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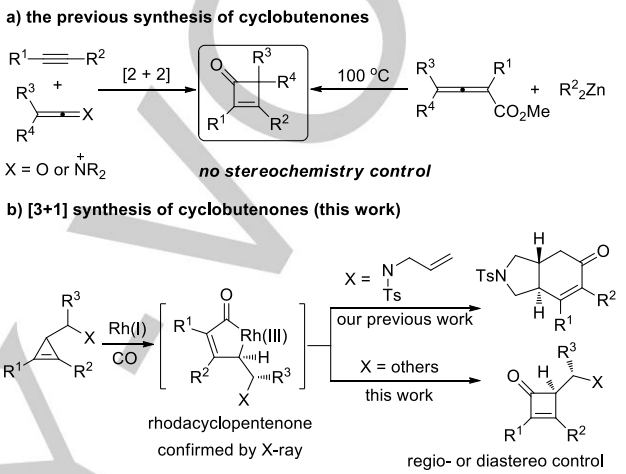
Rh(I)-Catalyzed Carbonylative [3+1] Construction of Cyclobutenones via C-C σ-Bond Activation of Cyclopropenes

Wen-Bin Xu,[a] Changkun Li*[a], Jianbo Wang[b]

Abstract: Upon exposure to a catalytic amount of $Rh(cod)_2BF_4$ and dppm, cyclopropenes undergo a direct carbonylative [3+1] cycloaddition reaction under the atmosphere of CO to produce the cyclobutenones in excellent yields, in which the regio- and diastereoselectivities can be controlled in certain cases with the help of chelating groups. 4-Chiral cyclobutenone was prepared by diastereoselctive induction. Rhodacyclopentenone has been proved to be the key intermediate, as it was synthesized and applied to the reductive elimination step.

Transition-metal-catalyzed C-C bond activation has emerged as one of the powerful and straightforward methods in terms of step economy for the construction of complex polycyclic frameworks.[1] But the main challenge is the high barrier for metals to have oxidative addition into C-C bonds (vs. C-H bonds) for kinetic and thermodynamic reasons.[2] To solve this problem, small rings with high strain energy are usually used as reactive substrates during the cycloaddition reactions. Although the driving force of releasing the energy in the small ring is thermodynamically favored, some directing groups for the metal to coordinate are still necessary for the kinetics. Up to now, there are numerous reports of catalytic cycloadditions involving cyclopropane and their derivatives, such as cyclopropyl ketones or imines, alkylidenecyclopropanes, vinyl cyclopropanes and cyclopropenes.[3] However, a direct [3+1] carbonylative ring extension reaction, in which the high strain energy is partially released and a highly strained cyclobutanone skeleton formation is still very rare. Uchida reported that rhodium catalyzed carbonylation of simple cyclopropane at high temperature, in which the yield of the cyclobutanone is very low, with propene as the main product.[4a] de Meijere realized a cobalt-mediated or catalyzed ring enlargement of alkylidene-cyclopropanes.[4b]

On the other hand, cyclobutenones, which bear a C-C double bond and a carbonyl group in a strained 4-membered ring, are not only important synthetic blocks in cycloaddition reactions,[5] but also ideal substrates for C-C bond cleavage and ring-expansion reactions under transition-metal catalysis or organocatalysis.[6] The synthesis of cyclobutenones is mainly based on [2+2] cycloaddition of alkynes and in-situ-generated ketene or keteniminium salt (Scheme 1, a).[7] Ma and coworkers reported an elegant synthesis starting from easily available allenes and organozinc reagents, in which multi-substituted cyclobutenones could be prepared regioselectively.[8] However, a stereoselective synthesis of cyclobutenones is not applicable and still highly desirable. Herein, we reported a rhodium-catalyzed C-C bond cleavage of cyclopropenes and subsequent carbonylative [3+1] construction cyclobutenones, allowing the control of regio- and diastereoselectivities.



Scheme 1. The synthesis of cyclobutenones.

