

화학과 세미나

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Photo-induced reductive elimination reactions of organonickel complexes

While photoexcitation had become one of the acknowledged methods to activate Ni-catalyzed cross-coupling reactions, factors that determine the photoactivity of organonickel complexes are still under debates. In this presentation, the C-to-Ni charge transfer (CT) states were proposed as key excited states for photo-induced reductive elimination (RE) reactions of nickelacycles, merging two different examples of photo-induced RE reactions:

1) C-S bond-forming RE reactions of Ni^{II} complexes and 2) C-C bond-forming RE reactions of Ni^{III} and Ni^{IV} complexes.

The excited-state RE activities of nickelacycles with the thiacycloneophyl ($-\text{SC}_6\text{H}_4\text{-O-C(CH}_3)_2\text{CH}_2-$) ligand have been measured with five different ancillary ligands, revealing that the RE activities depend on the excitation energy and are independent of the ancillary ligand.¹ The electronic structural analyses utilizing electronic absorption (Abs) and magnetic circular dichroism (MCD) spectroscopies in combination with density functional theory (DFT) computations have uncovered that d-d excitations can facilitate Ni-C bond homolysis to generate Ni^{I} intermediate via intersystem crossing to a dissociative (C-to-Ni CT) state. The sequential C-S bond formation occurring from Ni^{I} intermediate eventually produces the cross-coupled product.

Alternatively, with cycloneophyl ($-\text{C}_6\text{H}_4\text{-O-C(CH}_3)_2\text{CH}_2-$) Ni^{III} and Ni^{IV} complexes, C-to-Ni CT excited states are directly accessible utilizing visible light sources, exhibiting 10^5 -time enhanced C-C bond-forming activity compared to the ground state. These studies emphasize that the RE reactions can be promoted by accessing C-to-Ni CT excited states, showing the significance of an electronic structure level understanding of organometallic reaction mechanisms. Furthermore, an understanding of excited-state RE reactions of organonickel complexes can be utilized to design the Ni-catalyzed cross-coupling reactions incorporating photoexcitations.

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