Stoichiometry-Controlled FeP Nanoparticles from Single Source Precursor.

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Experimental Procedures

General Remarks: All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents were dried using standard procedures and distilled freshly prior to use. All NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400.132 MHz; ^{31}P: 161.975 MHz) with δ referenced to external $SiMe_4$ (^{1}H) or H_3PO_4 (^{31}P), respectively. The NMR spectra were simulated with the program WinDaisy.[1] IR spectra were measured with a Varian FTS-800 spectrometer. The mass spectrum was recorded on a Finnigan MAT SSQ 710 A. Microscopy samples were prepared by deposition of a drop of diluted colloidal solution onto a carbon-coated copper grid and observed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (TEMSCAN) on a JEOL 1011 microscope for bright-field transmission electronic microscopy (TEM), or a JEOL-2100F field-emission microscope for high resolution TEM (HRTEM), the latter two working at 100 and 200 kV, respectively. Magnetic studies were carried out on powder samples by SQuID (Quantum Design MPMS 5.5) and the iron state and environment were analyzed by Mössbauer spectroscopy (WISSEL, 57Co source). Elemental analyses were performed by the service de microanalyses du Laboratoire de Chimie de Coordination (C, H, N) or by Antellis Co. (Fe, P). Powder XRD spectra were recorded on a MPD Pro Panalytical spectrometer using Cu Kr radiation. A powder of the sample was placed on a glass slide for the analysis.

X-ray structure determination: Data of **$[(CO)_3Fe(\mu\text{-}PH_2)]_2$** and **$[(CO)_4Fe(PH_3)]$** were collected on a STOE IPDS area detector diffractometer using Mo-K_α ($\lambda = 0.71073$ Å) radiation. Analytical absorption correction from crystal faces was applied. The structure was solved by direct methods using SIR-97,[3] and full matrix least squares refinements on F^2 in SHELXL-97[4] was performed with anisotropic displacement parameters for non-H atoms. The coordinates of the hydrogen atoms were localized from difference Fourier map and refined isotropically.

$[(CO)_4Fe(PH_3)]$: A mixture of $[Fe(CO)_5]$ (1.96 g, 10 mmol) and $P(SiMe_3)_3$[2] (2.51 g, 10 mmol) was irradiated in THF (50 mL) for 3 hours. MeOH (1.15 g, 36 mmol) was added at 0 °C and the mixture was stirred for 5 hours. Removing the solvent under reduced pressure at 0 °C yielded a yellow crude product of **$[(CO)_4Fe(PH_3)]$**, which was purified by sublimation at room temperature and 10^{-3} mbar. Yield: 1.63 g (81 %). IR (KBr): $\tilde{\nu}_{CO} = 2065$(m), 1990(m), 1960(vs) cm^{-1}; $\tilde{\nu}_{PH} = 2353$(w) cm^{-1}. ^{1}H NMR (400.132 MHz, C_6D_6): $\delta = 2.80$ (d, $^{1}J_{PH} = 366$ Hz, 3 H, PH_3). ^{31}P{^{1}H} NMR (161.975 MHz, C_6D_6): $\delta = -108$ (s, PH_3). ^{31}P NMR (161.975 MHz, C_6D_6): $\delta = -108$ (q, $^{1}J_{PH} = 366$ Hz, PH_3).

