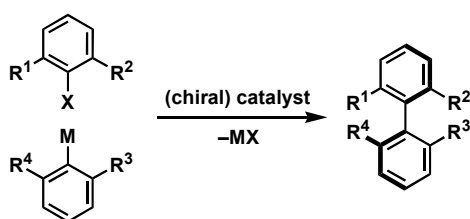


# Overcoming Steric Hindrance and Molecular Strain by Rhodium-Catalyzed Cycloaddition

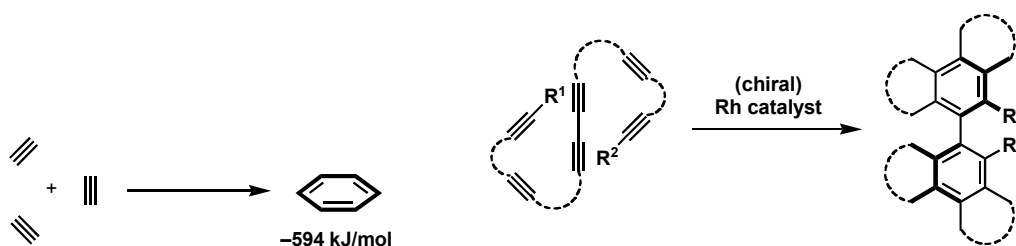
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Overcoming steric hindrance is crucial for the synthesis of sterically demanding aromatic compounds, such as biaryls and helicenes. For the synthesis of biaryls, the transition-metal-catalyzed cross-coupling reactions have been employed, however, this approach suffers from low efficiency due to the difficulty of the sterically demanding aryl-aryl bond formation.



On the other hand, the [2+2+2] cycloaddition of three acetylenes to form benzene is highly exothermic and irreversible process, although high temperature or a catalyst is required because of entropic and kinetic considerations. In 2003, our research group reported that a cationic rhodium(I)/biaryl bisphosphine complex shows exceptionally high catalytic activity and selectivity toward the [2+2+2] cycloaddition. This catalyst was successfully applied to the conceptually new biaryl synthesis by the double [2+2+2] cycloaddition, in which the sterically demanding aryl-aryl bond formation is replaced to the sterically less demanding alkyne-alkyne bond formation followed by the highly exothermic and irreversible benzene ring construction.



In this talk, I will disclose the application of this rhodium catalyst to the synthesis of various biaryls and helicenes. Overcoming molecular strain for the synthesis of highly strained cyclic  $\pi$ -conjugated compounds will also be disclosed.

## References

1. For reviews, see: a) K. Tanaka, *Chem. Asian J.* **2009**, 4, 508. b) Y. Shibata, K. Tanaka, *Synthesis* **2012**, 44, 323. c) *Transition-Metal-Mediated Aromatic Ring Construction*, ed. by K. Tanaka, Wiley, Hoboken, **2013**, part 1.
2. For our accounts, see: a) K. Tanaka, *Synlett* **2007**, 1977. b) K. Tanaka, Y. Kimura, K. Murayama, *Bull. Chem. Soc. Jpn.* **2015**, 88, 3375. c) K. Tanaka, *Bull. Chem. Soc. Jpn.* **2018**, 91, 187.