

Hidden Assemblies Switching Chemoselectivity in Photocatalytic Borylation Reactions of 1,4-Dicyanobenzene

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The reaction of Lewis-acid-base adducts obtained of *N*-heterocyclic carbenes and boranes have found application in alkene, arene, and alkyne functionalization under photochemical and photocatalytic conditions.^[1] The accessible product scope differs significantly in reactivity and selectivity from thermal hydroboration reactions. Intrigued by the mechanistic postulate of Curran and co-workers on their photocatalytic formal 1,4 hydroboration of electron-deficient alkenes^[2], we set out on a mechanistic study and to not only revise that mechanism but also use the gained understanding to derive the originally desired substitution reaction. The talk will provide complementary computational and spectroscopic (transient absorption spectroscopy, NMR) information on the mechanism at hand and will highlight the importance of variance in spatial and temporal evolution of the key open-shell intermediates for chemoselectivity.

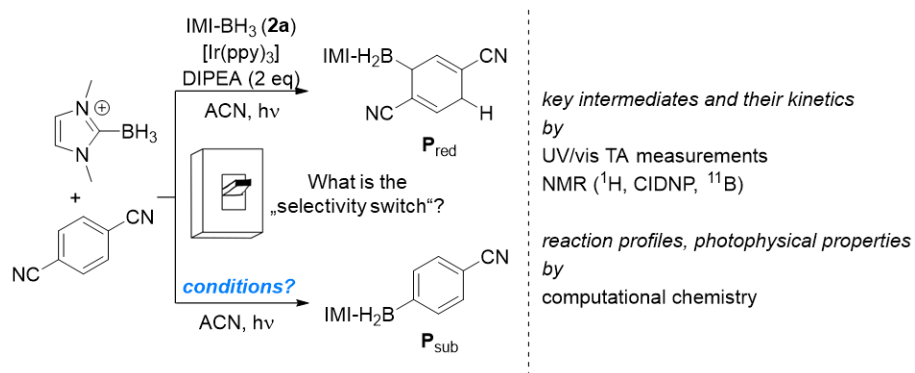


Figure 1: Reactions under study with identification of the “switch” by combination of spectroscopy and computational chemistry.

[1] D. P. Curran *et al.* *Angew. Chem. Int. Ed.* 2011, **50**, 10294, 10.1002/anie.201102717.

[2] W. Dai *et al.*, *J. Am. Chem. Soc.* 2020, **142**, 6261, 10.1021/jacs.0c00490.