$[(CO)_3Fe(\mu\text{-}PH_2)]_2$: $[(CO)_4Fe(PH_3)]$ (202 mg, 1 mmol) was dissolved in 75 mL toluene and irradiated for 2 hours. Removing the solvent under reduced pressure at 0 °C yielded a red crude product of **$[(CO)_3Fe(\mu\text{-}PH_2)]_2$**, which was purified by sublimation at room temperature and normal pressure. Yield: 58 mg (34 %). IR (KBr): $\tilde{\nu}_{CO} = 2071$(s), 2018(vs), 1995(vs) cm^{-1}; $\tilde{\nu}_{PH} = 2363$(w), 2331(w) cm^{-1}. ^{1}H NMR (400.132 MHz, C_6D_6): $\delta = 0.48 - 3.49$ (m, $^{1}J_{PH} = 380.5$ Hz, $^{1}J_{PH} = 377.5$ Hz, $^{3}J_{PH} = 26.4$ Hz, $^{3}J_{PH} = 26.9$ Hz, $^{2}J_{HH} = 10.5$ Hz, $^{4}J_{HH} = 7.5$ Hz, $^{4}J_{HH} = 1.1$ Hz, $^{4}J_{HH} = 0.7$ Hz, 4 H, PH_2) (coupling constants have been determined by simulation of the NMR spectra). ^{31}P{^{1}H} NMR (161.975 MHz, C_6D_6): $\delta = -10$ (s, PH_2). ^{31}P NMR (161.975 MHz, C_6D_6): $\delta = -10$ (m, $^{2}J_{PP} = 182.2$ Hz, $^{1}J_{PH} = 380.5$ Hz, $^{1}J_{PH} = 377.5$ Hz, $^{3}J_{PH} = 26.4$ Hz, $^{3}J_{PH} = 26.9$ Hz, PH_2)

(coupling constants have been determined by simulation of the NMR spectra). EI-MS (70 eV): *m/z* (%) = 346 (94) $[(CO)_3Fe(\mu\text{-}PH_2)_2Fe(CO)_3]^+$, 318 (71) $[(CO)_3Fe(\mu\text{-}PH_2)_2Fe(CO)_2]^+$, 290 (55) $[(CO)_2Fe(\mu\text{-}PH_2)_2Fe(CO)_2]^+$, 262 (55) $[(CO)_2Fe(\mu\text{-}PH_2)_2Fe(CO)]^+$, 234 (100) $[(CO)Fe(\mu\text{-}PH_2)_2Fe(CO)]^+$, 206 (99) $[(CO)Fe(\mu\text{-}PH_2)_2Fe]^+$, 178 (95) $[Fe(\mu\text{-}PH_2)_2Fe]^+$. Anal. Calcd for $C_6H_4Fe_2O_6P_2$: C, 20.84; H, 1.17. Found: C, 20.45; H, 1.08.

FeP NPs synthesis: $[(CO)_4Fe(PH_3)]$ (100.9 mg, 0.50 mmol), oleic acid (70.6 mg, 0.25 mmol) and hexadecylamine (60.4 mg, 0.25 mmol) with a molar ratio of 1:0.5:0.5 were dissolved in 10 mL mesitylene. The mixture was heated at 150°C for 1h. After cooling the reacted solution to room temperature, the black-colored FeP NPs were obtained as a black precipitate after centrifugation. This powder was then washed with pentane (3 x 10 mL) and dried under vacuum.

Magnetization calculation of annealed FeP NPs and conversion emu/g into µB: Magnetization measurements show an unsaturated magnetization at 5 T and 2 K of 8 emu/g. For converting it into µB, we need first to calculate the magnetic moment per gram of FeP. The chemical analysis performed by ICP-MS indicates a FeP content of 4.4% in the powder.

M (emu/gFeP) = M(emu/gpowder) / FeP content

M = 8 / (4.4%) = 181 emu/gFeP

The number of atom contained per gram of FeP is given by:

$n = N_A / (Mw_{FeP})$ with Mw_{FeP} = FeP molecular weight = $M_{WFe} + M_{WP}$ = 86 $g.mol^{-1}$ (N_A is the Avogadro constant)

M (emu/at) = M(emu/gFeP)/ n

To express this value in μ_B (= $9{:}274.10^{-24}$ $J.T^{-1}$) we need to convert the result in the international system unit $J.T^{-1}$(1 emu = 10^{-3} $J.T^{-1}$) thus $M(J.T^{-1}/at)$ = M(emu/gFeP)/ (n*1000)

