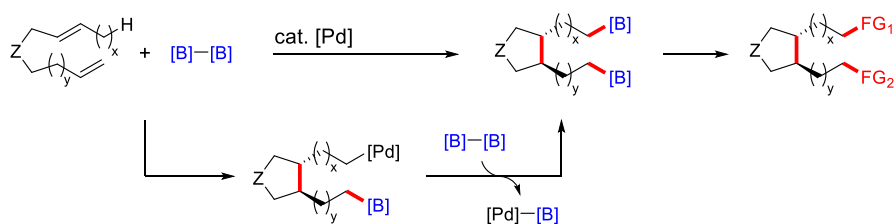


Palladium-Catalyzed Remote Diborylative Cyclization of Various 1,n-Dienes with Diborons

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Keywords: Palladium Catalyst; Chain Walking; Remote Functionalization; Borylation; Cyclization

Remote functionalization of alkenes has attracted growing interest because it allows for transformations at the positions which are difficult to functionalize selectively.¹ However, the examples of catalytic reactions of alkene substrates to form bonds at positions remote from each other, namely remote difunctionalization, are still limited.² Previously, we achieved intramolecular remote difunctionalization for a palladium-catalyzed hydrosilylation/cyclization of 1,n-dienes by using chain walking.³ In the course of the study, we recently found a reaction of 1,n-dienes with diborons to furnish five-membered carbocycles as well as two carbon-boron bonds which are distant from each other as the first example of remote bismetalation of alkene substrates by addition of dimetal reagents. Here we report the detail of the reaction development, as well as its application and the mechanistic studies.⁴ A variety of dienes and diborons can be used to form cyclopentane derivatives with two boryl groups at remote positions. Especially, the reaction of 1,n-dienes ($n \geq 7$) achieved the catalytic formation of three distant bonds between non-hydrogen atoms in one sequence for the first time. By transforming boron functional groups, we also achieved formal remote difunctionalizations that have not been reported so far. Furthermore, mechanistic studies revealed that the reaction is considered to proceed via regioselective conversion of an unactivated sp^3 C–H bond to a C–B bond by a rare process, formal σ -bond metathesis between a C–Pd and B–B bonds.



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