



**HAL**  
open science

## Iron-catalyzed C–C cross-coupling in the absence of additional ligands: active species and off-cycle pathways

Guillaume Lefèvre, Lidie Rousseau, P. Dorlet, Christian Herrero, Martin Clémancey, J.-M Latour

### ► To cite this version:

Guillaume Lefèvre, Lidie Rousseau, P. Dorlet, Christian Herrero, Martin Clémancey, et al.. Iron-catalyzed C–C cross-coupling in the absence of additional ligands: active species and off-cycle pathways. International Conference on Coordination Chemistry, Jul 2018, Sendai, Japan. cea-02340033

**HAL Id: cea-02340033**

**<https://cea.hal.science/cea-02340033>**

Submitted on 30 Oct 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

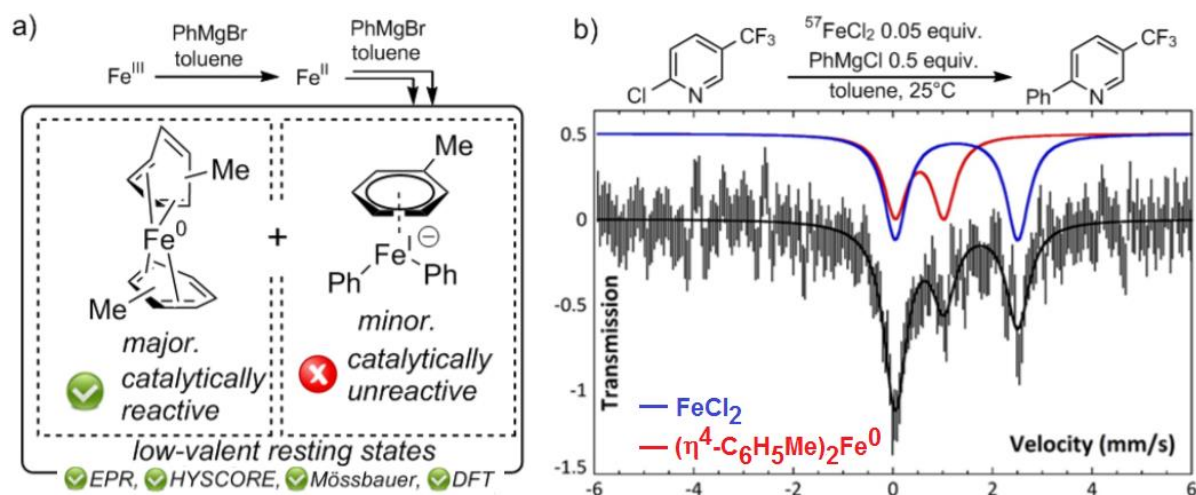
# Iron-catalyzed C—C cross-coupling in the absence of additional ligands: active species and off-cycle pathways

Guillaume Lefèvre,<sup>a\*</sup> Lidie Rousseau,<sup>a</sup> Pierre Dorlet,<sup>b</sup> Christian Herrero,<sup>c</sup>  
Martin Clémancey,<sup>d</sup> and Jean-Marc Latour<sup>d</sup>

<sup>a</sup> CEA Saclay, DRF/IRAMIS/NIMBE, Gif-sur-Yvette, France; <sup>b</sup> CEA Saclay, I2BC, Gif-sur-Yvette, France; <sup>c</sup> ICMMO, Univ. Paris-Sud Orsay, Orsay, France

<sup>d</sup> CEA Grenoble, BIG-LCBM-PMB, Grenoble, France  
guillaume.lefevre@cea.fr

Iron-catalyzed cross-coupling between a Grignard reagent RMgX and an electrophile R'—X was discovered by Kochi in the 1970s and witnessed recent improvements.<sup>1</sup> This transformation can be carried out using simple iron salts such as FeCl<sub>2</sub>, FeCl<sub>3</sub> or Fe(acac)<sub>3</sub> in the absence of additional ligand. However, these systems lead to short-lived reactive species, making *in-situ* mechanistic analysis challenging. By means of Mössbauer, cw- and pulse-EPR spectroscopies, we demonstrated that two arene-stabilized Fe<sup>0</sup> and Fe<sup>I</sup> resting states were obtained by reduction of the precursor in toluene (Fig. 1a). Analysis of the bulk revealed that the (η<sup>4</sup>-C<sub>6</sub>H<sub>5</sub>Me)<sub>2</sub>Fe<sup>0</sup> complex catalyzes efficiently aryl-heteroaryl coupling, via a Fe<sup>0</sup>/Fe<sup>II</sup> cycle (Fig. 1b).<sup>2</sup> Preliminary results moreover show that transient tris(aryl) species such as [Ph<sub>3</sub>Fe<sup>II</sup>]<sup>−</sup> are key intermediates in the formation of the lower oxidation states. Fe<sup>0</sup> and Fe<sup>I</sup> are respectively afforded by 2-electron reductive elimination and by redox disproportionation of the +II ox. state.



**Figure 1.** a) reduction of iron precursors (FeCl<sub>2/3</sub>, Fe(acac)<sub>3</sub>) by PhMgBr in toluene; b) iron distribution during a Ar-HetAr C—C cross-coupling (<sup>57</sup>Fe-Mössbauer, 80 K).

1 a) R. S. Smith, J. K. Kochi, *J. Org. Chem.*, **1976**, *41*, 502; b) I. Bauer, H.-J. Knölker, *Chem. Rev.*, **2015**, *115*, 3170; 2) M. Clémancey, T. Cantat, G. Blondin, J.-M. Latour, P. Dorlet, G. Lefèvre, *Inorg. Chem.*, **2017**, *56*, 3834.