Synthesis of Fused Cyclopentadienes and Cycloheptatrienes via Direct Carbon–Carbon Double Bond Cleavage of Cyclopropene Enabled by Ruthenium Catalysis

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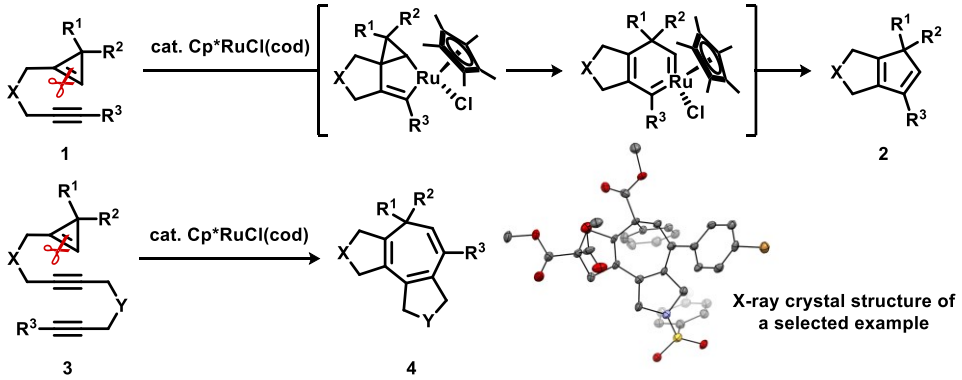
It is widely known that the transition-metal-mediated carbon–carbon single bond cleavage of a cyclopropene ring readily proceeds.[1] On the other hand, the ring opening of cyclopropenes via direct and selective carbon–carbon double bond cleavage of the cyclopropene ring is a formidable challenge.

Transition-metal-catalyzed cycloaddition reactions provide us with an opportunity to construct a variety of complex ring scaffolds in a single operation. In particular, η^5-cyclopentadienyl ruthenium complexes and 1,6-diynes generate five-membered cyclic biscarbenoids, which can lead to formation of various aromatic compounds in the presence of appropriate reactants.[2] Given the similarity of cyclopropenes and alkynes,[3] we hypothesized that the reaction of cyclopropene-ynes **1** with the ruthenium catalyst could form cyclopropane-fused ruthenacycles, which can be key intermediates for the formation of non-aromatic carbocycles. Herein, we report the ruthenium-catalyzed cycloaddition of **1** via carbon–carbon double bond cleavage of the cyclopropene ring to provide fused cyclopentadienes **2**. The density functional theory calculations indicate that the reaction proceeds via cyclopropane-fused ruthenacycles, which undergoes ring expansion to generate six-membered cyclic biscarbenoids. We also demonstrated a synthesis of fused cycloheptatrienes **4** via the cycloaddition of cyclopropene-diynes **3**.



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