

# Rhodium-Catalyzed [7 + 1] Cycloaddition of Exocyclic 1,3-Dienylcyclopropanes and Carbon Monoxide

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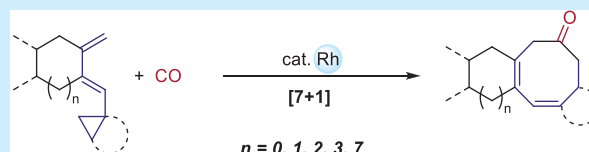
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**ABSTRACT:** A rhodium-catalyzed [7 + 1] reaction of exocyclic 1,3-dienylcyclopropanes and carbon monoxide has been developed to synthesize eight-membered carbocycle-embedded bicyclic and tricyclic molecules. In addition, *ab initio* calculations were conducted to reveal the reaction mechanism.

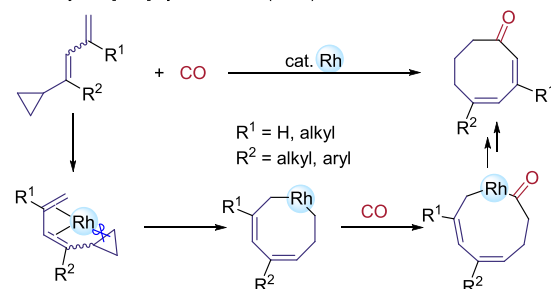


In the past decades, chemists have made tremendous advances in developing transition-metal-catalyzed cycloadditions for the synthesis of eight-membered carbocycles (EMCs),<sup>1</sup> which are common building blocks in natural products<sup>2</sup> and have applications in transition metal catalysis,<sup>3a</sup> polymer chemistry,<sup>3b</sup> and chemical biology.<sup>3c</sup> Among them, our group in 2007 developed a [5 + 2 + 1] reaction of enynylcyclopropanes and CO for synthesizing EMC-embedded bi- and tricyclic rings.<sup>4a,b</sup> This reaction has also been used to synthesize natural products with EMCs<sup>4c,d</sup> or a 5/5/5 tricyclic skeleton.<sup>5</sup> We have also developed a [7 + 1] reaction of dienyl cyclopropanes and CO for the synthesis of monocyclic EMCs in 2011 (Scheme 1a).<sup>6,7</sup> A Rh-catalyzed benzo/[7 + 1] cycloaddition for the *in situ* generated dienyl cyclopropanes (via thermal 4π electrocyclic ring-opening reaction of cyclopropyl-benzocyclobutenes) and CO was also achieved by us to reach aromatic-ring-fused EMCs (Scheme 1b).<sup>8</sup> Unfortunately, the [7 + 1] reaction has limitations, where cyclopropane of the substrates cannot be substituted. The success of benzo/[7 + 1] cycloaddition using aromatic exocyclic dienyl-cyclopropanes inspired us to use (non-aromatic) exocyclic 1,3-dienylcyclopropanes (EDCPs) as substrates (Scheme 1c). We reasoned that this reaction could also be accelerated by the rigid conformation of EDCPs, which consequently can tolerate substituents in the cyclopropyl (CP) ring and be used to construct EMC-embedded bi-, tri-, and polycyclic rings.

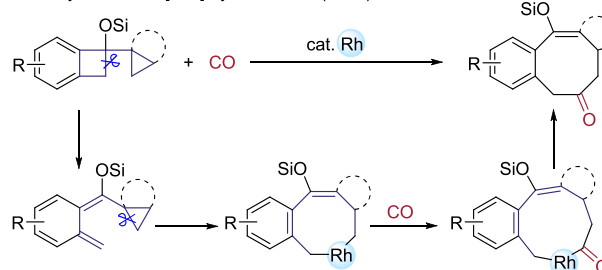
This design was attractive but faced several challenges. The benzo/[7 + 1] reaction was successful as a result of the existence of aromatization as a driving force, but this effect is absent in the designed [7 + 1] reaction of EDCPs shown in Scheme 1c. In addition, the new substrates could undergo alkene isomerization, moving exocyclic alkenes in the substrates into the ring moieties, and the resulting substrates were impossible for the desired cycloadditions. We are happy to report that such a design was successful, and the new [7 + 1] reaction can be used to synthesize bi- and tricyclic rings with EMCs. The mechanism of this reaction studied by *ab initio* calculations is also present here.

