Inorganic Chemistry

Structural Insights into the Nature of Fe⁰ and Fe¹ Low-Valent Species Obtained upon the Reduction of Iron Salts by Aryl Grignard Reagents

Martin Clémancey,[†] Thibault Cantat,[‡][©] Geneviève Blondin,[†] Jean-Marc Latour,^{*,†} Pierre Dorlet,^{*,§}[©] and Guillaume Lefèvre^{*,‡}[©]

[†]Université Grenoble Alpes, LCBM/PMB and CEA, BIG/CBM/PMB and CNRS, LCBM UMR 5249, PMB, 38000 Grenoble, France [‡]NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France

[§]Institute for Integrative Biology of the Cell (I2BC), CEA, CNRS, Univ. Paris-Sud, Université Paris-Saclay, Gif-sur-Yvette, France

S Supporting Information

ABSTRACT: Mechanistic studies of the reduction of Fe^{III} and Fe^{II} salts by aryl Grignard reagents in toluene/tetrahydrofuran mixtures in the absence of a supporting ligand, as well as structural insights regarding the nature of the low-valent iron species obtained at the end of this reduction process, are reported. It is shown that several reduction pathways can be followed, depending on the starting iron precursor. We



demonstrate, moreover, that these pathways lead to a mixture of Fe⁰ and Fe^I complexes regardless of the nature of the precursor. Mössbauer and ¹H NMR spectroscopies suggest that diamagnetic 16-electron bisarene complexes such as $(\eta^4 - C_6H_5Me)_2Fe^0$ can be formed as major species (85% of the overall iron quantity). The formation of a η^6 -arene-ligated low-spin Fe^I complex as a minor species (accounting for ca. 15% of the overall iron quantity) is attested by Mössbauer spectroscopy, as well as by continuous-wave electron paramagnetic resonance (EPR) and pulsed-EPR (HYSCORE) spectroscopies. The nature of the Fe^I coordination sphere is discussed by means of isotopic labeling experiments and density functional theory calculations. It is shown that the most likely low-spin Fe^I candidate obtained in these systems is a diphenylarene-stabilized species $[(\eta^6-C_6H_5Me)Fe^IPh_2]^-$ exhibiting an idealized $C_{2\nu}$ topology. This enlightens the nature of the lowest valence states accommodated by iron during the reduction of Fe^{III} and Fe^{II} salts by aryl Grignard reagents in the absence of any additional coligand, which so far remained rather unknown. The reactivity of these low-valent Fe^I and Fe⁰ species can be used efficiently as a precursor in this reaction, whereas the Fe^I oxidation state does not exhibit any reactivity.

INTRODUCTION

To reach a broad scope of cross-coupling reactions based on iron catalysis is an appealing alternative to the noble-metalbased cross-coupling catalysis because iron is a cost-efficient, abundant, and nontoxic metal.¹ The first iron-catalyzed crosscoupling reactions were reported by Kochi in the early 1970s, and they involved vinylic halides and alkyl Grignard reagents (Scheme 1a).^{2a,b} Several decades later, the methodology was successfully extended to heteroaryl halides and aryl Grignard reagents by Fürstner et al. (Scheme 1b) and was further explored by other groups.^{2c-n} This coupling reaction was first

Scheme 1. Representative Milestones in Iron-Catalyzed C-C Cross-Couplings



developed with simple iron catalysts, e.g., $Fe(\beta$ -diketonate)₃ and $FeCl_2$ or $FeCl_3$, without any stabilizing coligand. Iron salts combined with N-heterocyclic carbenes (NHCs) and fluoride anions proved to circumvent the homocoupling of the Grignard reagent, which was often observed as a side reaction.³

From a mechanistic standpoint, several low-valent iron species were suggested as catalytically relevant (e.g., Fe^{-II} , Fe^{0} , Fe^{I} , and Fe^{II} species).⁴ Fürstner et al. reported in 2005 that homoleptic "super-ate Fe^{II} -complexes" such as $[(Me_4Fe^{II})-(MeLi)][Li(OEt_2)]_2$ could exhibit activity toward organic electrophiles in catalytic and stoichiometric cross-coupling processes.⁵ Later, the Bedford group demonstrated that bis(diphosphine)iron(I) monoaryl complexes were catalytically active in Negishi-type couplings.⁶ The reactivity of in situ generated Fe^{I} species with organic halides (e.g., aryl,^{7a} benzyl,^{7b} or alkyl derivatives^{7c}) has been extensively investigated ever since, with electron paramagnetic resonance (EPR) spectroscopy being often used as an experimental characterization tool



Received: October 27, 2016

to support the involvement of Fe^I d⁷ complexes. Several reports focused on the possibility of promoting C-C bond formation reactions using tetramethylethylenediamine-7d and NHCstabilized^{7e-g} Fe^{II} well-defined species were also published recently. In 2015, the Neidig group reported that the catalytic activity observed in aryl-alkyl Kumada and Suzuki-Miyaura cross-couplings catalyzed by SciOPP-stabilized systems was due to $(\text{SciOPP})\text{Fe}^{II}(\text{Ph})_n$ species $[\text{SciOPP} = C_6H_4-1,2-(P(C_6H_3-1))]$ $3_{1}5$ -tBu₂)₂; n = 1 and 2]. They also demonstrated that the bisphenylated species (SciOPP)Fe^{II}(Ph)₂ was less selective and led to a significant amount of β -elimination products when secondary alkyl halides are employed as electrophiles. Importantly, it was also shown that Fe^I intermediates were obtained as minor reduced byproducts as well as catalytically nonrelevant Fe⁰ species.⁸ The authors demonstrated in this report the importance of the spin titration of EPR-detected species because iron oxidation states with an integer electronic spin (more specifically Fe^{II} and Fe⁰) cannot be detected by this technique. The matter of identification of the catalytically active species is also crucial and is still unanswered for systems based on the use of coligand-free iron salts and aryl Grignard reagents as reductants, as well as the exact nature of the metal oxidation states reached upon reduction under these conditions. Such coligand-free systems are more difficult to investigate because of the absence of stabilizing ligands, since the low-valent iron species have consequently shorter lifetimes and tend to lead to aggregates. A very representative case is the recent advancement made in the reduction of iron salts with methyl nucleophiles, with delineation of the structure of the $S = \frac{1}{2}$ species observed by Kochi in his first reports when reducing ferric chloride with the alkyl Grignard MeMgBr in tetrahydrofuran (THF).^{2b} This structure has remained unknown for almost 40 years, and Neidig et al. recently reported that this species was a cluster involving eight iron centers ($[Fe_8Me_{12}]^-$), which could exhibit catalytic activity when associated with an excess of MeMgBr.9 Therefore, the question of both the identification and titration of half-integer spin iron species that have been detected in similar systems remains crucial. In this paper, we focused our investigations on delineation of the nature of reduced metallic intermediates obtained upon the reaction of simple Fe^{III} or Fe^{II} salts with aryl Grignard reagents (herein PhMgBr or PhMgCl) in the absence of a stabilizing coligand. Some mechanistic insights regarding the redox events involved in the reduction steps (bielectronic or monoelectronic transfers) have been gained. We demonstrate that the same low-spin Fe^I species can be obtained upon the reduction of salts such as $Fe(acac)_n$ or $FeCl_n$ (n = 2, 3) by PhMgBr in toluene/ THF (10:1) mixtures. As evidenced by radical-trapping experiments, the Fe^I species originate from successive monoelectronic reductions of Fe^{II} and Fe^{III} precursors. Disproportionation of transient Fe^{II} intermediates also provides Fe^I oxidation state, associated with Fe^{III} species. For the first time, structural insights are gained for this Fe^I complex. Continuous-wave (cw-)EPR and pulsed-EPR spectroscopies were used to investigate its coordination sphere, which proved to feature η^6 -coordination of the solvent, as well as σ coordination of anionic C₆H₅⁻ ligands originating from PhMgX (X = Cl, Br). However, Fe^{I} oxidation state only represents ca. 15% of the overall iron quantity, with the distribution of the metallic species being quickly dominated by the formation of diamagnetic Fe⁰ species, as evidenced by Mössbauer spectroscopy. The nuclear parameters obtained for this Fe⁰ species are moreover similar to already reported

complexes featuring bisarene coordination of the metal. The presence of Fe⁰-arene ligation is also confirmed by low-temperature ¹H NMR spectroscopy. Fe⁰ molecular species then evolve to the formation of metallic aggregates. These results are supported by DFT calculations, which were performed to investigate the electronic structure of the above-mentioned Fe^I and Fe⁰ species. Moreover, it is demonstrated at the end of the manuscript that the zerovalent Fe⁰ complex can be used as an efficient precursor in Kumada aryl–heteroaryl cross-couplings, whereas the Fe^I species remains unreactive in the same conditions.

EXPERIMENTAL SECTION

General Considerations. All of the samples were prepared at 25 °C in a recirculating mBraun LabMaster DP inert-atmosphere (argon) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 °C before use. NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ¹H NMR spectra were referenced to solvent impurities (herein THF). Solvents (toluene- h_{8} , toluene- d_{8} , and THF- d_{8}) were dried over a sodium/benzophenone mixture and distilled before use.

EPR Spectroscopy. cw-EPR spectra were recorded on a Bruker Elexsys E500 spectrometer equipped with a continuous-flow cryostat (Oxford). Pulsed-EPR experiments were performed on a Bruker Elexsys E580 spectrometer at liquid-helium temperatures. Four-pulse hyperfine sublevel correlation (HYSCORE) spectra were recorded with the usual four-pulse sequence $(\pi/2)_y - \tau - (\pi/2)_y - t_1 - (\pi)_y - t_2 - (\pi/2)_y$ with pulse lengths $t_{\pi/2} = t_{\pi} = 24$ ns and different amplitudes for $\pi/2$ and π pulses. The size of the data was 256×256 , and the time intervals t_1 and t_2 were varied from 120 to 4200 ns in steps of 16 ns. A four-step phase cycle was used to eliminate unwanted echoes. The time domain spectra were baseline-corrected and zero-filled before 2D Fourier transformation to yield the frequency maps. Pulsed-EPR data were processed and simulations were performed by using the *Easyspin* software package and routines locally written with *Matlab* (The Mathworks, Inc.).

DFT Computations. DFT computations were performed using *Gaussian09*, version D.01. Unless specified otherwise, all structures were characterized as minima by frequency analysis (no imaginary frequency) and optimized without geometrical constraint. Unrestricted DFT methods were applied (see the SI for detailed methods).

Mössbauer Spectroscopy. Mössbauer spectra were recorded at 5 K on a low-field Mössbauer spectrometer equipped with a Janis CCR 5K cryostat or at 4.2 or 20 K on a strong-field Mössbauer spectrometer equipped with an Oxford Instruments Spectromag 4000 cryostat containing an 8 T split-pair superconducting magnet. Both spectrometers were operated in a constant-acceleration mode in transmission geometry. The isomer shifts are referenced against that of a metallic iron foil at room temperature. Analysis of the data was performed with the program *WMOSS* (WMOSS4 Mössbauer Spectral Analysis Software, www.wmosss.org, 2009–2015) and a homemade program.¹⁰ Computational modelings of Mössbauer parameters were carried out using *ORCA* software (version 3.0.3) at a BP86–TZVP/CP(PPP)(Fe) level [see the Supporting Information (SI) for detailed methods].

