

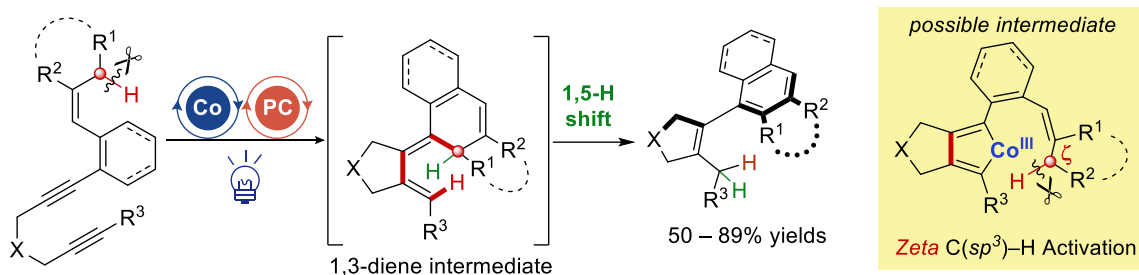
Cobalt/Organophotoredox Dual Catalysis-Enabled Cycloisomerization of 1,5,10-Enediynes via C(sp³)-H Activation

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C-H functionalization reactions using high-valent group 9 metal catalysts such as Rh^{III} and Co^{III} species have been recognized as a powerful method allowing access to various complex molecules from non-preactivated substrates. In particular, Rh^{III} and Co^{III} complexes generated in situ from the corresponding low-valent metal species by the oxidative cyclization of 1,6-diynes or 1,6-enynes have also been employed for such fascinating transformations.¹⁾ This type of transformation includes the cyclization process in addition to the C-H functionalization, which potentially leads to efficient construction of complex polycyclic frameworks. However, reports on such redox-neutral and highly atom-economic transformations have been significantly limited.

Herein, we report a novel cobalt/photoredox dual-catalysis-enabled cycloisomerization of 1,5,10-enediynes via C(sp³)-H bond activation at *zeta*-position to the metal center of cobaltacyclopentadiene intermediates. We performed several control experiments and theoretical calculations to elucidate the mechanism of this intriguing transformation, indicating that the C(sp³)-H bond cleavage proceeds through σ -bond metathesis in the cobaltacyclopentadiene intermediate. To the best of our knowledge, the site-selective C-H bond functionalization at *zeta*-position to the metal center of metallacycle species has not been reported to date although the cyclization reactions involving γ -, δ -, and ϵ -C-H activation have been developed²⁾.



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