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Rh^{I}-Catalyzed Benzo/[7+1] Cycloaddition of Cyclopropyl-Benzocyclobutenes and CO by Merging Thermal and Metal-Catalyzed C–C Bond Cleavages

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Abstract: A Rh-catalyzed benzo/[7+1] cycloaddition of cyclopropyl-benzocyclobutenes (CP-BCBs) and CO to benzocyclooctenones has been developed. In this reaction, CP-BCB acts as a benzo/7-C synthon and the reaction involves two C–C bond cleavages: a thermal electrocyclic ring-opening of the four-membered ring in CP-BCB and a Rh-catalyzed C–C cleavage of the cyclopropane ring.

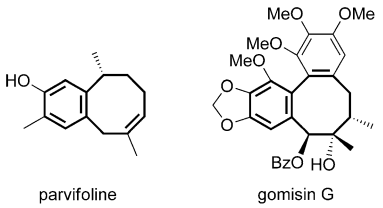
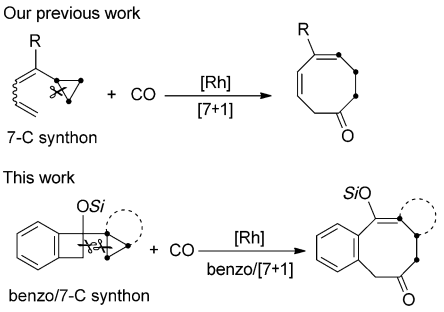


Figure 1. Selected natural products possessing benzo/8 skeletons.

Benzene-fused carbocyclic rings of various sizes (referred here as to benzo/*n* rings, $n \geq 4$) are widely found in natural products, pharmaceuticals, and material compounds. Therefore, developing reactions to access these skeletons is of great significance in today's science of synthesis. One of the powerful strategies to access benzo/*n* ring scaffolds is to utilize the chemistry of benzocyclobutenes.[1] For example, under thermal reaction conditions, the four-membered rings in benzocyclobutenes can generate *o*-quinodimethanes (the distal C–C bond in the four-membered ring is cleaved), which then undergo cycloadditions or electrocyclizations to furnish benzo/*n* rings ($n = 6$–8). Transition-metal-catalyzed cycloadditions of benzocyclobutene derivatives to benzo/*n* rings have been much less studied. Recently Dong and co-workers[2] reported benzocyclobutenones can undergo intramolecular [4+2] and [4+2–1] reactions by selective proximal C–C cleavage to give benzene-fused six- and five-membered rings, respectively, and in these reactions, benzocyclobutenones can be regarded as benzo/4-C and benzo/3-C synthons. Other elegant works from Barluenga and Aguilar's,[3a,b] Nemoto's,[3c] Murakami's,[3d] and Wang's[3e] groups also provide access to different sized (5- to 7-membered) benzene-fused rings. However, transition-metal-catalyzed cycloadditions of benzocyclobutenes to synthesize benzo/8 skeletons were not available.[4] Developing such a reaction will provide a new approach to the synthesis of natural products with a benzo/8 skeleton (Figure 1). This is also important to advance the field of transition-metal-catalyzed cycloadditions, in which a dozen of reactions to nonbenzenoid *n*/8 skeletons, but not benzo/8 skeletons, are available.[4,5] Following our long interest in discovering and developing new transition-metal-catalyzed cycloadditions,[6] we were eager to cover this gap and develop new benzo/*x*–C synthons ($x = 1$–8) that can be applied to synthesize the challenging benzo/8 skeletons. Here we report the first Rh-catalyzed benzo/[7+1] cycloaddition of cyclopropyl-benzocyclobutenes (CP-BCBs) and CO to access benzo/8 rings, in which CP-BCBs act as the benzo/7-C synthon (Scheme 1).



Scheme 1. [7+1] cycloaddition and new benzo/[7+1] cycloaddition.

