

Reductive Dimetalation of Unsaturated Bonds

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The reductive metalation of π bonds is a well-known reaction that typically leads to the formation of protonated products such as *trans*-alkenes and 1,4-cyclohexadienes via carbanions. However, the use of such reactions for *non-protonative* transformations has been limited due to the instability of radical anion or dianion intermediates. In this talk, I will discuss recent developments in the generation of carbanions by reductive metalation of unsaturated compounds in the presence of reduction-resistant electrophiles, aiming at adding values to simple unsaturated molecules by increasing molecular complexity.

Specifically, I will focus on the use of trialkoxyboranes as reduction-resistant electrophiles that can trap carbanions via their vacant p orbitals. This approach enables stereoselective reductive diboration of a range of unsaturated compounds, including alkenes (*Org. Lett.* **2020**, *22*, 2303), alkynes (*Bull. Chem. Soc. Jpn.* **2020**, *93*, 1171), cyclopropanes (*Synlett* **2021**, *32*, 219), and arenes (*Org. Lett.* **2021**, *23*, 4613). Additionally, I will describe recent advances in reductive *anti*-dimagnesiumation and -dialumination of alkynes using Mg- and Al-based reduction-resistant electrophiles (*Nat. Synth.* **2023**, *2*, 162), as well as reductive borylmetalation of alkynes by using flow microreactors (*Nat. Synth.* **2024**, *3*, 192).