe-P	AVG Fe-P
$AlP_3FeN_2^-$	1.744	1.159	2.487	2.203	2.221	2.238	2.221
AlP_3FeNNH	1.782	1.238	2.586	2.326	2.337	2.340	2.334

$AlP_3FeNNH_2^+$	1.741	1.271	2.669	2.370	2.410	2.417	2.399
AlP_3FeNNH_2	1.716	1.288	2.569	2.238	2.273	2.323	2.278
$AlP_3FeNNH_3^+$	1.795	1.414	2.666	2.393	2.468	2.419	2.427
AlP_3FeN^+	1.504	-	2.963	2.263	2.274	2.272	2.270
AlP_3FeN	1.548	-	2.720	2.228	2.234	2.233	2.232
AlP_3FeNH^+	1.747	-	2.764	2.432	2.440	2.438	2.437
AlP_3FeNH	1.766	-	2.603	2.344	2.416	2.370	2.377
$AlP_3FeNH_2^+$	1.865	-	2.736	2.422	2.436	2.425	2.428
AlP_3FeNH_2	1.905	-	2.616	2.346	2.357	2.373	2.359
$AlP_3FeNH_3^+$	2.104	-	2.601	2.346	2.402	2.386	2.378
AlP_3Fe^+	-	-	2.564	2.327	2.366	2.358	2.350
AlP_3Fe	-	-	2.460	2.249	2.253	2.250	2.251
AlP_3FeN_2	1.782	1.147	2.540	2.308	2.314	2.312	2.311

Table S15. Bond lengths in Å for the different intermediates involved in the catalytic cycle of NP_3Fe

	Fe-N	N-N	Fe-N_{anchor}	Fe-P	Fe-P	Fe-P	AVG Fe-P
$NP_3FeN_2^-$	1.764	1.160	2.827	2.227	2.283	2.232	2.247
NP_3FeNNH	1.773	1.250	2.916	2.254	2.333	2.238	2.275
$NP_3FeNNH_2^+$	1.732	1.278	2.835	2.287	2.397	2.327	2.337
NP_3FeNNH_2	1.627	1.353	3.303	2.169	2.184	2.194	2.182
$NP_3FeNNH_3^+$	1.812	1.400	2.884	2.342	2.344	2.422	2.369
NP_3FeN^+	1.517	-	2.483	2.221	2.223	2.223	2.222
NP_3FeN	1.561	-	2.487	2.194	2.210	2.219	2.208
NP_3FeNH^+	1.754	-	2.751	2.410	2.416	2.421	2.416
NP_3FeNH	1.759	-	2.911	2.290	2.360	2.325	2.325
$NP_3FeNH_2^+$	1.881	-	2.894	2.374	2.405	2.381	2.387
NP_3FeNH_2	1.917	-	2.955	2.257	2.281	2.272	2.270
$NP_3FeNH_3^+$	2.137	-	2.839	2.293	2.297	2.297	2.296
NP_3Fe^+	-	-	2.088	2.257	2.260	2.262	2.260
NP_3Fe	-	-	2.343	2.179	2.215	2.183	2.192
NP_3FeN_2	1.774	1.154	2.799	2.228	2.23	2.257	2.238

Table S16. Bond lengths in Å for the different intermediates involved in the catalytic cycle of PP_3Fe

	Fe-N	N-N	Fe-P_{anchor}	Fe-P	Fe-P	Fe-P	AVG Fe-P
$PP_3FeN_2^-$	1.745	1.156	2.165	2.183	2.194	2.190	2.189
PP_3FeNNH	1.740	1.233	2.134	2.199	2.227	2.209	2.212
$PP_3FeNNH_2^+$	1.726	1.292	2.204	2.243	2.307	2.250	2.267
PP_3FeNNH_2	1.785	1.309	2.140	2.181	2.227	2.186	2.198
$PP_3FeNNH_3^+$	1.815	1.458	2.208	2.253	2.318	2.289	2.287

