

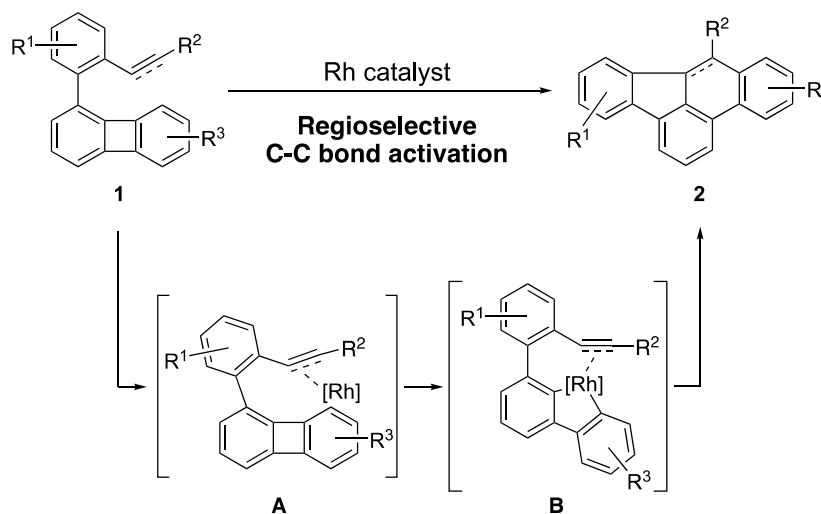
RHODIUM-CATALYZED REGIOSELECTIVE ACTIVATION OF STERICALLY HINDERED C-C BOND OF BIPHENYLENE

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Regioselective activation of sterically hindered C-C bond is one of the most challenging researches in recent organometallic chemistry, because it is difficult for transition metal complexes to approach it. In the field of biphenylene chemistry, there is only one example for regioselective C-C bond cleavage, which is a stoichiometric reaction of 1-(2-pyridyl)-biphenylene with iridium complex [1]. We here report catalytic transformation of biphenylene **1** having an unsaturated C-C bond such as alkene and alkyne moieties by intramolecular manner [2]. In the proposed mechanism, the coordination of unsaturated bond to metal center enables the access of sterically hindered C-C bond. Then, regioselective oxidative addition of C-C bond proceeded to form dibenzorhodacyclopentadiene **B**. Subsequent insertion and reductive elimination gave polycyclic hydrocarbon **2**. We will also disclose an enantioselective variant of the present regioselective C-C bond activation with chiral rhodium catalysts.



[1] Y. Koga, M. Kamo, Y. Yamada, T. Matsumoto, K. Matsubara, *Eur. J. Inorg. Chem.* **2011**, 2869-2878.

[2] H. Takano, T. Ito, K. S. Kanyiva, T. Shibata, *Chem. Eur. J.* **2018**, *24*, 15173-15177.