

SYNTHESIS AND REACTIVITY OF LOW-VALENT IRON COMPLEXES FOR THEIR RELEVANCE IN C-H ACTIVATION AND SINGLE ELECTRON TRANSFER REACTIONS

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The use of bulky bidentate phosphino ligands (such as bis(diisopropylphosphino)ethane (dippe) and bis(diisopropylphosphino)propane (dipp)) has led to the synthesis and characterization of a variety of tetra-coordinate iron complexes in which iron is in the 0, +1 and +2 oxidation states. The isolation of these very sensitive complexes has allowed us to explore the links between iron alkyl and iron olefin complexes for the understanding of C-H activation and C-C bond formation mediated by low-valent iron complexes.^[1] Specifically, reaction of LFeCl₂ with EtMgBr under ethylene atmosphere affords the bis-ethylene complex LFe(η²-C₂H₄)₂ (**1**) that reacts with dienes to mediate C-H activation cascade that is coaxed to induce stereoselective C-C bond formation. Moreover, monoalkylation of LFeCl₂ (**2**) with 1 equivalent of Grignard reagent furnished the iron alkyl species LFeCIR (R = cyclohexyl, isobutyl) with a 14-electron count but stable towards β-hydride elimination at low temperatures. In contrast, the exhaustive alkylation of **2** with cyclohexylmagnesium bromide triggers two consecutive C-H activation reactions mediated by a single iron center. The resulting complex has a diene dihydride character in solution, whereas its structure in the solid state is more consistent with an η³-allyl iron hydride rendition featuring an additional agostic interaction.

Moreover, single electron transfer reactions from zero-valent complexes to R-X electrophiles (X = Cl, Br, OTf) give access to the corresponding Fe(I) complexes. These studies are a valuable probe for mechanistic studies in iron-catalyzed Kumada-type cross-coupling reactions, where there is still some controversial about the nature of the active iron catalyst.^[2, 3]

1) A. Casitas, H. Krause, R. Goddard, A. Fürstner *Angew. Chem. Int. Ed.* **2015**, *54*, 1521-1526

2) S. L. Daifuku, J. L. Kneebone, B. E. R. Snyder, M. L. Neidig *J. Am. Chem. Soc.* **2015**, *137*, 11432-11444

3) R. B. Bedford *Acc. Chem. Res.* **2015**, *48*, 1485-1493