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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(I) species such as [Ar$_3$Fe$^{II}$]$^-$ (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 unwished organic byproducts.[3,4]

This work relates a study of the evolution of [Ar$_3$Fe$^{II}$]$^-$ complexes towards Fe$^0$ and Fe$^1$ oxidation states, through $^1$H 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$^{II}$ (Mes = 2,4,6-trimethylphenyl) species with Fe$^0$ and Fe$^1$ oxidation states