Supporting Information

Influence of the nacnac Ligand in Iron(I)-Mediated P₄ Transformations

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1. **Synthesis and Characterization**

General Remarks:
All manipulations were performed with rigorous exclusion of oxygen and moisture using Schlenk-type glassware on a dual manifold Schlenk line with Argon inert gas or glove box filled with N\textsubscript{2} containing a high-capacity recirculator (<0.1 ppm O\textsubscript{2}). Solvents were dried using a MB SPS-800 device of company MBRAUN, degassed and saturated with argon to prevent N\textsubscript{2} activation while reduction reactions. Mass spectrometry was performed using a ThermoQuest Finnigan TSQ 7000 (ESI-MS), Finnigan MAT 95 (LIFDI) and JEOL AccuTOF GCX (LIFDI), respectively. Elemental analysis (CHN) was determined using a Vario micro cube and Vario EL III instrument.

Fe(II) chloride, anhydrous; 98\% was purchased by ABCR and used without further purification. Ligands L\textsuperscript{1}H\textsuperscript{[1]} and L\textsuperscript{3}H\textsuperscript{[2]} were synthesized following literature-known routes.

**Synthesis of L\textsuperscript{2}H:**

L\textsuperscript{2}H was prepared using the standard β-diiimine ligand preparation except that 1,1,3,3-tetramethoxypropane was used instead of 2,4-peantadione as starting material.\textsuperscript{[28]} L\textsuperscript{2}H was crystallized from THF.

Analytical data:

| NMR (C\textsubscript{6}D\textsubscript{6}, 300 K) | 1H: δ [ppm] = 11.42 (1H, br s, a), 7.05 (2H, d, \textsuperscript{1}J\textsubscript{HH} = 6 Hz, d), 6.97 (4H, d, \textsuperscript{1}J\textsubscript{HH} = 7 Hz, f), 6.91 (2H, dd, \textsuperscript{1}J\textsubscript{HH} = 6 Hz, \textsuperscript{1}J\textsubscript{HH} = 9 Hz, e), 4.79 (1H, t, \textsuperscript{1}J\textsubscript{HH} = 6 Hz, c), 2.17 (12H, s, b). |
| --- | --- |
| Mass spectrometry (ESI-MS) | m/z: 279.19 (100\%) [M+H]\textsuperscript{+}. |

**Synthesis of [L\textsuperscript{1}Fe(tol)] (1a):**

Compound 1a was prepared analogue to literature method,\textsuperscript{[3]} beside that [L\textsuperscript{1}FeBr]\textsubscript{2} was used instead of [L\textsuperscript{1}CoI(2,4-lutidine)].

**Synthesis of [L\textsuperscript{2}Fe(tol)] (1b):**
A yellow slurry of 6.68 g (24.0 mmol) \( \text{L}^2\text{H} \) in 100 mL THF was treated with a solution of 15 mL (24.0 mmol) \( ^{\text{t}}\text{BuLi} \) (1.6 M) in n-hexane. The formed clear red solution was stirred at r.t. for 1 h. Within 1.5 h the solution was slowly transferred into a slurry of 3.04 g (24.0 mmol) anhydrous \( \text{FeCl}_2 \) in 5 mL THF, forming an intense dark yellow solution, which was stirred at r.t. for 12 h. After removal of solvent, the brownish solid was dissolved in 50 mL of toluene. The intense dark yellow solution was transferred into a slurry of 1.05 equivalents of potassium graphite in 10 mL toluene. The mixture was stirred at r.t. for 98 h and a color change to olive green was observed. Remaining graphite and salts were removed via filtration of the olive green solution over celite. The solvent was removed \text{i. vac.} and a dark green brown solid was obtained. The solid was dissolved in 100 mL n-hexane and the solution was filtered over celite. After concentration of the solution to a volume of ca. 20 mL, the intense green solution was stored at 5 °C for several h and at –15 °C for one night to yield 2.36 g of dark green crystalline blocks.

Crystalline yield: 2.36 g (5.55 mmol, 23 %)

Analytical data:

| NMR (Tol-\( \text{d}_8 \), 298 K) | \( ^1\text{H} \): \( \delta \) [ppm] = 512.9 (2H, s, b), 487.6 (1H, s, a), 10.9 (4H, s, d), 9.8 (2H, s, e), 7.76 and 7.65 (ca. 5H, s, g/h/i), 2.78 (3H, s, f), 1.9 (12H, s (broad), c). |
| Evans-NMR (Tol-\( \text{d}_8 \) solution) | \( \mu_{\text{eff}} = 2.01 \mu_\text{B} \) (298 K) |
| Elemental analysis (C\( _{26} \)H\( _{29} \)FeN\( _2 \)) | Calculated: C 73.41, H 6.87, N 6.59. Found: C 72.78, H 6.61, N 6.63. |
| Mass spectrometry (FD, toluene) | m/z: 425.18 (100%) \([\text{M}]^+\), 610.30 (24%) \([\text{L}^2\text{Fe}]^+\). |

\textbf{Synthesis of L}^3\text{Fe(tol)} \times 0.25 n\text{-hexane (1c):}
To a cooled (0 °C) solution of 6.03 g (14.4 mmol) $\text{L}^3\text{H}$ in 40 mL THF was added a solution of 9 mL (14.4 mmol) $\text{nBuLi}$ (1.6 M) in n-hexane. The solution was stirred for 3.5 h and allowed to warm up to room temperature. Within 10 min the clear intense yellow solution was slowly added to a slurry of 1.83 g (14.5 mmol) anhydrous FeCl$_2$ in 20 mL THF. A color change to intense dark yellow occurred and the reaction mixture was stirred for 17.5 h. After removal of the solvent, the dark yellow solid was dissolved in 45 mL of toluene. The intense dark yellow solution was added to a slurry of 1.05 equivalents potassium graphite in 10 mL toluene. The mixture was stirred at r.t. for 48 h. Remaining graphite and salts were removed by filtration over celite. The solvent was removed $i. \text{vac.}$ and the resulting dark brown solid was dissolved in 65 mL n-hexane, filtered over celite and stored at 5 °C for 3 d to yield 3.01 g of black crystals. The supernatant solution was concentrated and 1.20 g of a second crystalline crop was obtained.

Crystalline yield: 4.21 g (7.45 mmol, 52 %)

Analytical data:

| Test | Result |
|------|--------|
| $^1$H-NMR (Tol-$d_8$, 300 K) | Despite $^1$H spectra were measured from 1100 ppm to -1100 ppm, only three very broad signals could be detected. This might be due to line broadening caused by the paramagnetic nature of 1c. $^1$H-NMR Spectrum of obtained signals is shown in chapter “5. $^1$H-NMR and EPR Spectra”. |
| Evans-NMR (Tol-$d_8$ solution) | $\mu_{\text{eff}} = 1.89 \mu_B$ (300 K) |
| Elemental analysis (C$_{36}$H$_{49}$FeN$_2$) | Calculated: C 76.44, H 8.73, N 4.95. Found: C 76.24, H 8.79, N 4.83. |
| Mass spectrometry (FD, toluene) | m/z: 565.34 (100%) [M]$^+$ |

**Synthesis of $[(\text{L}^3\text{Fe})_4\text{P}_8]$ (2a):**
506 mg (4.0 mmol, 2 equivalents) of P₄ were dissolved in 20 mL toluene. The solution was added to an intense reddish brown solution of 943 mg (2.0 mmol, 1 equivalent) of 1a in 50 mL toluene. Within 1 h, a color change to red was observed. After 16 h, the solvent was concentrated and the solution was filtered over celite. Within 1 d red crystals were obtained by storing saturated solutions at 8 °C.

