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Formation of low-valent Fe^0 and Fe^1 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 Fe^0 and Fe^1 oxidation states. These low oxidation states were shown to be catalytically active in some cases, but they mostly lead to unwanted organic byproducts.^[3,4]

This work relates a study of the evolution of $[\text{Ar}_3\text{Fe}^{\text{II}}]^-$ complexes towards Fe^0 and Fe^1 oxidation states, through ^1H NMR, EPR and ^{57}Fe -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.

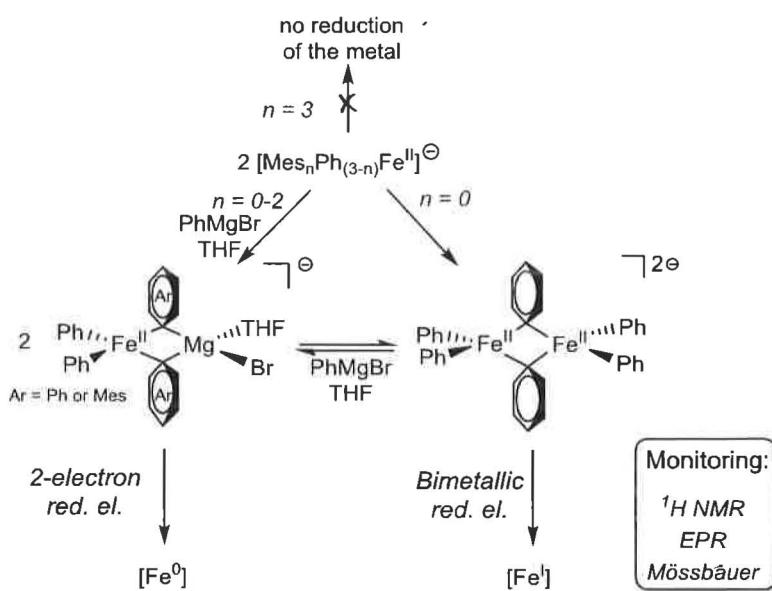


Figure 1: Pathways connecting ate- Fe^{II} ($\text{Mes} = 2,4,6$ -trimethylphenyl) species with Fe^0 and Fe^1 oxidation states

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