Following our interest about cyclopropenes in ring opening reactions,[9, 10] we reported that tethered cyclopropene-ene or cyclopropene-yne are able to participate in carbonylative cycloisomerization reactions to prepare bicyclic enones and phenols respectively, in which rhodacyclopentanone was proposed as the key intermediate via C-C σ-bond oxidative addition to rhodium and CO insertion. This intermediate can have further migratory insertion with intramolecular C-C double or triple bonds (Scheme 1, b). [11] We assume that a challenging reductive elimination from rhodacyclopentenone to form strained cyclobutenones could be realized by careful selection of the ligand on rhodium.

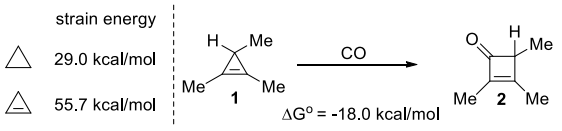


Figure 1. The strain energy of cyclopropene and cyclobutenone.

The strain energy of cyclopropene is 55.7 kcal/mol, which is almost doubled compared with the cyclopropane.[3,12] To check the thermodynamic tendency from cyclopropene to cyclobutenone, DFT calculation on M062X/6-311+G(d,p) level was conducted (Figure 1). The calculated ΔG^o from **1** to **2** is -18.0 kcal/mol, which means the reaction is very favorable

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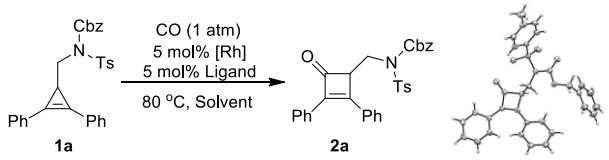
thermodynamically, although the cyclobutenone is still a highly strained molecule.

We commenced our studies with **1a** as the model substrate (Table 1). Moderate yields were obtained when **1a** was treated with catalytic amount of $[Rh(cod)Cl]_2$ or $[Rh(CO)_2Cl]_2$ in toluene at 80 °C under the balloon pressure carbon monoxide (entries 1 and 2), along with some starting material recovered. The structure of **2a** was unambiguously elucidated by X-ray single crystal diffraction analysis. We speculated that the reductive elimination process is reversible and the catalyst is captured by the product when higher conversion is reached.[13] Then, we examined several bidentate phosphine ligands, aiming at altering the equilibrium towards products. With $Rh(cod)_2BF_4$ as the rhodium source, small-bite-angle ligand dppm and its electron-rich counterpart dcypm could make the reaction reach full conversion (entries 3 and 4). The spacer between the phosphorus atoms could be further extended to two carbons (dppe and dcype) and similar yields could be obtained (entries 5 and 6). When dppp was applied, only 32 % of **2a** was isolated (entry 7). The trend was further confirmed by the fact that dppb and dppf gave only trace amount of product (entries 8 and 9). dppm was selected because it is more affordable. An optimization of solvents revealed that toluene is the best, and the yields are lower when THF, 1, 4-dioxane and DCE were used (entries 10-12). $Co_2(CO)_8$ was also examined under the same reaction condition and no any [3+1] product was detected.

Table 1. Optimization of the Rh-catalyzed [3+1] synthesis of cyclobutenones [a]



