

PHOTOPHYSICS OF Ni^{II} PYRIDINOPHANE PHOTOCATALYSTS USED FOR C-O CROSS-COUPLING REACTIONS PROBED VIA FEMTOSECOND OPTICAL ABSORPTION SPECTROSCOPY

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Ni catalysis has garnered much attention over the past decades as a low-cost, abundant alternative to Pd catalysis. Ni^{I/III} cycles are thought to be critically important to the cross-coupling step in the catalytic cycle, but typical Ni catalysts contain bipyridine ligands which are generally unable to stabilize high-valent Ni^{III}. Tridentate pyridinophane ligands, on the other hand, are able to stabilize both high- and low-valent Ni, making them optimal ligands to use in Ni catalysis. Tridentate pyridinophane Ni^{II} dichloride complexes form a highly reactive Ni^I catalyst upon photoexcitation of the metal-to-ligand charge transfer (MLCT) band. This process is thought to occur from the ³d-d charge transfer state, though there is no experimental evidence for this and little is known about the photophysics following photoexcitation of the MLCT transition. Optical transient absorption gives insight into the photophysics of the catalyst formation. We report highly-efficient back electron transfer (BET) following MLCT excitation. We will vary the excitation energy to investigate if the BET is suppressed or enhanced. We will perform transient XUV spectroscopy to probe the dynamics at the Ni M-edge and determine the states that are involved in the Ni^I catalyst formation.