## **On the Use of Amine–Borane Complexes To Synthesize Iron Nanoparticles**

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Abstract: The effectiveness of amineborane as reducing agent for the synthesis of iron nanoparticles has been investigated. Large (2-4 nm) Fe nanoparticles were obtained from [Fe{N-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]. Inclusion of boron in the nanoparticles is clearly evidenced by extended X-ray absorption fine structure spectroscopy and Mössbauer spectrometry. Furthermore, the reactivity of amine-borane and amino-borane com-

**Keywords:** boranes • dehydrogenation • inclusion compounds • iron • nanoparticles plexes in the presence of pure Fe nanoparticles has been investigated. Dihydrogen evolution was observed in both cases, which suggests the potential of Fe nanoparticles to promote the release of dihydrogen from amineborane and amino-borane moieties.

### Introduction

With the development of nanosciences, new strategies to reach advanced nanomaterials have been sought. In particular, due to their unique electronic properties, metal nanoparticles are key nanomaterials for many applications in catalysis,<sup>[1]</sup> electronics,<sup>[2,3]</sup> or even the biomedical field.<sup>[4]</sup> Consequently, considerable research effort has been devoted to the invention of cheap and reliable synthesis routes. In this context, in the last 10 years, amine–borane derivatives have been explored for the synthesis of metal nanoparticles. They proved to work in both organic and aqueous solutions, and even in the solid state, with tunable reducing activity de-

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pending on the nature of the amine. As recently reviewed,<sup>[5]</sup> the range of metal nanoparticles synthesized that way spans from noble metals, such as gold or iridium, to more electropositive ones, such as cobalt, nickel, or iron. Amine-borane derivatives are thus reported as promising mild reducing agents. In previous work, we investigated the use of diisopropylamine-borane (AeB) to produce bimetallic FeRh and CoRh nanoparticles<sup>[6]</sup> in an integrated two-step process: the reaction between AeB and an amido iron or cobalt complex generated diisopropylamino-borane (AoB) and the dihydrogen quantity necessary to reduce the Rh precursor on top of the first-formed Fe or Co seeds. Separation in time of the formation of the iron seeds and of the rhodium deposit favored a core-shell chemical distribution in the bimetallic nano-objects. The final size of the so-formed nanoparticles was around 1.9 nm, which suggested extremely small intermediate iron or cobalt seeds that we could only partially characterize at the time.<sup>[7]</sup> It is well established that elements such as cobalt, iron, and nickel display a huge tendency for boron incorporation when the nanoparticles are prepared by borohydride reduction of metal salts.<sup>[8]</sup> Similarly, reaction of FeCl<sub>3</sub> with ammonia-borane led to the formation of FeB nanoparticles.<sup>[9]</sup> As boron inclusion leads to important changes in the magnetic properties of the nanoparticles and also in their reactivity, it is thus important to scrutinize the possible incorporation of boron, especially in the case of iron, which constitutes the cheapest magnetic and catalytic material.

To shed some light on this issue, we investigated the synthesis of iron nanoparticles from AeB more thoroughly. The procedure was strongly inspired by that in reference [6] apart from the absence of additional ligand during the synthesis, which might have interfered during characterization. Notably, given the bulkiness of the two isopropyl substituents on nitrogen, the corresponding AoB does not form dimers or polymeric byproducts in solution,<sup>[10]</sup> again facili-

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- 6021

tating the characterization steps. Verifying the presence of boron inside ultrafine particles that are often poorly crystallized is not an easy task. Herein, a combination of techniques (extended X-ray absorption fine structure spectroscopy (EXAFS) and <sup>57</sup>Fe Mössbauer spectrometry) has been used to reveal the presence of boron.

### Results

The main characteristics of the samples—reaction conditions and morphology—are reported in Table 1. TEM images of the nanoparticles and size histograms can be found in the Supporting Information (Figure SI1).

Table 1. Preparation conditions and sizes for samples 1-9.