If we express this value in µB: M(µB) = $M(J.T^{-1}/at)$/µB = 2.78µB

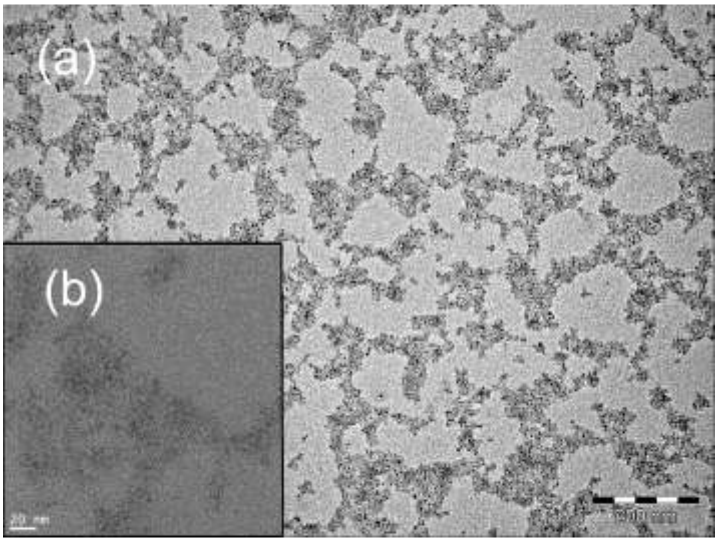


Figure S1. TEM (a) and HRTEM (b) pictures of the FeP nanoparticles.

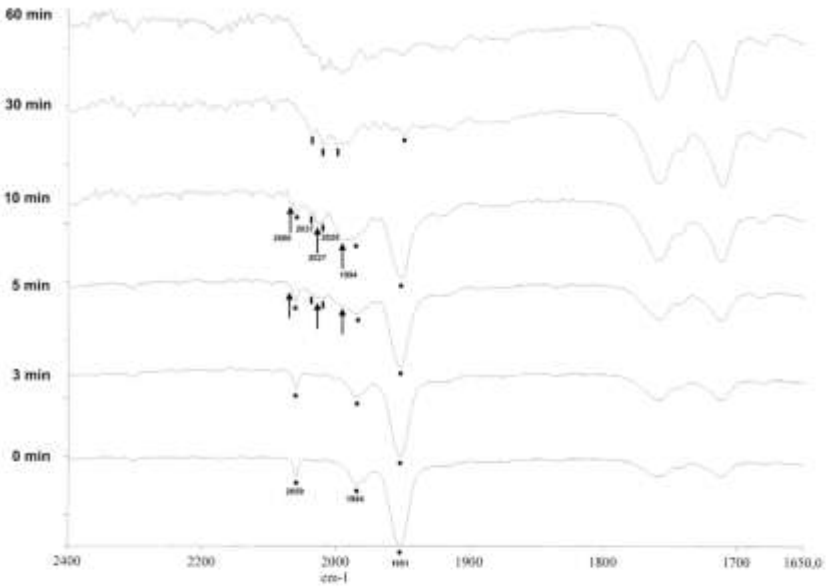


Figure S2. Temporal evolution of the FT-IR spectrum during the synthesis of FeP nanoparticles (●, $[(CO)_4Fe(PH_3)]$; ↑, $[(CO)_3Fe(\mu\text{-}PH_2)]_2$; ı unknown species)

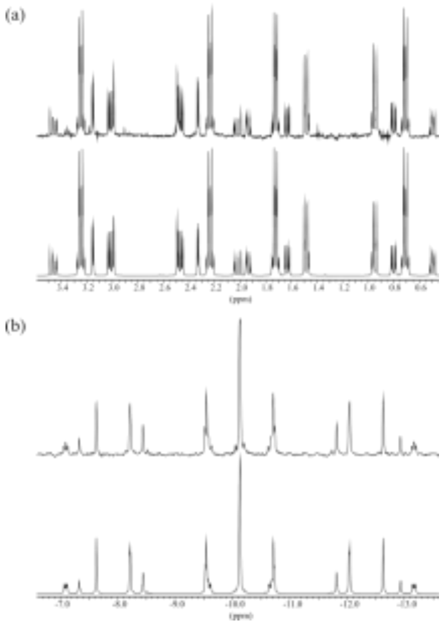


Figure S3. Experimental (C_6D_6, 300 K, top) and simulated (bottom) ^{1}H NMR (a) and ^{31}P NMR (b) spectra of $[(CO)_3Fe(\mu\text{-}PH_2)]_2$.

