

**SURPRISES WITH ALKYNES:  
A NEW REACTIVITY PARADIGM AND ITS APPLICATIONS**

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Metal catalyzed hydrogenation reactions invariably result in *cis*-delivery of the two H-atoms of H<sub>2</sub> to the  $\pi$ -bond of a given substrate. This canonical course, however, is violated in reactions of internal alkynes catalyzed with [Cp\**Ru*]-based complexes, which afford *E*-alkenes by direct *trans*-hydrogenation. Connected to this unorthodox transformation is an even more surprising reactivity mode, in which both H-atoms of H<sub>2</sub> are delivered to one and the same C-atom of the triple bond with concomitant formation of discrete metal carbene complexes; such *geminal* hydrogenation of stable carbogenic compounds is without precedent.

In this lecture I intend to describe the current state of the art and summarize our growing mechanistic understanding [1]. At the same time, it will be shown that *trans*-hydrogenation is by no means a singularity: rather, the underlying principle is also manifest in *trans*-hydroboration, *trans*-hydrosilylation and *trans*-hydrostannation reactions. These transformations are particularly robust and functional group tolerant and have already stood the test of natural product synthesis. A few selected examples will be presented to showcase scope and limitations of this novel catalytic reactivity paradigm.

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[1] A. Fürstner, *J. Am. Chem. Soc.* **2019**, *141*, 11.