Carbopalladation Cascades – Not only syn, but also anti

Daniel B. Werz
Prof. Dr. Daniel B. Werz, Technische Universität Braunschweig, Institute of Organic Chemistry, Hagenring 30, 38106 Braunschweig, Germany

A characteristic feature of carbopalladation reactions is the syn-attack of the organopalladium species L_nX[Pd]-R on the reacting π-system.\(^\text{[1]}\) 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 oligoenes.\(^\text{[1]}\)

We exploited this chemistry to synthesize not only chromans, isochromans\(^\text{[2]}\) and dibenzopentalfulvalenes,\(^\text{[3]}\) but also to access the most truncated π-helicenes which only consist of a Z,Z,Z,...-oligoene chain that is fixed in an all s-cis arrangement.\(^\text{[4]}\) 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 (Scheme 1). 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.\(^\text{[5]}\)

\[ \begin{align*}
 &\text{Pd} & &\text{PdL}_n \ 
 &\text{R} & &\text{R'}
\end{align*} \\
(R = CMe_2(OH); CMe_3; SiMe_3; SR'; CCR')
\]

**Scheme 1.** Formal anti-carbopalladation reaction embedded in a domino cascade.