## Scheme 1. Rh-Catalyzed [7 + 1] Reactions

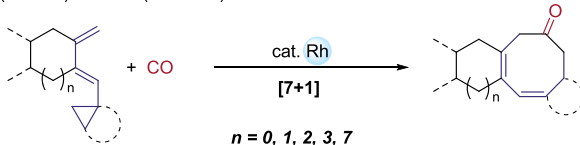
(a) Rh-catalyzed [7+1] cycloaddition (2011)



(b) Rh-catalyzed benzo/[7+1] cycloaddition (2015)



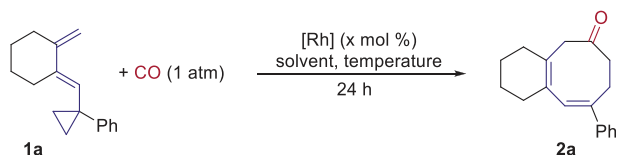
(c) Rh-catalyzed [7+1] cycloaddition of exocyclic 1,3-dienylcyclopropanes (EDCPs) and CO (this work)



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Table 1. Optimization of the Reaction Conditions<sup>a</sup>

entry	[Rh] (mol %)	solvent	T (°C)	yield (%)
1	[Rh(NBD)Cl] <sub>2</sub> (2 mol %)	<i>o</i> -DCB (0.1 M)	90	21
2	[Rh(NBD)Cl] <sub>2</sub> (2 mol %)	toluene (0.1 M)	90	10
3	[Rh(NBD)Cl] <sub>2</sub> (2 mol %)	dioxane (0.1 M)	90	24
4	[Rh(NBD)Cl] <sub>2</sub> (5 mol %)	dioxane (0.05 M)	90	35
5	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (10 mol %)	dioxane (0.05 M)	90	32
6	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.1 M)	80	47
7	[Rh(NBD)Cl] <sub>2</sub> (2 mol %)	DCE (0.1 M)	80	20
8	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	dioxane (0.1 M)	80	38
9	Rh(COD) <sub>2</sub> BF <sub>4</sub> (5 mol %)	DCE (0.1 M)	70	ND <sup>b</sup>
10 <sup>c</sup>	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.1 M)	80	28
11	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.05 M)	80	52
12	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.05 M)	75	46
13	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.05 M)	70	24
14 <sup>d</sup>	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (10 mol %)	DCE (0.1 M)	70	47
15 <sup>c,d</sup>	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (10 mol %)	DCE (0.05 M)	70	42
16 <sup>c,e</sup>	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (10 mol %)	DCE (0.05 M)	70	40
17	[Rh(CO) <sub>2</sub> Cl] <sub>2</sub> (5 mol %)	DCE (0.025 M)	80	39

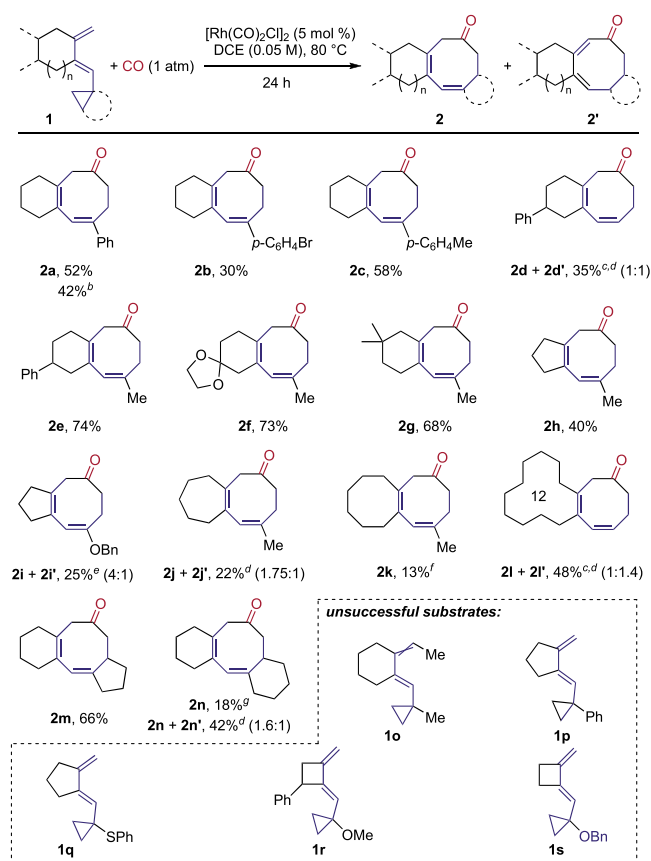
<sup>a</sup>All reactions were conducted on a 0.2 mmol scale, under 1.0 atm CO for 24 h at 600 revolutions per minute (rpm), and the reported yields were isolated yields. <sup>b</sup>Not detected. <sup>c</sup>Under 0.2 atm CO + 0.8 atm N<sub>2</sub>. <sup>d</sup>For 48 h. <sup>e</sup>For 120 h.