Synthesis of Isotopically Enriched Products. ${}^{57}\text{FeCl}_2$ was synthesized as follows. Elemental 94%-enriched ${}^{57}\text{Fe}$ was heated under a dry in situ generated chlorine atmosphere at 350 °C for 15 min. Dry chlorine was obtained by the dropwise addition of anhydrous sulfuric acid into a commercial bleach solution; the resulting chlorine gas was then dried by bubbling into sulfuric acid (98%). ${}^{13}\text{C}_6\text{H}_3\text{MgBr}$ was synthesized according to a reported microscale method using commercial ${}^{13}\text{C}_6\text{H}_3\text{Br}$ and elemental magnesium. 11

RESULTS AND DISCUSSION

Role of the Nature of the Precursor in the Reduction Mechanism. The reduction of $Fe(acac)_3$ by 1 equiv of

PhMgBr in THF- d_8 was monitored by ¹H NMR. Fe(acac)₃ was fully consumed, whereas Fe(acac)₂, acacMgBr, and PhPh were characterized by their ¹H NMR signals [Fe(acac)₂, -31.5 ppm (12H, CH₃), CH not detected in THF; acacMgBr, 5.2 ppm (1H, CH)], attesting that they were quantitatively obtained within 5 min at room temperature, leading to a bright-yellow solution (Scheme 2a).¹²

Scheme 2. Reduction of Iron Precursors by PhMgBr in the Absence (a and b) or Presence (c) of a Hydrogen $Donor^{a}$



 $^a(\ast)$ indicates that the presence of more than 100% PhH after an acidic quench is due to the presence of traces of benzene in the starting material. 13

In order to evidence the formation of putative transient radical intermediates, radical-trapping experiments were performed using tris(trimethylsilyl)silane [TTMSSH = (Me₃Si)₃SiH] as a hydrogen donor. The reduction of either $Fe(acac)_n$ or $FeCl_n$ (n = 2, 3) by an excess of PhMgBr in the presence of TTMSSH inhibits the formation of PhPh, usually observed as the sole byproduct upon the oxidation of PhMgBr by Fe^{III} or Fe^{II} (Scheme 2a), and only leads to the formation of benzene (Scheme 2c). This suggests that in the absence of TTMSSH, phenyl radicals Ph[•] are produced during reduction of the Fe^{III} or Fe^{II} precursor, with the recombination of these radicals leading to the formation of PhPh. In the presence of a strong hydrogen donor such as TTMSSH, Ph[•] is transformed into benzene by hydrogen-atom transfer in a process faster than dimerization. Therefore, this shows that the monoelectronic reduction of Fe(acac)₃ by PhMgBr is preferred to a classic bielectronic reductive elimination from a putative bisphenyl $(Ph)_2[Fe^{III}]$ species, which would directly yield from Fe^{III} to Fe^{I} in a radical-free process (with the formation of PhPh). The possibility of a reduction involving direct single electronic transfer proceeding by an outer sphere between PhMgBr and $Fe(acac)_3$ and leading to a Fe^{II} species (namely, $[Fe^{II}(acac)_3]^-$) would be unlikely because of the high gap between the oxidation potential of PhMgBr in THF (ca. 0.0 V vs SHE^{14a}) and the reduction potential of $Fe(acac)_3$ (-0.49 V vs SHE^{14b}).^{14c-e} DFT calculations were carried out to investigate the reduction of $Fe(acac)_3$ by inner-sphere-type electronic transfers. Coordination of C₆H₅⁻, transferred from PhMgBr onto the iron center, leading to PhFe^{III}(acac)₂, is thermodynamically favored (exothermicity of 15.8 kcal-mol⁻¹; Scheme 3a). However, a second phenyl anion transfer, leading to $[Ph_2Fe^{III}(acac)_2]^-$, requires an overall span of 27 kcal·mol⁻¹, precluding its formation under the reaction conditions (-30 to)+25 °C; Schemes 1 and 2). This explains why bielectronic reductive elimination directly connecting Fe^{III} and Fe^I oxidation states does not occur here.

The magnesium-to-iron phenyl anion transfer described in Scheme 3a can involve the formation of an adduct exhibiting a

Scheme 3. Computed Free Energies (kcal·mol⁻¹) of (a) Mono- and Bisphenyl-Fe^{III} Intermediate Formation, (b) Reduction of Fe(acac)₃ into Fe(acac)₂ by PhMgBr Involving a Dimeric Process^{*a*}



^{*a*}Ground spin multiplicities are superscripted (solvation THF molecules are omitted for clarity; see the SI).

Fe–O–Mg linkage ($\Delta G = -2.7 \text{ kcal} \cdot \text{mol}^{-1}$; Scheme 3b), thus weakening the coordination of one of the acac- ligands. This adduct prefigures the release of acacMgBr and the formation of the C-Fe^{III} bond (computed exothermicity of -15.8 kcal mol^{-1}). The ability of PhFe^{III}(acac)₂ to undergo homolytic C-Fe cleavage and generate Fe(acac)₂ in its ground spin state (quintet) was investigated. A global endothermicity of 16.4 kcal·mol⁻¹ has been obtained (Scheme 3a), which is incompatible with the experimental conditions (reaction time of ca. 5 min at room temperature). Moreover, the release of free Ph[•] radicals in a solvent such as THF could hardly explain the quantitative formation of PhPh as a recombination product because carboradicals can readily abstract hydrogen atoms from THF. However, it is known that $Fe(acac)_2$ can accommodate oligomeric structures thanks to the presence of vacant coordination sites.¹² An alternative pathway involving the formation of an O(acac)-bridged dimer, leading to [Fe- $(acac)_{2}_{2}$ has been computed and allows the reduction to process with a lower energy barrier (8.1 kcal·mol⁻¹; Scheme 3b). In this dimeric process, the phenyl radical Ph[•] and Fe^{III}bonded C₆H₅⁻ ligand can undergo in-cage recombination to lead to the formation of PhPh. The further reduction of $Fe(acac)_2$ to lower oxidation states can then proceed, most likely via the formation of an intermediate organo-Fe^{II} complex, similar to the Fe^{III} to Fe^{II} reduction route. The titration of the biphenyl obtained by the reduction of FeCl₂ by 30 equiv of PhMgBr showed that, after 30 min at room temperature and acidic quenching, ca. 1 equiv of PhPh was obtained per 1 mol of iron, which corresponds to an average transfer of 2 electrons per 1 mol of Fe^{II} (Scheme 2b).¹³

In a previous contribution mainly focused on cyclic voltammetry,^{14b} we demonstrated that chemical reduction of $Fe(acac)_3$ by PhMgBr in THF led to a mixture of Fe^{II} , Fe^{I} , and Fe^{0} oxidation states depending on the PhMgBr/Fe ratio. In the presence of a moderate excess of Grignard reagent (from 9 up to 15 equiv per 1 mol of iron), two well-defined paramagnetic species could be characterized by their ¹H NMR spectra. The addition of a larger amount of PhMgBr (>15 equiv overall per 1

mol of iron) led to a drastic alteration of the NMR spectra because no signal could be detected. This was associated with an evolution of the color of the sample, which switched from pale green to dark brown, and in these conditions, the formation of a low-spin Fe^I species was attested by cw-EPR spectroscopy and the formula $[PhFe^{I}(acac)(THF)]^{-}$ was tentatively attributed. However, as highlighted by Bedford,⁴ DFT-based computational analysis shows that this species exhibits a strong preference for the quartet spin state and therefore cannot account for the low-spin Fe^I complex detected by EPR spectroscopy. In order to investigate more closely the nature of the low-valent iron complexes obtained in these systems, we decided to examine and compare the EPR spectra of frozen solutions containing various Fe^{II} and Fe^{III} salts reduced by PhMgBr in toluene/THF (10:1) mixtures. The choice of toluene as a major cosolvent has been motivated by the fact that arene ligands often stabilize iron low oxidation states.¹⁵

Reduction of Fe^{II} and Fe^{III} Salts Monitored by EPR Spectroscopy in toluene/THF (10:1). In addition to the use of β -diketonate salts, the reduction of iron chloride precursors (FeCl₂ and FeCl₃) with PhMgBr was investigated by EPR spectroscopy. These salts are also excellent catalysts in Kumada coupling reactions.² They do not benefit from the presence of stabilizing acac⁻ ligands and are more electron-deficient, being thus more easily reduced by PhMgBr. Unlike the reduction of Fe(acac)₃, the reduction of FeCl₃ by 1 equiv of PhMgBr provides a mixture of a low-spin Fe^I complex and high-spin Fe^{III} unidentified species, as attested by EPR spectroscopy (Scheme 4 and the SI). These data support the formation of transient polyphenyl-Fe^{III} species,¹⁶ which can evolve to the formation of Fe^I.

Scheme 4. Reduction of Fe^{III} into Fe^{I} by 1 equiv of PhMgBr in Toluene/THF (10:1)

$$\operatorname{Fecl}_{3} \xrightarrow{1 \text{ eq. PhMgBr}} 1/n [\operatorname{Ph}_{n}\operatorname{Fe^{III}}]^{(3-n)+} \longrightarrow "\operatorname{Fe^{III}}$$

A comparison of the X-band EPR spectra of samples resulting from the reduction of Fe(acac)₃, FeCl₂, and FeCl₃ by a large excess of PhMgBr (30 equiv) carried out at room temperature (reaction time: 2 min) shows that the same $S = \frac{1}{2}$ species is formed, with g values of 2.21, 2.02, and 2.00 [see Figure 1 for the case of FeCl₂ and the SI for the spectra recorded using FeCl₃ and Fe(acac)₃ as precursors]. Interestingly, a similar EPR spectrum exhibiting very close g values (2.20, 2.02, and 1.99) was obtained when the reduction of Fe(acac)₃ was carried out in pure THF.^{14b} This signal is characteristic of a $S = \frac{1}{2}$ transition-metal-based system with resolved g anisotropy and is consistent with the formation of a low-spin Fe¹ mononuclear species. Moreover, the three g values are in good agreement with other reported EPR data for similar low-spin Fe¹ mononuclear systems (Table 1).^{6a,17}

The obtention of the same spectra regardless of the nature of the precursor implies that all of the acac⁻ ligands are displaced in the bielectronic reduction of Fe(acac)₃. A redistribution of the acac⁻ and Ph⁻ ligands is indeed observed, with the harder ligand (acac⁻) being transferred from iron to magnesium and the softer ligand (C₆H₅⁻) being transferred from magnesium to iron: [*trans*-(THF)₂Mg(acac)₂] μ^2 (O,O)FeBr₂ was obtained at -30 °C and characterized by single-crystal X-ray diffraction.¹⁸ When a Fe^{II} salt is used as a precursor, an alternative



Figure 1. cw-EPR spectrum (10:1 toluene- h_8 /THF- h_8 glass) of FeCl₂ + 30 equiv PhMgBr (frozen after 2 min at 25 °C). Inset: Spectrum under nonsaturating conditions of the g = 2 region (Fe¹ species; black, exptl; red, simul.). Experimental conditions: microwave frequency 9.50 GHz; microwave power 1 mW and 0.25 mW (inset); field modulation amplitude 1 and 0.25 mT (inset); field modulation frequency 100 kHz; T = 10 and 60 K (inset). Simulation parameters: g = 2.2059, 2.0230 and 2.0003; H_{strain} (MHz) = 50.5, 15.8, and 0.0; peak-to-peak line width 1 mT.

Table 1. Selection of EPR g Values for Low-Spin Fe^I Mononuclear Complexes

entry	complex	g values	ref				
1	$(p-tolyl)(1,2-C_6H_4(PPh_2)_2)_2Fe$	2.25/2.09/2.08	6a				
2	$(\eta^6$ -C ₆ H ₆)(NacNac)Fe ^a	2.20/2.01/1.98	17a				
3	Na(trop ₂ dae)(THF) ₃ Fe ^b	2.16/2.06/2.01	17b				
^{<i>a</i>} NacNac = HC(C[Me]N-(2,6-diisopropylphenyl)) ₂ . ^{<i>b</i>} trop = 5 dibenzo[<i>a</i> , <i>d</i>]cyclohepten-5-yl; dae = NCH ₂ CH ₂ N.							

mechanism for generation of the Fe^I oxidation state can be evidenced. The reduction of FeCl₂ by 30 equiv of PhMgBr provided a mixture containing a well-defined Fe^I species and high-spin Fe^{III} complexes, as attested by EPR spectroscopy (Figure 1). This shows that Fe^I and Fe^{III} oxidation states can be provided by a fast disproportionation process of intermediate polyphenyl-Fe^{II} complexes.^{19a} A similar hypothesis was formulated by Bedford et al., who reported that the benzylic ate-complex [Fe^{II}(benzyl)₃]⁻ yields Fe^{III} and Fe^I species by a disproportionation pathway.^{19b} Koszinowski et al. also reported that [Ph₄Fe^{III}]⁻ and [Ph₃Fe^{II}]⁻ could be detected concomitantly by electrospray ionization mass spectroscopy (ESI-MS) when Fe^{II} in situ generated species reacted with an excess of PhMgCl.^{19c}

A quantitation of the Fe^I species obtained by double integration of its EPR signal and a comparison with standard solutions of $CuSO_4$ recorded under the same nonsaturating conditions demonstrated that, after a reaction time of 2 min at room temperature (Figure 1), the Fe^I species represents about 15% of the overall iron quantity. This indicates that the most important part of the metal is under other forms or oxidation states, including EPR-silent species.



