Supplementary Material (ESI) for Chemical Communications

Growth of FePt nanocrystals by a single bimetallic precursor $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$

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Experimental Section

Preparation of $[(CO)_4Fe(C_6H_5)_2PCH_2P(C_6H_5)_2]$.

To the stirred solution of bis(diphenylphosphino)methane (2.00 g, 5.20 mmol) in 50 ml of tetrahydrofuran in 125 ml round-bottomed flask at 70 ^oC was added diiron nonacarbonyl (1.89 g, 5.20 mmol) in 15 ml of tetrahydrofuran with a syringe. The reaction mixture was stirred for 6 hours under nitrogen atmosphere. After checking TLC for the completion of reaction, column chromatography was performed with a mixture of ethyl acetate and hexane (1:8, v/v). First eluted product was discarded and the next eluted product (rf = 0.42 in ethyl acetate/hexane (1:4, v/v)) was collected to give a pale yellow solid in 65 % yield (m.p. 174 - 177 ^oC) and used for the subsequent reaction without any purification. ^1H NMR ($CDCl_3$) 3.38 (d, J = 9.2 Hz, CH_2), 7.25 (m, 10 H, C_6H_5), 7.40 (m, 10 H, C_6H_5); ^{31}P NMR ($CDCl_3$) -20.92 (Ph_2P), 68.14 (FeP).

Preparation of $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ (1) [dppm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$].

To the stirred solution of $[(C_6H_5)_2PCH_2P(C_6H_5)_2Fe(CO)_4]$ (1.20 g, 2.17 mmol) in 30 ml of toluene in a 125 ml round-bottom flask at room temperature was added dichloro(1,5-cyclooctadiene)platinum(II) (0.82 g, 2.17 mmol). After 20 minutes of stirring, the color of solution changed from pale yellow to bright grey. The mixture was stirred for 2 hours, and then the solvent was evaporated under vacuum. Recrystallization was done with dichloromethane to give the product $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ in 73 % yield (m.p. 146 - 149 ^oC). ^1H NMR ($CDCl_3$) δ 3.28 (t, J = 5.4 Hz, 2H, CH_2), 7.38 (m, C_6H_5), 7.47 (m, C_6H_5), 7.89 (m, C_6H_5); ^{31}P NMR ($CDCl_3$) δ 12.11 (dt, PtP_B, $J(PtP_B)$ = 1720 Hz, $J(P_AP_B)$ = 53.7 Hz), 61.82 (dt, FeP_A, $J(PtP_A)$ = 31.7 Hz); FT-IR (cm^{-1}) 2056, 1972, 1951, 1906, 1432, 744, 692. Anal. Calcd. for $C_{29}H_{22}O_4P_2Cl_2FePt$: C 42.57; H 2.71. Found: C 42.52; H 2.85.

Synthesis and characterization of FePt nanoparticles.

First, 0.95 g of $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ **(1)** (1.16 mmol) was added into 30 ml of *n*-dioctyl ether in a three-necked round-bottomed flask. The solution was heated for 15 minutes under nitrogen at 100 ^oC, and then oleic acid (0.25 ml, 0.79 mmol) and oleylamine (0.26 ml, 0.79 mmol) were added into the reaction mixture. The reaction temperature was increased to 220 ^oC and kept at that temperature for 10 minutes. Next, 1.5 ml of lithium triethylborohydride (1.0 M solution in tetrahydrofuran) was added dropwise into the mixture. The solution slowly turned to black and was further heated at 260 ^oC for 2 hours. Then, the reaction mixture was cooled down to room temperature with continuous stirring. After washing the resulting precipitate with ethanol, followed by centrifugation at 6000 rpm three times, about 0.185 g of FePt nanoparticles was obtained in 64 % yield. The collected particles were annealed at temperatures from 500 to 600 ^oC for 30 minutes in a 5 % H_2/ 95 % argon atmosphere. The phase purity of the nanoparticles was confirmed using a Rigaku RAD diffractometer (12 kW) utilizing Cu Kα radiation. The peak positions in our samples match those observed in the standard material (file JCPDS #43-1359). No other phases are detected in the annealed sample. The lattice constants of *a* and *c* were refined yielding values of 3.992(4) and 3.832(6) Å, respectively. Low and high resolution TEM was performed using a JEOL JEM - 4010 electron microscope with a 400 kV accelerating voltage. Temperature- and field-dependent magnetization measurements were carried out using a SQUID MPMS magnetometer (Quantum Design).

