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 (dippp)) 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 LFeCl$_2$ with EtMgBr under ethylene atmosphere affords the bis-ethylene complex LFe(η$_2$-C$_2$H$_4$)$_2$ (1) that reacts with dienes to mediate C-H activation cascade that is coaxed to induce stereoselective C-C bond formation. Moreover, monoalkylation of LFeCl$_2$ (2) with 1 equivalent of Grignard reagent furnished the iron alkyl species LFeClR (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 η$_3$-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]