

Expected and unexpected role of a second copper unit in copper catalyzed cross coupling reactions: the mechanism of the oxidative addition of aryl halides to copper(I) complexes

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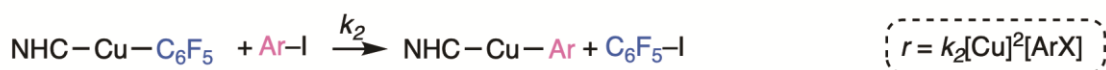
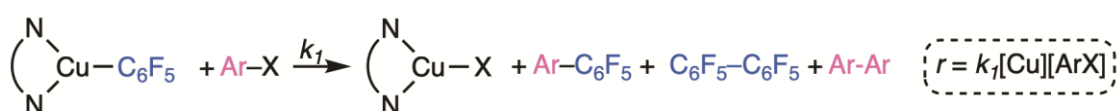
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Copper catalyzed cross-coupling reactions are being developed to replace those catalyzed by palladium, that is an much more expensive and scarce metal. One of the most remarkable differences between these metals is that the oxidative addition of alkyl halides to Pd(0) is fast and produces stable Pd(II) complexes, while the oxidative addition to Cu(I) is very slow, producing unstable Cu(III). Recently, our research group has undertaken a detailed study of the mechanism of oxidative addition / reductive elimination reactions of aryl halides to copper(I) complexes. As shown in the Scheme 1, in trigonal planar complexes of the type [Cu(bipy)(C₆F₅)] the oxidative addition of Ar-I produces C₆F₅-Ar and also C₆F₅-C₆F₅ and Ar-Ar, indicating that some kind of transmetalation between copper complexes has occurred, although the reaction kinetics are of order one in the metal. Paradoxically, when the linear complex [Cu(NHC)(C₆F₅)] is used, the reaction does not produce homocoupling products, but the rate law is second order on Cu.



NHC = N-Heterocyclic Carbene

Scheme 1

In this communication these experimental results and their mechanistic interpretations based on kinetic data and DFT calculations will be shown.

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