Crystalline yield: 50 mg (0.03 mmol, 6%)

Analytical data:

| Method                                      | Data                                      |
|---------------------------------------------|-------------------------------------------|
| NMR (THF-d₈, 300 K)                        | ¹H: δ [ppm] = 11.4 (8H, s, f/g), 3.9 (8H, s, f/g), -4.4 (4H, s, c/h/i), -5.0 (24H, s, d/e), -20.9 (12H, s, a/b), -21.6 (4H, s, c/h/i), -23.1 (24H, s, d/e), -26.1 (4H, s, c/h/i), -28.7 (12H, s, a/b). |
|                                             | ³¹P{¹H}: No signal could be detected between 1200 to -1200 ppm. |
| Evans-NMR (C₆D₆ solution)                  | µₑff = 6.79 µB (300 K)                    |
| VT SQUID                                    | χ₈₈₉ = 11.11·10⁻⁴ cm³·mol⁻¹               |
|                                             | µₑff = 7.04 µB (300 K)                    |
| Elemental analysis (C₉₁H₁₀₈Fe₄N₈P₈)        | Calculated: C 61.23, H 6.10, N 6.28.      |
|                                             | Found: C 61.42, H 6.28, N 6.59.           |
| Mass spectrometry (FD, toluene)            | m/z: 1692.7 (100%) [M]⁺                   |

Synthesis of [(L²Fe)₄P₈] (2b):
44 mg (0.35 mmol, 0.5 equivalents) of P₄ were dissolved in 12 mL toluene. Within 15 min at r.t., the solution was added to an intense dark green solution of 300 mg (0.71 mmol, 1 equivalent) 1b in 15 mL toluene. After 30 min the solution has changes color from olive green to dark brown. After stirring at r.t. for 20 h, the brown reaction solution was filtered over celite and the solvent was concentrated to a volume of 5 mL. Several crops of crystalline brown blocks were obtained by cooling the concentrated solution to 5 °C.

Crystalline yield: 185.8 mg (0.12 mmol, 67 %)

Analytical data:

| NMR (Tol-\textit{d₈}, 300 K) | ¹H: δ [ppm] = 273.1 (4H, s, a/b), 251.5 (4H, s, a/b), 12.3 (8H, broad s, f/g), 5.6 (8H, broad s, f/g), -5.0 (24H, s, d/e), -12.9 (4H, s, c/h/i), -14.8 (4H, s, c/h/i), -19.2 (4H, s, c/h/i), -19.3 (24H, s, d/e). |
| Evans-NMR (THF-\textit{d₈} solution) | ³¹P{¹H}: No signal could be detected between 1200 to -1200 ppm. |
| VT SQUID | ¹H-NMR Spectrum is shown in chapter “5. ¹H-NMR and EPR Spectra”. |
| Zero-field Mössbauer | Note: An accurate signal integration is possible in ¹H NMR spectra only with spectral width of 240 ppm or less. Therefore we could not compare the integral ratio of the signals at δ = 273.1 and 251.5 ppm with the rest of the signals. |
| Elemental analysis (C₇₆H₈₄Fe₄N₈P₈) | Calculated: C 57.75, H 5.36, N 7.09. |
| Mass spectrometry (LIFDI, toluene) | Found: C 57.85, H 5.22, N 6.53. |

Synthesis of [(L₃Fe)₂P₄] (2c):
33 mg (0.27 mmol, 0.5 equivalents) of \( P_4 \) were dissolved in 10 mL toluene. Within 8 min at r.t. this solution was added to an intense reddish brown solution of 300 mg (0.53 mmol, 1 equivalent) \( 1c \) in 15 mL toluene. After stirring at r.t. for 18 h, the brown reaction solution was filtered over celite and the solvent was removed i. vac. to obtain a brown microcrystalline product, which was washed with 10 mL \( \text{n-hexane} \) and dried.

Microcrystalline yield: 176.2 mg (0.17 mmol, 62 %)

Analytical data:

\[
\text{NMR (THF-}^d_8, 300 \text{ K)}
\]

\[ ^1\text{H: } \delta \text{ [ppm]} = 6.7 \text{ (8H, d, } ^1J_{\text{H-H}} = 7 \text{ Hz, f), 6.5 (12H, s, b), 2.3 (4H, t, } ^1J_{\text{H-H}} = 7 \text{ Hz, g), 2.1 (24H, s, c/d), 0.7 (2H, s, a), -0.6 (8H, s (broad), e), -2.0 (24H, s, c/d).} \]

\[ ^{31}\text{P\{^1\text{H}\}: No signal could be detected between 1200 to -1200 ppm.} \]

\[^1\text{H-NMR Spectrum is shown in chapter “5. } ^1\text{H-NMR and EPR Spectra”.} \]

\[
\text{Evans-NMR (THF-}^d_8 \text{ solution)}
\]

double determination:

\[ \mu_{\text{eff,1}} = 2.97 \mu_B, \]
\[ \mu_{\text{eff,2}} = 3.20 \mu_B \]

\[
\text{VT SQUID}
\]

\[ \chi_{\text{dia}} = 7.45 \cdot 10^{-4} \text{ cm}^3\text{mol}^{-1} \]
\[ \mu_{\text{eff}} = 3.46 \mu_B \text{ (300 K)} \]

\[
\text{Zero-field Mössbauer}
\]

\[ \delta = 0.74(1) \text{ mm}\text{s}^{-1}, \Delta E_Q = 1.74(1) \text{ mm}\text{s}^{-1} \]

\[
\text{Elemental analysis (C}_{58}\text{H}_{82}\text{Fe}_2\text{N}_4\text{P}_4)
\]

Calculated: C 65.05, H 7.72, N 5.23.

Found: C 65.08, H 7.56, N 5.23.

\[
\text{Mass spectrometry (LIFDI, toluene)}
\]

\[ m/z: 1070.49 \text{ (100%) [M]^+}, 1039.52 \text{ (22%) [M-P]^+}, 1008.54 \text{ (23%) [M-P}_2]^+}, 566.22 \text{ (4%) [L}^3\text{FeP}_3]^+, 535.26 \text{ (10%) [L}^3\text{FeP}_2]^+, 473.29 \text{ (7%) [L}^3\text{Fe}]^+, 418.37 \text{ (22%) [L}^3]^+. \]
2. Crystallographic Details

General remarks:

Single crystal structure analyses were performed using Agilent Technologies diffractometer (GV1000, Titan\textsuperscript{52} diffractometer (1b), Xcalibur, Atlas\textsuperscript{52}, Gemini ultra diffractometer (1c, 2b), SuperNova, Single source at offset, Atlas diffractometer (2a), SuperNova, Single source at offset, Eos diffractometer (2c). Frames integration and data reduction were performed with the CrysAlisPro\textsuperscript{41} software package. Using the software Olex2\textsuperscript{55} the structure solution was carried out using the programs ShelXT\textsuperscript{66} (Sheldrick, 2015) (1a, 1b, 2b, 2c) and SIR2004\textsuperscript{77} (2a). Least squares refinements on $F_0^2$ were performed using SHELXL-2014 (1b, 1c, 2a, 2b, 2c).\textsuperscript{88} Further details are given in Table S2.

