

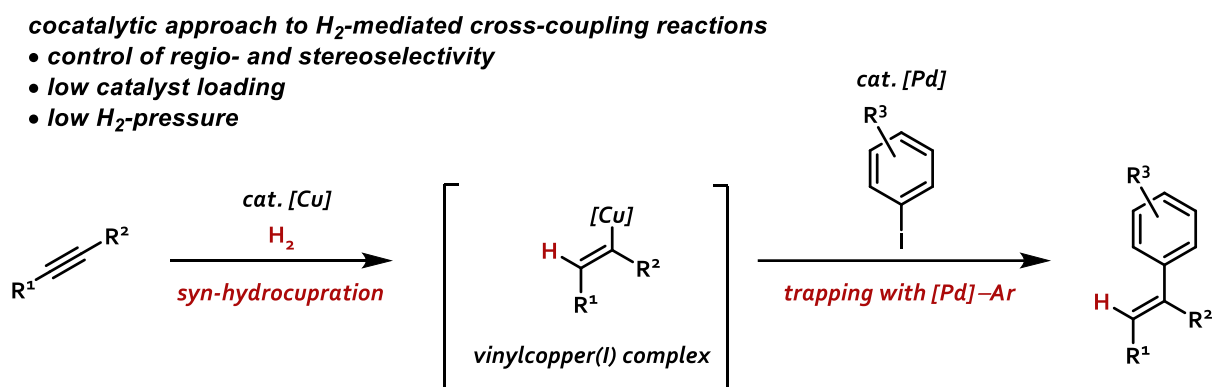
H₂-Mediated Cross-Coupling Reactions with a Cocatalysis Approach: Trapping of Copper Hydrogenation Intermediates by Palladium Catalyzed C–C-bond Formation Reactions

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The regio- and stereo-controlled synthesis of trisubstituted alkenes is challenging in organic synthesis.^[1] One of the most efficient synthetic approaches are palladium-catalyzed cross-coupling reactions.^[2] One downside is the fact that most of the cross-coupling reactions require a stoichiometric amount of organometallic compounds. If the organometallic cross-coupling partner could be generated in situ via a catalytic process only based on H₂, the overall reaction would be rendered much more atom-economic. Furthermore, the use of two separate catalysts would allow the control of stereo- and regioselectivity.^[3]

Based on highly efficient catalysts for stereoselective alkyne semihydrogenations to alkenes developed in our group.^[4] We envisioned the trapping of the key reactive intermediate, a vinylcopper complex, by a fast Pd-catalyzed cross-coupling reaction. The overall transformation with aryl iodides provides access to trisubstituted alkenes footing on just H₂ as stoichiometric reagent.



[1] J. Wang, *Stereoselective Alkene Synthesis*, In *Topics in Current Chemistry*, Vol. 327; Springer-Verlag: Berlin, **2012**.

[2] A. de Meijere, S. Bräse, M. Oestreich, *Metal-Catalyzed Cross-Coupling Reactions and More*, Ed.; Wiley-VCH: Weinheim, **2014**.

[3] Recently, such a Cu/Pd cocatalytic approach with a limited substrate scope has been published K. Semba, R. Kameyama, Y. Nakao, *Chem. Lett.* **2018**, 47, 213–216.

[4] J. F. Teichert, *Homogeneous Hydrogenation with Non-Precious Catalysts*, Ed.; Wiley-VCH: Weinheim, **2020**.