Previously, we have developed the first [7+1] cycloaddition of dienylcyclopropanes and CO (Scheme 1). Reported here is a benzo/[7+1] reaction using cyclopropyl-benzocyclobutene (CP-BCB) as a benzo/7-C synthon with CO as the 1-C synthon (Schemes 1 and 2). We hypothesized that, under thermal reaction conditions, ring opening[7] of the benzocyclobutene ring in CP-BCB would generate intermediate **I** first (Scheme 2). Then oxidative cyclometallation leads to intermediate **II**. Cyclopropane opening (β-C elimination) would convert **II** into an eight-membered metallacycle **III**. CO coordination and migratory in-

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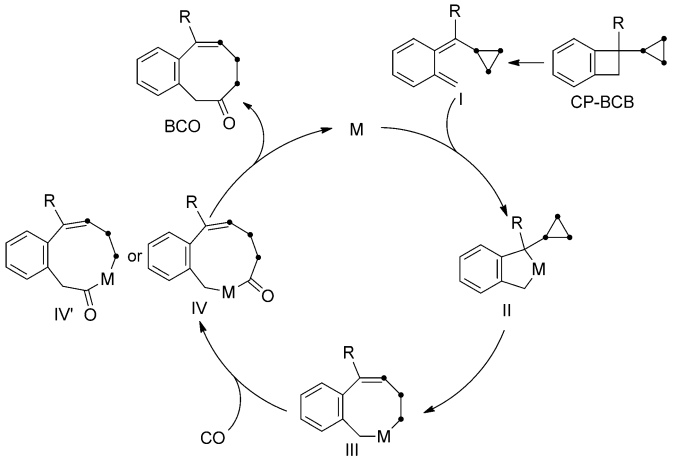


Scheme 2. Proposed benzo/[7+1] reaction pathway of CP-BCB with CO under transition-metal catalysis.

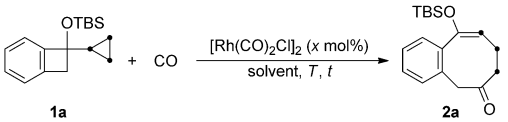
sertion then transforms **III** into intermediate **IV** or **IV′**. Finally reductive elimination gives the benzocyclooctenone (BCO). This designed benzo/[7+1] reaction involves two C–C bond cleavages: one is through the thermal opening of the four-membered ring in benzocyclobutene, the other through transition-metal-catalyzed cyclopropane opening.[8–10]

However, we had several concerns at the outset of this work. First, the opening of cyclobutene ring in CP-BCBs could be difficult because usually such processes were carried out under very harsh conditions, under which the starting materials may decompose. Therefore choosing an appropriate R group in CP-BCBs to facilitate the ring opening of benzocyclobutene would be the primary requirement for the success of the designed benzo/[7+1] reaction. Suzuki and co-workers have demonstrated that CP-BCBs can give benzocycloheptenes (structure is not given here) under thermal reaction conditions without catalyst, even though they had to use more reactive substrates in which the four-membered ring had two alkoxyl substituents.[11] As a result, the second obstacle of the designed benzo/[7+1] reaction is that, once intermediate **III** is generated, it could also undergo direct reductive elimination to give benzocycloheptene as a side product. In addition, β-hydrogen elimination could also happen for all possible intermediates and this may mess up the reaction.

It was reported that the electron-donating group could promote BCB's ring opening,[1b] so we envisioned the substituent (R-, Scheme 2) in the BCB ring of the substrate had better be some electron-donating group (here we chose the trimethylsiloxy (TMSO) or *tert*-butyldimethylsiloxy (TBSO) group). We chose Rh complexes as the catalysts since Rh-catalyzed cyclopropane opening from intermediates similar to **II** had been reported.[12] In addition, Rh-catalyzed cycloadditions of various species with CO had been well documented.[13] Previously it has been shown that $[RhCl(CO)_2]_2$ is an excellent catalyst in several CO carbonylation reactions;[6,13] therefore, we chose it as the catalyst to test our designed benzo/[7+1] reaction.