In 2c one disordered methyl group was refined to a chemical occupancy 68:32. Additionally the slightly disordered cyclo-P\textsubscript{4} middle deck was refined to a chemical occupancy of 97:3. Due to the low electron density of minor component two geometrical restraints (DFIX, SIMU) were used in case of the minor component (3% occupation).

**Table S1**: Comparison of geometrical details of major and minor component in 2c.

|                     | major component (97%)                                                                 | minor component (3%)                                                                 |
|---------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| P1-P2, P1-P2’       | 2.178(1), 2.207(1) Å                                                              | 2.18(1) Å (DFIX), 2.25(3) Å                                                        |
| Fe1-P1, Fe1-P2, Fe1-P1’, Fe1-P2’ | 2.4376(6), 2.5064(6), 2.5064(6), 2.5163(6) Å                                      | 2.43(2), 2.50(2), 2.55(2), 2.52(2) Å                                             |
| P2’-P1-P2, P1-P2-P1’ | 88.27(3)°, 91.73(3)°                                                              | 87(1)°, 94(1)°                                                                      |

Molecular structures of compounds 1b, 1c and 2a are shown on Figure S1-S3. Molecular structures of compounds 2b and 2c are shown in main part of publication.

Crystallographic data and details of the diffraction experiments are given in Table S2. CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for 1 and 2 are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-1435936–1435939 and CCDC-1436088.
### Table S2: Crystallographic data and details of diffraction experiments for 1b, 1c, 2a, 2b and 2c.

| Compound | 1b | 1c · 0.25 \text{^9} \text{hexan} | 2a · 2 tol | 2b · 1 tol | 2c |
|----------|----|---------------------------------|-----------|-----------|----|
| CCDC     | 1436088 | 1435936 | 1435937 | 1435938 | 1435939 |
| Formula  | C_{36}H_{49}FeN_{2} | C_{36}H_{49}FeN_{2} | C_{36}H_{16}Fe_{2}N_{2}P_{8} | C_{36}H_{16}Fe_{2}N_{2}P_{8} | C_{36}H_{16}Fe_{2}N_{2}P_{4} |
| \(D_{calc.}\) / g cm\(^{-3}\) | 1.297 | 1.140 | 1.298 | 1.352 | 1.249 |
| \(\mu\) / mm\(^{-1}\) | 5.637 | 3.837 | 6.385 | 7.400 | 0.661 |
| Formula Weight | 425.36 | 565.62 | 1877.14 | 1671.79 | 1070.85 |
| Colour | clear dark green | black | red | clear dark brown | clear dark black |
| Shape | block | block | block | Block | block |
| Max Size/mm | 0.26 | 0.42 | 0.32 | 0.23 | 0.18 |
| Mid Size/mm | 0.23 | 0.17 | 0.13 | 0.13 | 0.14 |
| Min Size/mm | 0.18 | 0.07 | 0.07 | 0.09 | 0.07 |
| \(T/K\) | 123(1) | 123(1) | 123(1) | 125(4) | 123(1) |
| Crystal System | orthorhombic | tetragonal | triclinic | monoclinic | monoclinic |
| Space Group | Pna\(_2\)_1 | I4\(_1\)/a | P-1 | C2/c | P2\(_1\)/n |
| \(a/\text{\AA}\) | 12.1516(2) | 37.7067(4) | 13.59902(16) | 24.7045(2) | 14.2409(3) |
| \(b/\text{\AA}\) | 25.9683(6) | 37.7067(4) | 14.59579(18) | 13.14969(13) | 13.5520(3) |
| \(c/\text{\AA}\) | 6.90447(16) | 9.27235(14) | 25.7434(4) | 26.0368(3) | 15.2276(3) |
| \(\alpha/\degree\) | 90 | 90 | 91.9532(11) | 90 | 90 |
| \(\beta/\degree\) | 90 | 90 | 105.1756(12) | 103.8325(9) | 104.288(2) |
| \(\gamma/\degree\) | 90 | 90 | 102.0298(10) | 90 | 90 |
| \(V/\text{\AA}^3\) | 2178.74(8) | 13183.4(3) | 4801.96(12) | 8212.95(14) | 2847.91(11) |
| \(Z\) | 4 | 16 | 2 | 4 | 2 |
| \(Z'\) | 1 | 1 | 1 | 0.5 | 0.5 |
| \(\Theta_{max}/\degree\) | 3.404 | 3.315 | 3.427 | 3.685 | 3.144 |
| \(\Theta_{max}/\degree\) | 74.165 | 66.624 | 73.093 | 66.647 | 28.282 |
| Measured Refl. | 9794 | 27919 | 35623 | 35496 | 46308 |
| Independent Refl. | 3724 | 5726 | 18648 | 7235 | 7046 |
| Reflections Used | 3614 | 5491 | 16595 | 6664 | 6142 |
| \(R_{int}\) | 0.0427 | 0.0297 | 0.0304 | 0.0296 | 0.0408 |
| Parameters | 268 | 393 | 1119 | 479 | 345 |
| Restraints | 1 | 0 | 131 | 0 | 7 |
| Largest Peak | 0.385 | 0.236 | 0.733 | 0.398 | 0.562 |
| Deepest Hole | -0.342 | -0.217 | -0.580 | -0.249 | -0.831 |
| Goof | 1.054 | 1.107 | 1.022 | 1.027 | 1.054 |
| \(wR_2\) (all data) | 0.1073 | 0.0848 | 0.1084 | 0.0625 | 0.1042 |
| \(wR_2\) | 0.1062 | 0.0779 | 0.1037 | 0.0607 | 0.1001 |
| \(R_1\) (all data) | 0.0393 | 0.0301 | 0.0462 | 0.0298 | 0.0473 |
| \(R_1\) | 0.0382 | 0.0280 | 0.0404 | 0.0260 | 0.0402 |
| Flack Parameter | -0.003(8) | | | | |
| Hooft Parameter | 0.041(7) | | | | |
Figure S1: Molecular structure of compound 1b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability level.

Figure S2: Molecular structure of compound 1b. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability level.

Figure S3: Molecular structure of compound 2a. Hydrogen atoms and three molecules toluene are omitted for clarity. Thermal ellipsoids are shown at 50% probability level.
3. Magnetic Measurements in Solution (Evans Method)

Magnetic susceptibilities $\chi_M$ and effective magnetic moments $\mu_{\text{eff}}$ of paramagnetic compounds in solution were determined by $^1$H NMR spectroscopy using Evans Method$^9$ with pure solvent as internal reference and neglecting diamagnetic contributions according to equations$^{10}$ (1) and (2). $^1$H NMR spectra were recorded on a Bruker Avance III HD 400 ($^1$H: 400.130 MHz) spectrometer.