Table S1. Crystallographic Data of $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ **(1)**.

Formula	$C_{29}H_{22}O_4P_2Cl_2FePt$
Formula weight	818.27
Temperature (K)	293(2)
Crystal size (mm)	0.20 x 0.17 x 0.10
Crystal color	pale yellow
Crystal description	block
Crystal system	monoclinic
Space group	$P2_1/n$ (SG No. 14), Z = 4
Dimension (Å, °, Å^3)	a = 12.535(1)
	b = 17.662(1)
	c = 13.211(1)
	β = 102.17(0)
	V = 2859.2(7)
Calculated density (g/cm^3)	1.901
Radiation	0.71073 (Mo Kα)
2θ range (°)	$3.9 < 2\theta < 52.1$
R_1[a] [$I > 2\ \sigma\ (I)$]	0.0294
wR_2[b] [$I > 2\ \sigma\ (I)$]	0.0561
R_1 [for all]	0.0447
wR_2 [for all]	0.0571
Goodness-of-fit	0.948
$(\Delta/\sigma)_{max}$ final cycle	0.002
Residual density (e. Å^{-3})	1.212/-1.014
No. of reflections collected	15966
No. of reflections used	5624 [$> 2\sigma$(I)]
No. of parameters	353
Diffractometer	Bruker APEX CCD
Monochromator	graphite
Structure determination	SHELXS-97 and SHELXL-97
Refinement	Full-matrix least-squares on F^2

[a] $R_1(F) = \Sigma(|F_o| - |F_c|)/\Sigma\ (|F_o|)$.

[b] $wR_2(F^2) = [\Sigma|w[F_o^2 - F_c^2)]^2|/\Sigma|w[F_o^2]^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (\mathrm{Max}(F_o^2,0) + 2\ F_c^2)/3$.

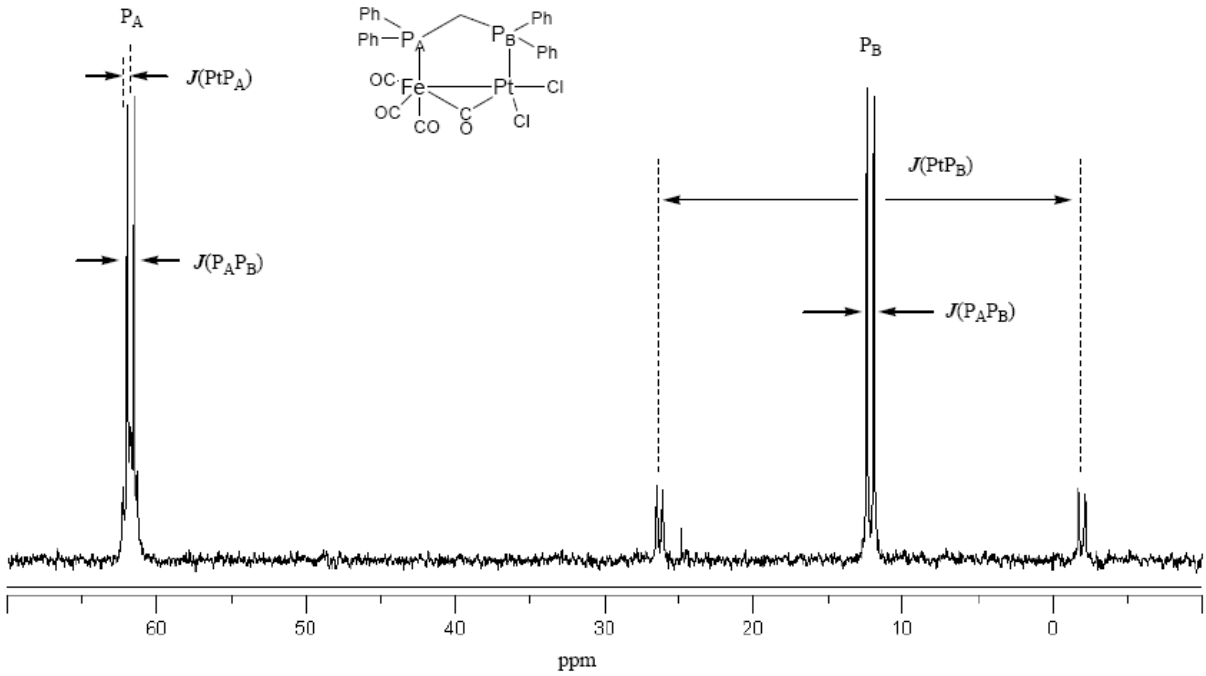

Figure S1. ^{31}P NMR spectrum of $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ **(1)** in $CDCl_3$.