Our research was commenced with the model substrate **1a**, which was subjected to the reaction conditions used for the [7+1] cycloaddition of butandienylcyclopropanes and CO previously reported by our group (Table 1).[4b] However, the reactant remained intact on heating for five days (Table 1, entry 1). Considering the difficulties associated with ring-opening of BCB, we surmised that a higher reaction temperature was needed. When the reaction was conducted at 140 °C in *p*-xylene, to our delight, the desired benzo/[7+1] cycloaddition product was obtained in a good yield (entry 2). Lowering the reaction temperature decreased the yield remarkably (entry 3). Reducing catalyst loading had little effect on the reaction yield (entries 4–6). It was noticed that the benzo/[7+1] reaction with 2.5 mol% loading of catalyst gave a comparable reaction yield as with 10 mol% catalyst loading (entry 5 vs. 2), but much lower loading (1 mol%, entry 6) led to a little lower yield. 1 and 0.5 atm. CO were both good to the reaction, but 0.2 atm. CO reduced the yield significantly (entries 7–8). Extra phosphine ligand was found to be detrimental to the reaction (entry 9). Wilkinson's catalyst cannot promote the reaction at all (entry 10). We found that the benzo/[7+1] reaction can also be carried out in a high boiling point solvent, such as *n*-butyl ether (nBu_2O), with a slightly lower yield (entry 11). In contrast, using toluene as the solvent gave a much lower yield (entry 12), and 1,2-dichloroethane (DCE) cannot be used as the reaction medium (entry 13). Consequently, the optimal reaction conditions of the benzo/[7+1] cycloaddition were determined: balloon pressured 1 atm. CO gas, 2.5 mol% $[RhCl(CO)_2]_2$ as the catalyst, *p*-xylene as the solvent at the temperature of 140 °C. We must point out here that the TBS protecting group is required for the success of the present reaction. Substrate with a free alcohol group gave the Murakami-type C–C cleavage product **3a** under $[RhCl(CO)_2]_2$ catalysis [Eq. (1)].[3d,14] In addition, we did not observe benzocycloheptene in the reaction system, which suggests reductive elimination from **III** is slower

Table 1. Optimization of the benzo/[7+1] reaction conditions.[a]

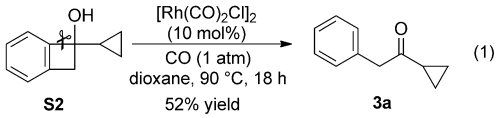


1a 2a

Entry	CO [atm]	*x* [mol%]	Solvent	*T* [°C]	*t* [h]	Yield [%][b]
1	1	10	dioxane	100	120	N.R.
2	1	10	*p*-xylene	140	6	84
3	1	10	*p*-xylene	130	9	52
4	1	5	*p*-xylene	140	6	79
5	1	2.5	*p*-xylene	140	4	84
6	1	1	*p*-xylene	140	6	72
7	0.5[c]	5	*p*-xylene	140	7	83
8	0.2[c]	5	*p*-xylene	140	8	49
9	0.5[c]	5[d]	*p*-xylene	140	22	0
10	1	10[e]	*p*-xylene	140	20	0
11	1	5	nBu_2O	140	10	72
12	1	5	$PhCH_3$	110	72	57
13	1	5	DCE	85	70	N.R.

[a] All reactions were carried out on a 0.2 mmol scale in 4 mL solvent. [b] Yield of isolated product. [c] Here 0.5 or 0.2 atm. CO means that we used balloon pressured mixed gas of CO/N_2 (ratio is 1:1 for 0.5 atm. CO and 1:4 for 0.2 atm. CO), whereas 1 atm. CO indicates using ballon pressured gas of CO. [d] 10 mol% PPh_3 was added. [e] $[RhCl(PPh_3)_3]$ was used. DCE = 1,2-dichloroethane, N.R. = no reaction.

than the competing CO insertion, and the followed reductive elimination from **IV** or **IV′**.[15] Without adding CO gas, the reaction of **1a** did not give benzocycloheptene either but some unidentified decomposition products, which suggests that CO is critical to the present benzo/[7+1] reaction.