Equations:

\[
\chi_M = \frac{3 \cdot \Delta f}{1000 \cdot f \cdot c} \quad (1)
\]

\[
\mu_{\text{eff}} = 798 \cdot \sqrt{T \cdot \chi_M} \quad (2)
\]

where

$\chi_M$ is the molar susceptibility of the sample in m$^3$ · mol$^{-1}$,

$\Delta f$ is the chemical shift difference between solvent in presence of paramagnetic solute and pure solvent in Hz,

$f$ is the operating frequency of NMR spectrometer in Hz,

$c$ is the concentration of paramagnetic sample in mol · L$^{-1}$,

$T$ is the absolute temperature in K, and

$\mu_{\text{eff}}$ is the effective magnetic moment in $\mu_B$. 

4. SQUID Magnetization Measurements and Mössbauer Spectra

General remarks:

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Measurements were obtained for a finely ground microcrystalline powder (15 - 30 mg) restrained within a polycarbonate gel capsule. Samples used for magnetization measurement were checked for chemical composition and purity by $^1$H NMR spectroscopy. Data reproducibility was checked on independently synthesized samples. Dc susceptibility data were collected in the temperature range 2-300 K under a dc field of 1 T. The data shown refer to the complete tetra- and dinuclear complexes, not mononuclear subunits. The data were corrected for core diamagnetism of the sample estimated using Pascal’s constants\textsuperscript{[11]} ($\chi_{\text{dia}} = 11.11 \cdot 10^{-4}$ cm$^3$·mol$^{-1}$ for 2a, $10.16 \cdot 10^{-4}$ cm$^3$·mol$^{-1}$ for 2b, and $7.451 \cdot 10^{-4}$ cm$^3$·mol$^{-1}$ for 2c). Magnetic susceptibility data was analyzed and simulated using the julX program written by E. Bill (MPI for Chemical Energy Conversion, Mülheim an der Ruhr).

$^{57}$Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. $^{57}$Co/Rh was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mm·s$^{-1}$. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N$_2$ cryostat within an accuracy of $\pm$0.3 K. Isomer shifts were determined relative to $\alpha$-iron at 298 K.
Figure S4: Molecular structure of 2a (R = Me) and 2b (R = H).

Figure S5: VT SQUID magnetization measurement of compounds 2a (left) and 2b (right).

Figure S6: Zero-field $^{57}$Fe Mössbauer spectrum of compound 2b.
Figure S7: Molecular structure of 2c.

Figure S8: VT SQUID magnetization measurement (left) and zero-field $^{57}$Fe Mössbauer spectrum (right) of compound 2c.
5. $^1$H NMR and EPR Spectroscopy

General remarks:

$^1$H and $^{31}$P NMR spectra were recorded on a Bruker Avance III HD 400 ($^1$H: 400.130 MHz, $^{31}$P: 161.976 MHz). The chemical shifts are reported in ppm relative to external TMS ($^1$H) and H$_3$PO$_4$ ($^{31}$P). The X-band EPR measurements were carried out with a MiniScope MS400 device equipped with a Magnettech GmbH rectangular TE102 resonator at a frequency of 9.5 GHz. The compounds were dissolved in a glovebox under N$_2$ inert gas atmosphere, placed in tip-sealed pasteur pipettes, and were rubber plugged. The measurements were conducted at room temperature and 77 K, respectively.

EPR spectrum of $[\text{L}_2\text{Fe(tol)}]$ (1b):

![EPR spectrum of $[\text{L}_2\text{Fe(tol)}]$ (1b)](image)

**Figure S9**: EPR spectrum of $[\text{L}_2\text{Fe(tol)}]$ (1b) in toluene (ca. 0.03 M) at r.t. (a): $g = 2.04$, and at 77 K (b): $g = 2.17$, 2.00, 1.97.
EPR spectrum of [L₃Fe(tol)] x 0.25 n-hexane (1c):

![EPR spectrum image](image)

**Figure S10:** EPR spectrum of [L₃Fe(tol)] x 0.25 n-hexane (1c) in toluene (ca. 0.03 M) at r.t. (a): $g = 2.06$, and at 77 K (b): $g = 2.20, 2.01, 1.98$.

**Note:** An EPR spectrum of [L₃Fe(benzene)] in toluene at 77 K has already been published,[¹²] containing identical signals like 1c in toluene at 77 K.
$^1$H NMR spectrum of [L$^2$Fe(tol)] (1b) in Tol-$d_8$:
$^1$H NMR spectrum of [L$_3$Fe(tol)] (1c) in Tol-$d_8$:
$^1$H NMR spectrum of [(L$^1$Fe)$_4$P$_8$] (2a) in THF-$d_8$:

$^1$H NMR spectrum of compound 2a. * = impurities (toluene, L$^1$H and silicon grease).
$^1$H NMR spectrum of [(L$_2$Fe)$_4$P$_3$] (2b) in Tol-$d_8$.
$^1$H NMR spectrum of [(L$^3$Fe)$_2$P$_4$] (2c) in THF-$d_8$:
6. Computational Details

Table S3: Oxidation states (obtained from NPA analysis for 2a,b,c at the BP86/def2-SVP level of theory), selected geometric and Mössbauer parameter of 2a,b,c and A.\textsuperscript{[13]}

| oxidation state | atomic distances | Mössbauer |
|-----------------|------------------|-----------|
|                 | d(N-Fe) / [Å]    | d(Fe-P) / [Å] | d(P-P) / [Å] | d(Fe-Fe\textsubscript{opposing}) / [Å] | δ / [mm s\textsuperscript{-1}] | ΔE\textsubscript{Q} / [mm s\textsuperscript{-1}] |
| 2a P\textsubscript{s}\textsuperscript{4} Fe(+2) | 1.983(2) - 2.006(2) | 2.4559(6) - 2.5006(6) | 1.991(8) - 2.2813(7) | 6.740 - 6.756 | n.a. | n.a. |
| 2b P\textsubscript{s}\textsuperscript{4} Fe(+2) | 1.982(2) - 1.990(2) | 2.4583(3) - 2.4807(5) | 2.2111(6) - 2.2792(6) | 6.765 | 0.73(1) | 1.93(1) |
| 2c P\textsubscript{2}\textsuperscript{2} Fe(+2) | 2.018(2) - 2.025(2) | 2.4376(6) - 2.5163(6) | 2.178(1) - 2.207(1) | 3.902 | 0.74(1) | 1.74(1) |
| A 2x P\textsubscript{2}\textsuperscript{2} Fe(+3) | 2.023(3) - 2.025(3) | 2.344(1) - 2.377(1) | 2.036(2) | 2.777 | 0.42(1) | 1.15(1) |