Figure 2. (a) cw-EPR spectrum (10:1 toluene- h_8 /THF- h_8 glass) of FeCl₂ + 30 equiv PhMgBr frozen after 5 min (black; vertical scale 1/1) or 24 h (blue; vertical scale 5/1) at 298 K. Inset: Zoom on the g_{max} area. Experimental conditions: microwave frequency 9.40 GHz; microwave power 0.06 mW (blue) and 0.02 mW (black); field modulation amplitude 0.5 mT (blue) and 0.2 mT (black); field modulation frequency 100 kHz; temperature 50 K. (b) Wide-field-range spectrum of the 24 h sample. Experimental conditions: microwave frequency 9.40 GHz; microwave power 1 mW; field modulation amplitude 0.5 mT; field modulation frequency 100 kHz; temperature 10 K.

Stability of the Fe^I Oxidation State. It is worth noting that the Fe^I complex, formed upon the reduction of FeCl₂ by PhMgBr, proved to be unstable over time. Indeed, a second minor complex is sometimes observed after 5 min at room temperature (Figure 2a, black, $g_{max} = 2.22$). After 24 h at room temperature, the overall Fe^I quantity only represents 20% of the starting Fe^I quantity detected in EPR (Figure 2a, blue, $g_{max} = 2.20$, 2.21, and 2.22). The system evolves toward the formation of clusters, potentially nanoparticles, as suggested by new broad EPR resonances observed (Figure 2b) over a wide range of magnetic field values (1 T).

The evolution of the intensity of the Fe¹ signal in EPR spectroscopy clearly shows that this complex is unstable over time. Importantly, the EPR spectrum recorded after 24 h suggests that the system evolved toward paramagnetic clusters. In order to investigate the formation and the fate of the EPR-silent integer spin species, the reduction of isotopically enriched 57 Fe^{II} precursors was investigated by Mössbauer spectroscopy, thus allowing an overview of the whole distribution of iron oxidation states reached in these systems.

Mössbauer Spectroscopy Investigations. Because bromine atoms strongly absorb γ radiation and are thus highly detrimental to the quality of Mössbauer spectra, we investigated the reduction of isotopically enriched ⁵⁷FeCl₂ with an excess (30 equiv) of PhMgCl in toluene/THF (10:1) for 3 min, inside an inert-atmosphere box. Mössbauer spectra of the frozen sample (Figure 3) were recorded at low temperatures (4.2–20 K) in the absence (Figure 3a) or presence (Figure 3b,c) of a high magnetic field (7 T) applied parallel to the γ -rays. In order to circumvent as efficiently as possible the fast formation of iron aggregates in the reduction process, spectra have been run at low ⁵⁷Fe concentration (2.5 mM).

In the absence of an applied field, the spectrum appears as a broad quadrupole doublet, and a similar doublet was observed at 80 K. The application of a magnetic field splits the doublet over a small velocity range $(-1 \text{ to } +2 \text{ mm} \cdot \text{s}^{-1})$. This is a typical

behavior of a spin S = 0 system, and all spectra could be simulated under this assumption with the following nuclear parameters: $\delta = 0.44 \text{ mm} \cdot \text{s}^{-1}$ and $\Delta E_Q = 0.93 \text{ mm} \cdot \text{s}^{-1}$. This simulation accounts for ca. 85% of the iron present in the sample (Figure 3, red lines). However, it does not totally reproduce parts of the spectrum on both sides of the central multiplet (velocity domains from -4 to -3 mm·s⁻¹ and from +3 to +4 $\text{mm}\cdot\text{s}^{-1}$). Moreover, these features are both field- and temperature-dependent (increase at 20 K). This suggests the occurrence of a minor additional species with a half-integer spin. The whole spectrum could be simulated by considering that the sample is a mixture of a spin S = 0 species and a spin S $= \frac{1}{2}$ species (Figure 3, blue lines) using the g values deduced from the EPR experiment and literature hyperfine values (Table 2).²⁰ The nuclear parameters for this paramagnetic species are δ = 0.28 mm s⁻¹ and ΔE_Q = 2.01 mm s⁻¹. Owing to the low signal-to-noise ratio of the spectrum and the intrinsic similarity of the spectra of both components, a precise determination of their respective contributions is not achievable; however, the content of the $S = \frac{1}{2}$ species can be estimated within the range of 10-20%. Mössbauer experiments are thus fully consistent with the EPR analysis pointing to the formation of a major S =0 species (EPR-silent) and a minor $S = \frac{1}{2}$ species. The nuclear parameters of the major iron center are not unambiguous, as is often the case for low-spin systems, and could be associated with Fe^{II,8} Fe^{I,21} or Fe⁰ species.²² However, formation of the Fe⁰ oxidation state as a major species is consistent with the overall transfer of 2 electrons per iron ion (vide supra). In addition, the nuclear parameters of the diamagnetic species evidenced herein ($\delta = 0.44 \text{ mm s}^{-1}$ and $\Delta E_Q = 0.93 \text{ mm s}^{-1}$) are similar to those published for related arene-stabilized Fe⁰ species: $(\eta^6 - C_6 H_6)(\eta^4 - C_6 H_8) Fe^0$ ($\delta = 0.51 \text{ mm} \cdot \text{s}^{-1}$ and $\Delta E_Q = 0.94 \text{ mm} \cdot \text{s}^{-1}$) and $(\eta^6 - C_6 H_6)(\eta^4 - C_6 H_6) Fe^0$ ($\delta = 0.64 \text{ mm} \cdot \text{s}^{-1}$) and $\Delta E_Q = 1.04 \text{ mm} \cdot \text{s}^{-1}$.^{22a} It, moreover, echoes the report of Neidig, who showed that the reduction of SciOPP-stabilized Fe^{II} precursors by PhMgBr led at room temperature to a similar



Figure 3. Mössbauer spectra of frozen solutions resulting from the reduction of ${}^{57}\text{FeCl}_2$ in toluene/THF by PhMgCl (30 equiv; overall ${}^{57}\text{Fe concentration } 2.5 \text{ mM}$) after 3 min at room temperature: (a) T = 5 K, no magnetic field; (b) T = 4.2 K, 7 T; (c) T = 20 K, 7 T. The low signal-to-noise ratio is due to the diluted conditions (2.5 mM ${}^{57}\text{FeCl}_2$) as well as the large excess of chloride anions.

diamagnetic Fe⁰ arene-stabilized species (η^6 -biphenyl)-Fe⁰(SciOPP) with a close isomer shift and a higher quadrupolar split ($\delta = 0.44 \text{ mm} \cdot \text{s}^{-1}$ and $\Delta E_Q = 1.75 \text{ mm} \cdot \text{s}^{-1}$).⁸ It is interesting to note that the high-spin Fe^{III} species detected in EPR spectroscopy (Figure 1) were not detected in Mössbauer spectroscopy, which shows that the overall concentration of Fe^{III} is significantly smaller than that of Fe^I. On this basis, it can be suggested that the most important part of Fe^I species is not formed by the disproportionation of polyphenyl-Fe^{II} intermediates.

Stabilization of "elemental iron atoms" at the zero oxidation state by arene and alkene neutral ligands [leading, e.g., to (η^{6} arene)(η^{4} -diene)Fe⁰ complexes] has already been reported in the past.^{22–24} These molecular species can be obtained by reducing bisarene-ligated Fe^{II} precursors with monoelectronic reductants such as sodium amalgam²³ or by cocondensing elemental iron atoms and organic ligands onto low-temperature frozen surfaces.²⁴ Three different modes of coordination can be accommodated by Fe⁰ centers in the presence of arene ligands depending on their hapticity. This can lead to the formation of 20-electron (Scheme 5a), 18-electron (Scheme 5b), or 16electron (Scheme 5c) species.

Scheme 5. Possible Coordination Modes (η^6 or η^4) of Fe⁰ Atoms by Arene Ligands



Binding modes of the arene ligand strongly depend on the nature of both the arene and temperature. Astruc et al. demonstrated by Mössbauer spectroscopy that the reduction of Fe^{II} to the Fe⁰ oxidation state in mesitylene led to formation of the bis- η^6 corresponding adduct (η^6 -C₆Me₆)₂Fe⁰ (Scheme 5a, R = Me₆).²³ It has been shown by low-temperature metal-atommatrix UV-visible and IR investigations that iron atoms condensed in benzene vapor led to formation of the 18-electron complex $(\eta^{6}-C_{6}H_{6})(\eta^{4}-C_{6}H_{6})Fe^{0}$ (Scheme 5b, R = H₆) as the sole product (in the range of T = 50-240 K).^{22a,24b} On the other hand, iron atoms condensed in toluene vapor could exhibit two coordination modes. A 18-electron (η^6 -C₆H₅Me)- $(\eta^4$ -C₆H₅Me)Fe⁰ complex is favored at medium temperatures (90-240 K; Scheme 5b, R = Me), whereas a 16-electron complex $(\eta^4\text{-}C_6\text{H}_5\text{Me})_2\text{Fe}^0$ is obtained at lower temperatures (<77 K; Scheme 5c, R = Me).^{24b} Both complexes lead to the formation of clusters upon warming. In our case, it seems unlikely that a bis- η^6 -toluene coordinated Fe⁰ complex is obtained because the analogue species $(\eta^6-C_6Me_6)_2Fe^0$ and $(\eta^6-C_6Me_6)_2Fe^0$ $C_6H_6)_2Fe^0$ exhibit much higher isomer shifts (respectively 1.06) and 1.22 $\text{mm} \cdot \text{s}^{-1}$) and higher quadrupolar splits (respectively -1.45 and +1.84 mm·s⁻¹).^{22a,23} More specifically, it has been demonstrated by Mössbauer spectroscopy that $(\eta^6-C_6Me_6)_2Fe^0$

Table 2. Best-Fit Parameters Deduced from the Simulation of the Mössbauer Spectra (See Figure 3 and the SI) Taking into Account a Mixture of S = 0 (Fe⁰) and $S = \frac{1}{2}$ (Fe^I) Species Using the Experimental EPR g Values Reported Herein and Nuclear Hyperfine Values Consistent with the Literature Data²⁰

entry	iron oxidation state	spin	$g_{x,y,z}$	$\delta~({\rm mm}\cdot{ m s}^{-1})$	$\Delta E_{\rm Q} ({\rm mm} \cdot {\rm s}^{-1})$	$\Gamma (mm \cdot s^{-1})$	η	A_x (T)	A_{y} (T)	A_{z} (T)	% ± 5%
1	Fe ⁰	0		0.44	0.93	0.60	0.97				85
2	Fe^{I}	$^{1}/_{2}$	2.21 (g_x)	0.28	2.01	0.48	0.63	19	13	18	15
			2.02 (g_y)								
			2.00 (g_z)								

Table 3	3.	Calcula	ated	and	Observed	Isomer	Shifts	(δ)	for	Several	Bisarene-	or	Bisd	liene-l	Fe ^o (Compl	exes
---------	----	---------	------	-----	----------	--------	--------	------------	-----	---------	-----------	----	------	---------	-------------------	-------	------

entry	complex	spin	$\rho_0(\text{calcd}) \ (\text{e-a}_0^{-3})$	$\delta({ m calcd})~({ m mm\cdot s^{-1}})$	$\delta(\text{exptl}) \ (\text{mm} \cdot \text{s}^{-1})$	ref
1	$(\eta^6$ -C ₆ Me ₆) ₂ Fe ⁰	1	11826.87	0.99	1.06	23
2	$(\eta^6 - C_6 H_6)(\eta^4 - C_6 H_6) Fe^0$	0	11827.85	0.58	0.64	22a
3	$(\eta^6 - C_6 H_6)(\eta^4 - C_6 H_8) Fe^0$	0	11827.87	0.57	0.51	22a
4	$(\eta^{6}\text{-}C_{6}\text{H}_{5}\text{Me})(\eta^{4}\text{-}C_{6}\text{H}_{5}\text{Me})\text{Fe}^{0}$	0	11827.83	0.59		
5	$(\eta^{6}-C_{6}H_{5}Me)(\eta^{4}-C_{6}H_{5}Me)Fe^{0}$	0	11827.88	0.57		
6	$(\eta^{6}\text{-}C_{6}\text{H}_{5}\text{Me})(\eta^{4}\text{-}C_{6}\text{H}_{5}\text{Me})\text{Fe}^{0}$	0	11827.85	0.58		
7	$(\eta^4$ -CH ₂ CMeCHCH ₂) ₂ Fe ⁰	0	11828.35	0.38		
8	$(\eta^4$ -C ₆ H ₅ Me) ₂ Fe ⁰	0	11828.04	0.50		

accommodated a spin triplet state (S = 1).²³ This is in stark contrast with the electronic structure of the Fe⁰ complex discussed here, which is a singlet spin state (Figure 3). The possibility of the formation of (η^6, η^4) - or (η^4, η^4) -bistoluene-ligated Fe⁰ complexes has been further investigated by theoretical modelings.