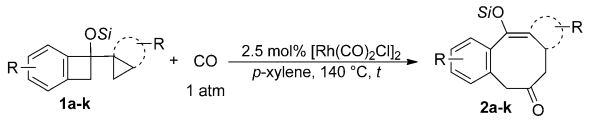
S2 3a

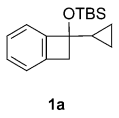
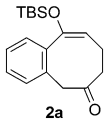
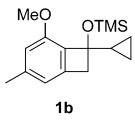
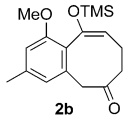
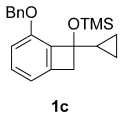
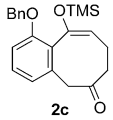
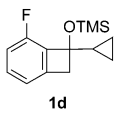
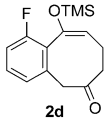
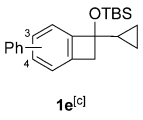
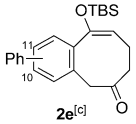
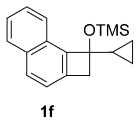
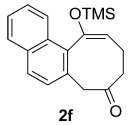
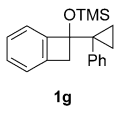
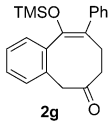
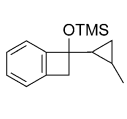
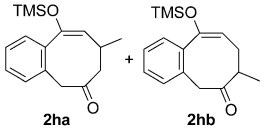
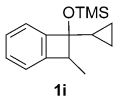
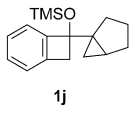
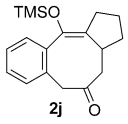
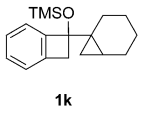
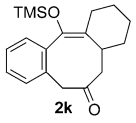
With the optimal reaction conditions in hand, we next investigated the substrate scope of the present benzo/[7+1] cycloaddition (Table 2). We found that the reaction showed a good tolerance with different functional groups and substitution patterns. For example, the electron-donating group on the phenyl ring had a negligible effect on the reaction: the substrates possessing a methoxy or benzyloxy group gave the corresponding benzo/[7+1] adducts in good yields (Table 2, entries 2 and 3). Additionally, the structure of **2b** was unambiguously confirmed by X-ray diffraction analysis (see the Supporting Information for details). An electron-withdrawing group can also be tolerated, as the substrate with a fluorine atom on the phenyl ring gave the desired product **2d** in 73% yield (entry 4). Phenyl as a substituent can be incorporated on the aromatic ring of the substrate (entry 5). The naphthalene-fused cyclopropylcyclobutene **1f** was also a suitable substrate, affording the corresponding naphthalene-fused cyclooctenone in a good yield (entry 6). Moreover, substituents can be introduced on the cyclopropane ring in the substrate. Substrate **1g** with a phenyl group at the junctional position on the CP ring gave the [7+1] cycloadduct in 50% yield (entry 7). The substrate **1h** with a methyl group at the nonjunctional position on the cyclopropane ring can also be tolerated, giving the corresponding cycloadduct in a moderate yield, with a little selectivity favoring the cleavage of the less-hindered C–C bond of the cyclopropane ring (leading to **2ha**) (entry 8). However, introducing another substituent (a methyl group) on the four-membered ring (**1i**) completely inhibited the reaction, probably because of unfavorable steric hindrance (entry 9).

We further tested whether the benzo/[7+1] reaction can be used for the synthesis of the tricyclic skeleton when the cyclopropane of the CP-BCB substrate is fused with another ring, which is difficult to achieve in our previously reported [7+1] cycloaddition of butandienylcyclopropanes and CO. Impressively, **1j** and **1k**, with five- and six-membered ring fused cyclopropane, respectively, were suitable substrates to give benzo/[7+1] cycloaddcuts in good yields (**2j** and **2k**) (Table 2, entry 10—11). In the case of **1j**, we did isolate the byproduct **4j** [Eq. (2)] originating from β-H elimination of the proposed rhodacyclooctene intermediate **III** (Scheme 2).[16] This may support our proposed reaction mechanism (Scheme 2) and account for the erosion of the reaction yield by the β-H elimination pathway.