DFT calculations on the complex \([L^1\text{Fe} \mu_{4}\cdot \eta^2; \eta^2; \eta^2; \eta^2-P\textsubscript{8}]\) (2a) and the hypothetical complex \([L^1\text{Fe} \mu_{4}\cdot \eta^2; \eta^2-P\textsubscript{4}]\) have been performed with the TURBOMOLE program package\textsuperscript{[14]} at the RI\textsuperscript{[15]}-BP86\textsuperscript{[16]}/def2-SVP\textsuperscript{[17]} level of theory, followed by single point calculations without the RI approximation and using the def2-TZVP basis set for N, P and Fe and the def2-SVP basis set for the C and H atoms. The Multipole Accelerated Resolution of Identity (MARI-J)\textsuperscript{[18]} approximation was used in the geometry optimization steps. The Natural Population Analysis (NPA) has been performed at the BP86/def2-SVP level of theory with the TURBOMOLE program. For 2c the BPW91/def2-SVP optimized geometry was used. The DFT calculations for \([L^3\text{Fe} \mu_{4}\cdot \eta^2-P\textsubscript{4}]\) (2c) have been performed with the ORCA program.\textsuperscript{[19]} The geometry optimization was performed at the BPW91\textsuperscript{[20]}/def2-SVP level followed by single point calculations in which for Fe and P the aug-cc-pVTZ\textsuperscript{[21]} basis set was used. Broken-symmetry (singlet spin-state) calculations for 2c were done using the converged high-spin (quintet spin-state) as initial guess and flipping the spin on one iron. We found an antiferromagnetic coupling E(High-Spin)-E(BrokenSym) of 486 cm\textsuperscript{-1}. For the constrained geometry of \([L^3\text{Fe} \mu_{4}\cdot \eta^2-P\textsubscript{4}]\) (Fe-Fe distance constrained to 2.777 Å) we obtained a E(High-Spin)-E(BrokenSym) coupling of 1360 cm\textsuperscript{-1}.

Table S4. Relative energies of \([L^1\text{Fe} \mu_{4}\cdot \eta^2; \eta^2; \eta^2; \eta^2-P\textsubscript{8}]\) (2a) in different spin-states at the BP86/def2-SVP level of theory.

| Spin-state | Singlet (unrestricted) | Triplet | Quintet | Septet | Nonet |
|------------|------------------------|---------|---------|--------|-------|
| Rel. Energy (kJ·mol\textsuperscript{-1}) | 0 | 79.00 | 52.29 | 82.91 | 134.92 |
Table S5. Relative energies of [(L^3Fe)₂(μ-η^4:η^4-P₄)] (2c) in different spin-states at the BPW91//def2-SVP/aug-cc-pVTZ (Fe, P) level of theory.

| Spin-state     | Singlet (unrestricted) | Triplet | Quintet |
|----------------|-------------------------|---------|---------|
| Rel. Energy (kJ·mol⁻¹) | 0                       | 26.75   | 32.79   |

Table S6. Relative energies of the constrained geometry of [(L^3Fe)₂(μ-η^4:η^4-P₄)] (geometry optimized with constrained Fe-Fe distance of 2.777 Å) in different spin-states at the BPW91//def2-SVP/aug-cc-pVTZ (Fe, P) level of theory.

| Spin-state     | Singlet (unrestricted) | Quintet |
|----------------|-------------------------|---------|
| Rel. Energy (kJ·mol⁻¹) | 0                       | 20.01   |

Table S7. Cartesian coordinates of the optimized geometry of [(L^1Fe)₄(μ-η²:η²:η²:η²-P₈)] (nonet spin-state) (2a) at the BP86/def2-SVP level of theory. Total Energy: -11168.28440919 a.u.

| Atom | x          | y          | z          |
|------|------------|------------|------------|
| Fe   | 0.145172100| 2.455462800| 2.480034200|
| Fe   | -1.046185100| -2.387140000| 2.233742900|
| Fe   | 1.048027600| -2.341831100| -2.254303300|
| Fe   | -0.153392600| 2.448535700| -2.461434700|
| P    | 0.011266200| 2.284478900| 0.004470700|
| P    | 1.328405700| -0.766884000| 1.141096600|
| P    | -0.461136900| 0.033041900| 2.237509400|
| P    | -1.652542700| 0.855898800| 0.512751200|
| N    | 2.975957500| 2.0034279100| 3.087007000|
| C    | 0.3234279100| 3.855211700| 4.291016000|
| C    | 1.078674600| -4.005656500| 3.607858900|
Table S8. Cartesian coordinates of the optimized geometry of [(L\textsuperscript{1}Fe)\textsubscript{4}(\mu-\eta^2:\eta^2:\eta^2:\eta^2-P)\textsubscript{8}] (unrestricted singlet spin-state) (2a) at the BP86/def2-SVP level of theory. Total Energy: -11482.579767331 a.u.

| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| Fe   | 13.0002636| 2.1986698 | 4.5072346 |
| P    | 13.8180399| 1.8383504 | 6.8320542 |
| P    | 14.7707360| 0.4318347 | 4.1241124 |
| N    | 11.1777691| 1.7243123 | 3.8850187 |
|  |  |  |  |
|---|---|---|---|
| N | 12.9418417 | 4.0331098 | 3.7517639 |
| Fe | 14.4499648 | 1.8131098 | 5.7779494 |
| P | 13.2487317 | -0.2938826 | 7.2620403 |
| Fe | 16.4533431 | -1.3532248 | 3.4767794 |
| P | 13.2487317 | -0.2938826 | 7.2620403 |
| C | 10.3404847 | 2.5484842 | 3.2211746 |
| C | 10.7442056 | 0.3857614 | 4.1434737 |
| C | 11.8897677 | 4.5647996 | 3.0878897 |
| C | 14.0968718 | 4.8582562 | 3.9329368 |
| P | 15.0710807 | -0.5389178 | 8.5594425 |
| N | 13.1278199 | 2.3588000 | 10.620995 |
| P | 13.1278199 | 2.3588000 | 10.620995 |
| N | 16.3105030 | -2.9696902 | 2.3087869 |
| N | 18.2198528 | -0.7982742 | 2.7615011 |
| C | 8.9600148 | 2.0528918 | 2.8287412 |
| C | 10.6816546 | 3.8709968 | 2.8584871 |
| C | 10.0734673 | 0.0886179 | 5.3604470 |
| C | 10.9695271 | -0.6189631 | 3.1626163 |
| C | 11.9912943 | 5.9767978 | 2.5376468 |
| C | 14.1574533 | 5.7472920 | 5.0414778 |
| C | 15.1445473 | 4.8079213 | 2.9739512 |
| Fe | 15.8270883 | -2.9211747 | 8.1284608 |
| C | 13.3701543 | 3.2395802 | 11.6190611 |
| C | 11.819276 | 1.7844126 | 10.5487982 |
| C | 15.8099077 | 3.7239630 | 11.0728411 |
| C | 12.2687308 | 0.1657747 | 2.1656967 |
| C | 14.6136170 | 3.8811149 | 11.8084771 |
| C | 10.7879297 | 2.4715948 | 9.8509720 |
| C | 11.5602529 | 0.5577972 | 11.2187364 |
| C | 17.0184947 | 4.5207396 | 11.530744 |
| C | 17.5482040 | 3.6357856 | 8.3075600 |
| Attributed | C   | 18.7337063 | 2.8235421 | 2.0103913 |
|-----------|-----|------------|-----------|-----------|
| Attributed | C   | 17.4971462 | 1.0445235 | 0.6845473 |
| Attributed | C   | 19.7618033 | 2.3260456 | 4.1484455 |
| Attributed | C   | 19.7439939 | -0.0097689 | 5.1308208 |
| Attributed | H   | 9.4377397 | -3.2437874 | 4.7743148 |
| Attributed | H   | 17.1582490 | 7.2649822 | 4.3000705 |
| Attributed | C   | 13.9738191 | -6.7782651 | 8.9760541 |
| Attributed | C   | 16.3671344 | -6.0787143 | 8.7495615 |
| Attributed | C   | 12.8645845 | -3.8116634 | 10.2242083 |
| Attributed | C   | 12.2671128 | -4.1014106 | 7.8399514 |
| Attributed | C   | 18.8398207 | -5.9468763 | 9.0838246 |
| Attributed | C   | 18.9904261 | -2.7012965 | 10.1498250 |
| Attributed | C   | 19.6267868 | -3.0098135 | 7.7780143 |
| Attributed | C   | 9.2143956  | 0.7273707  | 10.5418820 |
| Attributed | H   | 8.6806470  | 2.4614669  | 9.3444961 |
| Attributed | H   | 10.211319  | 4.0940516  | 8.5293144 |
| Attributed | H   | 11.9495212 | 3.6370156  | 8.4411945 |
| Attributed | H   | 11.3536703 | 4.5833270  | 9.8202174 |
| Attributed | H   | 10.0384933 | -0.8992051 | 11.7242400 |
| Attributed | H   | 13.5094366 | -0.3871154 | 11.2511654 |
| Attributed | H   | 12.3158000 | -1.1077843 | 12.3842252 |
| Attributed | H   | 13.1032512 | 0.4607217  | 12.7594844 |
| Attributed | C   | 19.7529421 | 2.5770388  | 8.2284774 |
| Attributed | H   | 19.1079690 | 4.1832133  | 6.9100963 |
| Attributed | H   | 16.8897865 | 5.0872800  | 6.8373312 |
| Attributed | H   | 16.4718043 | 5.5179607  | 8.5282400 |
| Attributed | H   | 15.5608461 | 4.2401701  | 7.6914401 |
| Attributed | H   | 20.0992428 | 0.9617733  | 9.6428693 |
| Attributed | H   | 18.5236453 | 0.1537669  | 11.2145856 |
| Attributed | H   | 16.7922504 | 0.3421432  | 10.7735175 |
| Attributed | H   | 17.5264541 | 1.4556601  | 11.9473252 |
| Attributed | C   | 12.5703443 | -4.8758344 | 1.6685538 |
| Attributed | H   | 12.3297078 | -3.4807655 | 0.0180960 |
| Attributed | H   | 13.8581016 | -1.7490927 | -0.5577694 |
| Attributed | H   | 15.5737743 | -2.2368291 | -0.3626043 |
| Attributed | H   | 14.8500254 | -1.1026455 | 0.7951467 |
| Attributed | H   | 13.0873230 | -6.1334100 | 3.3627158 |
| Attributed | H   | 16.4866810 | -5.9597766 | 3.6818151 |
| Attributed | H   | 15.0405990 | -5.9491739 | 4.6768136 |
| Attributed | H   | 15.8356436 | -4.3409926 | 4.7516172 |
| Attributed | C   | 19.4661589 | 3.2423035  | 3.1318992 |
| Attributed | H   | 18.5039876 | 3.5387281  | 1.2043701 |
| Attributed | H   | 17.3005940 | 1.8877277  | -0.0050508 |
| Attributed | H   | 16.5215603 | 0.6129640  | 0.9926051 |
| Attributed | H   | 18.0186681 | 0.2484094  | 0.1123034 |
| Attributed | H   | 20.3315023 | 2.6492669  | 5.0330340 |
| Attributed | H   | 20.7139387 | -0.5007145 | 4.8914356 |
| Attributed | H   | 18.9907144 | -0.8136516 | 5.2277553 |
| Attributed | H   | 19.8530595 | 0.4823629  | 6.1157082 |
| Attributed | H   | 13.4318697 | -6.6228724 | 9.9318863 |
| Attributed | H   | 14.4499312 | -7.7755251 | 9.0064807 |
| Attributed | H   | 13.2015803 | -6.7777625 | 8.1809959 |
| Attributed | H   | 16.5513266 | -7.1563200 | 8.8525984 |
| Attributed | C   | 11.5115562 | -3.5554647 | 10.5098803 |
| Attributed | C   | 13.9074283 | -3.8014018 | 11.3153365 |
| Attributed | C   | 10.9255607 | -3.8221012 | 8.1730497 |
| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Fe   | -0.518933221 | 0.969466542 | -1.540574531 |
| Fe   | 0.519666327  | -1.011151160 | 1.565244811 |
| P    | 0.202792371  | -1.365206524 | -0.826384937 |
| P    | -0.256163515 | 1.168230218  | 0.978855343 |
| P    | -1.527516707 | -0.530038572 | 0.252168806 |
| P    | 1.510857519  | 0.321557633  | -0.116334357 |
| N    | 0.421585619  | 1.286055617  | -3.324356122 |
| N    | -2.192737187 | 2.049981058  | -2.036171868 |
| N    | -0.369858247 | -1.297407662 | 3.290086791 |
| N    | 2.101199711  | -2.090384535 | 2.003772252 |
| C    | 1.847572704  | 1.108509326  | -3.426156974 |
| C    | -0.203789551 | 1.836379651  | -4.388655256 |
| C    | -3.145138685 | 2.405480526  | -1.015995895 |
| C    | -2.426609539 | 2.479667446  | -3.290788485 |
| C    | 2.111924671  | 3.428112675  | -2.303914611 |

