

# CARBOPALLADATION CASCADES – NOT ONLY SYN, BUT ALSO ANTI

Prof. Daniel B. Werz  
Technische Universität Braunschweig, Germany

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A characteristic feature of carbopalladation reactions is the *syn*-attack of the organo-palladium species  $\text{LnX}[\text{Pd}]\text{-R}$  on the reacting  $\pi$ -system. Such a step results in compounds bearing Pd and R on the same side of the originating alkene moiety. Embedded into longer domino sequences complex structures are efficiently obtained by a repetition of this *syn*-carbopalladation step. In this way, linear oligoynes were cyclized in a dumbbell-mode and led to benzene-type structures or higher oligoynes.

We exploited this chemistry to synthesize not only chromans, isochromans and dibenzopentafulvalenes, but also to access the most truncated  $\pi$ -helicenes which only consist of a *Z,Z,Z,..*-oligoene chain that is fixed in an all *s-cis* arrangement. All these domino processes are based on a *syn*-carbopalladation cascade.

However, a carbopalladation cascade involving formal *anti*-carbopalladation steps opens new avenues to create compounds with tetrasubstituted double bonds. Such a process was realized, and mechanistically and computationally investigated. The synthetic potential was demonstrated for the preparation of various oligocyclic frameworks (including natural products) by making use of a variety of different terminating processes.



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Instituto de Ciencia  
de Materiales de Aragón

/ Facultad de Ciencias, Universidad de Zaragoza - CSIC /  
C/ Pedro Cerbuna 12. 50009 Zaragoza. Spain

