Supplementary Information for;

Non-Volatile Iron Carbonyls as Versatile Precursors for the Synthesis of Iron-Containing Nanoparticles.

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Experimental.

Materials. Triiron dodecacarbonyl (Fe₃(CO)₁₂), diiron nonacarbonyl (Fe₂(CO)₉), dodecylamine (DDA), platinum acetylacetonate (Pt(acac)₂), cobalt carbonyl (Co₂(CO)₈), 1-octadecene (ODE) and dibenzyl ether were all purchased from Sigma Aldrich. All reagents were purified and degassed using standard Schlenk line techniques. All solution preparations were carried out in a nitrogen filled glove box and transferred to the reaction set-up using standard air-free techniques.

Synthesis of Fe(0) nanoparticles using Fe₃(CO)₁₂. A reaction flask was charged with ODE (3 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air free Schlenck line under a nitrogen atmosphere and heated to 200 °C. The reaction solution was prepared by adding together Fe₃(CO)₁₂ (0.04 g, 0.08 mmol), DDA (0.4 g, 2.2 mmol) and ODE (8 mL) in an inert atmosphere. This was heated to 75 °C, with stirring, to give a blood-red solution. An 8 mL aliquot of the blood-red solution was taken up in a syringe and injected into the reaction flask (kept at 200 °C) at a rate of 33 μ L/min. The reaction was aged for 120 min at 200 °C following the completion of the drip. The reaction was then cooled to room temperature and transferred back into a nitrogen filled glove box. The product was isolated from the magnetic stir bar and resuspended in clean octadecene. For characterization an aliquot was removed from the glovebox for HRTEM and SAXS analysis. This was purified by washing three times with chloroform and isopropanol before being suspended in hexane.

Synthesis of $Fe_{I-x}Co_x$ nanoparticles using $Fe_3(CO)_{12}$. A reaction flask was charged with ODE (3 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air free Schlenck line under a nitrogen atmosphere and heated to 200 °C. The reaction solution was prepared by adding together $Fe_3(CO)_{12}$ (30 mg, 0.06 mmol), $Co_2(CO)_8$ (12 mg, 0.04 mmol), DDA (0.3 g, 1.7 mmol),

and ODE (3 mL) in an inert atmosphere. This was heated to 80 °C with stirring to give a brown solution. A 2.5 mL aliquot of the brown solution was taken up in a syringe and injected into the reaction flask (kept at 200 °C) at a rate of 33 μ L/min. The reaction was prepared for analysis as above.

Synthesis and thermal annealing of $Fe_{1-x}Pt_x$ nanoparticles using $Fe_3(CO)_{12}$. A reaction flask was charged with ODE (3 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air free Schlenck line under a nitrogen atmosphere and heated to 200 °C. The reaction solution was prepared by adding together $Fe_3(CO)_{12}$ (5 mg, 0.015 mmol), $Pt(acac)_2$ (7.5 mg, 0.02 mmol), DDA (0.3 g, 1.7 mmol) and dibenzyl ether (5 mL) in an inert atmosphere. This was heated to 40 °C with stirring to give a blood-red solution. A 4 mL aliquot of the blood-red solution was taken up in a syringe and injected into the reaction flask (kept at 125 °C) at a rate of 33 μ L/min. The product was exposed to atmosphere and purified as above. Nanoparticles were then dropcast from toluene onto an Aduro Thermal E-chipTM and thermally annealed in-situ at 750 °C for 30 min in the TEM using a Protochips Aduro heating holder.

Synthesis of Fe(0) nanoparticles using Fe₂(CO)₉. A reaction flask was charged with ODE (3 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air-free Schlenck line under a nitrogen atmosphere and heated to 180 °C. The reaction solution was prepared by adding together Fe₂(CO)₉ (0.02 g, 0.06 mmol), DDA (0.25 g, 1.3 mmol), and ODE (4 mL). This was heated to 70 °C, with stirring, to give an orange-red solution. A 4 mL aliquot of the orange-red solution was taken up in a syringe and injected into the reaction flask (kept at 180 °C) at a rate of 33 μ L/min. The reaction was aged for 15 min at 180 °C following the completion of the drip. The reaction was then cooled to room temperature and transferred back into a nitrogen filled glove box. The product was isolated from the magnetic stir bar and resuspended in clean

octadecene. For characterization an aliquot was removed from the glovebox for HRTEM and SAXS analysis. This was purified by washing three times with chloroform and isopropanol before being suspended in hexane.

Synthesis of $Fe_{1-x}Co_x$ nanoparticles using $Fe_2(CO)_9$. A reaction flask was charged with ODE (2 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air free Schlenck line under a nitrogen atmosphere and heated to 200 °C. The reaction solution was prepared by adding together $Fe_2(CO)_9$ (30 mg, 0.08 mmol), $Co_2(CO)_8$ (12 mg, 0.04 mmol), DDA (0.3 g, 1.7 mmol), and ODE (3 mL) in an inert atmosphere. This was heated to 40 °C with stirring to give a brown solution. A 2.5 mL aliquot of the brown solution was taken up in a syringe and injected into the reaction flask (kept at 200 °C) at a rate of 33 μ L/min. The reaction was prepared for analysis as above.