Fe sample	Conditions	Size [nm] <sup>[a</sup>	
1	AeB (2 equiv)	3–3.5	
2	AeB/RT (0.16 equiv) then $H_2$	2.8 (0.5)	
3	AeB/RT (0.5 equiv) then $H_2$	3.4 (0.7)	
4	AeB/RT (1 equiv) then $H_2$	3.5 (0.7)	
5	AeB/RT (1.6 equiv) then $H_2$	4 (0.9)	
6	AoB (1 equiv)	2.9 (0.7)	
7 <sup>[b]</sup>	$H_2$	1.8 (0.3)	
8	sample 7, AeB (1 equiv)	1.8 (0.4)	
9	sample 7, AoB (1 equiv)	2.2 (0.5)	

[a] From a Gaussian fit of the size distribution observed by TEM ( $\sigma$  given in brackets) for nonagglomerated samples. [b] From ref. [16].

**Direct formation of nanoparticles in the presence of AeB or AoB**: Sample 1 was obtained by following an already published procedure,<sup>[6]</sup> by reacting a stoichiometric amount of AeB with  $[Fe{N(SiMe_3)_2}_2]$  according to Scheme 1. The nanoparticles obtained were strongly agglomerated with an estimated diameter in the range 3–3.5 nm.

Samples 2-5 were obtained by a two-step procedure. In



the first step, 0.16, 0.5, 1.1, or 1.6 equivalents of AeB, respectively, were reacted with  $[Fe{N(SiMe_3)_2}_2]$  followed by a hydrogenation step at 110°C designed to convert the unreacted iron precursor. TEM analysis shows better-dispersed nanoparticles with an average diameter of 2.8, 3.4, 3.5, and 4 nm, respectively, for samples 2–5. Samples 1 and 4 were further analyzed by Mössbauer spectrometry. Typical Möss-





Figure 1. a) Mössbauer spectra recorded at 10 K, 0 T or 10 K, 8 T. b) Hyperfine field distributions  $B_{\rm eff}$ =effective field,  $B_{\rm hyp}$ =hyperfine field for sample 1; •: 10 K, 0 T,  $\odot$ : 10 K, 8 T.  $B_{\rm eff}$ =effective field,  $B_{\rm hyp}$ =hyperfine field.

bauer spectra recorded at 10 K on sample 1 are illustrated in Figure 1 (similar ones were obtained for sample 4, not shown here, and give rise to the same conclusions). The zero-field Mössbauer spectrum consists of a weakly asymmetrical magnetic sextet with broadened and overlapped lines; one does consider a distribution of hyperfine fields linearly correlated to that of isomer shift.

The distribution exhibits a prevailing Gaussian-like peak centered at around 27 T (with a mean isomer shift value of  $\delta = 0.28 \text{ mm s}^{-1}$ ) and a small peak located at about 39 T ( $\delta =$  $0.32 \text{ mm s}^{-1}$ ; about 2–3 Fe at %), whereas the lower-field peak results from a fitting artifact (corresponding to intermediate lines). In the presence of an external magnetic field oriented parallel to the y beam, it can be clearly observed that the intermediate lines disappear, which allows one to conclude that the magnetic moments are ferromagnetically coupled. In addition, the distribution of effective fields is exactly shifted by 7.2 T from the hyperfine field distribution, which suggests that the ferromagnetic domains are weakly canted with respect to the external magnetic field. From the hyperfine field and isomer shift values, the main contribution is attributed unambiguously to some FeB amorphous alloy in which the B content is close to 25 at % and the structure consists of a dense polytetrahedral atomic packing (for comparison the mean values of hyperfine field and isomer shift reported for  $Fe_{75}B_{25}$  amorphous alloys are 27 T<sup>[11–13]</sup> and 0.25 mm s<sup>-1</sup>,<sup>[12–14]</sup> respectively). The mean hyperfine field value is consistent with that of Fe surrounded by B whereas the width of the distribution is consistent with a chemically homogeneous system; indeed, a nonhomogeneous distribution of B within the metallic matrix with B-rich and B-poor regions would give rise to a broadened and non-Gaussian hyperfine field distribution. The second minor contribution associated with a larger isomer shift value can be assigned to Fe species with lower electron density, that is, having suffered a partial oxidation process.<sup>[15]</sup>

Sample 6 was prepared by reacting 1 equivalent of AoB with  $[Fe{N(SiMe_3)_2}]$ , at 110 °C to ensure completion of the reaction in a reasonable time. The nanoparticles display an average size of 2.9 nm. Samples 1 and 4–6 all display polyte-trahedral atomic packing, as shown by wide-angle X-ray scattering (WAXS) investigation with coherence lengths of 1.2, 1.6, 1.7, and 1.1 nm for samples 1 and 4–6 (Figure SI3 in the Supporting Information), respectively.

