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## Aryl-Alkyl Cross-coupling *versus* Homo-coupling: A Mechanistic Study On The Catalytic Performance Of A Bulky Silylamide Iron(II) Complex

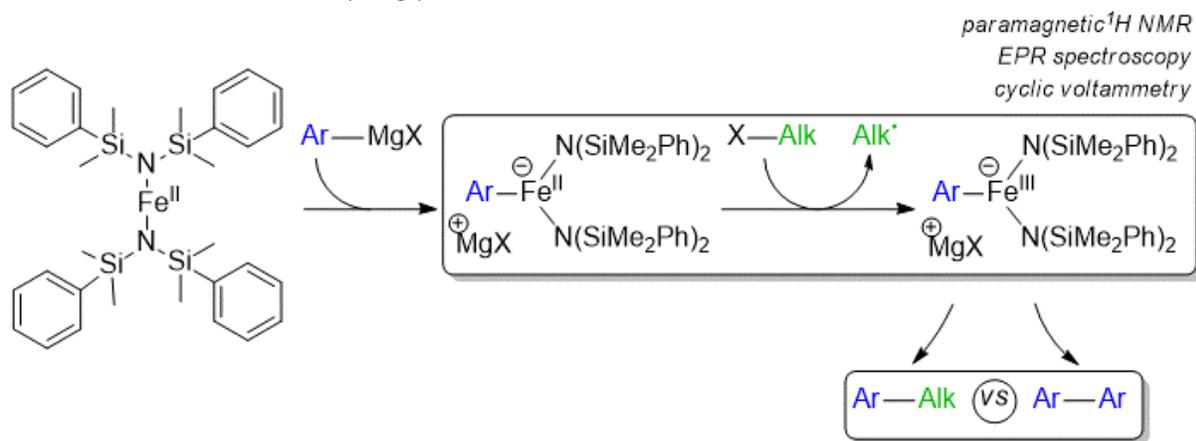
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Iron catalysis has raised a great interest in the organometallic field since the 1970s and the first successful Fe-catalyzed cross-coupling reactions developed by Kochi,<sup>1</sup> as it is a cheaper, more earth-abundant and less toxic alternative 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. Nakamura<sup>2</sup> 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) complex<sup>3</sup> [Fe(N(SiMe<sub>2</sub>Ph)<sub>2</sub>)<sub>2</sub>] 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 <sup>1</sup>H paramagnetic NMR, EPR spectroscopy and cyclic voltammetry were lead in order to discuss the mechanism of the reaction, evidencing transient Fe<sup>III</sup> species responsible for the formation of the homocoupling product.



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

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

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