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► **To cite this version:**

Guillaume Lefèvre, Lidie Rousseau, Christian Herrero, Martin Clémancey, Geneviève Blondin, et al.. Formation of low-valent  $\text{Fe}^0$  and  $\text{Fe}^I$  species in Fe-catalyzed cross-coupling chemistry: key role of ate- $\text{Fe}^{II}$  intermediates. International Symposium on Metal Complexes 2019, Jun 2019, Debrecen, Hungary. cea-02329104

**HAL Id: cea-02329104**

**<https://cea.hal.science/cea-02329104>**

Submitted on 23 Oct 2019

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## Formation of low-valent Fe<sup>0</sup> and Fe<sup>I</sup> species in Fe-catalyzed cross-coupling chemistry : key role of *ate*-Fe<sup>II</sup> intermediates

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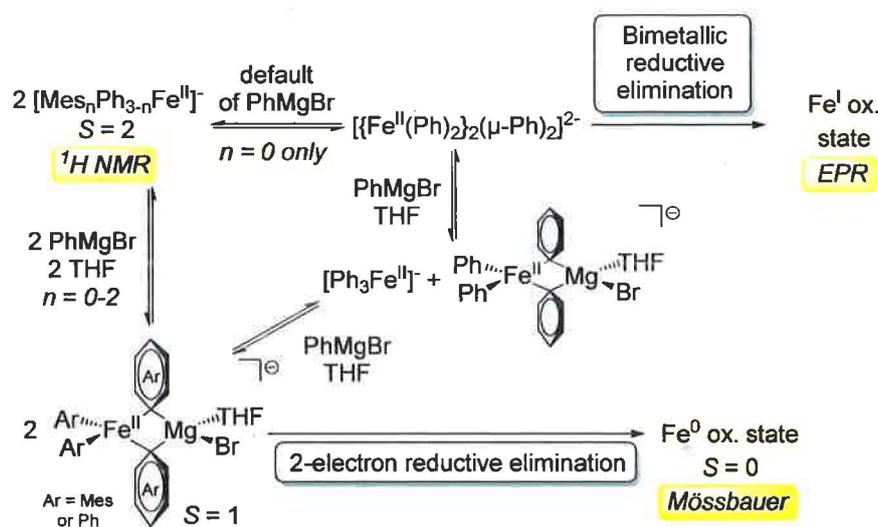
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*ate*-iron(II) species such as [Ar<sub>3</sub>Fe<sup>II</sup>]<sup>-</sup> (Ar = aryl) are key intermediates in Fe-catalyzed cross-coupling reactions between aryl Grignard reagents (ArMgX) and organic electrophiles. They can be active species in the catalytic cycle, or lead to Fe<sup>0</sup> and Fe<sup>I</sup> oxidation states.[1] In some cases, these low oxidation states can be themselves active in the coupling process.[2] However, their presence in the reaction medium most often leads to unwished organic byproducts. The development of new and efficient Fe-mediated cross-coupling processes therefore requires new frameworks enabling a fine control of the iron species distribution in the reaction medium, giving the possibility to inhibit the formation of unwanted oxidation states. So far, the formation of Fe<sup>0</sup> and Fe<sup>I</sup> species in cross-coupling mediums can be hardly controlled. A deep understanding of the formation mechanism of these oxidation states is thus fundamental if one wants to finely monitor their presence in the reaction medium.

We report in this work our efforts related to the understanding of the elementary steps connecting *ate* [Ar<sub>3</sub>Fe<sup>II</sup>]<sup>-</sup> species (Ar = Mes, Ph), formed by transmetallation of aryl Grignard reagents with FeCl<sub>2</sub>, to the formation of Fe<sup>0</sup> and Fe<sup>I</sup> low oxidation states. A particular focus is put on the role of the steric and electronic effects of the aryl group in the reduction process. We demonstrate that a steric decompression induced by progressive substitution of the mesityl groups in [Mes<sub>3</sub>Fe<sup>II</sup>]<sup>-</sup> by phenyl anions leads to the formation of [Mes<sub>n</sub>Ph<sub>3-n</sub>Fe<sup>II</sup>]<sup>-</sup> species (n = 0-2; observation by <sup>1</sup>H NMR). Thanks to this steric decompression, formation of Fe<sup>0</sup> and Fe<sup>I</sup> oxidation states is concomitantly observed by EPR and Mössbauer spectroscopies (Scheme 1).



**Schemes 1:** summary of the different pathways connecting *ate*-Fe<sup>II</sup> species with Fe<sup>0</sup> and Fe<sup>I</sup> oxidation states; *S* denotes the spin multiplicity.

Analysis of the reactivity pattern by DFT computation shows that at early stages of the transmetalation process, for low PhMgBr:Fe ratios, dimerization of  $[\text{Ph}_3\text{Fe}^{\text{II}}]^-$  into  $[\{\text{Fe}^{\text{II}}(\text{Ph})_2\}_2(\mu\text{-Ph})_2]^{2-}$  [3] leads to the formation of Fe<sup>I</sup> oxidation state by a bimetallic reductive elimination, enabled by an antiferromagnetic coupling between the two Fe<sup>II</sup> subunits. This dimerization is hampered for  $[\text{Mes}_n\text{Ph}_{3-n}\text{Fe}^{\text{II}}]^-$  intermediates involving one or more bulky aryl groups (Ar = Mes), which explains why Fe<sup>I</sup> oxidation state is not detected when sterically hindered Grignard reagents are used as nucleophiles in these systems. In the presence of an excess of PhMgBr, quaternarization of the Fe<sup>II</sup> ions in  $[\text{Mes}_n\text{Ph}_{3-n}\text{Fe}^{\text{II}}]^-$  species affords  $[\text{Mes}_n\text{Ph}_{4-n}\text{Fe}^{\text{II}} \bullet \text{MgBr}(\text{THF})]^-$  ( $n = 0-2$ ), which leads to the formation of Fe<sup>0</sup> oxidation state by 2-electron reductive elimination. This two-step mechanism involves two successive intersystem crossings, and connects high-spin  $[\text{Ar}_3\text{Fe}^{\text{II}}]^-$  species with a diamagnetic Fe<sup>0</sup> complex, demonstrating the importance of spin acceleration in this process.

Overall, this work enlightens the role played by steric and electronic factors in the evolution of *ate*-Fe<sup>II</sup> species towards the low-valent Fe<sup>0</sup> and Fe<sup>I</sup> oxidation states. Such mechanistic findings can give new guidelines for the design of finely tailored ligands in iron-mediated C–C bond formation strategies, opening up the possibility to selectively obtain a sole iron oxidation state upon the reduction process.[4]

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