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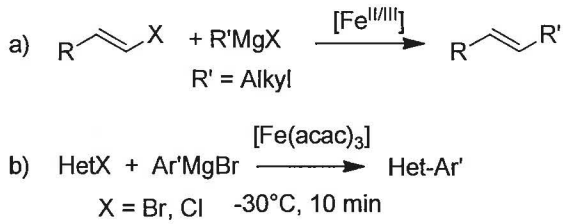
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Structural analysis and Quantitation of Low-valent Iron Species in Fe-Catalyzed Kumada Cross-Coupling: insights from Mössbauer and EPR Spectroscopies

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Iron chemistry is an inexpensive and non-toxic alternative to the noble-metal-based systems used in organometallic catalysis. The field of iron-catalyzed C—C bond formation, which was discovered by Kochi in the 1970s, is still in its infancy, and witnessed recent improvements thanks to the work of Fürstner, Nakamura and Bedford during the two last decades. [1] One of the main advantages of Fe-mediated Kumada cross-coupling is that no additional ligand is required, and simple salts such as $FeCl_2$, $FeCl_3$ or $Fe(acac)_3$ exhibit excellent catalytic performances (Scheme 1).

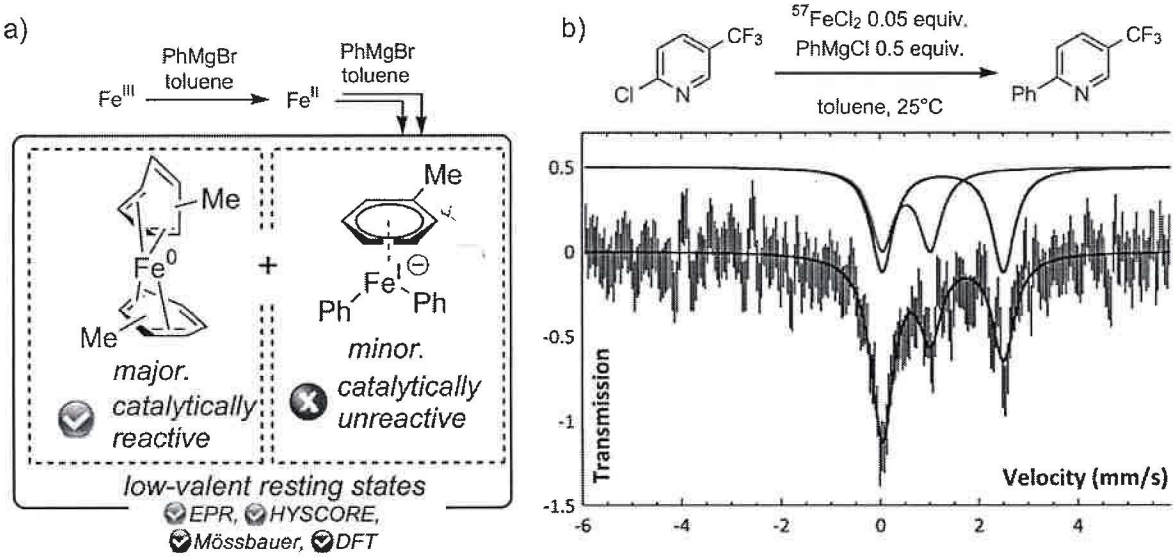


Scheme 1. Representative examples of Fe-catalyzed C–C cross-couplings.

However, the mechanistic features of such transformations are still unclear, since numerous oxidation states can be reached by iron upon reduction by Grignard reagents. The absence of stabilizing co-ligand moreover leads to the formation of short-lived active species, thus making *in-situ* mechanistic investigations challenging. An illustrating example of these difficulties is the very recent structural elucidation of the paramagnetic cluster $[Fe_8Me_{12}]^-$ by Neidig. This allowed the identification of a species whose EPR spectrum had first been reported by Kochi in the context of the reduction of $FeCl_3$ by MeMgBr almost 40 years earlier. [2,3]

By means of Mössbauer, cw-EPR and pulsed-EPR spectroscopies, we demonstrated that the reduction of FeX_n salts (X = $acac^-$, halide, n = 2 or 3) by aryl Grignard reagents in toluene led to the formation of two low-valent arene-stabilized resting states (Scheme 2a). A major

bis-arene-ligated diamagnetic Fe^0 species $(\eta^4\text{-}C_6H_5Me)_2Fe^0$ (accounting for ca. 85% of the overall iron quantity), and a homoleptic organoferrate low-spin Fe^I minor complex $[(\eta^6\text{-}C_6H_5Me)Fe^I(Ph)_2]^-$ (S = 1/2, ca. 15% of the overall iron quantity) could therefore be characterized.



Scheme 2. a) low-valent resting states obtained by reduction of FeX_n (X = $acac^-$, halide, n = 2 or 3) by PhMgBr in toluene; b) *In-situ* "Mössbauer snapshot" of the iron distribution during a aryl-heteroaryl Kumada cross-coupling process (recording conditions: frozen solution; 80 K – blue lines: $FeCl_2$, red lines: $(\eta^4\text{-}C_6H_5Me)_2Fe^0$).

The reactivity of these low-valent Fe^I and Fe^0 species in aryl-heteroaryl Kumada cross-coupling conditions was also investigated. Mössbauer analysis showed that the zerovalent Fe^0 species can be used efficiently as a catalyst in this reaction. However, the Fe^I oxidation state does not exhibit any reactivity, as attested by EPR spectroscopy. In-situ Mössbauer analysis of the reaction bulk reveals that both Fe^0 and Fe^{II} oxidation states coexist during the cross-coupling process (Scheme 2b), suggesting that a Fe^0/Fe^{II} redox cycle can be operative in such systems. [4]

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