Synthesis of $Fe_{1-x}Pt_x$ nanoparticles using $Fe_2(CO)_9$. A reaction flask was charged with ODE (3 mL) and DDA (0.24 g, 1.3 mmol). This was transferred to an air free Schlenck line under a nitrogen atmosphere and heated to 200 °C. The reaction solution was prepared by adding together $Fe_2(CO)_9$ (5.6 mg, 0.015 mmol), $Pt(acac)_2$ (7.5 mg, 0.02 mmol), DDA (0.3 g, 1.7 mmol), and dibenzyl ether (5 mL) in an inert atmosphere. This was heated to 40 °C with stirring to give an orange-red solution. A 4 mL aliquot of the solution was taken up in a syringe and injected into the reaction flask (kept at 125 °C) at a rate of 33 μ L/min. The product was exposed to atmosphere and purified as above.

Characterization. Infrared spectra of synthesized iron precursors were collected on a Bruker IFS 66vS infrared spectrometer (Bruker Optik GmbH, Germany). Aliquots were characterized using a grazing angle attenuated total reflectance (GATR) accessory (Harrick Scientific Products

Inc., Pleasantville, NY). Nanoparticle products were characterized using high resolution transmission electron microscopy (HRTEM), small angle X-ray scattering (SAXS) and X-ray diffraction (XRD). HRTEM samples were prepared by dropcasting the hexane dispersion on a carbon coated copper grid. Images were collected using a Philips Tecnai HRTEM operating at 300 keV. SAXS analysis was performed by injecting concentrated solutions of samples suspended in hexanes into glass capillary tubes with a 1.0 mm diameter (Charles Supper Company, Natick, MA). Samples were analyzed using a Rigaku SmartLab II diffractometer system with the SmartLab Guidance system control software. Data analysis was performed using Rigaku NANO-Solver v.3.5 software, assuming a spherical form factor and Gaussian size distribution. XRD samples were prepared by placing several drops of concentrated nanoparticle suspension onto a silicon substrate and allowing the solvent to evaporate. Powder X-ray diffractograms were collected using a Rigaku SmartLab II diffractometer system with SmartLab Guidance system. Data analysis was completed using Rigaku PDXL 2.0 analytical software with the ICDD (International Center for Diffraction Data) PDF2 database for phase identification. Magnetization measurements were collected using a Quantum Design MPMS-7 SQUID Samples were prepared by depositing a small amount of the synthesized magnetometer. nanoparticles suspended in ODE onto glass wool and vacuum sealing in a NMR tube. Magnetization curves were recorded from -50kA/m to +50kA/m at 250K. Zero-field cooled (ZFC) magnetization curves were obtained by cooling the sample to 5K with no applied field, then applying a field of 0.8 kA/m, and recording the magnetization from 5K to 250K. With the field still applied, the sample was then cooled from 250K to 5K to obtain the field-cooled (FC) magnetization. The precise iron mass of each sample was determined destructively by heating the sample in a 600°C furnace for 1 hour to incinerate the organic material and then dissolving the iron containing residue in hydrochloric acid. A phenanthroline/Fe²⁺ complex was formed in solution and spectrophotometrically quantified. ESI-MS spectra were recorded on Waters Synapt G2 model using direct injection of iron cluster solution in CH_2Cl_2 . Molecular ion was observed at cone voltages below 10eV. The spectra below were recorded at cone voltage 5eV. Capillary voltage was 2.2kV, cone temperature 80°C, desolvation temperature 120°C.



Figure S1. Experimental (red) and calculated (blue) ESI-MS peak profiles^{*} for $[HFe_3(CO)_9]^-$ (m/z=420.7) and $[HFe_3(CO)_{11}]^-$ ion (molecular ion, m/z=476.7).

*Slight discrepancy between experimental and calculated relative intensities of $[M-H]^-$ and M^- peaks is due to the expected formation of small amounts of anion-radical $[Fe_3(CO)_{11}]^-$ and its decarbonylation products.



Figure S2. UV-vis spectroscopy measurements performed on the as-prepared reaction solution and the $[HFe_3(CO)_{11}]^-$ ion isolated using high performance liquid chromatography (HPLC) : absorption spectra (*a*) and their first derivatives (*b*). The similarities in the absorption profiles confirms that the $[HFe_3(CO)_{11}]^-$ anion is the majority species in solution.



