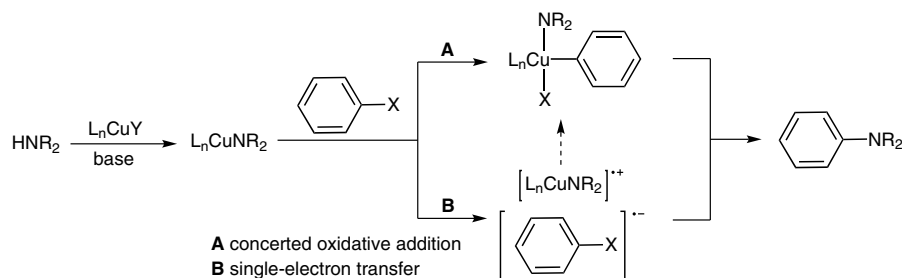


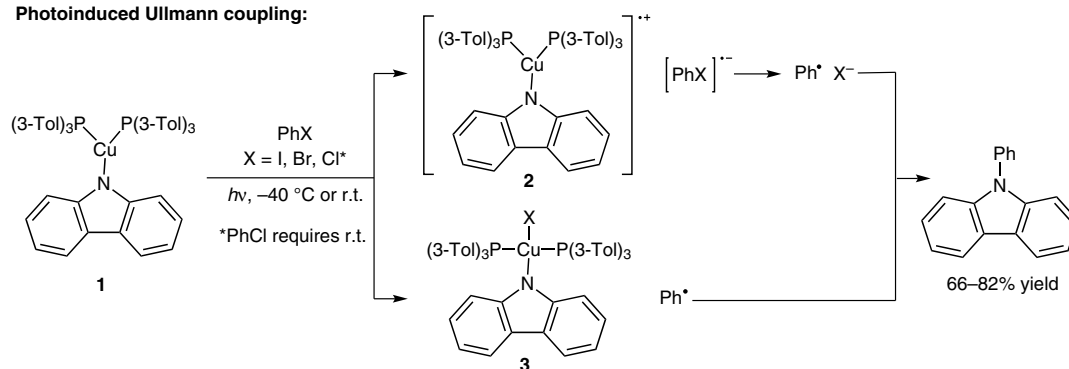
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Photoinduced Ullmann C–N Coupling: Demonstrating the Viability of a Radical Pathway
Science **2012**, 338, 647–651.

C–N Bond Formation Through a Single-Electron Transfer Pathway

Ullmann coupling and possible mechanistic pathways:



Photoinduced Ullmann coupling:



Significance: For the last century, Ullmann couplings have been used to synthesize anilines from amines and aryl halides, despite the relatively harsh conditions necessary for C–N bond formation (stoichiometric copper under high temperatures). Although many groups have focused their attention on improving the traditional Ullmann coupling, the mechanism of aryl halide bond cleavage has remained unsettled within the chemical community. Two possible mechanistic pathways include concerted oxidative addition (**A**) and single-electron transfer (**B**). In this report, Peters, Fu and co-workers provide the first experimental evidence for a single-electron transfer mechanism.

Comment: Radical intermediates were able to be observed for the first time during an Ullmann reaction by the development of a mild, photo-induced coupling of aryl halides and carbazole. Carbazole-containing copper complex **1** is excited with 300–400 nm light, which promotes an electron-transfer reaction, ultimately leading to an aryl radical. Reaction of the aryl radical with the resulting copper-carbazole complex (**2** or **3**) leads to C–N bond formation. It was shown that this transformation proceeds at -40°C with phenyl iodide or phenyl bromide. For coupling to phenyl chloride, longer reaction times at room temperature were necessary. The coupling does not occur in the dark and kinetic isotope effects, radical traps, competition experiments, by-product formation analysis, and EPR spectra all support one-electron chemistry in the photo-induced Ullmann coupling.

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