PP_3FeN^+	1.553	-	2.317	2.234	2.238	2.237	2.236
PP_3FeN	1.597	-	2.283	2.191	2.244	2.235	2.223
PP_3FeNH^+	1.678	-	2.238	2.214	2.231	2.325	2.257
PP_3FeNH	1.772	-	2.173	2.205	2.231	2.241	2.226
$PP_3FeNH_2^+$	1.857	-	2.183	2.284	2.313	2.297	2.298
PP_3FeNH_2	1.864	-	2.151	2.237	2.279	2.250	2.255
$PP_3FeNH_3^+$	2.042	-	2.108	2.235	2.277	2.244	2.252
PP_3Fe^+	-	-	2.196	2.297	2.297	2.302	2.299
PP_3Fe	-	-	2.228	2.221	2.216	2.210	2.216
PP_3FeN_2	1.763	1.152	2.244	2.277	2.278	2.279	2.278

2.4. ADCH charges

Table S17. ADCH charges for the different intermediates involved in the catalytic cycle of BP_3Fe

	Fe	N1	N2	P	P	P	AVG P	B
$BP_3FeN_2^-$	-0.373	0.173	-0.308	0.146	0.185	0.202	0.177	-0.092
BP_3FeNNH	-0.125	-0.034	-0.380	0.204	0.202	0.201	0.202	-0.085
$BP_3FeNNH_2^+$	-0.044	-0.129	-0.286	0.193	0.192	0.194	0.193	-0.038
BP_3FeNNH_2	-0.248	-0.086	-0.331	0.149	0.172	0.207	0.176	-0.202
$BP_3FeNNH_3^+$	-0.013	-0.397	-0.123	0.185	0.187	0.199	0.190	-0.051
BP_3FeN^+	-0.165	-0.141	-	0.219	0.217	0.217	0.218	0.100
BP_3FeN	-0.225	-0.219	-	0.208	0.209	0.207	0.208	0.041
BP_3FeNH^+	0.007	-0.394	-	0.199	0.189	0.196	0.195	0.048
BP_3FeNH	-0.067	-0.426	-	0.208	0.208	0.207	0.208	-0.072
$BP_3FeNH_2^+$	0.043	-0.680	-	0.194	0.175	0.189	0.186	0.083
BP_3FeNH_2	-0.032	-0.707	-	0.198	0.162	0.208	0.189	-0.060
$BP_3FeNH_3^+$	-0.073	-0.454	-	0.165	0.168	0.180	0.171	-0.056
BP_3Fe^+	-0.019	-	-	0.187	0.191	0.170	0.183	-0.067
BP_3Fe	-0.084	-	-	0.169	0.171	0.172	0.171	-0.116
BP_3FeN_2	-0.198	0.104	-0.155	0.194	0.195	0.194	0.194	-0.088

Table S18. ADCH charges for the different intermediates involved in the catalytic cycle of GaP_3Fe

	Fe	N1	N2	P	P	P	AVG P	Ga
$GaP_3FeN_2^-$	-0.435	0.187	-0.306	0.139	0.174	0.188	0.167	0.154
GaP_3FeNNH	-0.183	-0.044	-0.343	0.192	0.190	0.182	0.188	0.163
$GaP_3FeNNH_2^+$	-0.123	-0.201	-0.014	0.180	0.188	0.191	0.187	0.223
GaP_3FeNNH_2	-0.189	-0.413	0.040	0.146	0.186	0.211	0.181	0.162
$GaP_3FeNNH_3^+$	-0.074	-0.393	-0.121	0.178	0.188	0.192	0.186	0.188
GaP_3FeN^+	-0.209	-0.100	-	0.211	0.210	0.211	0.211	0.336
GaP_3FeN	-0.282	-0.191	-	0.197	0.196	0.195	0.196	0.232
GaP_3FeNH^+	-0.033	-0.366	-	0.186	0.190	0.197	0.191	0.284
GaP_3FeNH	-0.100	-0.477	-	0.200	0.189	0.193	0.194	0.164
$GaP_3FeNH_2^+$	0.011	-0.653	-	0.195	0.175	0.184	0.185	0.256
GaP_3FeNH_2	-0.109	-0.647	-	0.192	0.155	0.196	0.181	0.157
$GaP_3FeNH_3^+$	-0.156	-0.430	-	0.168	0.162	0.180	0.170	0.191
GaP_3Fe^+	-0.003	-	-	0.180	0.183	0.152	0.172	0.187
GaP_3Fe	-0.117	-	-	0.161	0.160	0.162	0.161	0.085
GaP_3FeN_2	-0.276	0.146	-0.101	0.179	0.179	0.179	0.179	0.135