Figure S3. Transmission electron microscopy (TEM) image of Fe(0) nanoparticles synthesized using Fe₃(CO)₁₂, with small angle X-ray spectroscopy (SAXS) analysis showing the raw data (black circles) overlaid by the model fit (red line), as well as the model residuals (blue circles). (a-b) When synthesized at 180 °C nanoparticles 11.1 ± 2.0 nm in size were formed. (c-d) When synthesized at 280 °C nanoparticles 7.2 ± 0.7 nm in size were formed.



Figure S4. X-ray diffraction (XRD) profile of Fe(0) nanoparticles synthesized from $Fe_3(CO)_{12}$. The nanoparticles were oxidized during sample preparation. The broad reflections can be indexed to the iron oxide magnetite (Fe_3O_4), with no reflections from bcc iron present. This indicates the particles possess a polycrystalline iron oxide shell and an amorphous iron core.



Figure S5. Energy dispersive X-ray spectroscopy (EDX) measurement of FePt branched nanoparticles.

Element (Edge)	Weight %	Atomic %	Uncertainty %
Fe (K)	21.68	49.17	0.12
Pt (L)	78.31	50.82	0.30

Table S2. Quantification of the energy dispersive X-ray spectroscopy (EDX) measurement of $Fe_{1-x}Pt_x$ branched nanoparticles synthesized from $Fe_3(CO)_{12}$.



Figure S6. (a) High resolution transmission electron microscopy of $Fe_{1-x}Pt_x$ nanoparticles synthesized from $Fe_3(CO)_{12}$ cluster. (b) Lattice plan resolution of a single FePt nanoparticle which can be indexed to the (111) plane of cubic-FePt. (c) After annealing *in-situ* at 750 °C for 30 min using a TEM heating stage. The particles have become more rounded indicating a reduction in surface area. Both single crystal and polycrystalline nanoparticles are present indicating conversion to the tetragonal phase does not guarantee the removal of twin planes and defects. The contrast difference between nanoparticles possessing the tetragonal crystal structure (c) can be explained by the deflection of the electron beam by the magnetically active nanoparticles. (d) Lattice plan resolution of a single FePt nanoparticle after annealing which can be indexed to the (111) plane of tetragonal-FePt.





Figure S7. Characterization of the [HFe₃(CO)₁₁] anion formed from mild heating of diiron nonacarbonyl Fe₂(CO)₉ in excess DDA. (a) FTIR absorption spectrum of Fe₂(CO)₉, (b) FTIR absorption spectrum of the [HFe₃(CO)₁₁]⁻ anion. It shows a large absorbance at ~ 2800 cm⁻¹ corresponding to C-H stretches of the DDA backbone and terminal and bridging CO stretches around 2000 cm⁻¹, characteristic of the formation of the multi-metal center [HFe₃(CO)₁₁]⁻. Photo of the [HFe₃(CO)₁₁]⁻ cluster anion containing solution formed from Fe₃(CO)₁₂ and Fe₂(CO)₉, respectively. When formed from the equivalent amount of Fe2(CO)9, the red color is less intense, indicating a lower concentration of [HFe₃(CO)₁₁]⁻ in solution.



Figure S8. (a) Transmission electron microscopy (TEM) image of Fe(0) nanoparticles synthesized from Fe₂(CO)₉. (b) Small angle X-ray spectroscopy (SAXS) analysis of the Fe(0) nanoparticles showing the raw data (black circles) overlaid by the model fit (red line), as well as the model residuals (blue circles).



Figure S9. TEM size analysis of nanoparticles synthesized using Fe₂(CO)₉.



Figure S10. (a) Transmission electron microscopy (TEM) image of $Fe_{1-x}Co_x$ nanoparticles synthesized from $Fe_2(CO)_9$ cluster. (b) Small angle X-ray spectroscopy (SAXS) analysis of the $Fe_{1-x}Co_x$ nanoparticles showing the raw data (black circles) overlaid by the model fit (red line), as well as the model residuals (blue circles). (c) Data from EDAX measurements showing the presence of Fe and Co and (d) deconvolution of the overlapping CoK α and FeK β peaks allowing for quantitative analysis to give an elemental composition of $Fe_{55}Co_{45}$.



Figure S11. (a) Transmission electron microscopy (TEM) image of FePt nanoparticles synthesized from $Fe_2(CO)_9$. (b) Small angle X-ray spectroscopy (SAXS) analysis of the $Fe_{I-x}Pt_x$ nanoparticles showing the raw data (black circles) overlaid by the model fit (red line), as well as the model residuals (blue circles).



Figure S12. Energy dispersive X-ray spectroscopy (EDX) measurement of the $Fe_{1-x}Pt_x$ nanoparticles synthesized using $Fe_2(CO)_9$.

Table S3. Quantification of the energy dispersive X-ray spectroscopy (EDX) measurement of the FePt nanoparticles synthesized from Fe₂(CO)₉ cluster.

Element (Edge)	Weight %	Atomic %	Uncertainty %
Fe (K)	13.40	35.10	0.20
Pt (L)	86.59	64.89	0.65