

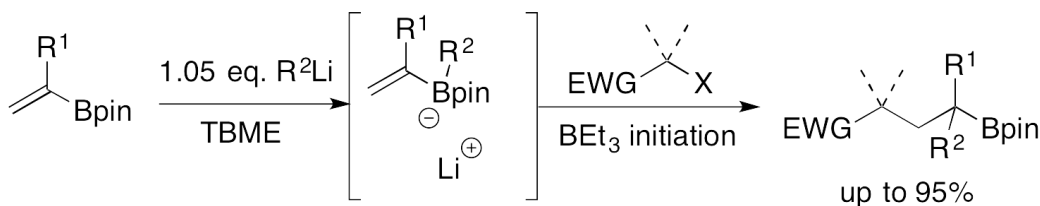
Radical Triggered Three-Component Coupling of Alkenylboronates, Halides, and Organolithiums

N. Tappin¹, M. Gnägi¹, P. Renaud^{1*}

¹University of Bern

The Atom Transfer Radical Addition (ATRA) reaction over alkenylboronates was employed by Matteson to showcase his now eponymous [1,2]-metalate shift.^[1] However, the ATRA reaction suffers from poor efficiency arising from the stabilization that the vacant p-orbital of the boron gives to the radical product. Modifying the hybridization of boron from sp^2 to sp^3 can resolve this problem as has been seen with MIDA-alkenylboronates.^[2] Better still is the combination of this logic to a [1,2]-metalate shift in order to exploit the synthetic utility of the vacant orbital.

Here, we report that the reaction takes place with good to excellent yields, initiated simply with triethylborane. In the late stages of our study other groups reported similar reactions,^[3-4] but our mechanistic insight has allowed us to design a versatile reaction with simple conditions and operation. For example, we may couple tertiary organolithiums with relatively acidic alkenylboronates or radical precursors. Our system tolerates a wide range of radical precursors and primary-, secondary-, tertiary-, and aryl-organolithiums. We also present evidence to distinguish between alternative mechanisms; one involving a true ATRA or one involving a SET-oxidation and boron-ylid.



- [1] Matteson, D. S.; Mah, R. W. H., *J. Am. Chem. Soc.* **1963**, 85 (17), 2599-2603.
[2] Quiclet-Sire, B.; Zard, S. Z., *J. Am. Chem. Soc.* **2015**, 137 (21), 6762-6765.
[3] Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A., *Science* **2017**, 355 (6328), 936-938.
[4] Silvi, M.; Sandford, C.; Aggarwal, V. K., *J. Am. Chem. Soc.* **2017**, 139 (16), 5736-5739.