Table S19. ADCH charges for the different intermediates involved in the catalytic cycle of AlP_3Fe

	Fe	N1	N2	P	P	P	AVG P	Al
$AlP_3FeN_2^-$	-0.440	0.187	-0.301	0.185	0.139	0.172	0.165	0.145
AlP_3FeNNH	-0.198	-0.047	-0.329	0.193	0.190	0.184	0.189	0.180

$AlP_3FeNNH_2^+$	-0.117	-0.228	0.097	0.184	0.189	0.197	0.190	0.211
AlP_3FeNNH_2	-0.222	-0.387	0.090	0.150	0.189	0.214	0.184	0.161
$AlP_3FeNNH_3^+$	-0.074	-0.392	-0.121	0.181	0.192	0.193	0.189	0.185
AlP_3FeN^+	-0.204	-0.099	-	0.213	0.212	0.213	0.213	0.246
AlP_3FeN	-0.280	-0.187	-	0.199	0.199	0.197	0.198	0.215
AlP_3FeNH^+	-0.024	-0.361	-	0.188	0.191	0.199	0.193	0.254
AlP_3FeNH	-0.106	-0.480	-	0.203	0.188	0.193	0.195	0.172
$AlP_3FeNH_2^+$	0.021	-0.652	-	0.197	0.177	0.188	0.187	0.232
AlP_3FeNH_2	-0.121	-0.624	-	0.194	0.157	0.193	0.182	0.159
$AlP_3FeNH_3^+$	-0.162	-0.426	-	0.172	0.162	0.182	0.172	0.191
AlP_3Fe^+	0.030	-	-	0.172	0.176	0.149	0.166	0.173
AlP_3Fe	-0.100	-	-	0.156	0.156	0.157	0.156	0.080
AlP_3FeN_2	-0.280	0.117	-0.073	0.173	0.174	0.175	0.174	0.148

Table S20. ADCH charges for the different intermediates involved in the catalytic cycle of NP_3Fe

	Fe	N1	N2	P	P	P	AVG P	N_{anchor}
$NP_3FeN_2^-$	-0.293	0.077	-0.347	0.120	0.183	0.189	0.164	-0.032
NP_3FeNNH	-0.211	-0.113	-0.413	0.152	0.149	0.190	0.164	-0.054
$NP_3FeNNH_2^+$	-0.069	-0.305	-0.151	0.141	0.179	0.180	0.167	-0.067
NP_3FeNNH_2	-0.319	-0.204	-0.498	0.162	0.159	0.164	0.162	0.005
$NP_3FeNNH_3^+$	-0.055	-0.514	-0.116	0.174	0.180	0.146	0.167	-0.075
NP_3FeN^+	-0.203	-0.174	-	0.205	0.203	0.204	0.204	0.000
NP_3FeN	-0.260	-0.393	-	0.178	0.190	0.190	0.186	0.014
NP_3FeNH^+	0.023	-0.458	-	0.165	0.163	0.165	0.164	-0.065
NP_3FeNH	-0.082	-0.685	-	0.190	0.197	0.147	0.178	-0.060
$NP_3FeNH_2^+$	0.070	-0.821	-	0.166	0.145	0.166	0.159	-0.082
NP_3FeNH_2	-0.153	-0.759	-	0.155	0.149	0.166	0.157	-0.049
$NP_3FeNH_3^+$	-0.213	-0.439	-	0.146	0.143	0.146	0.145	-0.057
NP_3Fe^+	-0.220	-	-	0.159	0.159	0.160	0.160	0.022
NP_3Fe	-0.359	-	-	0.118	0.136	0.142	0.132	-0.001
NP_3FeN_2	-0.359	0.200	-0.359	0.180	0.120	0.174	0.158	-0.034

