

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 $[\text{Ar}_3\text{Fe}^{\text{II}}]^-$ (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 works relates a study of the evolution of $[\text{Ar}_3\text{Fe}^{\text{II}}]^-$ 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.

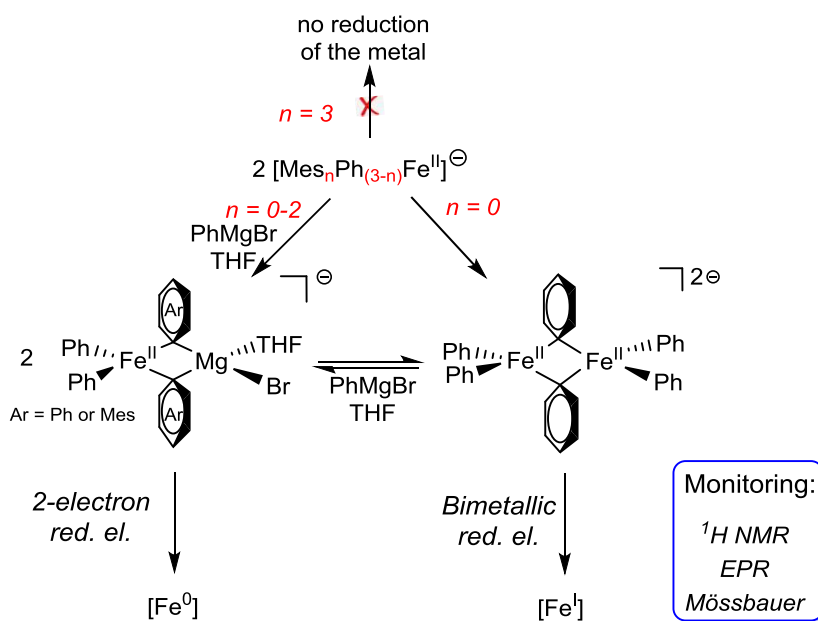


Figure 1: Pathways connecting ate-Fe^{II} (Mes = 2,4,6-trimethylphenyl) species with Fe⁰ and Fe^I oxidation states

[1] S. L. Daifuku, J. L. Kneebone, B. E. R. Snyder, M. L. Neidig, *J. Am. Chem. Soc.*, **2015**, 137, 11432

[2] P. B. Brenner, E. Carter, P. M. Cogswell, M. F. Haddow, J. N. Harvey, D. M. Murphy, J. Nunn, C. H. Woodall, R. B. Bedford, *Angew. Chem. Int. Ed.*, **2014**, 53, 1804

[3] F. E. Zhurkin, M. D. Woodrich, X. Hu, *Organometallics*, **2017**, 36, 499

[4] M. Clémancey, T. Cantat, G. Blondin, J.-M. Latour, P. Dorlet, G. Lefèvre, *Inorg. Chem.*, **2017**, 56, 3834