Analysis of the Mössbauer Spectra: Insights from DFT Calculations. Mössbauer parameters can indeed be easily evaluated using straightforward DFT techniques, which allow computation of the electronic density at the ⁵⁷Fe nucleus, denoted as ρ_0 (unit: $e \cdot a_0^{-3}$, where a_0 is the Bohr radius). A reliable estimation of the isomer shift (δ) can thus be obtained with a linear extrapolation from $\rho_0^{.25a}$ To do so, a benchmark of Fe⁰ and Fe¹ complexes^{25b,c} has been used to calibrate the chosen level of theory. All calculations were performed with *ORCA 3.0.3* software, using the BP86 functional in the gas phase, associated with the TZVP basis set for all atoms except iron, which was treated with the CP(PPP) enlarged basis set. This choice has been motivated because it allows a good compromise between the accuracy and computational time. It has indeed been demonstrated that the use of the CP(PPP) basis set on iron allowed a more accurate linear fit between ρ_0 and δ for a very modest additional computational cost.^{25a}

The level of theory used in this benchmark allowed us to compute the isomer shift of the already reported complexes $(\eta^6-C_6Me_6)_2Fe^0$, $(\eta^6-C_6H_6)(\eta^4-C_6H_6)Fe^0$, and $(\eta^6-C_6H_6)(\eta^4-C_6H_8)Fe^0$ with good accuracy (Table 3, entries 1–3). For model complexes involving η^4 toluene-coordinated species, the position of the methyl group (borne by C₁ atom) in the η^4 ligand did not have a significant impact on either the calculated isomer shift or the average Fe–C_{arene} distances; see Table 3, entries 4 $(\eta^4-C_1C_2C_3C_4)$, 5 $(\eta^4-C_1C_2C_3C_6)$, and 6 $(\eta^4-C_2C_3C_4C_5)$. It can be noted that these species exhibit isomer shifts very close to their bis-C₆H₆ analogue (Table 3, entry 2).

A noticeable trend that can be drawn from this computational analysis is that the average Fe-C_{arene} bond is slightly longer for η^6 -coordinated arene ligands than for their η^4 analogues. In the case of $(\eta^6-C_6H_5Me)(\eta^4-C_6H_5Me)Fe^0$ (Table 3, entries 4–6), the average computed Fe– $C_{\eta^6-arene}^{6}$ distance is 2.11 Å, whereas the average $\text{Fe}-\text{C}_{\eta^{4}\text{-arene}}$ distance is 2.06 Å. This trend is confirmed by the optimized structure of the model complex $(\eta^4$ -CH₂CMeCHCH₂)₂Fe⁰ (Table 3, entry 7), which features an average $\text{Fe}-\text{C}_{\eta^{4}\text{-diene}}$ distance close to 2.04 Å. A smaller $Fe-C_{sp}^2$ distance leads to a higher computed electronic density ρ_0 and, therefore, to a smaller computed isomer shift [0.38 mm·s⁻¹ for $(\eta^4$ -CH₂CMeCHCH₂)₂Fe⁰ (entry 7) versus 0.57–0.59 mm·s⁻¹ for $(\eta^6$ -C₆H₅Me)(η^4 - $C_6H_5Me)Fe^0$ (entries 4–6)]. Taking this into account, analysis of the bis- η^4 -arene complex $(\eta^4$ -C₆H₅Me)₂Fe⁰ nuclear parameters was performed. The computed electronic density ρ_0 was significantly higher (11828.04 $e \cdot a_0^{-3}$, entry 8) than that for the

 $(\eta^{6}-C_{6}H_{5}Me)(\eta^{4}-C_{6}H_{5}Me)Fe^{0}$ complexes (entries 4–6), and the corresponding isomer shift (0.50 mm·s⁻¹) is in good agreement with the experimentally observed data ($\delta = 0.44$ mm·s⁻¹; Figure 3). It must be stated that the two η^{4} coordinated toluene ligands do not play a symmetric role: one of them is strongly twisted, whereas the second one is almost planar (Scheme 6). The η^{4} -coordination onto the planar toluene is due to a displacement of the iron atom, which is slightly shifted from the pseudo- C_{6} -symmetry axis of the η^{6} ligand.

Scheme 6. Computed Structure of $(\eta^4-C_6H_5Me)_2Fe^0$, Suggested as a Model for the Diamagnetic Fe⁰ Species Detected in Figure 3^{*a*}



"Selected metric data for the η^4 -(C₂C₃C₄C₅) toluene moiety: Fe-C₁ = 2.15 Å; Fe-C₂ = 2.08 Å; Fe-C₃ = 1.95 Å; Fe-C₄ = 1.95 Å; Fe-C₅ = 2.08 Å; Fe-C₆ = 2.14 Å; Fe-C_n bonds (n = 2-5) frozen during optimization.

Suggestion of a bisarene-ligated Fe⁰ species as a major complex obtained in the conditions depicted above [reduction of FeX_n salts by 30 equiv of PhMg(Hal), 2 min in toluene] is therefore in good agreement with the literature^{24b} and with the Mössbauer spectroscopy analysis reported herein (using ⁵⁷FeCl₂ as a precursor). This species evolves toward the formation of paramagnetic aggregates, as evidenced by the strongly distorded EPR spectrum in Figure 2b. However, the computed isomer shift δ is extremely sensitive to the Fe–C_{arene} bond distances and consequently to the theoretical level applied (δ variation of more than 30% for less than 5% of difference between the average Fe–C_{arene} distances in the structures depicted in Table 3, entries 4–6 and 8). Therefore, care must be taken in the interpretation of the experimental data, especially because of the low signal-to-noise ratio of the spectra displayed in Figure 3. An average error of $\pm 0.05 \text{ mm} \cdot \text{s}^{-1}$ on the simulation of the nuclear parameters should be acknowledged. Consequently, it can be anticipated that several geometrically close species featuring arene-ligated Fe⁰ centers that could fall in this error range coexist in solution.

¹H NMR Spectroscopy. The formation of transient arenecoordinated Fe⁰ species was also suggested by ¹H NMR spectroscopy when Fe(acac)₃ was used as a precursor in toluene- d_8 . At low iron concentrations (0.7 mM) and low temperature (-40 °C), the reduction of Fe(acac)₃ by PhMgBr (50 equiv) in the presence of PhPh as an additive (50 equiv of which were added to ensure the presence of a large excess of arene ligands in the bulk) led to the observation of transient resonances in the 4–5 ppm area (δ = 5.00, 4.72, 4.45, 4.31, and 4.15 ppm; see the SI). Such resonances are usually observed in this range for diamagnetic Fe⁰ arene-coordinated species, with arene protons being upfielded by retrodonation from the metal: Ittel et al. reported that the arene proton resonances of the analogue complex (η^6 -toluene)Fe⁰(butadiene) were observed between 4.66 and 4.87 ppm.^{24a} The number of resonances observed in our conditions (vide supra) also suggests that multiple arene-coordinated Fe⁰ species are obtained in the bulk upon chemical reduction of the precursor by PhMgX (X = Cl, Br). Consistent with the evolution of these Fe⁰ complexes toward paramagnetic aggregates, the resonances described above quickly disappeared. The only ¹H NMR signals observed after 10 min at -40 °C or upon slow warming at room temperature in the 4–6 ppm area belonged to the free acac ligand (δ = 5.25 ppm, CH), which was released in the reduction process (Scheme 2a). Concomitantly, the color of the solution evolved from very pale-red-brown to a deep-dark-brown.

The nature of the minor Fe^{I} complex evidenced in EPR and Mössbauer spectra (Figures 1 and 3) is discussed in the next section. As evidenced by spin titration in both aforementioned techniques, this oxidation state only represents a small fraction of the overall iron quantity (ca. 15%).

Nature of the Fe^I Complex: Insights from Pulsed-EPR **Spectroscopy.** In order to investigate the nature of the Fe^I coordination sphere, pulsed-EPR experiments (HYSCORE) were realized in toluene/THF (10:1) glass. HYSCORE is a powerful 2D pulsed-EPR technique that allows the study of hyperfine coupling of nuclei coupled to the paramagnetic species of interest. Figure 4 shows the HYSCORE quadrant plots obtained for magnetic field values corresponding to the three principal g values of the Fe^I complex. Here, ridges well separated from the ¹H Larmor frequency are observed and extend over nearly 12 MHz, indicating specific proton coupling to the Fe^I ion. These ridges disappear when the same experiments are performed in fully deuterated toluene (associated with 10% THF- h_8 ; see the SI), indicating that the signals can be attributed to the protons of the toluene solvent in close interaction with the metal ion. Therefore, the signals observed are compatible with a toluene molecule in η^6 coordination to Fe^I. The strong affinity of low-valent iron ions for arene ligands is already known (vide supra), and several well-defined arene-coordinated Fe^I complexes have been reported and, for some of them, investigated with spectroscopic and theoretical methods.^{17a,26a}

HYSCORE experiments performed in deuterated toluene unambiguously show that arene coordination of the Fe^I species implies ligation of a toluene molecule and not a biphenyl



Figure 4. HYSCORE contour plots for Fe^I (FeCl₂ + 30 equiv of PhMgBr; 10:1 toluene- h_8 /THF- h_8 glass) at g_{max} (315 mT), g_{mid} (343 mT), and g_{min} (347 mT). Experimental parameters: microwave frequency 9.71 MHz; τ = 120 ns; shot repetition time 5 ms; T = 10 K.

progressively formed in the bulk by oxidation of the Grignard reagent. However, it cannot be excluded that biphenyl acts as a η^6 -coordinating arene ligand in other solvents, e.g., when the reduction is carried out in THF. The competition between the iron coordination by toluene and biphenyl is discussed at the end of the next section.

On the basis of cw-EPR and HYSCORE experiments, it is thus reasonable to suggest that a η^6 -arene-stabilized Fe^I species is formed upon reduction of the iron precursor by PhMgBr. The nature of the other ligands of the coordination sphere was then investigated. Fe^I complexes often feature strongly σ donating ligands, such as β -diketiminate,^{17a} NHCs,^{21b} aryl groups,^{26a} or trimethylsilylamides.^{26b} In the presence of strongly coordinating species such as the C₆H₅⁻ anion, it is likely that the Fe^I center is coordinated by anionic phenyl ligands. To investigate this hypothesis, the reduction of FeCl₂ was carried out using isotopically enriched ¹³C₆H₅MgBr, synthesized at a microscale from commercial ¹³C₆H₅Br. The cw-EPR spectrum obtained for the reduction of FeCl₂ by 30 equiv of ${}^{13}C_6H_5MgBr$ for 2 min at room temperature is shown in Figure 5. The resonances are centered on the same g values as those observed when FeCl₂ was reduced with nonenriched C_6H_5MgBr (Figure 1) but exhibit significant broadening, reflecting hyperfine couplings between the Fe^I ion and ¹³C nuclei.