Action of AeB and AoB on preformed Fe nanoparticles: As a reference sample (hereafter labeled sample 7) pure iron nanoparticles with diameters of 1.8 nm were produced according to an already published procedure avoiding the use of boron derivatives: hydrogenation of  $[Fe{N(SiMe_3)_2}_2]$ .<sup>[16]</sup> One equivalent of AeB (sample 8) or AoB (sample 9) was reacted with nanoparticles of sample 7. In both cases dihydrogen evolution was observed upon addition of the boron derivative to the iron nanoparticles in solution. The diameter of the nanoparticles was checked at the end of the reaction. No variation could be detected given the error inherent to the analysis of TEM images at this scale, thus ruling out any significant atom redistribution or coalescence process.

Measurements of the EXAFS at the Fe<sub>K</sub> absorption edge were carried out on the most significant samples, namely samples 1, 4, and 6-9, to extract the crystallographic structure and type of backscattering atoms around Fe. As an example, Figure 2 shows the  $k^3$ -weighted EXAFS oscillations for sample 1 compared with sample 7 (pure Fe nanoparticles produced by hydrogenation) and the oxidized sample 7 after exposure to air. In the lower panel of Figure 2, the corresponding Fourier transforms (FTs) are presented. Note that due to the EXAFS phase shift, the radial distance is not the geometric distance between atoms. Despite the slightly different amplitudes, the FT calculated from the EXAFS of sample 1 is quite similar to that of sample 7 and close to that of amorphous Fe,<sup>[17]</sup> thus indicating the polytetrahedral packing already observed by WAXS. The two peaks at small radial distances (below 0.16 nm) may indicate traces of oxide. EXAFS data and FTs of samples 1, 4, and 6-9 are shown in Figures SI5 and SI6, respectively, in the Supporting Information.

However, the  $k^3$  weighting of EXAFS data suppresses contributions of light elements to the total EXAFS signal, as discussed in the Supporting Information. To shift the focus to the light elements incorporated in the sample, the  $k^1$ -weighted EXAFS and the corresponding FTs were also



FULL PAPER

Figure 2. EXAFS oscillations weighted with  $k^3$  and the corresponding Fourier transforms (FTs) for samples 1 and 7 and oxidized sample 7, that is, after exposure to air. Note the different scaling for the oxidized sample 7. Due to the EXAFS phase shift, the radial distance obtained after Fourier transformation is not the geometric distance between atoms.

analyzed (Figure 3). It can be seen that the oxide contribution is enhanced. Additionally, the shape of the FT related to sample 1 now looks significantly different from that of sample 7 in the range between 0.2 and 0.3 nm.

For the  $k^1$ -weighted data, it is not possible to obtain a similar FT for these two samples by just scaling one of the FTs by a constant factor. The contribution of oxygen has already decreased in this region of radial distances, which might indicate the presence of another light element at similar radial distances to the regular lattice sites of the polytetrahedral Fe structure. However, it is not possible to further specify the type of backscattering atoms in a straightforward manner by using the standard Fourier-based analysis. A possible approach to identify these atoms is given by the wavelet transform (WT). Due to the different *k* dependence of backscattering amplitude of Fe, B, and O (see Figure SI4 in the Supporting Information), the WT offers the possibility to visualize the chemical environment of absorbing atoms



Figure 3. EXAFS oscillations weighted with  $k^1$  and the corresponding FTs for samples 1 and 7 and oxidized sample 7, that is, after exposure to air. Note the different scaling for the oxidized sample 7. Due to the EXAFS phase shift, the radial distance obtained after Fourier transformation is not the geometric distance between atoms.

