

Reductive Dimetalation of Alkynes

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Electron injection into alkynes is a well-known process that ends up with providing *trans*-alkenes via protonations of vinylic carbanions. However, applications of such reactions for *nonprotonative* transformations have been limited due to the inherent instability of radical anion intermediates. Here we will discuss recent developments in the generation of *vic*-dimetalated alkenes by reductive metalation of alkynes in the presence of reduction-resistant metal electrophiles: (1) *syn*-diboration with trialkoxyboranes as reduction-resistant electrophiles (Figure 1a),¹ (2) *anti*-dimagnesiation and -dialumination with Mg- and Al-based electrophiles (Figure 1b),² (3) *syn*-borylmetalation using flow microreactors (Figure 2).³

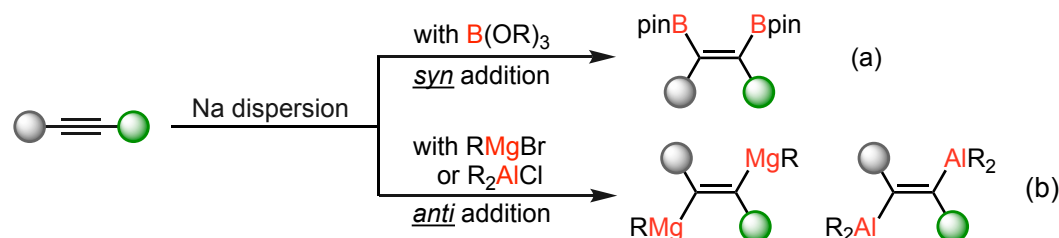


Figure 1. Reductive *syn*-diboration and *anti*-dimagnesiation and -dialumination of alkynes.

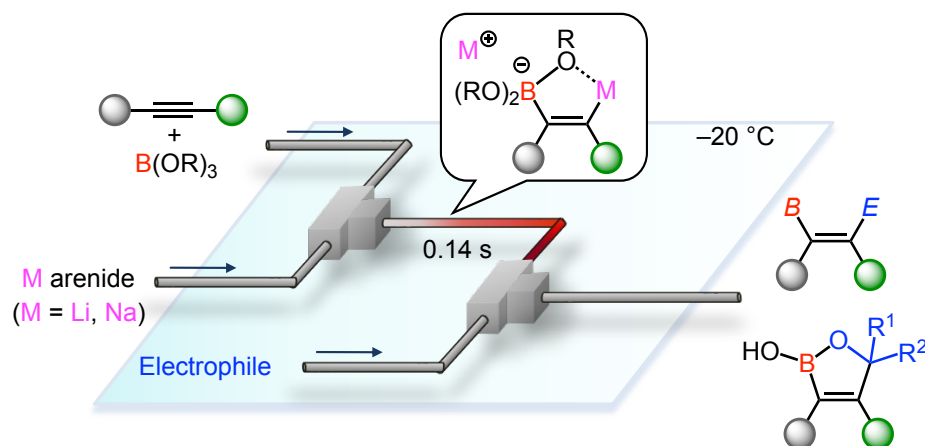


Figure 2. Unsymmetrical borylmetalation of alkynes using flow microreactors.

- [1] S. Ito, M. Fukazawa, F. Takahashi, K. Nogi, H. Yorimitsu, *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1171-1179.
 [2] F. Takahashi, T. Kurogi, H. Yorimitsu, *Nat. Synth.* **2023**, *2*, 162-171.
 [3] Y. Jiang, T. Kurogi, H. Yorimitsu, *Nat. Synth.* **2024**, *3*, 192-201.