Because the coupling is not resolved on the cw-EPR spectrum, we performed HYSCORE measurements on this



Figure 5. Experimental (black) and simulated (red) cw-EPR spectrum (10:1 toluene- h_8 /THF- h_8 glass) of FeCl₂ + 30 equiv of ${}^{13}C_6H_5$ MgBr. Experimental parameters: microwave frequency 9.38 GHz; microwave power 0.01 mW; field modulation amplitude 0.5 mT; field modulation frequency 100 kHz; temperature 50 K. Simulation parameters : g = 2.2059, 2.0230, and 2.0003; H_{strain} (MHz) = 50.5, 15.8, and 0.0; peak-to-peak line width 1 mT; two ${}^{13}C$ nuclei with $A_{iso} = 35$ MHz, four ${}^{13}C$ nuclei with A = 9.0, 8.8, and 9.2 MHz.

sample. The contour plots obtained at magnetic field values corresponding to the principal g values are shown in Figure 6. Signals were observed in both quadrants, corresponding to strong and weak coupling cases. The cross peaks in the (+-)



Figure 6. HYSCORE contour plots of FeCl₂ + 30 equiv of ${}^{13}C_6H_5MgBr$ (10:1 toluene- h_8/THF - h_8 glass) at g_{max} (315 mT), g_{mid} (343 mT), and g_{min} (347 mT). Experimental parameters: microwave frequency 9.71 MHz; τ = 140 ns; shot repetition time 3 ms; T = 10 K.

quadrant do not exhibit significant changes in their position suggesting that the hyperfine coupling of the corresponding ¹³C nuclei is essentially isotropic. On the basis of the distance between the cross peaks, the value of the coupling was estimated to be about 9 MHz. The fact that the coupling is isotropic indicates that some spin density is localized on ¹³C nuclei and therefore that at least one ¹³C₆H₅⁻ anion is a ligand to the Fe^I ion. In the (++) quadrant, the cross peaks are not resolved and are close to the ¹³C Larmor frequency, indicating rather weak hyperfine coupling.

On the basis of these results, it can be proposed that the carbon bonding the Fe^I ion (C_{ipso}) bears the strongest spin density in the $C_6H_5^-$ ligands. It is therefore quite strongly coupled to the iron and is not detectable by HYSCORE. This is in agreement with the simulated spectrum depicted in Figure 5 that includes a parameter $A_{iso} = 35$ MHz (red lines). The two carbon atoms in the ortho position are those responsible for the cross peaks observed in the (+-) quadrant with a hyperfine coupling of 9 MHz, and the carbon atoms in the meta and para positions are very weakly coupled and detected close to the ¹³C Larmor frequency in the (++) quadrant. With this in mind, simulations were performed for the cw-EPR spectrum of the sample. Keeping the same parameters (g values, strain, and line width) as those for the spectrum without ¹³C labeling (Figure 1, inset), the best fit was obtained when considering two equivalent C₆H₅⁻ ligands compared to only one (see the SI). The simulation is shown in Figure 5 with the experimental data, and the parameters are reported in the caption. The overall results obtained with cw- and pulsed-EPR thus allow the suggested structure, which is represented in Scheme 7 for the S = $1/_2$ Fe^I complex, namely, $[(\eta^6 - C_6 H_5 Me) Fe^I (Ph)_2]^-$.

Scheme 7. Structure Suggested for the Minor Fe^I Complex Obtained by the Reduction of FeX_n (X = acac, Cl; n = 2, 3) by an Excess of PhMgBr in Toluene, on the Basis of cw- and Pulsed-EPR Experiments^a



^{*a*}The starred atoms correspond to ¹³C atoms, which allowed detection of the hyperfine $Fe^{I}-^{13}C$ couplings when $^{13}C_6H_5MgBr$ was used as a reductant.

In order to support the structure suggested above (Scheme 7), the most likely number of $C_6H_5^-$ ligands, and, therefore, the most likely topology that can be accommodated by the Fe^I center to afford a spin doublet arene-ligated polyphenyl-Fe^I complex $[(\eta^6-C_6H_5Me)Fe^I(Ph)_n]^{(n-1)-}$, was then examined using DFT calculations.

Theoretical Investigations of the Fe^I Electronic Structure. The gap between the doublet and quartet spin states was evaluated for a benchmark of representative Fe^I organometallic complexes reported in the literature and featuring for some of them η^6 -arene-coordinated Fe^I centers (1a, 1b, 1c, and 1d in Scheme 8).²⁷ Benzene was used as a Scheme 8. $\Delta E_{Q-D} = E_Q - E_D$ DFT Quartet-Doublet Split (kcal·mol⁻¹; Gas Phase; See the SI for the Assignments) for $1a-1f^{a}$



^aBasis sets for carbon, hydrogen, nitrogen, and phosphorus: see the SI.

model for the coordinated arene solvent in each case. Different dispersion-fitted functionals (PBE0-D3, B3LYP-D3, and M06) as well as two pseudopotentials for the iron ion (SDD and CEP-31G) were used. The complexes $[(\eta^6-C_6H_6)Fe^I(Ph)_2]^-$ (1e) and $[(\eta^6-C_6H_6)Fe^I(Ph)_3]^{2-}$ (1f) have been used as models of η^6 -arene-coordinated polyphenyl-Fe^I complexes exhibiting respectively idealized $C_{2\nu}$ and $C_{3\nu}$ environments, in order to be compared with 1d, a bulkier terphenyl analogue of which having been experimentally characterized as a quartet spin ground state.^{26a}

Regarding the energetic features, the DFT methods reproduce well the stabilization of the quartet states (1c and 1d), with a significantly high quartet-doublet gap (23.8-34.0 kcal·mol⁻¹, 1c, and 16.0-33.4 kcal·mol⁻¹, 1d). However, the stabilization of doublet states is not efficiently reflected by DFT analysis. All methods returned to a ground quartet state for complex 1a (stabilized by $3.1-7.6 \text{ kcal} \cdot \text{mol}^{-1}$). Either a slight preference for the doublet state for 1b (by 2.2–8.9 kcal·mol⁻¹ PBE0-D3 and B3LYP-D3) or a slight preference for the quartet state (by 1.4-1.5 kcal·mol⁻¹, M06) is returned. Moreover, natural bond orbital (NBO) analysis shows that natural orbital occupancy numbers (NOONs) for the d-block molecular orbitals strongly differ from integers (0, 1, or 2) for the computed Fe^I complexes (Table 4). The computed NOONs for Fe^{I} complexes 1a, 1b, 1c, 1d, 1e, and 1f (entries 1-6) can be compared with the computed NOONs for $Fe(acac)_3$ (entry 7). The latter is essentially monoconfigurational (high-spin d^5 complex), and its electronic structure is therefore accurately described by DFT.

Table 4. DFT-Computed NOONs for d-Block Orbitals of Complexes Depicted in Scheme 8 (PBE0, Gas Phase, SDD, and Pseudopotential for Iron)

entry	complex	d-NOONs
1	² 1a	$d_{xy}^{1.73} d_{xz}^{0.81} d_{yz}^{1.20} d_{x^2-y^2}^{1.79} d_{z^2}^{1.93}$
2	² 1b	$d_{xy}^{1.47} d_{xz}^{0.86} d_{yz}^{1.29} d_{x^2-y^2}^{2.32} d_{z^2}^{1.78}$
3	⁴ 1c	$d_{xy}^{1.27} d_{xz}^{1.60} d_{yz}^{1.57} d_{x^2-y^2}^{1.31} d_{z^2}^{1.09}$
4	⁴ 1d	$d_{xy}^{1.14} d_{xz}^{1.17} d_{yz}^{1.73} d_{x^2-y}^{2.131} d_{z^2}^{1.64}$
5	² 1e	$d_{xy}^{0.97} d_{xz}^{1.61} d_{yz}^{1.08} d_{x^2-y^2}^{2.78} d_{z^2}^{1.62}$
6	⁴ 1f	$d_{xy}^{1.14} d_{xz}^{1.37} d_{yz}^{1.26} d_{x^2-y^2}^{2.30} d_{z^2}^{1.30}$
7	⁶ Fe(acac) ₃	$d_{xy}^{1.14} d_{xz}^{1.16} d_{yz}^{1.16} d_{x^2-y^2}^{2.14} d_{z^2}^{1.05}$

This suggests that a correct description of the Fe^I ion electronic structure cannot be obtained with a single electronic configuration and is then beyond the limit of an accurate DFT analysis (see the SI).²⁸ Nevertheless, several trends can be drawn from this analysis in the case of complexes 1a and 1b. The experimentally attested stability of the doublet state can indeed arise from the multiconfigurational character of the Fe¹ center, counterbalancing the slight quartet stabilization predicted by DFT methods. Among the three examined candidates for arene-ligated polyphenyl-Fe^I complexes (1d, 1e, and 1f) that could account for the doublet species reported herein, a monophenyl species such as $(\eta^6 - C_6 H_5 Me) Fe^{I}Ph$ seems unlikely because its structural topology is very close to Power's terphenyl complex (model 1d), which has a strongly stabilized quartet ground state, as attested by EPR spectroscopy.^{26a} Similar to **1d**, DFT computations of $(\eta^6 - C_6H_6)Fe^IPh$ indeed return a strong preference for the quartet configuration as well (18.7 kcal·mol⁻¹ at the PBE0-D3/SDD level).^{29,30} The triphenyl species $[(\eta^6\text{-} \text{arene})\text{Fe}^{I}\text{Ph}_3]^{2-}$ (1f) seems also unlikely because of the strong stabilization of the quartet state (Scheme 8). However, in the case of the bisphenyl analogue 1e, the doublet-quartet gap is small enough $(-1.1 \text{ to } -9 \text{ kcal} \cdot \text{mol}^{-1})$ depending on the functional used) to consider multiconfigurational effects, similar to 1a and 1b. Preliminary computational analysis run at the CCSD(T) level indeed shows that the correlation energy is much stronger, by almost 0.1 au, in the doublet configuration of 1e than in the quartet analogue. Such a discrepancy between the correlation effects involved in the doublet and quartet electronic structures can lead to reinterpretation of the DFT-computed tendencies, mainly dominated by exchange energies and, therefore, favoring high-spin multiplicities. Small doublet-quartet DFT-computed gaps (complexes 1a, 1b, and 1e; Scheme 8) could therefore be counterbalanced by taking into account the multiconfigurational effects. As highlighted by Bedford,⁴ an acac-ligated monophenyl species such as [PhFe^I(acac)(THF)]⁻ exhibits a strongly stabilized quartet configuration with a computed doublet-quartet gap higher than 20 kcal·mol⁻¹ [DFT level: PBE0/6-31+G(d)/SDD basis set and pseudopotential for iron]. This high gap could be overcome with difficulty by multiconfigurational effects, and, consequently, on the basis of the experimental and computational work reported herein, $[(\eta^6-C_6H_5Me)Fe^IPh_2]^-$ seems to be a closer model for the description of the minor Fe^I species obtained upon the reduction of a $Fe^{I/III}$ precursor with aryl Grignard reagents. Moreover, it is consistent with the recent report of Koszinowski et al., who reported that the [Ph2FeI]- fragment could be detected by ESI-MS when Fe(acac)₃ was reduced with PhMgCl in THF in cross-coupling conditions (presence of iPrCl as an electrophile).^{19c} Determination of the structure of this Fe^I complex also allowed us to compute an estimation of the energetic barrier required to ensure disproportionation of the trisphenylated species $[Ph_3Fe^{II}]^-$ into the Fe^{III} and Fe^I oxidation states (thus affording $[Ph_4Fe^{III}]^-$ and $[(\eta^6-C_6H_5Me)-$ Fe^IPh₂]⁻), which was brought up by Koszinowski and Bedford (vide supra). At a DFT level (see the SI), this reaction is quite athermic ($\Delta E = 0.2 \text{ kcal·mol}^{-1}$) and could therefore occur in short times at room temperature.³¹

The plausibility of the bisphenylated structure $[(\eta^6 - C_6H_5Me)Fe^IPh_2]^-$ depicted above (Scheme 7) has, moreover, been strengthened by the computation of its Mössbauer isomer shift following the DFT-based method mentioned in the previous section (ORCA 3.0.3 software; BP86–TZVP/CP-

(PPP) for the iron atom). According to the calibration curve using the benchmark of Fe⁰ and Fe^I complexes described earlier,^{25b} the computed density at the ⁵⁷Fe^I nucleus (ρ_0) for the structure $[(\eta^6-C_6H_5Me)Fe^I(Ph)_2]^-$ corresponds to a predicted isomer shift of 0.24 mm·s⁻¹ (computed ρ_0 : 11828.69 e·a₀⁻³). This is in good agreement with the experimental value obtained from Mössbauer spectra (Figure 3), which was $\delta = 0.28$ mm·s⁻¹.