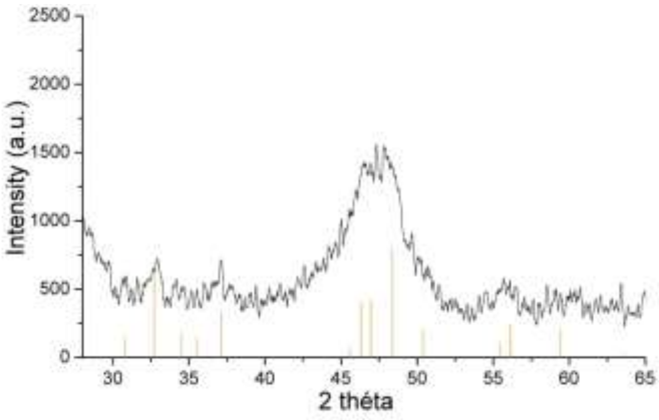


Figure S4. X-ray diffractogram of the annealed FeP nanoparticles

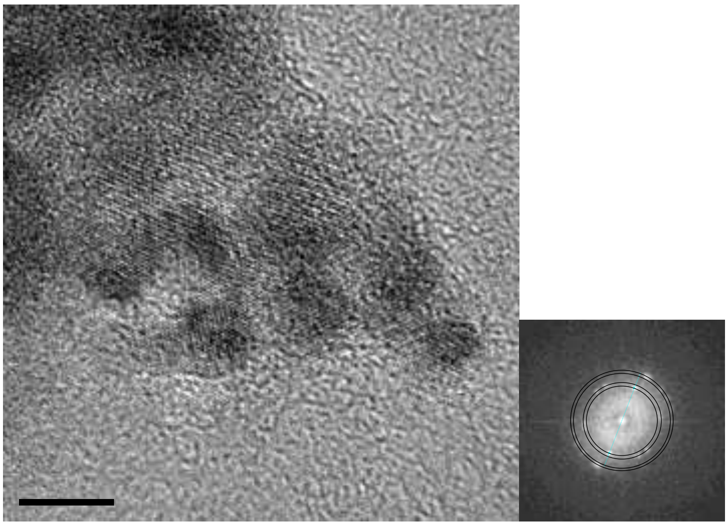


Figure S5. HRTEM picture and selected area diffraction pattern of annealed FeP nanoparticles

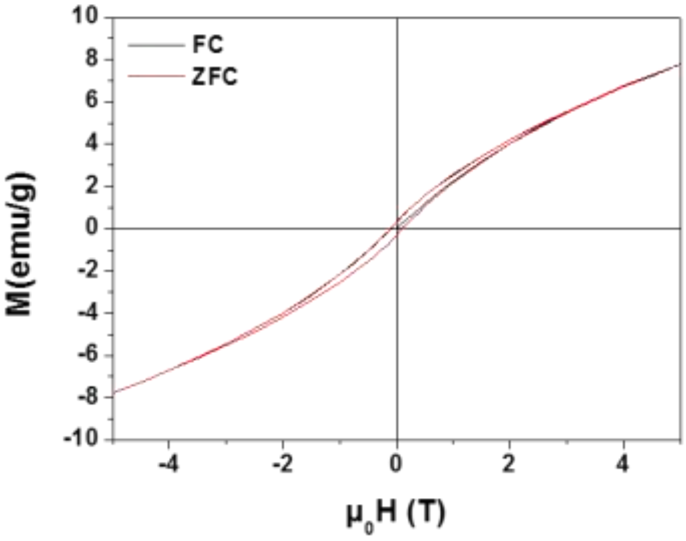


Figure S6. Temperature dependence ZFC-FC magnetization of annealed FeP nanoparticles at 2 K.