Table S21. ADCH charges for the different intermediates involved in the catalytic cycle of PP_3Fe

	Fe	N1	N2	P	P	P	AVG P	P_{anchor}
$PP_3FeN_2^-$	-0.459	0.103	-0.219	0.162	0.163	0.162	0.163	0.174
PP_3FeNNH	-0.393	-0.049	-0.354	0.181	0.179	0.176	0.179	0.157
$PP_3FeNNH_2^+$	-0.282	-0.209	-0.177	0.202	0.191	0.192	0.195	0.154
PP_3FeNNH_2	-0.404	-0.335	-0.234	0.181	0.151	0.173	0.168	0.148
$PP_3FeNNH_3^+$	-0.253	-0.448	-0.142	0.182	0.201	0.186	0.190	0.154
PP_3FeN^+	-0.278	-0.185	-	0.214	0.213	0.213	0.213	0.163
PP_3FeN	-0.335	-0.375	-	0.193	0.189	0.189	0.190	0.173

PP_3FeNH^+	-0.234	-0.376	-	0.207	0.207	0.203	0.206	0.158
PP_3FeNH	-0.292	-0.557	-	0.188	0.197	0.186	0.191	0.159
$PP_3FeNH_2^+$	-0.180	-0.646	-	0.198	0.212	0.195	0.202	0.146
PP_3FeNH_2	-0.316	-0.680	-	0.192	0.184	0.165	0.180	0.148
$PP_3FeNH_3^+$	-0.360	-0.419	-	0.146	0.180	0.191	0.172	0.138
PP_3Fe^+	-0.181	-	-	0.179	0.177	0.179	0.178	0.056
PP_3Fe	-0.413	-	-	0.127	0.162	0.171	0.153	0.106
PP_3FeN_2	-0.464	0.099	-0.168	0.163	0.164	0.164	0.164	0.161

2.5. cDFT indices

Table S22. cDFT indices (electrophilicity, nuceolphilicity, hardness, softness, and mulliken electronegativity indices) for intermediates prone to underdo reduction (all values are in ev)

Anchor atom	Intermediate	E Index	N Index	Hardness	Softness	Mulliken Electronegativity
B	**$EP_3FeNNH_2^+$**	5.193	-0.862	4.842	0.207	7.091
	EP_3FeN^+	5.001	-1.862	4.827	0.207	6.949
	EP_3FeNH^+	5.462	-1.357	4.487	0.223	7.001
	$EP_3FeNH_2^+$	3.745	-1.29	5.54	0.181	6.442
	EP_3Fe^+	4.265	-1.394	5.752	0.174	7.005
	EP_3FeN_2	0.478	2.474	6.265	0.160	2.448
P	**$EP_3FeNNH_2^+$**	3.157	-0.366	5.462	0.183	5.663
	EP_3FeN^+	3.198	-1.616	5.804	0.172	6.093
	EP_3FeNH^+	3.371	-0.814	5.498	0.182	6.088
	$EP_3FeNH_2^+$	2.606	-0.773	6.011	0.166	5.597
	EP_3Fe^+	3.19	-0.362	5.195	0.193	5.757
	EP_3FeN_2	0.4769	3.0013	4.656	0.2148	2.1073
N	**$EP_3FeNNH_2^+$**	3.058	1.85	5.56	0.18	5.831
	EP_3FeN^+	3.084	-1.577	5.959	0.168	6.063
	EP_3FeNH^+	4.11	-1.09	5.009	0.2	6.417
	$EP_3FeNH_2^+$	2.543	-1.029	6.484	0.154	5.743
	EP_3Fe^+	2.752	-0.532	6.244	0.16	5.862
	EP_3FeN_2	0.4389	3.7079	4.3956	0.2275	1.9643
Al	**$EP_3FeNNH_2^+$**	4.807	1.094	4.867	0.206	6.84
	EP_3FeN^+	5.565	-2.042	4.657	0.215	7.2
	EP_3FeNH^+	5.365	-1.603	4.786	0.209	7.166
	$EP_3FeNH_2^+$	2.928	-1.594	6.717	0.149	6.271
	EP_3Fe^+	4.173	-1.463	6.014	0.166	7.084
	EP_3FeN_2	0.4353	2.503	6.1899	0.1616	2.3214
Ga	**$EP_3FeNNH_2^+$**	5.1159	-1.384	4.9309	0.2028	7.103
	EP_3FeN^+	5.4324	-2.0047	4.6943	0.213	7.1416
	EP_3FeNH^+	5.3105	-1.5454	4.7539	0.2104	7.1057
	$EP_3FeNH_2^+$	3.0481	-1.5299	6.4588	0.1548	6.2749
	EP_3Fe^+	4.0905	-1.3364	5.9626	0.1677	6.9843
	EP_3FeN_2	0.4484	2.4857	6.2664	0.1596	2.3706