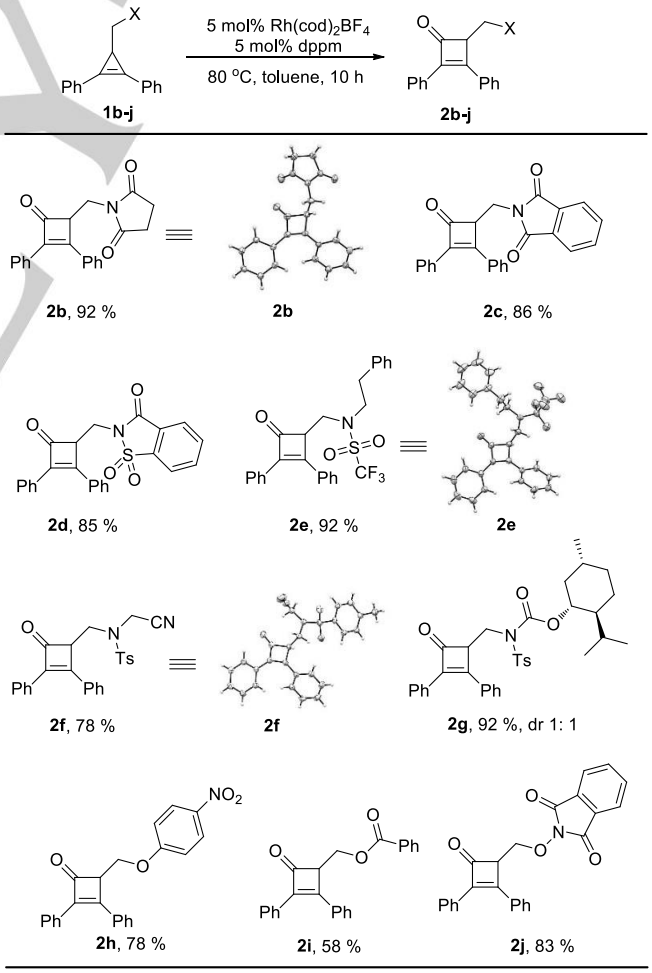
Entry	Catalyst	Ligand	Solvent	Yield[b]
1	$[Rh(cod)Cl]_2$	none	Toluene	69%
2	$[Rh(CO)_2Cl]_2$	none	Toluene	62%
3	$Rh(cod)_2BF_4$	dppm	Toluene	89%
4	$Rh(cod)_2BF_4$	dcypm	Toluene	92%
5	$Rh(cod)_2BF_4$	dppe	Toluene	85%
6	$Rh(cod)_2BF_4$	dcype	Toluene	90%
7	$Rh(cod)_2BF_4$	dppp	Toluene	32%
8	$Rh(cod)_2BF_4$	dppb	Toluene	trace
9	$Rh(cod)_2BF_4$	dppf	Toluene	trace
10	$Rh(cod)_2BF_4$	dppm	THF	58%
11	$Rh(cod)_2BF_4$	dppm	1,4-Dioxane	75%
12	$Rh(cod)_2BF_4$	dppm	DCE	67%

[a] All reactions were run with 5 mol% rhodium catalyst (based on Rh) and 5 mol% ligand on a 0.2 mmol scale at 80 °C for 10 hours unless otherwise noted. [b] Yield of isolated product.

dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,1-bis(diphenylphosphino)ethane, dppp = 1,1-bis(diphenylphosphino)propane, dppb = 1,1-bis(diphenylphosphino)butane, dppf = 1,1-bis(diphenylphosphino)ferrocene, dcypm = 1,2-bis(dicyclohexylphosphino)methane, dcype = 1,2-Bis(dicyclohexylphosphino)-ethane, THF = tetrahydrofuran, DCE = 1,2-dichloroethane

With the optimized reaction conditions in hand, we sought to investigate the scope of the [3+1] cycloaddition for the synthesis of various substituted cyclobutenones. As summarized in Table 2, two phenyl substituted cyclopropene substrates **1b** to **1j** were examined. The yields of carbonylation products are good to excellent. Different protecting groups on the nitrogen atom (carbonyl, alkyl and sulfonyl) could be tolerated The structures of **2b**, **2e** and **2f** were confirmed by X-ray diffraction. A cyano group in the substrate **1f** does not participate in the reaction as the C-C triple bond to give a six-membered heterocycle.[11] The cyclobutenone **2f** was isolated in 78 % yield. The attempt to use menthol as chiral auxiliary to get chiral cyclobutenones via desymmetrization is not successful and **2g** is obtained in 92% yield and 1 : 1 dr. The reaction of substrate bearing a free hydroxyl group gave complicated mixture. When the hydroxyl group is masked as aromatic ether (**2h**) and protected hydroxylamine (**2j**), the products were obtained smoothly, while the corresponding ester **2i** can only be isolated in moderate yield.