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Figure 4. b–d) WT compared with the a) FT of the  $k^1$ -weighted EXAFS data for sample 1. Due to the EXAFS phase shift, the radial distance obtained after wavelet transformation is not the geometric distance between atoms.

directly without any structural assumptions or further data treatment. Figure 4 displays the result for sample 1 obtained by this method (see Figure SI7 in the Supporting Information for the WT of EXAFS data of samples 1, 4, and 6–9). For comparison, the FT for this sample is presented in Figure 4a. The FT is equivalent to the sum over all k values of the WT. Here, the k-weighted EXAFS data have been used for the WT to emphasize the light elements' contributions to the overall signal. To better visualize the B content in the samples, the contribution of pure Fe and Fe surrounded by O or N (Figure 4c) to the total WT (Figure 4a) was subtracted.<sup>[18]</sup> In the difference signal, the B contribution is thus well observed (Figure 4d). The two maxima reflect the complex k dependence of the B backscattering amplitude (see Supporting Information for details). In all samples but sample 7, B is found in iron first neighbours shell (Figure SI7 in the Supporting Information). This EXAFS study only gives qualitative evidence of the presence of B. However, a rough estimation of the B content by comparison with the WT of EXAFS measured on an Fe<sub>2</sub>B reference sample yields  $(15\pm5)$  at % B in sample 1. All other samples studied by means of EXAFS in this work have less B included.

### Discussion

**Growth mechanism (samples 1–5, with 6 and 7 as controls)**: It is well established that the final size of nanoparticles depends first on the nucleation step; each nucleus develops into seeds that can grow further into nanoparticles. Growth

itself proceeds either from atom addition at the surface of the seeds or from aggregation of a few seeds to form a nanoparticle, and it is often difficult to tell which mechanism is at play. As such, evidence of the aggregation process can only be obtained when the synthesis is carried out at mild temperatures. Indeed, elevated temperature favors reconstruction of the possible crystallographic defects present in the metal lattice and coalescence of aggregated seeds into a well-crystallized nanoparticle is efficient; thus any trace of possible aggregation of the initial seeds is lost. However, when the synthesis is carried out at mild temperatures, it is possible to trap this intermediate stage at which grain boundaries are still present between the initial seeds. For example, Pt nanoparticles coalesce in solution at room temperature into multiply twinned wormlike structures, with inner grain sizes close to the size of the initial nanoparticles.<sup>[19]</sup>

The nanoparticles in sample 1 present a coherence length (1.6 nm) much shorter than their overall diameter (3-3.5 nm). Given the high tendency for agglomeration observed from TEM images, this discrepancy between the length of the crystalline domains and that of the nanoparticles can be explained as the result of growth governed by coalescence of seeds. This notion is in agreement with the quasi-instantaneous reaction between AeB and [Fe{N- $(SiMe_3)_2]_2$  at a temperature as low as -93 °C (melting point of toluene), which is bound to induce a burstlike nucleation (i.e., burstlike consumption of the iron precursor under stoichiometric conditions). In the absence of long-chain stabilizing agents, aggregation and coalescence of the seeds into larger polycrystalline nanoparticles would naturally follow. As a comparison, when the synthesis was carried out in the presence of tetramethylpiperidine, it afforded well-dispersed nanoparticles of average size (1.7 nm).<sup>[6]</sup> The aggregation process is further supported in this specific case by the atomic packing adopted by the seeds (polytetrahedral in nature), the formation and growth of which was already suggested to progress through aggregation of small units.<sup>[20]</sup>

As AoB derivatives have already been reported for the synthesis of metal nanoparticles,<sup>[21]</sup> we also investigated the use of AoB to produce Fe nanoparticles. The average size measured in this case is 3 nm, close to the average size observed in sample 4, with crystalline domains not exceeding 1.1 nm. This evidences once again that coalescence processes are at play during the growth of the particles.

Surprisingly, in sample 7, which contains reference iron nanoparticles prepared by direct hydrogenation of  $[Fe{N-(SiMe_3)_2}_2]$ , the average size of the nanoparticles (1.8 nm) is identical to that of the crystalline domains (within experimental error). This finding indicates that the use of borane derivatives most probably promotes coalescence of the iron seeds, as it favors the formation of nanoscale iron-boron metallic glass (see below), which is an amorphous material with densely packed polytetrahedral units.

