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Lidie Rousseau, Guillaume Lefèvre

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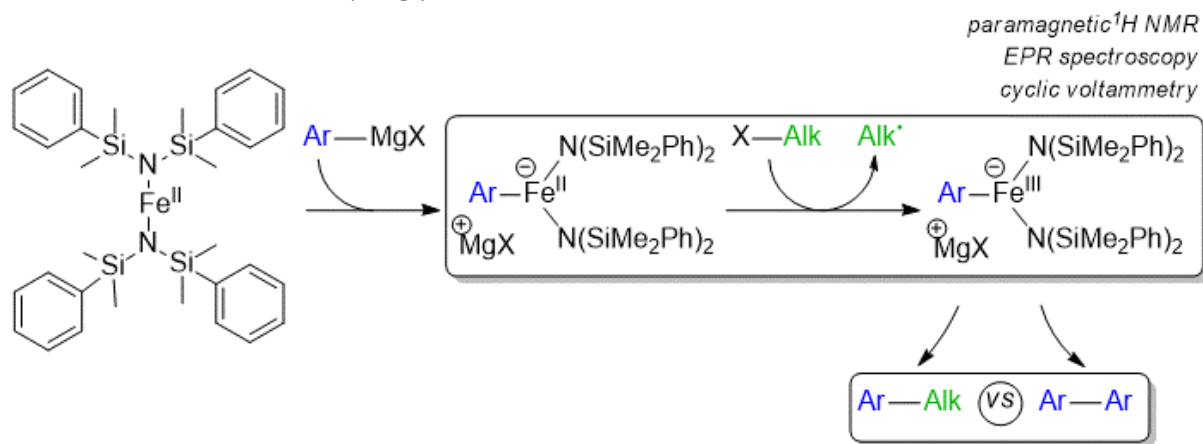
Lidie Rousseau ^{a,b}, Guillaume Lefèvre*^a

^a CSB2D, Institute of Chemistry for Life and Health Sciences, Chimie ParisTech, PSL University, CNRS, 75005 Paris, France ;

^b LCMCE, NIMBE, CEA, CNRS, Univ. Paris-Saclay, 91191 Gif-sur-Yvette, France ;

lidie.rousseau@chimieparistech.psl.eu

Iron catalysis has raised a great interest in the organometallic field since the 1970s and the first successful Fe-catalyzed cross-coupling reactions developed by Kochi,¹ as it is a cheaper, more earth-abundant and less toxic alternative to many other transition metals. Kumada-type reactions between aryl Grignard reagents and organic electrophiles are of high importance, but a significant issue remains in the competition between effective cross-coupling, and homocoupling of the Grignard reagent affording unwanted symmetrical biaryl byproducts. Nakamura² proposed an explanation for the large presence of this byproduct in the presence of several aryl groups on the iron center resulting from multiple Mg-to-Fe transmetallations, and proposed the addition of a source of fluoride anions to block this possibility. However, our study of the catalytic behavior of the bulky silylamide iron(II) complex³ [Fe(N(SiMe₂Ph)₂)₂] in an aryl-alkyl cross-coupling reaction refutes the hypothesis that the multi-transmetallations are the only cause of homocoupling. The steric hindrance of the ligands effectively prevents more than one transmetallation on the iron atom, affording a stable Ar–Fe bond, but it does not quite impede the homocoupling. Stoichiometric and catalytic tests involving ¹H paramagnetic NMR, EPR spectroscopy and cyclic voltammetry were lead in order to discuss the mechanism of the reaction, evidencing transient Fe^{III} species responsible for the formation of the homocoupling product.



¹ Kochi, J. K.; Tamura, M.; *J. Am. Chem. Soc.* **1971**, *93* (6), 1483–1485.

² Hatakeyama, T.; Nakamura, M.; *J. Am. Chem. Soc.* **2007**, *129* (32), 9844–9845.

³ Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P.; *J. Am. Chem. Soc.* **1989**, *111* (12), 4338–4345.