Table 2. The reaction scope of diphenyl substituted cyclopropenes[a]



[a] All reactions were conducted with 5 mol% rhodium catalyst and 5 mol% ligand on a 0.2 mmol scale at 80 °C for 10 hours unless otherwise noted.

10.1002/chem.201804170

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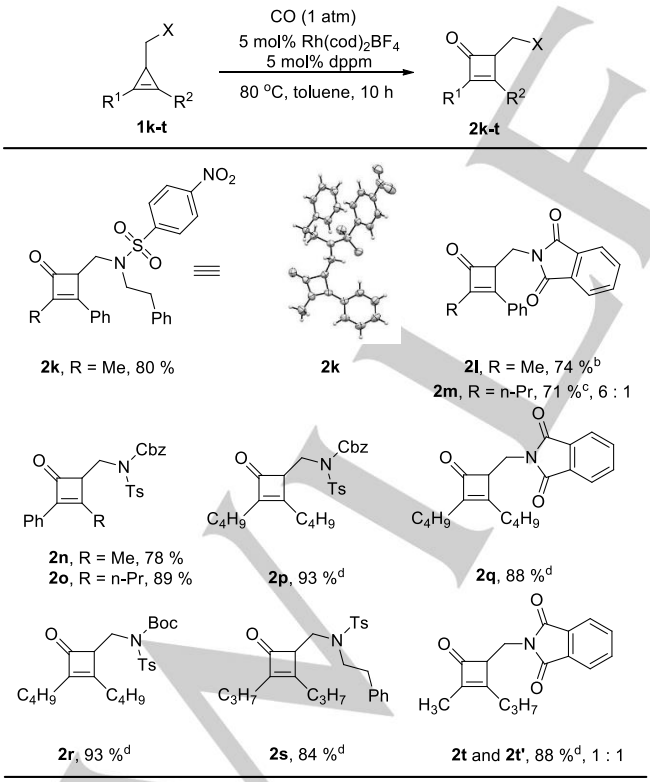
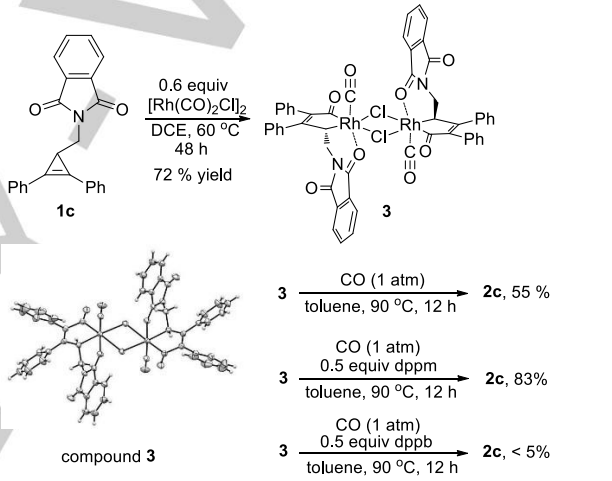
The groups on the double bonds in cyclopropenes were also examined (Table 3). When unsymmetric cyclopropene **1k** with phenyl and methyl groups on the double bond was checked under the standard reaction condition, cyclobutenone **2k** was isolated in 80% yield exclusively. The rhodium can selectively have oxidative addition with σ-bond in cyclopropene at the less hindered methyl group side. The same selectivity was also observed in **2l** with phthalimide function, although the reactivity is lower and 24 hours is needed. To our surprise, Ts and Cbz protected substrate **1n** with the same cyclopropenyl moiety lead to the regio-reversed product **2n**. By simply turning the protecting groups, the opposite selectivity could be realized. This phenomenon suggests that the atoms in the protecting groups coordinate with the rhodium. A similar regio-divergent [3+1] cyclobutenones synthesis is realized when bulkier n-propyl substituted cyclopropenes are used (**2m** and **2o**), although the regioselectivity is lower (6 : 1) in this case with **2m** as the major product. The symmetric dialkyl-group substituted cyclopropenes could also participate in this [3+1] reaction. Compounds **2p** to **2s** were isolated in excellent yields. The reactivities are higher and the reactions were conducted at 60 °C, probably because of the higher strain energy of alkyl substituted cyclopropenes without the stabilization effect of aromatic groups. However, cyclopropenes with a hydrogen on the double bonds lead to complex mixture. Unsymmetric methyl and n-propyl substituted cyclopropene **1t** leads to a 1 : 1 mixture of **2t** and **2t'**.

