C−C Bond Formation Through Iridium Photoredox and Ni Catalysis

Michaela Carlson Literature Seminar October 14, 2014

The formation of carbon-carbon bonds is a recurring challenge owing to their pervasiveness. Thus, while many C−C cross-coupling reactions exist, there is always an interest in new methods. A new photochemical route for the formation of C−C bonds has been developed within the past ten years [1,2]. This method is of interest to inorganic chemists because it entails metal-based redox agents. In conjunction with metal-based photosensitizers, this new reactivity is termed "dual catalysis" [2].

Dual catalysis involves two concurrent catalytic cycles to effect C−C cross-coupling. The process of this dual catalysis entails the following steps: reduction of the excited state of a photosensitizer, formation of an aryl radical, oxidative addition of the radical to a transition metal, and reductive elimination of the desired C−C product. For the reduction of an excited state step, a transition metal reduces the excited state of a photosensitizer via a single electron transfer (SET). This reduced photosensitizer is then reductively quenched, via a SET, by reagents that generate the desired aryl radical, Ar•. In the second catalytic cycle, this radical attacks an unsaturated metal center and the resulting Ar−M complex, after a transmetalation process, undergoes reductive elimination of the desired C−C product (Figure 1) [1,2,3,4].

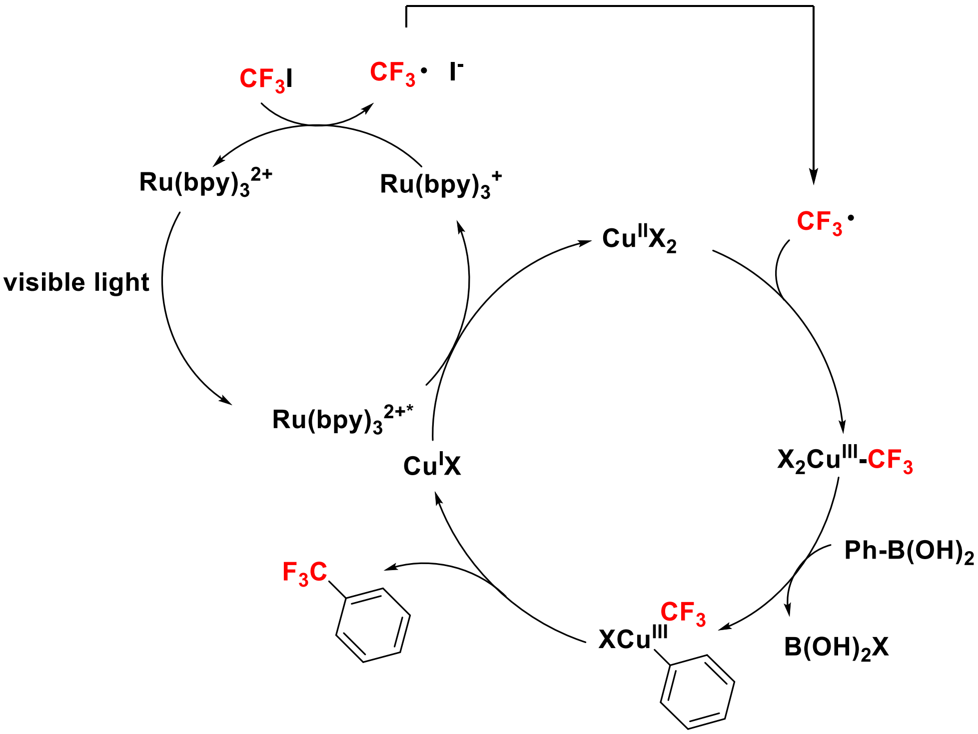

Figure 1: Proposed mechanism of dual catalysis $Ru(bpy)_3^{2+}$ and CuOAc [2]

The latest advancements to this relatively young field of dual catalysis use Ir(III) instead of Ru(II) as the photosensitizer due to its strong reductive behavior (Figure 3) [5,6]. To form a radical using $[Ru(bpy)_3]Cl_2$, an electron donor must be used to generate Ru(I), a strong reductant. However, the excited state of some Ir(III) complexes are able to directly reduce not only aryl radicals but also C−B and C−COOH bonds [5,7,8]. The reduction strength of Ir(III)* can be tuned via the ligands attached to Ir to become stronger or weaker [6,9]. Thus, Ir(III) complexes can be used to form radicals for a larger variety of reagents than Ru(II).

One of the newest implementations of dual catalysis uses Ir(III)-based photosensitizers in conjunction with a Ni(0) catalyst to couple certain amino acid derivatives with a variety of aryl halides (Figure 2). The amino acid derivative is first deprotonated via a weak base. After photoexcitation to Ir(III)* occurs, a SET releases CO_2 and an alkyl radical. This alkyl radical then attacks the unsaturated Ni(II), which forms a saturated Ni(III) species which reductively eliminates the desired product. The Ni(I) then via a SET reduces the Ir(IV) to a Ir(III), reforming both catalysts.[7]

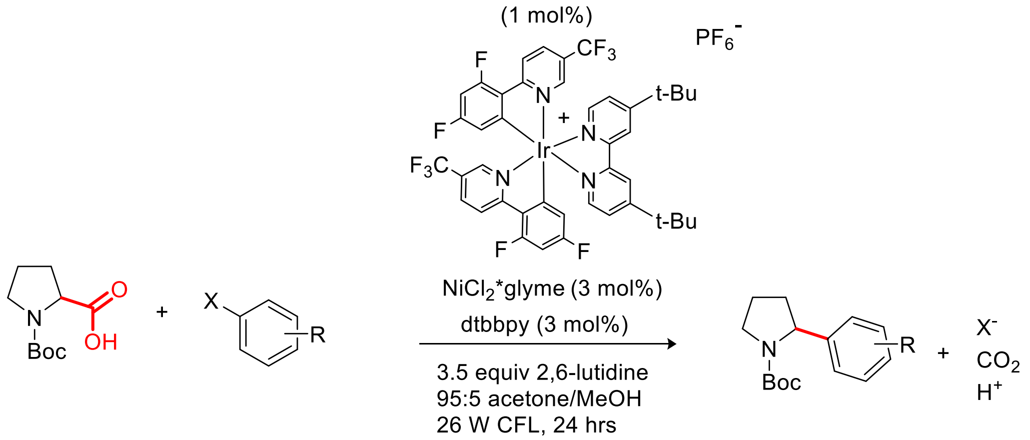

Figure 2: Reaction to couple aryl halides with Boc-protected amino acid derivatives [7]

Organoboron cross-coupling reactions can also be achieved via dual catalysis of Ir(III)/Ni(0) catalysts. Instead of the traditional two-electron mechanism, this process utilizes one-electron transfers. This system, also, supports formation of $C_{sp}^{3}-C_{sp}^{2}$ bonds, unlike the traditional method which generally effect $C_{sp}^{2}-C_{sp}^{2}$. This difference is attributed to stronger heterolytic C−B bonds being more reactive. This one-electron mechanism tolerates a wide range of electrophiles, such as protic functional groups, amino acid derivatives and nitrogen-containing heteroaryl bromides [8].

In summary, dual catalysis is an emerging class of reactions that utilize both photoredox and transition metal-based catalysts and is still a developing field. The latest advancements in the field highlight the versatility of the recently popularized Ir-based phenylpyridine sensitizers. It is noteworthy due to the unusual mechanisms that feature multiple SET pathways. However, one weakness is the lack of versatility within the coupling reagents. The reduction potential of the Ir(III)* must be greater than the oxidation potential of the radical-forming reagent. Due to this fact, this system cannot be overly generalized.

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