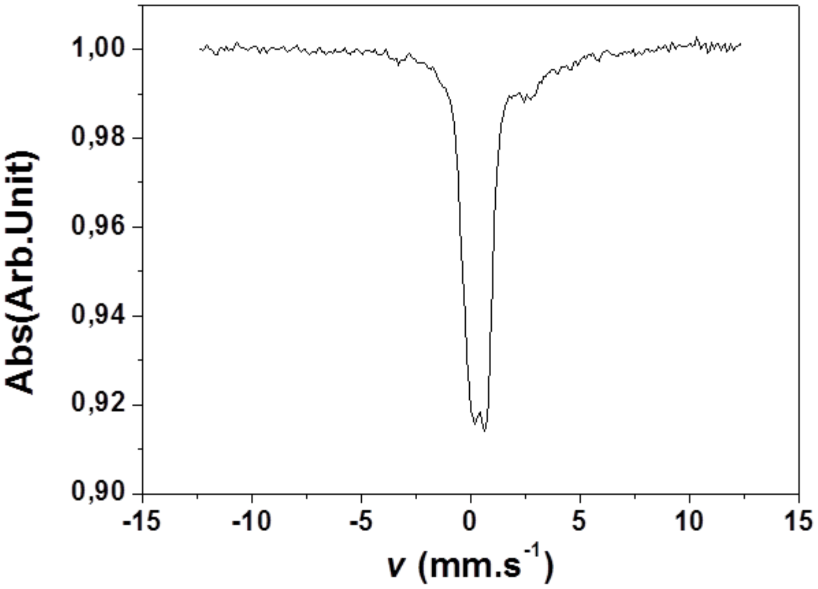
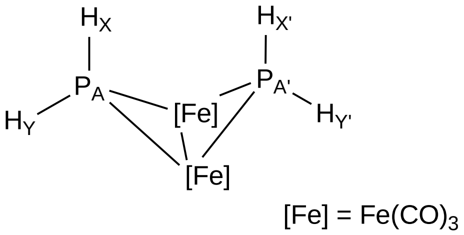


Figure S7. Mössbauer spectrum of annealed FeP nanoparticles at 5 K.

NMR data:

The ^{1}H and simultaneously the ^{31}P NMR spectra of **[(CO)$_3$Fe(μ-PH$_2$)]$_2$** were modeled with an AA'XX'YY' spin system using WINDAISY.[1]The obtained coupling constants are listed in table S1 while the corresponding notations can be found below.



$^2J(P_AP_{A'})$ = 182.16 Hz

$^1J(P_AH_X)$ = 380.45 Hz

$^1J(P_AH_Y)$ = 377.46 Hz

$^3J(P_{A'}H_X)$ = 26.35 Hz

$^3J(P_{A'}H_Y)$ = 26.89 Hz

$^2J(H_XH_Y)$ = 10.53 Hz

$^4J(H_XH_{X'})$ = 7.52 Hz

$^4J(H_XH_{Y'})$ = 0.74 Hz

$^4J(H_YH_{Y'})$ = 1.09 Hz

(a) The correlation of the coupling constants ^xJ (x = 1, 3, 4) are set randomly, because the concrete identification is not possible via simulation.

Table S1. Obtained coupling constants (a) of **[(CO)$_3$Fe(μ-PH$_2$)]$_2$** using WINDAISY.[1]

(1) WinDaisy, Version 4. 05, Bruker-Franzen Analytik GmbH

(2) Uhlig, F.; Gremler, S.; Dargatz, M.; Scheer, M.; Herrmann, E. *Z. Anorg. Allg. Chem.* 1991, ***606***, 105–108.

(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* 1999, ***32***, 115–119.

(4) Sheldrick, G. M. *Acta Cryst.* 2008, ***A64***, 112–122