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

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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.¹ This transformation can be carried out using simple iron salts such as FeCl₂, FeCl₃ or Fe(acac)₃ 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 Fe⁰ and Fe^I resting states were obtained by reduction of the precursor in toluene (Fig. 1a). Analysis of the bulk revealed that the (η⁴-C₆H₅Me)₂Fe⁰ complex catalyzes efficiently aryl-heteroaryl coupling, via a Fe⁰/Fe^{II} cycle (Fig. 1b).² Preliminary results moreover show that transient tris(aryl) species such as [Ph₃Fe^{II}][−] are key intermediates in the formation of the lower oxidation states. Fe⁰ and Fe^I are respectively afforded by 2-electron reductive elimination and by redox disproportionation of the +II ox. state.

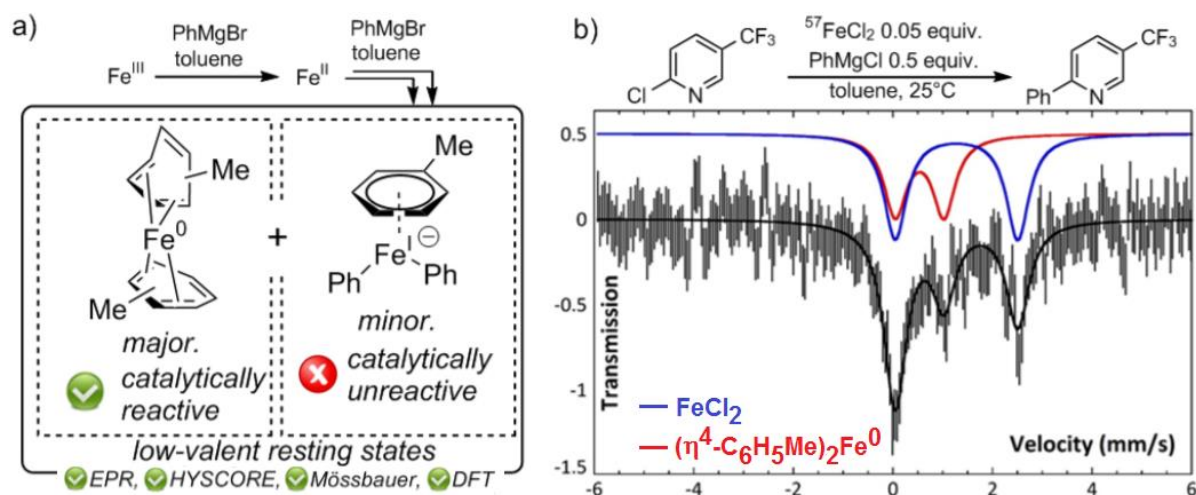


Figure 1. a) reduction of iron precursors (FeCl_{2/3}, Fe(acac)₃) by PhMgBr in toluene; b) iron distribution during a Ar-HetAr C—C cross-coupling (⁵⁷Fe-Mössbauer, 80 K).

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.