Samples 2 to 5 were produced in a two-step process initially designed to control the size of the nanoparticles. AeB was added under substoichiometric conditions to produce iron seeds upon which more iron atoms were supposed to

6024

# **FULL PAPER**

deposit during reduction of the excess iron precursor. However, despite the fact that the iron precursor was successfully and completely decomposed at the end of the reaction, the average diameter of the nanoparticles was similar to that in sample 1 (within experimental error) although with an enlarged size distribution. These observations are in agreement with the fact that coalescence of the seeds is a dominant growth process even when they are produced in limited quantity (low concentration of seeds).

**Origin of B inclusion**: Reduction of  $[Fe{N(SiMe_3)_2}_2]$  by AeB and AoB derivatives led to samples 1–6. Surprisingly, the presence of boron in close proximity to iron atoms has been evidenced independently of reaction conditions. More specifically, boron inclusion was clearly demonstrated by Mössbauer spectrometry in samples 1 and 4. Given the mechanism depicted in Scheme 1, the use of AeB as a reducing agent should not give B inclusion directly. Indeed, trapping of the byproducts of the reaction at low temperature indicated the formation of a stoichiometric amount of AoB.<sup>[6]</sup> However, the presence of AoB during warming of the reacting medium might very well be at the origin of the observed boron content. Thus, to ascertain the origin of boron inclusion, we investigated the reactivity of preformed pure iron nanoparticles with AeB and AoB.

Upon addition of AeB to a solution of preformed iron nanoparticles (sample 7) at room temperature, fast dihydrogen evolution was observed evidencing the efficiency of these iron nanoparticles for dehydrogenation of AeB, as depicted in step 1, Scheme 2. However, the reactivity does not stop with the release of AoB, as incorporation of B is revealed from EXAFS measurements.

In a second experiment, AoB was reacted with the preformed iron nanoparticles. Here again, dihydrogen evolution was observed, thus evidencing the activity of the iron nanoparticles towards dehydrogenation of the amino-borane moiety (step 2, Scheme 2). EXAFS investigation again indicated the incorporation of boron in the nanoparticles (sample 9). Based on these observations, the presence of boron in the nanoparticles of sample 1 is attributed to a side reaction involving AoB, the byproduct of the reaction, and the iron nanoparticles. Moreover, as boron inclusion is less pronounced when AoB is reacted with preformed nanoparticles than when it is produced in situ, inclusion of boron in



Scheme 2. Proposed steps for boron incorporation in reference iron nanoparticles (sample 7).

the nanoparticles of sample 1 most probably occurs at the early stage of nanoparticle formation, that is, at the nucleation stage, at least before coalescence of the seeds. This is further supported by the chemical homogeneity of the sample revealed by Mossbauer spectrometry.

These results also suggest that pure Fe nanoparticles might be efficient catalysts for dehydrogenation of AeB and AoB derivatives. As a promising source of dihydrogen, dehydrogenation of amine-borane complexes is the subject of intense research.<sup>[22]</sup> In water-free conditions,<sup>[23]</sup> it has been shown in certain cases that metal nanoparticles form during the catalytic dehydrogenation of amine-borane by organometallic complexes.<sup>[24]</sup> Further work has shown the catalytic efficiency of nanoclusters and particles in organic solutions, especially those of Rh<sup>[25]</sup> and Ru.<sup>[26]</sup> However, even though some iron complexes have been recently studied for the photoactivated dehydrogenation of AeB,<sup>[27]</sup> Fe nanoparticles have only been investigated under hydrolytic conditions.<sup>[28]</sup> To the best of our knowledge, the closest related system is that published by He et al.,<sup>[9]</sup> who reported the use of FeB nanoparticles for the thermolysis of ammonia borane in the solid state. Notably, the fate of AoB has been much less studied than that of AeB.<sup>[29]</sup> However, recent studies have shown the double activation of the B-H bonds of the simplest amino-borane NH2-BH2,<sup>[30]</sup> and borylene complexes have been demonstrated to be possible intermediates in their dehydrogenation.<sup>[31]</sup> Such intermediates might form at the surface of iron nanoparticles, but it is not clear how B inclusion can proceed from there. The study of the dehydrogenation of AeB and/or AoB catalyzed by iron nanoparticles is clearly outside the scope of this article, but the results reported herein show that iron nanoparticles might be a cheap alternative of low toxicity, capable of generating more than one equivalent of H<sub>2</sub> per AeB unit.