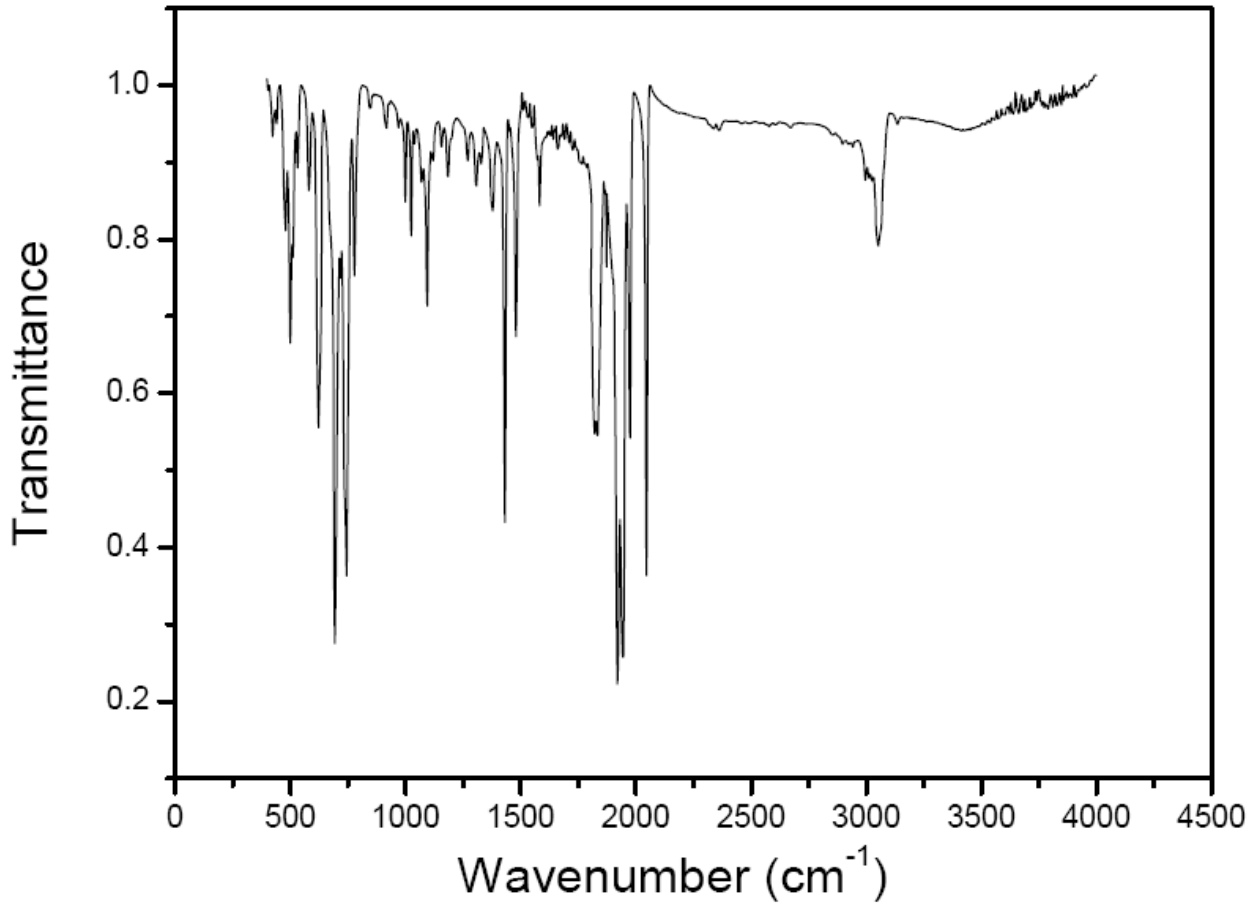

Figure S2. FT-IR spectrum of $[(CO)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ **(1)**.

