Carbopalladation Cascades – Not only syn, but also anti

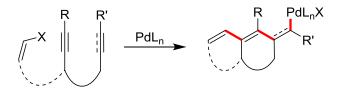
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A characteristic feature of carbopalladation reactions is the *syn*-attack of the organopalladium species $L_nX[Pd]$ -R on the reacting π -system.^[1] Such a step results in compounds bearing Pd and R on the same side of the originating alkene moiety. 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.^[1]

We exploited this chemistry to synthesize not only chromans, isochromans^[2] and dibenzopentafulvalenes,^[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.^[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.^[5]



 $(R = CMe_2(OH); CMe_3; SiMe_3; SR'; CCR')$

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

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