**Table S9.** Cartesian coordinates of the optimized geometry of \( [(L^{3}\text{Fe})_2(\mu-\eta^1:\eta^1-P_4)] (2c) \) (quintet spin-state) \( (2c) \) at the BPW91/def2-SVP level of theory.
|      |  1        |  2        |  3        |
|------|-----------|-----------|-----------|
| H    | -3.849455059 | 4.919816387 | 1.217221286 |
| H    | -1.241803774 | 4.19186514  | -1.408917318 |
| C    | -0.984340985 | 4.925954934 | 0.596041114 |
| H    | -2.445107555 | 5.968026423 | -1.186854013 |
| C    | -4.06548149  | -1.90544895 | 3.386985844 |
| C    | -1.332912352 | 1.369675191 | 4.323792626 |
| H    | -3.638254344 | 0.314526023 | 4.245640073 |
| H    | -1.425505816 | -2.723211598| 5.515660187 |
| H    | 0.100347981  | -2.520534963| 6.433394201 |
| C    | -0.952273860 | -1.119125656| 6.062953930 |
| C    | 5.076744778  | -1.959008901| -0.296974901|
| C    | 4.450465620  | -0.315736949| 1.532598190 |
| C    | 3.814240198  | -3.963993592| -0.772715098|
| H    | 1.754685292  | -4.65912605 | 0.524971142 |
| H    | 4.355258113  | -3.411382561| 2.726591187 |
| H    | 4.062771812  | -3.12024596 | 4.475347793 |
| C    | 3.276000494  | -4.84368978 | 3.659815409 |
| H    | 4.309031926  | -4.765401168| 3.880081334 |
| H    | -1.938056576 | -5.532464447| 3.030210898 |
| C    | -1.629661270 | -4.421828302| 4.389093895 |
| C    | -2.976260807 | -2.988150680| 0.480119097 |
| H    | -2.601517775 | -4.715093822| 0.777829334 |
| H    | -4.089519117 | -3.999836375| 1.450896862 |
| C    | 5.745316305  |  0.807109839| -3.765949534 |
| H    | 2.915485101  | -2.862951331| -4.007129329 |
| H    | 1.201434139  | -3.334592426| -4.204433293 |
| H    | 1.718071253  | -2.422409194| -2.754691216 |
| H    | 1.621888278  | -0.527723481| -6.707918455 |
| H    | 1.124258496  | -2.228191242| -6.476921891 |
| H    | 2.839415885  | -1.764584390| -6.312217243 |
| C    | -5.762742248 |  3.405101715| 1.727117906 |
| H    | -4.462367286 | -1.006780097| 0.326935536 |
| H    | -5.010036695 | -1.866470098| -1.147578418|
| H    | -6.099061002 | -0.715078171| -0.339582719|
| H    | -6.376977756 |  0.796045564| -2.441725114 |
| H    | -5.546733232 | -0.577189529| -3.231140248 |
| H    | -4.954258397 |  1.083516248| -3.486770694 |
| H    | -1.558404072 |  5.386298825| 1.424771233 |
| H    | -0.172814471 |  5.631376227| 0.327707139 |
| H    | -0.524864829 |  3.996593884| 0.980830347 |
| C    | -3.094349674 |  5.804246403| -2.066925177 |
| H    | -1.621088020 |  6.644786462| -1.489888501 |
| H    | -3.04951485  |  6.503624863| -0.427058851 |
| C    | -4.537479354 | -0.717686588| 3.959680765 |
| H    | -4.777971905 | -2.708004386| 3.145664478 |
| H    | -0.363701799 |  1.170091930| 3.824927514 |
| C    | -1.888923757 |  2.692816170| 3.757307290 |
| C    | -1.055461294 |  1.551980682| 5.833026769 |
| H    | -4.018249455 |  1.251606290| 4.676321834 |
| H    |  5.942848960 | -1.315033426| -0.500836911 |
| C    |  4.908278678 | -3.134293638| -0.103787447 |
| H    |  3.485671724 | -0.000758229| 1.97998093 |
| C    |  4.970712664 |  0.851369063| 0.672560925 |
| C    |  5.441602583 | -0.569484858| 2.690501388 |
| H    |  3.693348203 | -4.894687157| -1.344827365 |
Table S10. Cartesian coordinates of the optimized geometry of \([\text{L}_3\text{Fe}_2(\mu-\eta^1;\eta^1-\text{P}_3)]\) (2c) (unrestricted singlet spin-state) (2c) at the BPW91/def2-SVP level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Fe   | -0.49557622 | 0.947899852 | -1.517143463 |
| Fe   | 0.49546827 | -0.947308914 | 1.517323742 |
| P    | 0.457646929 | -1.221140580 | -0.911563413 |
| P    | -0.458099499 | 1.221764270 | 0.911079106 |
| P    | -1.433714028 | -0.702169113 | 0.041885729 |
| P    | 1.433782633 | 0.701754232 | -0.041228977 |
| N    | 0.428410775 | 1.296933108 | -3.223801953 |
| N    | -2.114082883 | 1.974158146 | 1.979816875 |
| N    | -0.428706294 | 1.296933108 | 3.223751335 |
| N    | 2.113505866 | -1.974500241 | 1.979921682 |
| C    | 1.852075405 | 1.068905308 | -3.32940703 |
| C    | -0.177175541 | 1.828646524 | -4.30598361 |
| C    | -3.059767548 | 2.329769709 | -0.945955224 |
| C    | -2.383394472 | 2.426513714 | -3.222491589 |
| C    | 2.235701877 | 3.475111894 | -2.435489265 |
| C    | 2.740779122 | 2.123418022 | -2.953055849 |
| C    | 2.357230964 | -0.153350572 | 3.869758583 |
| C    | -1.514320338 | 2.263879768 | -4.316191555 |
| C    | 0.566806494 | 2.083621305 | -5.611942328 |
| C    | -4.192378852 | 1.495088946 | -0.690779167 |
| C    | -2.883465246 | 3.558235883 | -0.237052173 |
| C    | -3.628308776 | 3.247167689 | -3.534410585 |
| C    | 2.367782165 | 4.579078371 | -3.507942374 |
| C    | 2.932132143 | 3.922358254 | -1.135608589 |
| C | -1.852548529 | -1.069784296 | 3.328915686 |
| C | 0.176810375 | -1.82677734 | 4.305917081 |
| C | 3.059961354 | -2.329069055 | 0.946407455 |
| C | 2.382910941 | -2.426708906 | 3.222654709 |
| C | -2.235366618 | -3.477140650 | 2.437311590 |
| C | 4.124881424 | 1.930458119 | -3.126496662 |
| C | 1.454015783 | -1.300193207 | -4.342221707 |
| C | 3.753317957 | -0.285202424 | -0.401951329 |
| H | -1.877304161 | 2.659533737 | -5.273392948 |
| H | 0.609630473 | 3.172342390 | -5.810210583 |
| H | 0.005726868 | 1.636260959 | -6.454627111 |
| H | 1.595713024 | 1.694498534 | -5.623109616 |
| C | -5.115941938 | 1.911565041 | 0.289171661 |
| C | -4.473198898 | 0.205886161 | -1.475030757 |
| C | -3.843267950 | 3.919193055 | 0.729387129 |
| C | -1.733468771 | 4.530038052 | -0.531398137 |
| H | -1.157781942 | -3.351491011 | 2.210720153 |
| H | 1.158447291 | 3.350643879 | -2.207560146 |
| H | -4.078037823 | 2.899349238 | -4.483507822 |
| H | -3.342379753 | 4.306844474 | -3.692376470 |
| H | 3.430420485 | 4.755178006 | -3.770240554 |
| H | 1.953948498 | 5.537250806 | -3.135086064 |
| H | 1.834910179 | 4.323869056 | -4.441449861 |
| H | 2.834598043 | 3.156313098 | -0.343201179 |
| H | 2.481866286 | 4.863575656 | -0.763571022 |
| H | 4.012240175 | 4.117558874 | -1.289228888 |
| C | -2.358160207 | -2.125065442 | 2.953589623 |
| C | 1.514221990 | 0.152541374 | 3.868602511 |
| C | -0.566625731 | -2.082160708 | 5.612551262 |
| C | 4.192256557 | -1.493448888 | 0.696262651 |
| C | 2.885063953 | -3.557142946 | 0.236523542 |
| C | 3.626721524 | -3.249220451 | 3.533726566 |
| C | -2.369376723 | -4.580711036 | 3.509961033 |
| C | -2.930328431 | -3.924659808 | 1.136727435 |
| C | 4.633880434 | 0.739917518 | -3.657486382 |
| H | 4.819526404 | 2.736968091 | -2.848918336 |
| H | 0.450557522 | -1.123803703 | 3.905771286 |
| C | 1.946630536 | -2.676250588 | 3.852412422 |
| C | 1.302616201 | -1.342872151 | -5.879916806 |
| H | 4.159364870 | -1.215082962 | -4.441564943 |
| H | -5.991298030 | 1.282072874 | 0.497359070 |
| C | 4.951917064 | 3.108698297 | 0.995315065 |
| C | -3.511178461 | -0.115895807 | -1.922766258 |
| C | -4.976417151 | -0.938924117 | -0.575935480 |
| C | -5.479684662 | 0.418006507 | -2.628347845 |
| H | -3.723310384 | 4.863875665 | 1.278475484 |
| C | -1.061669204 | 4.032365712 | -1.258334945 |
| C | -0.895465241 | 4.866243059 | 0.718193655 |
| C | -2.245498217 | 5.837220007 | -1.178320783 |
| C | -4.125044158 | -1.931955050 | 3.125442393 |
| C | -1.455175408 | 1.299822766 | 4.34050037 |
| C | -3.754392384 | 0.284512761 | 4.016871206 |
| H | 1.876798086 | -2.659633685 | 5.273561569 |
| H | -0.610957957 | -3.170822818 | 5.810902276 |
### Table S11. Cartesian coordinates of the optimized geometry (restricted) of $[(\text{L}^3\text{Fe})_2(\mu-\eta^4:\eta^4-\text{P}_4)]$ (2c) (quintet spin-state) with the Fe-Fe distance fixed to 2.777 Å, at the BPW91/def2-SVP level of theory.