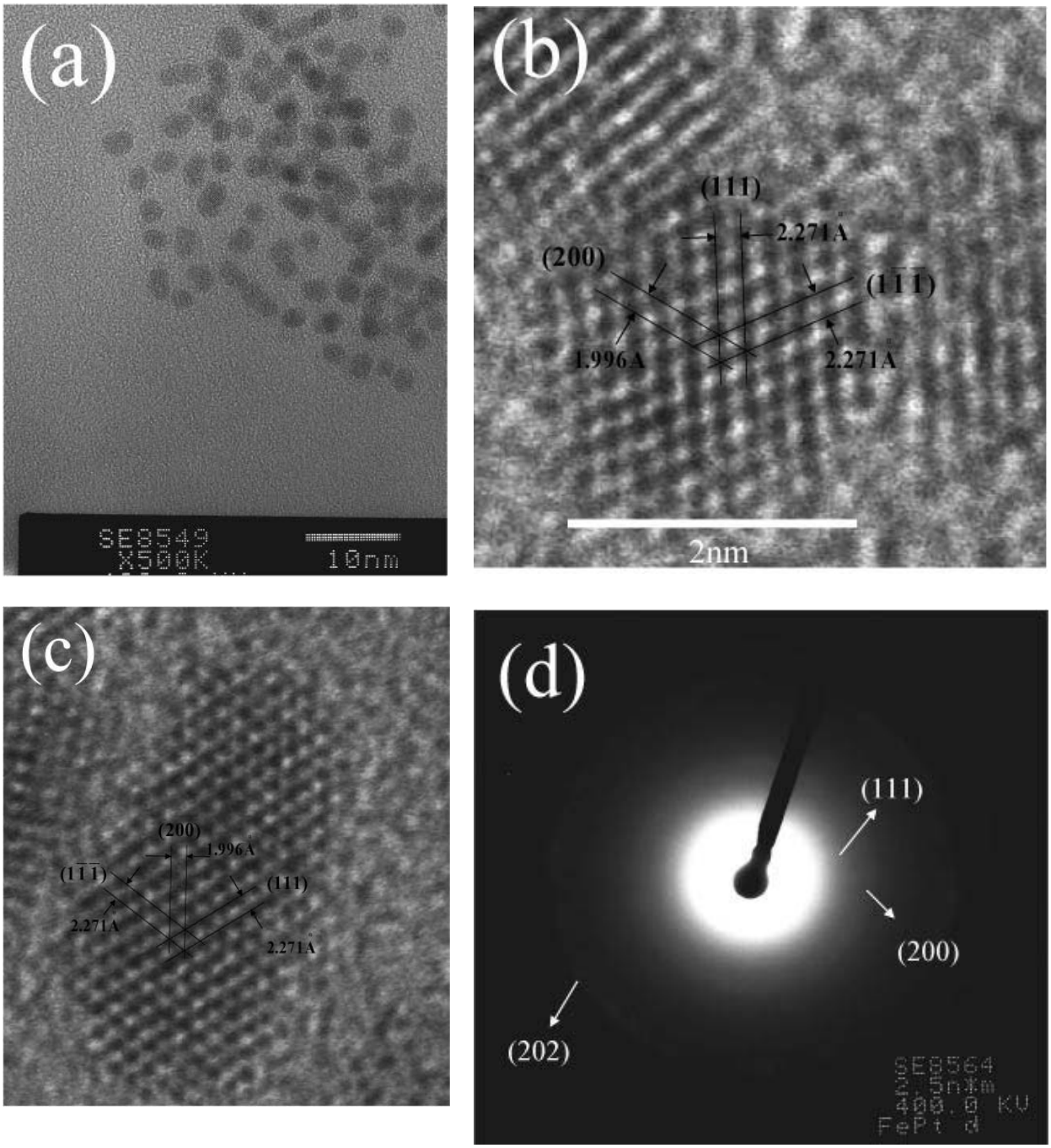

Figure S3. (a) Low resolution TEM micrograph of as-synthesized FePt nanocrystals. High resolution TEM images of the same sample are in (b) and (c). (d) SAED pattern of the same FePt nanocrystal.