We used compound **1a** as the model substrate for the reaction optimization (Table 1). Excitingly, bicyclic product **2a** was obtained in 21% yield in the presence of 2 mol % [Rh(NBD)Cl]<sub>2</sub> in *ortho*-dichlorobenzene (*o*-DCB) at 90 °C for 24 h (entry 1). A series of tests (entries 2–8) showed that a combination of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> and 1,2-dichloroethane (DCE) gave improved results, among which the desired product **2a** was formed in 47% yield (entry 6). We investigated other catalysts and found that Rh(COD)<sub>2</sub>BF<sub>4</sub> was not competent (entry 9). Unfortunately, lowering the pressure of CO to 0.2 atm afforded an inferior reaction result (28% yield, entry 10). Reducing the substrate concentration can slightly increase the reaction yield (52%, entry 11). No encouraging results were observed when we lowered the reaction temperature because 70% of substrate **1a** was recovered at 70 °C for 24 h (entries 12 and 13). To our disappointment, applying a higher catalyst loading, longer reaction time, or lower concentration of the substrate cannot improve the reaction yields (entries 14–17).

The above results prompted us to use the conditions in entry 11 of Table 1 as the optimized conditions to investigate the scope of this reaction (Scheme 2). This reaction can be scaled up to 1 mmol with a slight decrease in the yield (**2a**, 42% yield). We found delightfully that the aryl group in EDCP can tolerate both electron-withdrawing and -donating groups, where bicyclic products **2b** and **2c** were obtained in moderate yields (30 and 58%, respectively). Product **2b** with a Br group in the aryl ring was expected to be a platform molecule, because various coupling products can be envisioned from here. If the aryl group in EDCP was replaced by hydrogen, a significant decrease in reactivity was observed for the corresponding substrate **1d**. We emphasize that a higher temperature was needed for compound **1d**, and two separable alkene isomers **2d** and **2d'** were obtained in a combined yield of 35% yield. Excitingly, good results were achieved when Me was installed on the cyclopropyl group of EDCPs (**2e–2g**, 68–

74% yields). Then, different sized rings in EDCPs were scrutinized, showing that 5/8 bicyclic product **2h** can be synthesized in a moderate yield (40%). Substrate **1i** with OBn in its cyclopropyl ring delivered product **2i** as a mixture of two alkene isomers in a combined yield of 25%. We noticed that the fused rings in EDCPs can be medium- and large-sized, and the corresponding *n*/8 (*n* = 7, 8, and 12) bicyclic products were obtained (**2j–2l**, 13–48% yields). The present [7 + 1] reaction can be applied to prepare tricyclic products: product **2m** with a 6/8/5 skeleton was obtained in 66% yield, while only product **2n** with a 6/8/6 skeleton was obtained within 3 h, in 18% yield. A longer reaction time (24 h) for substrate **1n** led to a mixture of product **2n** (separable, 26%) and products **2n'** (with two inseparable diastereomers, *ca.* 1:1, 16%). There are some unsuccessful substrates for this [7 + 1] reaction: we hypothesized that the extra Me group introduced in substrate **1o**, which failed to give the desired [7 + 1] product, slows the reductive elimination, which consequently makes other side reactions compete; for substrates **1p** and **1q**, their failure in the [7 + 1] reactions could be imposed by the steric hindrance of the substituents. Complex mixtures were obtained for substrates **1r** and **1s**, which have four-membered rings and could be too active to be tuned for the [7 + 1] reactions.

Our previous study showed that the [7 + 1] reaction of dienyl cyclopropanes and CO gave both non-conjugated (minor) and conjugated (major) products because the initially formed non-conjugated cycloadducts isomerized to more stable conjugated cycloadducts, also catalyzed by the used Rh catalyst (but not by the base).<sup>6,9</sup> In most cases, we observed only non-conjugated [7 + 1] cycloadducts when there is a substituent in the eight-membered ring (Scheme 2). We hypothesized that this isomerization was controlled thermodynamically. When both products have similar stabilities, isomerization takes place, as indicated by the formation of product **2d'**.

Scheme 2. Substrate Scope of the [7 + 1] Reaction<sup>a</sup>

<sup>a</sup>Unless otherwise specified, all reactions used 5 mol %  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in 0.05 M DCE under 1 atm CO at 80 °C for 24 h. Substrates were 0.06–0.2 mmol scale, and the reported yields represent an average of the yields of the isolated products from two runs. <sup>b</sup>On a 1 mmol scale. <sup>c</sup>At 120 °C, with *o*-DCB as the solvent. <sup>d</sup>Separable isomers. <sup>e</sup>Inseparable isomers. <sup>f</sup>Product 2k' (conjugated isomer of product 2k) < 5%. <sup>g</sup>The reaction time was 3 h.