Competition between η^6 -**Toluene- and** η^6 -**Biphenyl-Fe**^I **Ligations.** As discussed earlier, the coordination of a η^6 biphenyl molecule onto the Fe^I ion cannot be ruled out in nonaromatic solvents such as THF. The competition between the coordination of toluene and biphenyl (i.e., the equilibrium between $[(\eta^6-C_6H_5Me)Fe^IPh_2]^-$ and $[(\eta^6-C_6H_5Ph)Fe^IPh_2]^-)$ has been investigated by DFT (Scheme 9). The equilibrium is

Scheme 9. Competition between the Toluene-Fe^I and Biphenyl-Fe^I Ligation



shifted toward the formation of the biphenyl species $^{PhPh}1e$, with a slight stabilization of ca. 4.9 kcal·mol⁻¹ with respect to the toluene analogue $^{Tol}1e$. Therefore, it is likely that coordination of the biphenyl molecule accumulated by the oxidation of PhMgBr can occur in nonaromatic solvents, with this ligand being replaced by a toluene molecule when the latter is used as a solvent.

Very recently, the X-ray structure of the biphenyl complex $^{\rm PhPh}1e$ was obtained by Hu et al. by reducing the iron–sulfur cluster $[Fe_4S_4Cl_4]^{2-}$ with an excess of phenyllithium. The authors, moreover, also assessed a low-spin ground state for this complex. 32

Reactivity of In Situ Generated Fe⁰ and Fe¹ Complexes in Aryl–Heteroaryl Kumada Cross-Couplings. The relevance of the complexes described in this Article as possible active species in aryl–heteroaryl Kumada cross-couplings has been examined. 2-Chloro-5-(trifluoromethyl)pyridine (HetArCl) has been used as an electrophilic partner in catalytic conditions (Scheme 10): chloropyridines proved indeed to be efficient cross-coupling partners in coligand-free iron-catalyzed methodologies.^{2e}

Scheme 10. Aryl–Heteroaryl Kumada Cross-Coupling between PhMgCl and HetArCl Investigated at Room Temperature (Nonoptimized Conditions): (a) Catalytic One-Pot Conditions; (b) Step-by-Step Conditions with Generation of Fe^0 Prior to the Addition of HetArCl^a



^aThe HetArPh yield was calculated with respect to HetArCl.

In the one-pot catalytic conditions described above (Scheme 10a), the first Mössbauer spectrum with 57 FeCl₂ as an iron source was recorded (Figure 7a).



Figure 7. Mössbauer spectra at 80 K in toluene: (a) solution containing 2.5 mM 57 FeCl₂ and **HetArCl** (20 equiv), frozen after the addition of PhMgCl (10 equiv; reaction time of 1 min at room temperature); (b) solution containing 57 FeCl₂ reduced in situ by PhMgCl (10 equiv; reaction time of 3 min at room temperature) followed by the addition of **HetArCl** (20 equiv) and freezing (reaction time of 1 min at room temperature). See the remarks regarding the low signal-to-noise ratio in the caption of Figure 3.

The spectrum displayed in Figure 7a exhibits a signal that could be simulated with two doublets. The first one (Figure 7a, red lines) accounts for ca. 39% of the overall iron quantity, with the following nuclear parameters: $\delta = 0.53 \text{ mm} \cdot \text{s}^{-1}$ and $\Delta E_Q = 0.98 \text{ mm} \cdot \text{s}^{-1}$. This signal is well-fitted to the Fe⁰ species described in the previous section, which featured similar parameters (Figure 3). The second doublet (Figure 7a, green lines) accounts for ca. 51% of the iron quantity with the following parameters: $\delta = 1.28 \text{ mm} \cdot \text{s}^{-1}$; $\Delta E_Q = 2.46 \text{ mm} \cdot \text{s}^{-1}$. This doublet corresponds to the regenerated Fe^{II} precursor (⁵⁷FeCl₂) with nuclear parameters corresponding to a high-spin Fe^{II} center (see the SI for the spectrum of ⁵⁷FeCl₂). These data are gathered in Table 5 (entry 1).

In agreement with the previous analysis, no transmetalated phenyl-Fe^{II} species can be detected during catalysis (Figure 7a). However, at this point, the origin of the regeneration of the Fe^{II} precursor is unclear. Fe^{II} can indeed be provided by two drastically different pathways: it could either be formed by the reaction of the reduced Fe⁰ species with the electrophile **HetArCl** (Scheme 11, path b) or come from the reaction of **HetArCl** with a transient, short-lived, phenylated organo-Fe^{II} intermediate formed prior to the Fe⁰ oxidation state (Scheme

Table 5. Best-Fit Parameters Deduced from the Simulation of the Mössbauer Spectra Displayed in Parts a (Entry 1) and b (Entry 2) of Figure 7^a

entry	iron oxidation state	spin	$\delta \pmod{s^{-1}}$	$\Delta E_{\mathbb{Q}} (\underset{s^{-1}}{\operatorname{mm}})$	$\frac{\Gamma \ (mm \cdot s^{-1})}{s^{-1}}$	% ± 5%
1	Fe ⁰	0	0.53	0.98	0.55	39
	Fe ^{II}	2	1.28	2.46	0.55	51
2	Fe ⁰	0	0.46	0.75	0.50	24
	Fe ^{II}	2	1.24	2.55	0.30	72

^{*a*}An average error of $\pm 0.05 \text{ mm} \cdot \text{s}^{-1}$ must be acknowledged in the simulations because of the low signal-to-noise ratio of the experimental spectra.

Scheme 11. Two Possible Pathways for the Regeneration of FeCl₂ under Catalytic Conditions



11, path a). In the second case, the bisarene-ligated Fe^0 species would be an off-cycle intermediate.³³

A second Mössbauer spectrum has therefore been recorded in order to selectively examine the reactivity of the Fe⁰ species (Figure 7b), in the step-by-step conditions depicted in Scheme 10b. ⁵⁷FeCl₂ has been reduced by an excess of PhMgCl to the Fe⁰ oxidation state, and an excess of HetArCl has been added to the resulting solution, which was frozen after 1 min at 25 °C. It turned out that the same Fe⁰ and Fe^{II} species are observed in both one-pot (Figure 7a) or step-by-step conditions (Figure 7b and Table 5, entry 2). When Fe⁰ is accumulated prior to the addition of the electrophile (conditions of Scheme 10b), the ratio Fe^{II}/Fe⁰ slightly increases (3:1 vs 1.3:1 in the conditions of Scheme 10a). Therefore, regeneration of the Fe^{II} precursor by the reaction of Fe⁰ reduced species with the electrophile (Scheme 11, path b) seems to be operative at room temperature within a couple of minutes, and formation of the cross-coupling product HetArPh was observed concomitantly (Scheme 10b).

cw-EPR spectra were also recorded in the conditions depicted in Scheme 10a, with nonenriched FeCl₂ as a precursor. These spectra showed that the Fe^I signal was not affected by the presence of **HetArCI**. This result therefore suggests that the minor low-spin Fe^I species obtained in these coligand-free systems is actually an off-cycle species and does not contribute to catalytic processes involving aryl Grignard reagents and heteroaryl chlorides. In their recent report, Hu et al. demonstrated that the analogue biphenyl complex $[(\eta^6-C_6H_5Ph)Fe^IPh_2]^-$ was unreactive toward the addition of chloroarenes but that stoichiometric C–C cross-coupling reactions could be observed while using organic bromides as electrophiles, albeit with low yield and the concomitant formation of biphenyl.³²

There is a strong similarity between the behavior of the SciOPP-stabilized systems reported by Neidig and the coligand-free systems investigated in this report. In both cases, the lowest oxidation state obtained upon the reduction of Fe^{II} precursors by PhMgX (X = Cl, Br) is a Fe⁰ complex, which can be used as a precursor in Kumada-type catalytic cross-couplings. However, before it can be stated that arene-ligated Fe⁰ complexes can be on-cycle intermediates in the case of coligand-free aryl-heteroaryl cross-coupling chemistry, the

reactivity of transient, short-lived nonstabilized polyphenyl-Fe^{II} intermediates $[Ph_nFe^{II}]^{(n-2)-}$ must be investigated. It was indeed demonstrated that the SciOPP-stabilized analogues (SciOPP)Fe^{II}(Ph)_n were extremely reactive in Kumada and Suzuki–Miyaura cross-couplings⁸ and that the reactivity of the zerovalent complex (η^6 -biphenyl)Fe⁰(SciOPP) was totally overwhelmed by the phenylated Fe^{II} complexes. Such investigations are currently in progress, and the results will be reported in due time.

CONCLUDING REMARKS

We established in this paper that several reduction mechanisms could take place when Fe^{II} or Fe^{III} salts were reduced by aryl Grignard reagents in the absence of a stabilizing coligand. In THF, Fe(acac)₃ undergoes a first ligand exchange with PhMgBr, leading to PhFe(acac)₂, which is prompted to lead to the formation of PhPh and $Fe(acac)_2$ in a dimeric pathway, as suggested by DFT. The formation of PhPh involves a monoelectronic reduction of the Fe^{III} center, which can proceed by the homolytic cleavage of Ph–Fe^{III} bonds. A second phenyl transfer, which would lead from PhFe(acac)₂ to $[Ph_2Fe(acac)_2]^-$, requires an overall high energetic span that cannot be reached in the experimental conditions, making the possibility of a classic bielectronic reductive elimination directly connecting the Fe^{III} and Fe^I oxidation states unlikely. Fe^I can be obtained by further reduction of the Fe^{II} intermediates, as attested by cw-EPR spectroscopy in 10:1 toluene/THF mixtures. Unlike $Fe(acac)_3$, the electron-deficient precursors FeCl₂ and FeCl₃ are more easily reduced by PhMgBr to the Fe^I level: FeCl₃ only requires 1 equiv of PhMgBr to provide Fe¹ oxidation state, and FeCl₂ can also provide Fe^I by disproportionation of the intermediate polyphenyl-Fe^{II} species. It was shown by EPR spectroscopy that the reduction of either $Fe(acac)_n$ or $FeCl_n$ (n = 2, 3) led to a common low-spin Fe^I species regardless of the nature of the starting iron salt, suggesting the possible formation of a polyphenyl-Fe^I species. This complex has been proven to be unstable over time and represents, moreover, a minor fraction (ca. 15%) of the overall iron amount, as attested by EPR-based spin titration and Mössbauer spectroscopy. Mössbauer analysis actually showed that the distribution of the metallic species is quickly dominated after 3 min by diamagnetic Fe⁰ complexes. Computational analysis of the experimental Mössbauer data and a comparison with the already reported Fe⁰ mononuclear complexes allowed us to suggest that the major iron species detected herein featured Fe⁰ centers that were stabilized by arene ligation, specifically by toluene when the latter was used as a solvent. The best model obtained by confronting the experimental nuclear parameters and computed data was $(\eta^4 - C_6H_5Me)_2Fe^0$. Because of the low signal-to-noise ratio of the Mössbauer spectra and the average error in the corresponding simulations, it can however be anticipated that multiple arene-stabilized Fe⁰ species coexist in solution. The presence of several areneligated Fe⁰ complexes was also confirmed by low-temperature ¹H NMR spectroscopy. These complexes are prompt to undergo aggregation and finally provide iron nanoparticles. Structural data were also gained for the minor Fe^I complex. Pulsed-EPR spectroscopy (HYSCORE) unambiguously demonstrated that the Fe^I ion is ligated by a toluene molecule in η^6 coordination. When iron salts were reduced with isotopically enriched ¹³C₆H₅MgBr, cw-EPR showed a significant broadening of the resonances due to hyperfine $Fe^{I}-{}^{13}C$ coupling, attesting to a ligation of the Fe^I ion by σ -donating anionic

C₆H₅⁻ ligands. Analysis of the cw-EPR and HYSCORE hyperfine patterns suggests that the coordination sphere of the Fe^I ion involves two σ -ligated C₆H₅⁻ ligands. This hypothesis was strengthened by DFT calculations and NBO analysis using different functionals (PBE0-D3, B3LYP-D3, and M06) as well as two pseudopotentials for iron (SDD and CEP-31G). Evaluation of the quartet-doublet energetic gap was computed for a benchmark of low-spin and high-spin Fe^I complexes reported in the literature, showing that multiconfigurational effects were predominant for low-spin Fe^I species. On the basis of the experimental and computational results, a bisphenyl structure $[(\eta^6-C_6H_5Me)Fe^IPh_2]^-$ has been suggested. We, moreover, demonstrated that the $[(\eta^6 C_6H_5Me)Fe^{I}Ph_2$ complex was not reactive in the arylheteroaryl Kumada cross-coupling conditions because its concentration remained roughly constant upon the addition of an heteroaryl chloride. On the other hand, the major bisarene-ligated Fe⁰ complex was able to react with HetArCl and could be used as an efficient precursor for aryl-heteroaryl Kumada cross-couplings. The results reported in this paper are focused on the structural nature and reactivity of the low-valent resting states that were observed at room temperature. The in situ observation of transient short-lived intermediates at lower temperatures (such as polyphenyl-Fe^{II} species) and their relevance in similar catalytic processes are currently being investigated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02616.