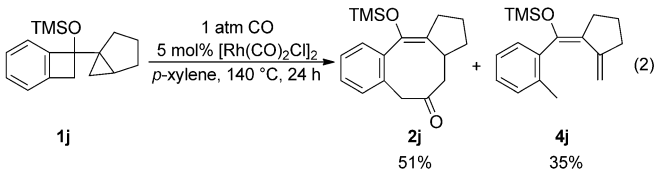
In summary, we have developed a benzo/[7+1] cycloaddition of cyclopropyl-benzocyclobutenes and CO for the synthe-

Table 2. Substrate scope of the benzo/[7+1] cycloaddition.[a]



Entry	Substrate	Product	t [h]	Yield[b] [%]
1	 1a	 2a	4	84
2	 1b	 2b	20	79
3	 1c	 2c	20	84
4	 1d	 2d	24	73
5	 1e[c]	 2e[c]	20	74
6	 1f	 2f	24	81
7	 1g	 2g	24	50
8[d]	 1h	 2ha : 2hb = 1.6 : 1	10	55[e]
9	 1i	–	20	no reaction
10[d]	 1j	 2j	24	51
11[d]	 1k	 2k	20	62[f]

[a] General reaction conditions: 0.2 mmol **1**, 2.5 mol% $[RhCl(CO)_2]_2$, 1 atm. CO, *p*-xylene (4 mL), 140 °C. [b] Yield of isolated products. [c] Inseparable mixture of isomers with the substituent at the 3- and 4-position. [d] 5 mol% $[RhCl(CO)_2]_2$ was used. [e] Average result of two diastereoisomers (see the Supporting Information). [f] See note [16] for the other unidentified byproduct.



sis of benzocyclooctenones. The reaction features high efficiency and broad substrate scope. This represents the first example of using transition-metal-catalyzed cycloaddition chemistry of benzocyclobutenes for the synthesis of challenging eight-membered carbocycles fused with aryl rings. Further mechanistic study on understanding the reaction sequences and how the four-membered[1] and three-membered rings are cleaved will be reported in due course. The development of other cycloadditions through the use of C–C bond cleavage of benzocyclobutene derivatives is ongoing in our laboratory.

Experimental Section

A solution of **1a** (55.3 mg, 0.201 mmol) in *p*-xylene (2.0 mL) was added to a solution of $[RhCl(CO)_2]_2$ (2.0 mg, 0.005 mmol) in anhydrous *p*-xylene (2.0 mL) in a flame-dried reaction tube under argon. Then the reaction mixture was bubbled with CO gas in a balloon for 5 min. After that, the reaction tube was immersed into a 140 °C oil bath and stirred under the atmosphere pressure of CO gas. When TLC analysis (by phosphomolybdic acid staining) indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated under reduced pressure to remove *p*-xylene. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to afford **2a** as a pale-yellow oil (51.2 mg, 84% yield).

Acknowledgements

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Keywords: benzo/[7+1] · benzocyclobutene · carbonylation · eight-membered ring · rhodium

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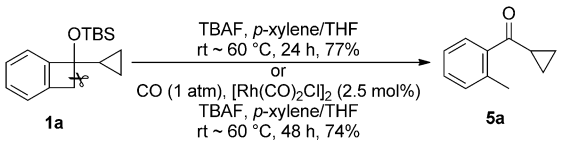

1a **5a**

[15] This can be understood by the hypothesis that reductive elimination between two sp^3 carbon atoms is more difficult than that between a sp^3 carbon and a sp^2 carbon (refs. [6a] and [4b]).

[16] The reaction of **1k** gave the desired benzo/[7+1] product **2k** together with another unidentified mixture, which could include the β-H elimination product, as judged by crude NMR spectroscopy.

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Organic Synthesis

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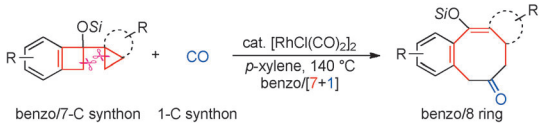
Rh^{I}-Catalyzed Benzo/[7+1] Cycloaddition of Cyclopropyl-Benzocyclobutenes and CO by Merging Thermal and Metal-Catalyzed C–C Bond Cleavages



Transition-metal-catalyzed benzo/[7+1] cycloaddition of cyclopropyl-benzocyclobutenes (CP-BCB) and CO to synthesize benzocyclooctenones is reported. In the reaction, CP-BCB acts as a benzo/7-C synthon and the reaction involves two C–C bond cleavages: thermal electrocyclic ring-opening of the cyclobutene ring and Rh-catalyzed C–C cleavage of the cyclopropane ring.