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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 $FeCl_2$, $FeCl_3$ 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 Fe^0 and Fe^I resting states were obtained by reduction of the precursor in toluene (Fig. 1a). Analysis of the bulk revealed that the $(\eta^4\text{-}C_6H_5Me)_2Fe^0$ complex catalyzes efficiently aryl-heteroaryl coupling, via a Fe^0/Fe^{II} cycle (Fig. 1b).[2] Preliminary results moreover show that transient tris(aryl) species such as $[Ph_3Fe^{II}]^-$ are key intermediates in the formation of the lower oxidation states. Fe^0 and Fe^I are respectively afforded by 2-electron reductive elimination and by redox disproportionation of the +II ox. state.

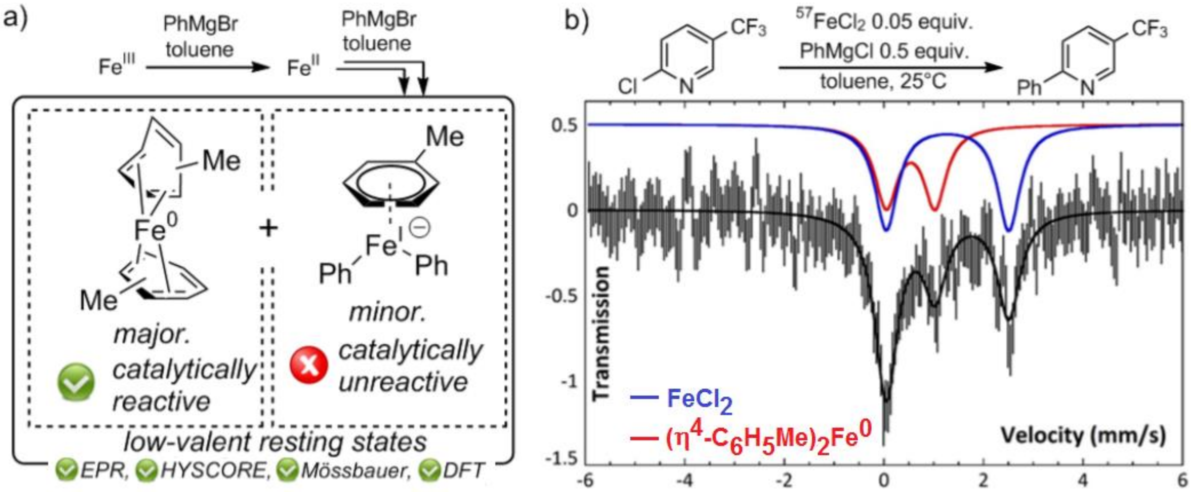

Figure 1. a) reduction of iron precursors ($FeCl_{2/3}$, $Fe(acac)_3$) by PhMgBr in toluene; b) iron distribution during a Ar-HetAr C–C cross-coupling (^{57}Fe-Mössbauer, 80 K).

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.