Experimental procedures, parameters, and software used for EPR and Mössbauer data analysis as well as Cartesian coordinates of optimized structures with the corresponding energies and lowest frequencies (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jean-marc.latour@cea.fr.

- *E-mail: pierre.dorlet@cea.fr.
- *E-mail: guillaume.lefevre@cea.fr.

ORCID ©

Thibault Cantat: 0000-0001-5265-8179 Pierre Dorlet: 0000-0001-7394-3374 Guillaume Lefèvre: 0000-0001-9409-5861

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge CEA, CNRS, ANR (Project JCJC SIROCCO-16 to G.L.), and the French Infrastructure for Integrated Structural Biology (Grant ANR-10-INSB-05-01 to P.D.). Dr. Pierre Thuéry (CEA) and Dr. Christian Herrero (Université Paris-Sud, Orsay) are thanked for technical assistance (X-ray diffraction and EPR spectroscopy).

REFERENCES

(1) Bedford, R. B.; Brenner, P. B. The development of iron catalysts for cross-coupling reactions. In *Iron Catalysis II*; Bauer, E., Ed.; Springer International: 2015.

(2) (a) Tamura, M.; Kochi, J. K. Vinylation of Grignard reagents. Catalysis by iron. J. Am. Chem. Soc. 1971, 93, 1487-1489. (b) Smith, R. S.; Kochi, J. K. Mechanistic studies of iron catalysis in the cross coupling of alkenyl halides and Grignard reagents. J. Org. Chem. 1976, 41, 502-509. (c) Quintin, J.; Franck, X.; Hocquemiller, R.; Figadère, B. Iron-catalysed arylation of heteroaryl halides by Grignard reagents. Tetrahedron Lett. 2002, 43, 3547-3549. (d) Fürstner, A.; Leitner, A. Iron-Catalyzed Cross-Coupling Reactions of Alkyl-Grignard Reagents with Aryl Chlorides, Tosylates, and Triflates. Angew. Chem., Int. Ed. 2002, 41, 609-612. (e) Fürstner, A.; Leitner, A.; Mendez, M.; Krause, H. Iron-Catalyzed Cross-Coupling Reactions. J. Am. Chem. Soc. 2002, 124, 13856-13863. (f) Martin, R.; Fürstner, A. Cross-Coupling of Alkyl Halides with Aryl Grignard Reagents Catalyzed by a Low-Valent Iron Complex. Angew. Chem., Int. Ed. 2004, 43, 3955-3957. (g) Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. Iron-Catalyzed Cross-Coupling of Primary and Secondary Alkyl Halides with Aryl Grignard Reagents. J. Am. Chem. Soc. 2004, 126, 3686-3687. (h) Nagano, T.; Hayashi, T. Iron-Catalyzed Grignard Cross-Coupling with Alkyl Halides Possessing β -Hydrogens. Org. Lett. 2004, 6, 1297– 1299. (i) Sherry, B. D.; Fürstner, A. The Promise and Challenge of Iron-Catalyzed Cross Coupling. Acc. Chem. Res. 2008, 41, 1500-1511. (j) Czaplik, W. M.; Mayer, M.; Cvengros, J.; von Wangelin, A. J. Coming of Age: Sustainable Iron-Catalyzed Cross-Coupling Reactions. ChemSusChem 2009, 2, 396-417. (k) Kuzmina, O. M.; Steib, A. K.; Flubacher, D.; Knochel, P. Iron-Catalyzed Cross-Coupling of N-Heterocyclic Chlorides and Bromides with Arylmagnesium Reagents. Org. Lett. 2012, 14, 4818-4821. (1) Kuzmina, O. M.; Steib, A. K.; Markiewicz, J. T.; Flubacher, D.; Knochel, P. Ligand-Accelerated Ironand Cobalt-Catalyzed Cross-Coupling Reactions between N-Heteroaryl Halides and Aryl Magnesium Reagents. Angew. Chem., Int. Ed. 2013, 52, 4945-4949. (m) Nakamura, E.; Hatakeyama, T.; Ito, S.; Ishizuka, K.; Ilies, L.; Nakamura, M. Org. React. 2013, 83, 1. (n) Bauer, I.; Knölker, H.-J. Iron Catalysis in Organic Synthesis. Chem. Rev. 2015, 115, 3170-3387.

(3) Hatakeyama, T.; Nakamura, M. Iron-Catalyzed Selective Biaryl Coupling: Remarkable Suppression of Homocoupling by the Fluoride Anion. *J. Am. Chem. Soc.* **2007**, *129*, 9844–9845.

(4) Bedford, R. B. How Low Does Iron Go? Chasing the Active Species in Fe-Catalyzed Cross-Coupling Reactions. *Acc. Chem. Res.* **2015**, *48*, 1485–1493.

(5) Fürstner, A.; Krause, H.; Lehmann, C. W. Unusual Structure and Reactivity of a Homoleptic "Super-Ate" Complex of Iron: Implications for Grignard Additions, Cross-Coupling Reactions, and the Kharasch Deconjugation. *Angew. Chem., Int. Ed.* **2006**, *45*, 440–444.

(6) (a) Adams, C. J.; Bedford, R. B.; Carter, E.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Huwe, M.; Cartes, M. A.; Mansell, S. M.; Mendoza, C.; Murphy, D. M.; Neeve, E. C.; Nunn, J. Iron(I) in Negishi Cross-Coupling Reactions. J. Am. Chem. Soc. 2012, 134, 10333–10336. (b) Bedford, R. B.; Carter, E.; Cogswell, P. M.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Murphy, D. M.; Neeve, E. C.; Nunn, J. Simplifying Iron–Phosphine Catalysts for Cross-Coupling Reactions. Angew. Chem., Int. Ed. 2013, 52, 1285–1288.

(7) (a) Kleimark, J.; Hedström, A.; Larsson, P.-F.; Johansson, C.; Norrby, P.-O. Mechanistic Investigation of Iron-Catalyzed Coupling Reactions. *ChemCatChem* **2009**, *1*, 152–161. (b) Guisán-Ceinos, M.; Tato, F.; Buñuel, E.; Calle, P.; Càrdenas, D. J. Fe-catalysed Kumadatype alkyl–alkyl cross-coupling. Evidence for the intermediacy of Fe(I) complexes. *Chem. Sci.* **2013**, *4*, 1098–1104. (c) Hedström, A.; Izakian, Z.; Vreto, I.; Wallentin, C.-J.; Norrby, P.-O. On the Radical Nature of Iron-Catalyzed Cross-Coupling Reactions. *Chem. - Eur. J.* **2015**, *21*, 5946–5953. (d) Noda, D.; Sunada, Y.; Hatakeyama, T.; Nakamura, M.; Nagashima, H. Effect of TMEDA on Iron-Catalyzed Coupling Reactions of ArMgX with Alkyl Halides. *J. Am. Chem. Soc.* **2009**, *131*, 6078–6079. (e) Liu, Y.; Xiao, J.; Wang, L.; Song, Y.; Deng, L. Carbon–Carbon Bond Formation Reactivity of a Four-Coordinate NHC-Supported Iron(II) Phenyl Compound. Organometallics 2015, 34, 599–605. (f) Liu, Y.; Wang, L.; Deng, L. Three-Coordinate Iron(II) Dialkenyl Compound with NHC Ligation: Synthesis, Structure, and Reactivity. Organometallics 2015, 34, 4401–4407. (g) Liu, Y.; Luo, L.; Xiao, J.; Wang, L.; Song, Y.; Qu, J.; Luo, Y.; Deng, L. Four-Coordinate Iron(II) Diaryl Compounds with Monodentate N-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Their Tetrahedral-Square Planar Isomerization in Solution. Inorg. Chem. 2015, 54, 4752–4760.

(8) Daifuku, S. L.; Kneebone, J. L.; Snyder, B. E. R.; Neidig, M. L. Iron(II) Active Species in Iron–Bisphosphine Catalyzed Kumada and Suzuki–Miyaura Cross-Couplings of Phenyl Nucleophiles and Secondary Alkyl Halides. *J. Am. Chem. Soc.* 2015, *137*, 11432–11444.
(9) Muñoz, S. B., III; Daifuku, S. L.; Brennessel, W. W.; Neidig, M. L. Isolation, Characterization, and Reactivity of Fe₈Me₁₂⁻: Kochi's S = 1/2 Species in Iron-Catalyzed Cross-Couplings with MeMgBr and Ferric Salts. *J. Am. Chem. Soc.* 2016, *138*, 7492–7495.

(10) (a) Charavay, C.; Segard, S.; Edon, F.; Clémancey, M.; Blondin, G. *SimuMoss software*; CEA/DRF/BIG, CNRS, Université Grenoble Alpes, 2012. (b) Carboni, M.; Clémancey, M.; Molton, F.; Pécaut, J.; Lebrun, C.; Dubois, L.; Blondin, G.; Latour, J.-M. Biologically Relevant Heterodinuclear Iron–Manganese Complexes. *Inorg. Chem.* **2012**, *51*, 10447–10460.

(11) Williamson, K. L.; Masters, K. M. Macroscale and microscale organic experiments, 6th ed.; Cengage Learning: 2010.

(12) Xue, Z.; Daran, J.-C.; Champouret, Y.; Poli, R. Ligand Adducts of Bis(acetylacetonato)iron(II): A ¹H NMR Study. *Inorg. Chem.* **2011**, *50*, 11543–11551.

(13) It was reported by Neidig that in situ acidic quenching at short times (within ca. 30 s; see ref 8) could artificially lead to the formation of biphenyl, thus leading to an overestimation of its quantity formed by the reduction of iron. This is due to the quenching process of transient short-lived aryl-Fe^{II} species.

