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

Frédéric-Georges Fontaine

Département de Chimie, Université Laval,
1045 Avenue de la Médecine, Québec (Qc), Canada G1V 0A6
frederic.fontaine@chm.ulaval.ca , http://fontaine.chm.ulaval.ca/

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-BH_2-2-NR_2-C_6H_4 framework, where the -BH_2 and the -NR_2 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.

References:

1) Stephan, D. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032. 2) Fontaine, F.-G; Rochette, É. *Acc. Chem. Res.* **2018,** *51*, 454-464. 3) Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. *Science* **2015**, *349*, 513 – 516. 4) Légaré Lavergne, J.; Jayaraman, A.; Misal-Castro, L.; Rochette, É.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2017**, *139*, 14714-14723. 5) Légaré, M.-A.; Rochette, É; Légaré Lavergne, J.; Bouchard, N.; Fontaine, F-G. *Chem. Commun.* **2016**, *52*, 5387-5390. 6) Rochette, É.; Desrosiers, V.; Soltani, Y.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2019**, *141*, 12305-12311. 7) Desrosiers, V.; Zavaleta Garcia, C.; Fontaine, F.-G. *ACS Catal.* **2020**, *10*, 11046-11056. 8) Desrosiers, V.; Knight, S. M.; Fontaine, F.-G. *ACS Catal.* **2022**, *12*, 13609-13618. 9) Someswara Ashwathappa, P. K.; Higashi, T.; Desrosiers, V.; Omana, A. A.; Fontaine, F-G. *Angew. Chem. Int. Ed.* **2023**, *e202309295.*

2)

UNIVERSITÉ LAVAL

Frédéric-Georges Fontaine *was born in Montréal in 1975. He received his Ph.D in 2002 at the Université de Montréal with Prof. Davit Zargarian, working on the nickel catalysts for silane polymerization. He was an NSERC postdoctoral fellow at UC Berkeley in 2003 and 2004 with Prof. T. Don Tilley developing scandium catalysts for the hydromethanation reaction. He joined Laval University in Quebec City, Canada, in July 2004 and he became full professor in 2013. He has been working on the development of metal-free catalysts for the C-H and CO_2 functionalization reactions and he has been developing materials for the CO_2 utilization reaction and the recycling of electronic waste. He has been holding a Canada Research Chair in Green Catalysis and Metal-Free Processes since 2018 and he is the director of CIRCUIT, an NSERC training center on CO_2 utilization technologies in industrial applications. The quality of his teaching and training was recognized by more than 20 awards. His ground-breaking research, published in top tier journals like Science, Journal of the American Chemical Society and Angewandte Chemie was awarded several recognitions, such as the discovery of the year 2015 by Quebec Science and he was chosen as a JSPS fellow for touring Japan in 2019.*