

University of Louisville
Department of Chemistry

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Literature Seminar

When: September 3, 2020
Time: 2:30 PM
Location: Microsoft TEAMS

Elucidation of Nickel-Catalyzed Cross-Coupling Reductive Elimination Reactions Mechanism through MLCT State

Abstract

Transition metal-catalyzed cross-coupling reactions have profoundly changed the protocols for the construction of natural products, building blocks for supramolecular chemistry and self-assembly, organic materials and polymers, and lead compounds in medicinal chemistry from simpler entities. These methods being largely limited to sp^2 -hybridised carbon reagents until recently, the advent of cross-coupling of sp^3 -hybridized organoboron reagents via novel photoredox/nickel dual catalysis represented a new paradigm in transition metal catalysis. The development invoked an interest in understanding the catalytic mechanism of organometallic Nickel aryl halide complexes relevant to cross-coupling reactions. This seminar will attempt to understand the catalytic mechanism of the Ni complex.

First, the viability of excited-state organometallic (Ni) catalysis via direct photoexcitation and triplet sensitization by energy transfer will be shown in terms of $C(sp^3)$ -H functionalization¹ of organic compounds and halide (bromine) radical generation from excited state Ni catalyst. Then, a detailed photophysics and photochemistry of Ni catalyst will be uncovered with the help of computational (DFT and TDD-DFT) and transient absorption spectroscopic methods². This will be followed by illumination of the Ni catalyst possessing a long-lived charge-transfer (MLCT) state which can participate in photoinduced disproportionation² reactions that holds important implications for the interpretation and design of photochemical reactions with Ni. Finally, multiconfigurational methods will illustrate that the long-lived MLCT state of the Ni catalyst is directly involved in reductive elimination of cross-coupling reactions owing to its intramolecular oxidized nature³ of the excited state.

References

1. Heitz, Drew R.; Tellis, John C.; Molander, Gary A. Photochemical Nickel-Catalyzed C–H arylation: Synthetic Scope and Mechanistic Investigations. *J. Am. Chem. Soc.* **2016**, *138*, 12715-12718.
2. Shields, Benjamin J.; Kudisch, Bryan; Scholes, Gregory D.; Doyle, Abigail G.; Long-Lived Charge-Transfer States of Nickel(II) Aryl Halide Complexes Facilitate Bimolecular Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **2018**, *140*, 3035-3039.
3. Ma, Pengchen; Wang, Shaohong; Chen, Hui. Reactivity of Transition-Metal Complexes in Excited States: C–O Bond Coupling Reductive Elimination of a Ni(II) Complex is Elicited by the Metal-to-Ligand Charge Transfer State. *ACS Catal.* **2020**, *10*, 1-6.