Formation of low-valent Fe⁰ and Fe¹ species in Fe-catalyzed cross-coupling chemistry: key role of ate-Fe¹Ι intermediates

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Ate-iron(II) species such as [Ar₃Fe]⁻ (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 Fe¹ 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 [Ar₃Fe]⁻ complexes towards Fe⁰ and Fe¹ 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 ates-Fe¹Ι (Mes = 2,4,6-trimethylphenyl) species with Fe⁰ and Fe¹ oxidation states]