

Rh(I)-Catalyzed [2+2+1] Carbonylative Cycloaddition Reaction of Diynes

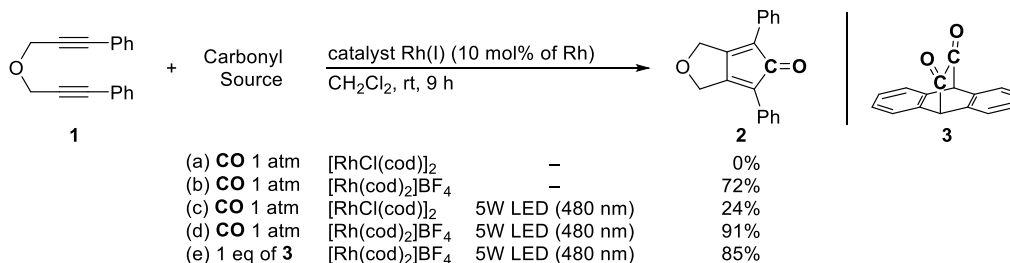
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Cyclopentadienones (CPDs) are a diverse class of fascinating molecules with broader potential in synthetic organic chemistry, biology, materials science, and nanotechnology. [2+2+1] Carbonylative cycloaddition of two alkynes, especially diynes, with carbon monoxide (CO) represents one of the accessible synthetic strategies to CPDs. Although there have been some reports using, such as cobalt,¹ iridium,^{2,3} and palladium complexes,⁴ rhodium complexes have not shown high catalytic activity on this transformation.^{3,5} Herein we will present a highly catalytic [2+2+1] carbonylative cycloaddition of diynes with Rh(I) complexes.

First, the reaction of diyne **1** with atmospheric CO in the presence of a catalytic amount of a neutral rhodium(I) complex at room temperature, $[\text{RhCl}(\text{cod})]_2$, resulted in no formation of CDP **2** as the previous report (Scheme (a)).⁵ When a cationic rhodium complex, $[\text{Rh}(\text{cod})_2]\text{BF}_4$, was used instead of $[\text{RhCl}(\text{cod})]_2$ as a catalyst, the [2+2+1] carbonylative cycloaddition proceeded efficiently to afford CDP **2** in 72% yield (b).⁶ Photoirradiation made the $[\text{RhCl}(\text{cod})]_2$ -mediated reaction catalytic. The irradiation of visible light (5W LED (480 nm)) in the presence of $[\text{RhCl}(\text{cod})]_2$ complex promoted catalytically the reaction of **1** with CO to give CPD **2** in 24% yield (c). The combined utilization of the irradiation of visible light with a cationic rhodium(I) catalyst, $[\text{Rh}(\text{cod})_2]\text{BF}_4$, also led to more highly efficient catalysis to give **2** in 91% yield (d). Both the cationic character of rhodium catalyst and the irradiation of visible light would contribute to provide the essential vacant site on the rhodium center to which diyne coordinates in the catalysis. Furthermore, the reaction of **1** with anthracene α -diketone (**3**), which is easily decarbonylated under photoirradiation to release two molecules of CO,⁷ in the presence of $[\text{Rh}(\text{cod})_2]\text{BF}_4$ catalyst under the irradiation of visible light resulted in the transformation without the direct use of CO to yield **2** in high yield (e). This is the first demonstration of the use of acene α -diketone as a substitute for CO.



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