2.6. Binding affinities (A)

Table S23. N_2 and H_2 binding affinities (A) in kcal/mol for the different anchor atom complexes.

Complex	N_2 Binding Affinity (kcal/mol)	H_2 Binding Affinity (kcal/mol)
BP_3Fe	2.5	-1.4
CP_3Fe	-0.6	-11.3
SiP_3Fe	11.3	3.1
AlP_3Fe	2.6	0.5
GaP_3Fe	2.9	1.5
NP_3Fe	8.8	7.1
PP_3Fe	19.7	18.5

2.7. ***Orbital energies***

Table S24. $EP_3FeNNH_2^+$ LUMO and EP_3FeNNH_2 HOMO alpha orbital energies (calculated at ωB97xD/TZVP level of theory) across various anchor atom complexes (all energies are in eV).

Complex	Alpha HOMO	Alpha LUMO	Alpha Gap	Beta HOMO	Beta LUMO	Beta Gap
BP_3FeNNH_2	-6.510	1.055	7.565	-6.474	0.959	7.433
$BP_3FeNNH_2^+$	-8.585	-0.227	8.359	-7.952	-0.962	6.990
AlP_3FeNNH_2	-6.504	1.159	7.663	-6.684	0.790	7.474
$AlP_3FeNNH_2^+$	-8.572	-0.231	8.341	-8.557	-1.130	7.427
NP_3FeNNH_2	-5.656	0.984	6.640	-5.615	0.880	6.495
$NP_3FeNNH_2^+$	-7.816	0.053	7.869	-7.980	-0.243	7.737
PP_3FeNNH_2	-5.614	0.812	6.425	-	-	-
$PP_3FeNNH_2^+$	-7.799	-0.116	7.683	-7.470	-0.150	7.320
N(Cl-1) P_3FeNNH_2	-6.369	0.749	7.117	-	-	-
N(Cl-1) $P_3FeNNH_2^+$	-8.001	-0.183	7.818	-8.172	-0.429	7.743
N(Cl-2) P_3FeNNH_2	-6.392	0.676	7.068	-	-	-
N(Cl-2) $P_3FeNNH_2^+$	-8.000	-0.249	7.752	-8.075	-0.446	7.629
N(Cl-3) P_3FeNNH_2	-6.417	0.666	7.083	-	-	-
N(Cl-3) $P_3FeNNH_2^+$	-8.019	-0.255	7.764	-8.114	-0.470	7.644
N(Cl-4) P_3FeNNH_2	-6.359	0.658	7.016	-	-	-
N(Cl-4) $P_3FeNNH_2^+$	-7.894	-0.318	7.576	-7.989	-0.435	7.554