Table 3. The scope of substitutions on the cyclopropene bouble bonds[a]



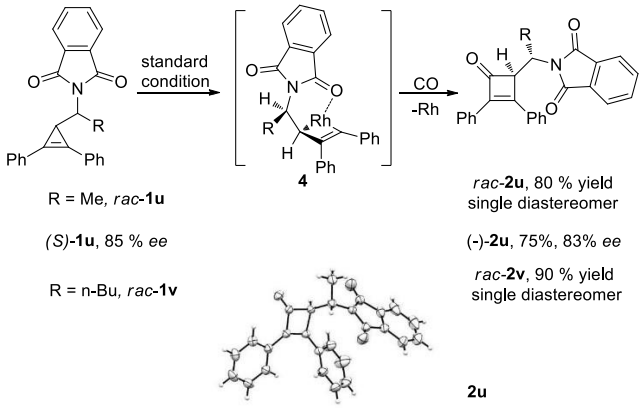
[a] All reactions were conducted with 5 mol% rhodium and 5 mol% ligand on a 0.2 mmol scale at 80 °C for 10 hours unless otherwise noted. [b] 24 hours. [c] with 5 mol% $[Rh(cod)_2Cl]_2$ for 24 hours, 6 : 1 regioselectivity. [d] at 60 °C.

We propose a mechanism involving a rhodacyclopentenone intermediate, which was formed by oxidative addition of rhodium and CO migratory insertion.[14] By heating substrate **1c** with stoichiometric $[Rh(CO)_2Cl]_2$ at 60 °C, a dimeric rhodacyclopentenone **3** was isolated (Scheme 2). The compound **3** was characterized by X-ray single crystal diffraction.[15] The coordination of phthalimide carbonyl group to rhodium is consistent with the reversed regioselectivities in Table 3. To gain more insight into the reaction mechanism, complex **3** was heated in the atmosphere of CO at 90 °C. 4-Membered product **2c** was isolated in 55% yield. The addition of dppm makes the reaction reach full conversion, while dppb inhibits the reaction and only trace amount of **2c** can be detected. These experiments also support that the strong ligand effect in Table 1 is assigned to the reductive elimination step.[16] The small bite angle ligands are probably prone to coordinate cis to metal centre and make the reductive elimination easier.



Scheme 2. Rhodacyclopentenone **3** synthesis and its reductive elimination

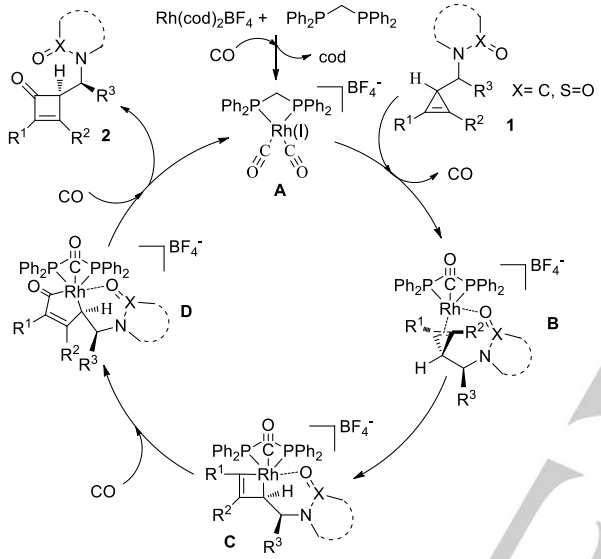
Not only the regioselectivity, the diastereoselectivity can also be controlled by rhodium complex.[17] When racemic cyclopropene **1u** and **1v** were subjected to the standard condition,



Scheme 3. The diastereoselective [3+1] synthesis of chiral cyclobutanone.