To obtain mechanistic insights into this [7 + 1] reaction, we computed the Gibbs free energy profile shown in Figure 1. We used compound 1e as the model substrate and proposed that the catalytic species is a monomer,  $[\text{Rh}(\text{CO})_2\text{Cl}]$ , as suggested in several other cycloadditions developed in our group.<sup>4b,10</sup> First, substrate 1e can undergo ligand exchange to generate intermediate INT1, which is then followed by the oxidative addition of cyclopropane via transition state TS1, with an activation free energy of 20.8 kcal/mol. Conformational change happens next, converting intermediate INT2 into intermediate INT3, which then coordinates a CO to give intermediate INT4. Then, CO insertion occurs via transition state TS2, with an activation free energy of 23.0 kcal/mol. Finally, product 2e can be obtained through irreversible reductive elimination (TS3, 18.6 kcal/mol) and catalyst transfer. The rate-determining step of the [7 + 1] reaction is CO insertion via transition state TS2. We checked the crude <sup>1</sup>H nuclear magnetic resonance (NMR) of the reaction of compound 1a, speculating that vinylicyclopropane (VCP) rearrangement and “VCP to diene” were responsible for two possible side reactions giving byproducts. Density functional theory (DFT) calculations were performed to show that these side reactions can compete with the desired [7 + 1] reaction (see the Supporting Information for details).

In conclusion, a rhodium-catalyzed [7 + 1] cycloaddition of EDCPs and CO was developed, providing a new and efficient way for the synthesis of EMC-embedded bi- and tricyclic products. Besides, we investigated the reaction mechanism in detail using *ab initio* calculations, showing that the [7 + 1] reaction proceeds through the oxidative addition of VCP, CO coordination/insertion, and reductive elimination.

## ■ ASSOCIATED CONTENT

## Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

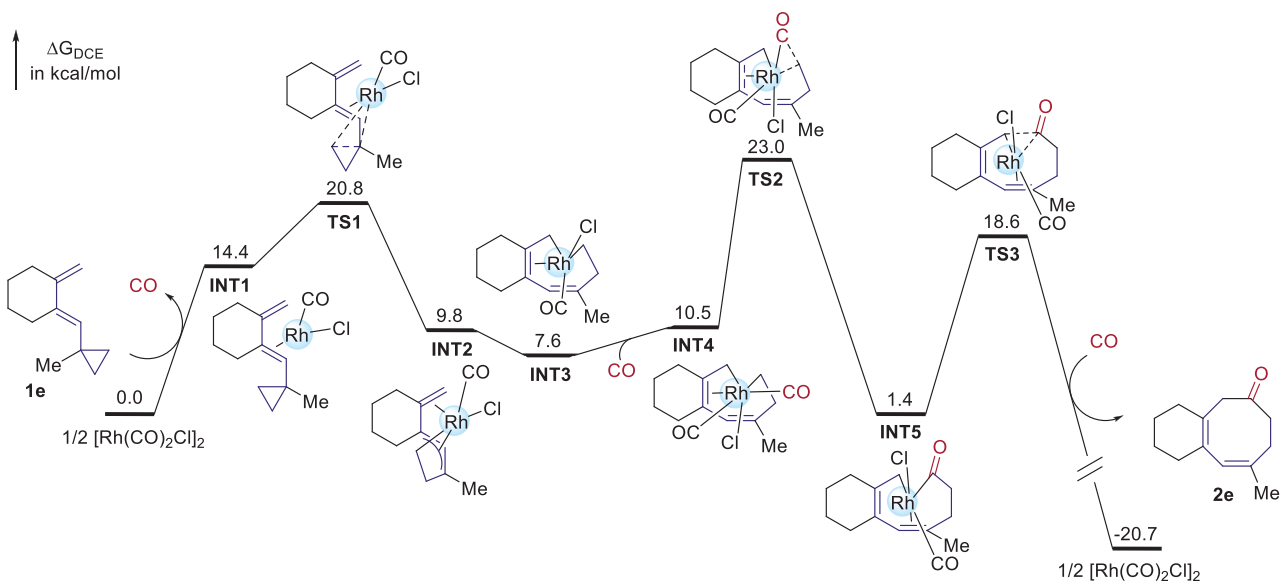


Figure 1. Gibbs energy profile for [7 + 1] cycloaddition of exocyclic 1,3-dienylcyclopropane 1e and CO, computed at the DLPNO-CCSD(T)-SMD(DCE)/def2-TZVPP//BMK/def2-TZVP level.

**SI** Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.3c03471>.

DFT study, experimental procedures, characterization data, and NMR spectra for new compounds (PDF)

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**Author Contributions**

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**Notes**

The authors declare no competing financial interest.

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