### Conclusion

The use of diisopropylamine-borane (AeB) as a cheap, mild reducing agent for the synthesis of iron nanoparticles has been investigated. Ultrafine iron particles (2-4 nm in size) have been produced under various reaction conditions, with the concomitant release of amino-borane and dihydrogen. By a combination of complementary techniques we determined that the nanoparticles contained a non-negligible amount of boron most probably resulting from the reaction of the amino-borane byproduct at the surface of the firstformed nanoparticles. This highlights the difficulty encountered in the search for alternative reducing agents for the synthesis of pure iron nanoparticles, especially emphasizing the role of the reaction byproducts. Up to now, dihydrogen<sup>[16]</sup> and amines<sup>[32]</sup> have been the sole reactants affording pure iron nanoparticles. This study opens a route for the preparation of iron boride nanoparticles and evidences the activity of iron nanoparticles for dehydrogenation of both AeB and AoB derivatives.

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### **Experimental Section**

**General synthesis methods**: All operations (material preparation, sampling, and packaging) were carried out by using standard Fischer–Porter bottle techniques and a glovebox under argon, commercial reactants, and carefully dried and degassed solvents.

**Compound 1:** [Fe{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (100 mg, 0.266 mmol) was dissolved in toluene (10 mL, H<sub>2</sub>O <3 ppm) in a Fischer–Porter bottle (200 mL) in a glovebox. The homogeneous green solution was frozen under liquid nitrogen and *i*Pr<sub>2</sub>NHBH<sub>3</sub> (2.2 equiv) in toluene (67 mg, 0.583 mmol in 4 mL toluene) was transferred through a cannula into the Fischer–Porter bottle. The mixture was allowed to warm to room temperature to afford a dark solution. The mixture was further stirred overnight, and then toluene was evaporated to afford a black sticky solid.

**Compounds 2–5**: [Fe{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (200 mg, 0.532 mmol) was dissolved in toluene (18 mL, H<sub>2</sub>O < 3 ppm) in a Fischer–Porter bottle (200 mL) in a glovebox. The homogeneous green solution was frozen under liquid nitrogen and *i*Pr<sub>2</sub>NHBH<sub>3</sub> (0.16, 0.5, 1.1, or 1.6 equiv, respectively) in toluene (4 mL) was transferred through a cannula into the Fischer–Porter bottle. The mixture was allowed to warm to room temperature to afford a dark brown solution. The solution was then pressurized under H<sub>2</sub> (3 bar) and stirred at 110 °C overnight. Then toluene was evaporated to afford a black sticky solid.

**Compound 6:** [Fe{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (100 mg, 0.266 mmol) was dissolved in toluene (18 mL, H<sub>2</sub>O <3 ppm) in a Fischer–Porter bottle (200 mL) in a glovebox. The homogeneous green solution was frozen under liquid nitrogen and *i*Pr<sub>2</sub>NBH<sub>2</sub> (1 equiv) diluted in toluene (30 mg, 0.266 mmol in 4 mL toluene) was transferred through a cannula into the Fischer–Porter bottle. The mixture was allowed to warm to room temperature to afford a dark brown solution. The solution was then stirred at 110 °C overnight. Evaporation of toluene afforded a black sticky solid.

**Compounds 7–9:** [Fe{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (1.128 g, 3 mmol) was dissolved in mesitylene (60 mL, H<sub>2</sub>O <1 ppm) in a Fischer–Porter bottle (500 mL). The green solution was pressurized under H<sub>2</sub> (3 bar) and stirred overnight in a 150 °C oil bath. Then the black solution was distributed equally into three Fischer–Porter bottles (200 mL). The first solution was evaporated directly and recovered with a few spatulas of poly(2,6-dimethyl-1,4-phe-nylenoxide) (PPO) to afford a black solid as a reference, sample 7. The other two solutions were charged respectively with 1 equivalent of  $iPr_2NBH_3$  (115 mg, 1 mmol) or  $iPr_2NBH_2$  (113 mg, 1 mmol) with respect to the iron content. After reaction they were treated the same way as sample 7 to afford black solids (samples 8 and 9, respectively).

**General measurement methods**: Full details of TEM, WAXS, Mössbauer spectrometry, and EXAFS investigations are reported in the Supporting Information.

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