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► To cite this version:

Lidie Rousseau, C. Herrero, M Clémancey, A Imberdis, G Blondin, et al.. Formation of low-valent Fe^0 and Fe^I species in Fe-catalyzed cross-coupling chemistry: key role of ate- Fe^{II} intermediates. GECOM-CONCOORD 2019, May 2019, Erquy, France. cea-02339541

HAL Id: cea-02339541

<https://cea.hal.science/cea-02339541v1>

Submitted on 30 Oct 2019

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Formation of low-valent Fe⁰ and Fe^I species in Fe-catalyzed cross-coupling chemistry: key role of ate-Fe^{II} intermediates

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Ate-iron(II) species such as [Ar₃Fe^{II}]⁻ (Ar = aryl) are key intermediates in Fe-catalyzed cross-coupling reactions between aryl Grignard reagents (ArMgX) and organic electrophiles.^[1] They can be active species in the catalytic cycle,^[2] or lead to Fe⁰ and Fe^I oxidation states. These low oxidation states were shown to be catalytically active in some cases, but they mostly lead to unwished organic byproducts.^[3,4]

This work relates a study of the evolution of [Ar₃Fe^{II}]⁻ complexes towards Fe⁰ and Fe^I oxidation states, through ¹H NMR, EPR and ⁵⁷Fe-Mössbauer spectroscopies, as well as DFT calculations, so as to discuss the role of both steric parameters and spin states in the reduction processes. Such mechanistic insights give a better understanding of iron-catalyzed C-C bond formation reactions, and can be exploited in the design of new ligands in order to selectively obtain a sole iron oxidation state in a catalytic process.

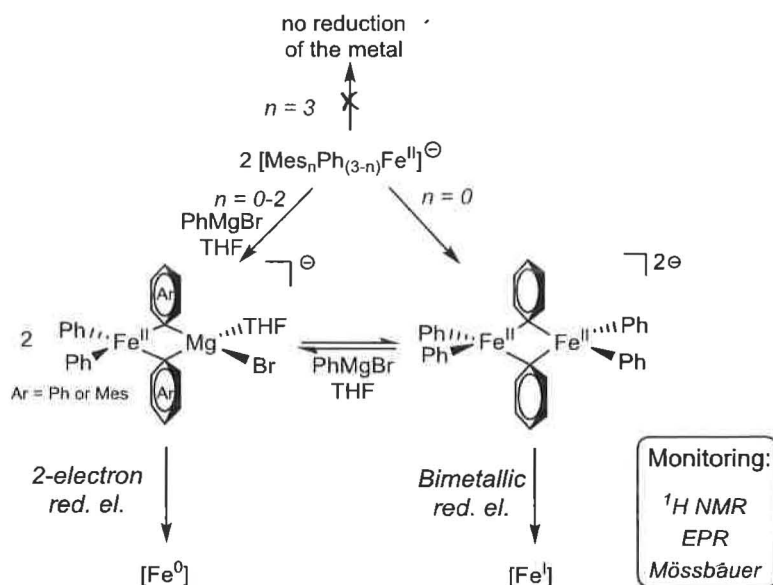


Figure 1: Pathways connecting ate-Fe^{II} (Mes = 2,4,6-trimethylphenyl) species with Fe⁰ and Fe^I oxidation states

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