10.1002/chem.201804170

single diastereomeric **2u** and **2v** were isolated in 80% and 90 % yield respectively (Scheme 3). We propose that rhodium firstly coordinates with both of carbonyl oxygen and C-C double bond. The R group blocks one σ-bond of the cyclopropene and the rhodium selectively reacts with the less hindered σ-bond to form intermediate **4** diastereoselectively, which finally generates the cyclobutenone **2u** and **2v**. The relative configuration of **2u** was confirmed by crystal structure and it is consist with the above-mentioned stereo-model. When enantio-enriched cyclopropene (*S*)-**1u** with 85 % *ee* was subjected to the standard condition, (-)-**2u** could be isolated in 75 % yield and the chirality of 4-position in cyclobutenone is obtained diastereoselectively with 83 % *ee*.



Scheme 4. The proposed catalytic cycle.

Based on the experiments above, we proposed a catalytic cycle (Scheme 4). The complexation of dppm ligand to $Rh(cod)_2BF_4$ in the atmosphere of carbon monoxide leads to the formation of active Rh(I) species **A**. Both of carbonyl (or sulfonyl) group and the C-C double bond in substrate **1** could coordinate with **A** to obtain complex **B**. Direct oxidative addition of rhodium(I) to the σ bond in cyclopropene generates Rh(III) intermediate **C,** which is the key step for the regio-divergent (Table 3, **2k** vs **2n**) or diastereoselective (**2u** and **2v**) formation of different cyclobutenones. The reason for regio-divergent formation of **C** is not clear at this moment. The different Lewis basicity of directing group (X = C or SO) may account for the divergent oxidative addition.[14g] The selective migratory insertion of CO to the sp^2 carbon-rhodium bond produces the key rhodacyclopentenone complex **D** with the releasing of the strain energy of cyclopropene moiety. The subsequent reductive elimination of **D** forms the product cyclobutenone **2** and regenerates the active rhodium **A**.

In summary, we have developed the rhodium-catalyzed [3+1][18] carbonylative cycloaddition reaction by C-C bond activation of cyclopropenes to prepare cyclobutenones under mild conditions. The regioselectivity can be controlled by different protecting groups when phenyl and alkyl substituted cyclopropenes were used, which are not possible in the [2+2] cyclobutenones synthesis. The diastereoselective synthesis of cyclobutenones could also be realized with the help of chelating protecting groups and chiral cyclobutenone was obtained for the first time from chiral cyclopropene. The rhodacyclopentenone intermediate was characterized and ligand effect was elucidated. The [3+1] asymmetric cyclobutenones preparation by desymmetrization and kinetic resolution are under investigation in our group.

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Keywords: rhodium • cyclopropene • cyclobutenone • C-C bond activation • rhodacyclopentenone

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[15] CCDC 1826690, 1826693, 1826692, 1851400, 1826703, 1840320 and 1826725 (**2a**, **2b**, **2e**, **2f**, **2i**, **2q** and **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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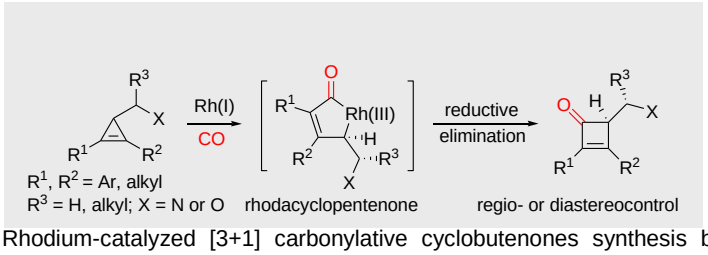

Rhodium-catalyzed [3+1] carbonylative cyclobutenones synthesis by C-C bond activation of cyclopropenes is reported, in which the regio- and diastereoselectivies can be controlled.

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Page No. – Page No.

Rh(I)-Catalyzed Carbonylative [3+1] Construction of Cyclobutenones via C-C σ-Bond Activation of Cyclopropenes