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Fe   | -0.320976920 | 0.801339516 | -1.086904970 |
| Fe   | 0.327411613  | -0.805320190 | 1.083340565  |
| P    | 0.244856151  | -1.455966223 | -1.137514807 |
| P    | -0.335708298 | 1.425016694  | 1.141046645  |
| P    | -1.578063430 | -0.950675964 | -0.220623556 |
| N    | 1.536699199  | 1.009902786  | 0.279740318  |
| N    | 0.667135667  | 1.239083926  | -2.865650445 |
| N    | -2.036212477 | 1.894569320  | -1.590586524 |
| N    | -0.662388388 | -1.251159048 | 2.873508428  |
| N    | 2.034936386  | -1.88984087 | 1.578375075  |
| C    | 2.101528005  | 1.228554952  | -3.067967545 |
| C    | -0.053739497 | 1.576892041  | -3.953683545 |
| C    | -2.976514586 | 2.467930281  | -0.651126828 |
| C    | -2.310216250 | 2.115164581  | -2.889518755 |
| C    | 2.225973208  | 3.660796487  | -2.156612504 |
| C    | 2.855963230  | 2.403528403  | -2.762475738 |
| C    | 2.738248809  | 0.111788879  | -3.698397873 |
| C    | -1.446152537 | 1.799042122  | -3.960270839 |
| C    | 0.600132830  | 1.902054569  | -5.293428452 |
| C    | -4.227636485 | 1.830935137  | -0.374309256 |
| C    | -2.690252823 | 3.753260744  | -0.093936078 |
| C    | -3.561234011 | 2.858774849  | -3.352454544 |
| C    | 2.130672592  | 4.802474704  | -3.192083931 |
| C    | 2.973168235  | 4.147520737  | -0.898625586 |
| C    | -2.095363976 | -1.228192585 | 3.079747553  |
| C    | 0.060844886  | -1.600843664 | 3.954250922  |
| C    | -2.972145994 | -2.466851550 | 0.637009356  |
| C    | 2.317111928  | -2.112929879 | 2.876953855  |
| C    | -2.246261579 | -3.643508857 | 2.130122707  |
|   | C   | H     | H     | H     | H     | H     | H     | C     | H     | H     | H     | H     | H     | H     |
|---|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | 1.409731905 | -4.526551915 | 0.429384563 |
| H | 4.304965211 | -3.039578640 | 2.527346932 |
| H | 4.075078728 | -2.258413887 | 4.129878802 |
| H | 3.301089142 | -3.815684172 | 3.779390905 |
| H | -3.160071427 | -5.096165754 | 3.511243121 |
| H | -1.684761684 | -5.689271780 | 2.697546369 |
| H | -1.555789352 | -4.518838844 | 4.041361422 |
| H | -3.055684491 | -3.308209173 | 0.111346557 |
| H | -2.489085369 | -4.980227425 | 0.412697399 |
| H | -4.037911918 | -4.431012161 | 1.103550993 |
| H | 5.926431598 | 1.399724170 | -3.960203553 |
| H | 3.637239297 | -2.607620742 | -3.904179132 |
| H | 2.003934349 | -3.310014973 | -3.771741148 |
| H | 2.675174134 | -2.351290860 | -2.418847414 |
| H | 1.456133772 | -0.475622795 | -6.187285521 |
| H | 1.380492886 | -2.239853655 | -5.938203150 |
| H | 2.962295652 | -1.429774518 | -6.102688830 |
| H | -5.620157542 | 4.254464292 | 1.646783932 |
| H | -4.211878030 | -0.659233370 | 0.838583464 |
| H | -5.223408101 | -1.525393849 | -0.354082628 |
| H | -5.939082350 | -0.243911625 | 0.657933687 |
| H | -6.768230612 | 1.010646819 | -1.417785135 |
| H | -6.131769595 | -0.353294378 | -2.373645549 |
| H | -5.672448109 | 1.319841470 | -2.790159569 |
| H | -1.337164095 | 5.899485932 | 1.307279596 |
| H | 0.246736919 | 5.559769404 | 0.566480535 |
| H | -0.538160558 | 4.321575367 | 1.594210609 |
| H | -2.088413820 | 5.229027593 | -2.394977244 |
| H | -0.727099415 | 6.162248807 | -1.710951879 |
| H | -2.382041960 | 6.833488663 | -1.065603416 |
| C | 4.856386926 | -1.324401918 | 3.703311167 |
| H | -4.827148637 | -3.305143494 | 2.841502055 |
| H | -0.929301235 | 1.064983090 | 3.803624874 |
| C | -2.586398786 | 2.425641518 | 3.609404185 |
| H | -1.893685299 | 1.269864407 | 5.726751693 |
| H | 4.584769342 | 0.659098687 | 4.512709324 |
| H | 6.104708225 | -2.014467855 | -0.699553932 |
| C | 4.883122511 | -3.768595659 | -0.997834088 |
| H | 3.798104182 | -0.083284325 | 1.534212527 |
| C | 4.972346819 | 0.543815424 | -0.155948140 |
| C | 5.865999912 | -0.597245538 | 1.894241743 |
| H | 3.459429709 | -5.390253785 | -1.108616845 |
| H | 0.704470124 | -3.792473693 | 0.865222594 |
| C | 0.736651098 | -5.131708257 | -0.818297098 |
| C | 1.666774280 | -5.623829890 | 1.485344477 |
| H | -5.926204559 | -1.363573953 | 3.953162526 |
| H | -3.592094647 | 2.621358094 | 4.032228932 |
| H | -1.954007288 | 3.301018147 | 3.857084111 |
| H | -2.685085956 | 2.377606011 | 2.510767503 |
| H | -1.389070694 | 0.415662951 | 6.209567811 |
| H | -1.334367998 | 2.185996017 | 6.003742113 |
| H | -2.905779494 | 1.355417850 | 6.170923408 |
| H | 5.630138497 | -4.275465920 | -1.625740672 |
| H | 4.138972538 | 0.651672672 | -0.871823229 |
| H | 5.170540883 | 1.539057510 | 0.287944188 |
| H | 5.874690599 | 0.255449361 | -0.730830782 |
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