

From Flatland to the mountain top: a quest for the metal-free catalytic C-H borylation reaction

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Frustrated Lewis Pairs (FLPs) have been used as catalysts in many important transformations, including notably the hydrogenation reaction.¹ Whereas FLP are defined as Lewis pairs having no interaction between a Lewis acid and a Lewis base because of steric or geometric constraints, many Lewis pairs exhibit typical FLP chemistry.² To better exemplify how the classic definition of a FLP does not perfectly describe FLP catalysis, we developed several generations of metal-free catalysts to do the C_{sp2}-H and C_{sp3}-H bond activation. The first generation of catalysts relied on the 1-BH₂-2-NR₂-C₆H₄ framework, where the -BH₂ and the -NR₂ were shown to activate C-H bonds of heteroarenes.^{3,4} It was shown, in a second generation of catalysts, that the fluoride-protected analogues could be used as air-stable precatalysts for the same borylation reaction.⁵ While this reaction could be carried on the kilogram scale, in presented several drawbacks, including an intolerance to many functional groups. To circumvent these problems, we developed an isodesmic borylation, aka transfer borylation, using a third generation of catalysts.⁶ By avoiding the presence of reactive B-H moieties throughout the catalytic cycle, we have been able to borylate heteroarenes, alkynes, and electron-rich alkenes in high yields.^{7,8} Using the knowledge developed in these processes, we are now looking at one of the most challenging transformation for metal-free and FLP chemistry: the C_{sp3}-H borylation, which was demonstrated in stoichiometric fashion.^{9,10} This presentation will present the advances that were made in order to better understand and do the rational design of novel generations of catalysts.

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