(14) (a) Carloni, P.; Greci, L.; Stipa, P.; Eberson, L. Electron-Transfer Reactions. Oxidation of Grignard Reagents in the Presence of an Aminoxyl as a Radical-Trapping Agent. J. Org. Chem. 1991, 56, 4733-4737. and references cited therein (b) Lefevre, G.; Jutand, A. Activation of Aryl and Heteroaryl Halides by an Iron(I) Complex Generated in the Reduction of [Fe(acac)₃] by PhMgBr: Electron Transfer versus Oxidative Addition. Chem. - Eur. J. 2014, 20, 4796-4805. (c) This is confirmed by a DFT-computed barrier of 45.1 kcalmol⁻¹. Grignard reagents can act as monoelectronic reductants with oxidants weaker than Fe(acac)₃ but under harsher conditions. See: Eberson, L.; Greci, L. Experimental Evidence for an Electron-Transfer Mechanism in the Reaction between 2-Phenyl-3-(phenylimino)-3Hindole and Grignard Reagents: Application of the Marcus Theory. J. Org. Chem. 1984, 49, 2135-2139. (oxidation of alkyl Grignard reagents by iminoindoles). (d) Uchiyama, N.; Shirakawa, E.; Hayashi, T. Single electron transfer-induced Grignard cross-coupling involving ion radicals as exclusive intermediates. Chem. Commun. 2013, 49, 364-366. (oxidation of PhMgBr by aryl iodides); see also ref 14a for oxidation of Grignard reagents by indole bisnitrone. (e) A bisarylmagnesium species such as Ph2Mg, in-situ-formed by Schlenk equilibrium, could more likely be involved in outer-sphere monoelectronic transfer with Fe(acac)₃. Bisorganomagnesium compounds are indeed more easily oxidized than their Grignard analogues. See: Psarras, T.; Dessy, R. E. Organometallic Electrochemistry. X. Organomagnesium reagents. J. Am. Chem. Soc. 1966, 88, 5132-5135. (15) Transition Metal Arene π -Complexes in Organic Synthesis and Catalysis; Kündig, E. P., Ed.; Springer International: 2004.

(16) (a) For the formation of a well-defined tetraaryl-Fe^{III} species, see: Alonso, P. J.; Arauzo, A. B.; Fornies, J.; Garcia-Monforte, M. A.; Martin, A.; Martinez, J. I.; Menjon, B.; Rillo, C.; Saiz-Garitaonandia, J. J. A Square-Planar Organoiron(III) Compound with a Spin-Admixed State. *Angew. Chem., Int. Ed.* **2006**, *45*, 6707–6711. (b) For the formation of a $[Me_4Fe^{III}]^-$ anion by transmetalation of MeMgBr onto FeCl₃, see: Al-Afyouni, M. H.; Fillman, K. L.; Brennessel, W. W.; Neidig, M. L. Isolation and Characterization of a Tetramethyliron(III)

Ferrate: An Intermediate in the Reduction Pathway of Ferric Salts with MeMgBr. J. Am. Chem. Soc. 2014, 136, 15457–15460.

(17) (a) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. Studies of Low-Coordinate Iron Dinitrogen Complexes. J. Am. Chem. Soc. 2006, 128, 756–769. (b) Lichtenberg, C.; Viciu, M.; Adelhardt, L.; Sutter, J.; Meyer, K.; de Bruin, B.; Grützmacher, H. Low-Valent Iron(I) Amido Olefin Complexes as Promotors for Dehydrogenation Reactions. Angew. Chem., Int. Ed. 2015, 54, 5766– 5771.

(18) The structure was an isomorph of the chloride analogue reported in: Döring, M.; Uhlig, E.; Dahlenburg, L. Die binuklearen Produkte der Umsetzung von Grignardreagenzien mit Acetylacetonaten der späten 3d-Elemente und ihre katalytische Wirkung bei der Kreuzkopplung. Z. Anorg. Allg. Chem. **1989**, 578, 58–68.

(19) (a) For the formation of polyphenyl-Fe^{II} species using PhLi, see: Fürstner, A.; Martin, R.; Krause, H.; Seidel, G.; Goddard, R.; Lehmann, C. W. Preparation, Structure, and Reactivity of Non-stabilized Organoiron Compounds. Implications for Iron-Catalyzed Cross Coupling Reactions. J. Am. Chem. Soc. 2008, 130, 8773-8787.
(b) Bedford, R. B.; Brenner, P. B.; Carter, E.; Cogswell, P. M.; Haddow, M. F.; Harvey, J. N.; Murphy, D. M.; Nunn, J.; Woodall, C. H. TMEDA in Iron-Catalyzed Kumada Coupling: Amine Adduct versus Homoleptic "ate" Complex Formation. Angew. Chem., Int. Ed. 2014, 53, 1804-1808. (c) Parchomyk, T.; Koszinowski, K. Ate Complexes in Iron-Catalyzed Cross-Coupling Reactions. Chem. - Eur. J. 2016, 22, 15609-15613.

(20) (a) Schilter, D.; Nilges, M. J.; Chakrabarti, M.; Lindahl, P. A.; Rauchfuss, T. B.; Stein, M. Mixed-Valence Nickel–Iron Dithiolate Models of the [NiFe]-Hydrogenase Active Site. *Inorg. Chem.* **2012**, *51*, 2338–2348. (b) Silakov, A.; Olsen, M. T.; Sproules, S.; Reijerse, E. J.; Rauchfuss, T. B.; Lubitz, W. EPR/ENDOR, Mössbauer, and Quantum-Chemical Investigations of Diiron Complexes Mimicking the Active Oxidized State of [FeFe]Hydrogenase. *Inorg. Chem.* **2012**, *51*, 8617–8628. (c) Stoian, S. A.; Hsieh, C.-H.; Singleton, M. L.; Casuras, A. F.; Darensbourg, M. Y.; McNeely, K.; Sweely, K.; Popescu, C. V. Hyperfine interactions and electron distribution in Fe^{II}Fe^I and Fe^IFe^I models for the active site of the [FeFe] hydrogenases: Mössbauer spectroscopy studies of low-spin Fe^I. *JBIC, J. Biol. Inorg. Chem.* **2013**, *18*, 609–622.

(21) (a) Bedford, R. B.; Brenner, P. B.; Carter, E.; Clifton, J.; Cogswell, P. M.; Gower, N. J.; Haddow, M. F.; Harvey, J. N.; Kehl, J. A.; Murphy, D. M.; Neeve, E. C.; Neidig, M. L.; Nunn, J.; Snyder, B. E. N.; Taylor, J. Iron Phosphine Catalyzed Cross-Coupling of Tetraorganoborates and related Group 13 Nucleophiles with Alkyl Halides. *Organometallics* **2014**, *33*, 5767–5780. (b) Ouyang, Z.; Meng, Y.; Cheng, J.; Xiao, J.; Gao, S.; Deng, L. Three- and Four-Coordinate Homoleptic Iron(I)–NHC Complexes: Synthesis and Characterization. *Organometallics* **2016**, *35*, 1361–1367.

(22) (a) Parker, S. F.; Peden, C. H. F. Iron benzene reactions: a matrix isolation Mössbauer investigation. *J. Organomet. Chem.* **1984**, 272, 411–416. (b) Blom, B.; Tan, G.; Enthaler, S.; Inoue, S.; Epping, J. D.; Driess, M. Bis-N-Heterocyclic Carbene (NHC) Stabilized η^6 -Arene Iron(0) Complexes: Synthesis, Structure, Reactivity, and Catalytic Activity. *J. Am. Chem. Soc.* **2013**, *135*, 18108–18120.

(23) Michaud, P.; Mariot, J.-P.; Varret, F.; Astruc, D. Improved Synthesis and Electronic Structure of the 19- and 20-Electron Complexes $[Fe(\eta^6-C_6Me_6)_2]^{n+}$, n = 0,1. J. Chem. Soc., Chem. Commun. 1982, 1383–1385.

(24) (a) Ittel, S. D.; Tolman, C. A. Metal Vapor Synthesis of Iron η^6 -Arene Complexes. *Organometallics* **1982**, *1*, 1432–1436. (b) Morand, P. D.; Francis, C. G. Modeling Macroscale Metal Vapor Reactions. 2. Bis(arene)iron Revisited. *Organometallics* **1985**, *4*, 1653–1659.

(25) (a) Römelt, M.; Ye, S.; Neese, F. Calibration of Modern Density Functional Theory Methods for the Prediction of ⁵⁷Fe Moössbauer Isomer Shifts: Meta-GGA and Double-Hybrid Functionals. *Inorg. Chem.* **2009**, *48*, 784–785. and references cited therein. (b) Low-spin Fe⁰ complexes: Fe(CO)₅, $(\eta^4-C_4H_4)$ Fe(CO)₃, $(\eta^6-C_6H_6)(\eta^4-C_6H_8)$ Fe, $(\eta^6-C_6H_6)(\eta^4-C_6H_6)$ Fe, $(\eta^6$ -biphenyl)Fe(SciOPP), and Fe[bis[*N*-(2,6diisopropylphenyl)imidazole-2-ylidene]methylene](η^6 -C₆H₆). Highspin Fe⁰ complex: $(\eta^6 - C_6 Me_6)_2$ Fe. Low-spin Fe^I complexes: (p-tolyl) $(Ph_2PCH_2CH_2PPh_2)_2Fe$, NaFe $(trop_2dae)(THF)_3$ (trop = 5H-dibenzo[a,d]cyclohepten-5-yl and dae = NCH₂CH₂N). See the SI for the corresponding reported nuclear parameters and related references. (c) Computation of the quadrupolar split was more problematic because this nuclear parameter is highly dependent on the symmetry of the occupied electronic levels. For several complexes in the benchmark depicted earlier,^{25b} the experimental value of ΔE_Q could not be reproduced with a satisfying accuracy. Therefore, minor differences between the optimized geometries and the experimental structures can induce strong discrepancies between the experimental and calculated values of ΔE_{0} . For a report of the computational analysis of quadrupolar splits, see: Pàpai, M.; Vankò, G. On Predicting Mössbauer Parameters of Iron-Containing Molecules with Density-Functional Theory. J. Chem. Theory Comput. 2013, 9, 5004-5020.

(26) (a) Ni, C.; Ellis, B. D.; Fettinger, J. C.; Long, G. J.; Power, P. P. Univalent transition metal complexes of arenes stabilized by a bulky terphenyl ligand: differences in the stability of Cr(I), Mn(I) or Fe(I) complexes. *Chem. Commun.* **2008**, 1014–1016. (b) Werncke, C. G.; Bunting, P. C.; Duhayon, C.; Long, J. R.; Bontemps, S.; Sabo-Etienne, S. Two-Coordinate Iron(I) Complex [$Fe{N(SiMe_3)_2}_2$]⁻: Synthesis, Properties, and Redox Activity. *Angew. Chem., Int. Ed.* **2015**, *54*, 245–248.

(27) (a) **1a** is a model for $(\eta^6 - C_6H_6)Fe^I(HC(C[Me]N-(2,6-diisopropylphenyl))_2)$ and **1c** for its PPh₃ analogue.^{17a}. (b) For **1b**, see ref 17b. (c) **1d** is a model for $(\eta^6 - C_6H_6)Fe^I(C_6H-2,6-(C_6H_2-2,4,6-iPr_3)_2-3,5-iPr_2).^{26a}$

(28) Schmidt, M. W.; Gordon, M. S. The construction and interpretation of MCSCF wavefunctions. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233–266.

(29) The same conclusion was reported by Norrby regarding $PhFe^{I}(THF)_{n}$ complexes: Hedström, A.; Lindstedt, E.; Norrby, P.-O. On the oxidation state of iron in iron-mediated C–C couplings. *J. Organomet. Chem.* **2013**, 748, 51–55.

(30) Moreover, the computed density at the ⁵⁷Fe nucleus in the monophenyl spin doublet species (η^6 -C₆H₆)Fe¹Ph would lead to an isomer shift of 0.67 mm s⁻¹ (computed $\rho_0 = 11827.64 \text{ e-}a_0^{-3}$), which is strongly different from the experimental value.

(31) $[Ph_3Fe^{II}]^-$ has been computed in the quintet spin state, which is the usual spin state for trishydrocarbyl ate-Fe^{II} species; see ref 19b and references cited therein. A sextet ground state has been found for $[Ph_4Fe^{III}]^-$; $[(\eta^6-C_6H_5Me)Fe^{I}Ph_2]^-$ has been computed in the doublet state.

(32) Zhurkin, F. E.; Wodrich, M. D.; Hu, X. A Monometallic Iron(I) Organoferrate. *Organometallics* **2017**, *36*, 499–501.

(33) This second scenario is preferred for the aryl–alkyl Kumada coupling mediated by SciOPP-Fe $^{\rm II}$ systems. 8