Asymmetric Catalysis

Deutsche Ausgabe: DOI: 10.1002/ange.201502505
Internationale Ausgabe: DOI: 10.1002/anie.201502505

Rhodium-Catalyzed [3+2+2] and [2+2+2] Cycloadditions of Two Alkynes with Cyclopropylideneacetamides**

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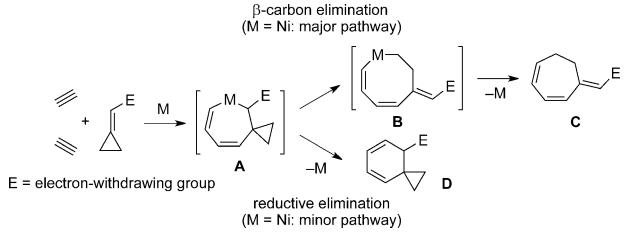
Abstract: *It has been established that a cationic rhodium(I)/H_8-binap complex catalyzes the [3+2+2] cycloaddition of 1,6-diynes with cyclopropylideneacetamides to produce cycloheptadiene derivatives through cleavage of cyclopropane rings. In contrast, a cationic rhodium(I)/(S)-binap complex catalyzes the enantioselective [2+2+2] cycloaddition of terminal alkynes, acetylenedicarboxylates, and cyclopropylideneacetamides to produce spiro-cyclohexadiene derivatives which retain the cyclopropane rings.*

Transition-metal-catalyzed [3+2+2] cycloaddition reactions involving cyclopropylidene compounds are valuable methods for the construction of seven-membered rings.[1] Previously, a cyclopropylideneacetate as a cycloaddition partner and a nickel(0)/phosphine complex as a catalyst were used.[2,3] For example, Saito and co-workers reported the nickel(0)/phosphine-complex-catalyzed intermolecular [3+2+2] cycloaddition of two identical alkynes with the cyclopropylideneacetate.[2h] Subsequently, they developed the cycloaddition of two different alkynes with the cyclopropylideneacetate, although the slow addition of substrates and the large excess of one alkyne component were required.[2g] They also developed the partial intramolecular [3+2+2] cycloaddition of a 1,6-diyne with cyclopropylideneacetate.[2e] A proposed mechanism of the nickel(0)-catalyzed [3+2+2] cycloaddition reactions is shown in Scheme 1.[2a,c–h,4] Two alkynes and cyclopropylideneacetate react with the nickel(0) complex to generate the nickelacycloheptadiene intermediate **A**. A β-carbon atom elimination affords the nickelacyclooctadiene intermediate **B** and subsequent reductive elimination furnishes the cycloheptadiene derivative **C**. Although direct reductive elimination from **A** would furnish the spiro-cyclohexadiene derivative **D**, such reactions are limited to the case using sterically demanding phosphine ligands and proceeded in low yields.[2f,5]



Scheme 1. Transition-metal-catalyzed [3+2+2] and [2+2+2] cycloadditions of two alkynes with methylenecyclopropane derivatives.

Importantly, both cycloheptane[6] and spiro-cyclohexane[7] skeletons are frequently found in biologically active natural products. Therefore, their selective syntheses are important targets for organic synthesis. Herein, we have applied a cationic rhodium(I)/biaryl bis(phosphine) catalyst, which is known to be a highly active catalyst for the [2+2+2] cycloaddition,[8,9] to the cycloaddition reactions involving cyclopropylidene compounds.[10]

Our research group reported that acrylamide derivatives are highly reactive substrates in cationic rhodium(I)-complex-catalyzed [2+2+2] cycloaddition reactions.[11] Therefore, we first examined the reaction of the 1,6-diyne **1a** and *N*-methyl-*N*-phenylcyclopropylidene-acetamide (**2a**) in the presence of cationic rhodium(I)/bisphosphine complexes, as shown in Table 1. We were pleased to find that the [3+2+2] cycloaddition of **1a** with **2a** proceeded using a cationic rhodium(I)/segphos catalyst (20 mol%) to give the [3+2+2] cycloaddition product **3aa** in moderate yield along with the [2+2+2] cycloaddition product **4aa** (entry 1). Screening of bis(phosphine) ligands (entries 1–5) revealed that the use of H_8-binap, which possesses the largest dihedral angle, afforded **3aa** in the highest yield without formation of **4aa** (entry 3), and non-biaryl bis(phosphine) ligands failed to afford **3aa** (entries 4 and 5). The catalyst loading could be reduced to 10 mol% with a slight erosion of the product yield, although prolonged reaction time was required (entry 6).

The scope of the cationic rhodium(I)/H_8-binap-complex-catalyzed [3+2+2] cycloaddition of 1,6-diynes and cyclo-

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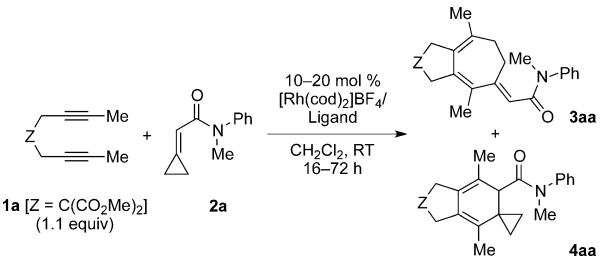
[**] This work was supported partly by a Grant-in-Aid for Scientific Research (No 25105714) from the the Ministry of Education, Culture, Sports, Science and Technology [MEXT (Japan)] and by ACT-C from the Japan Science and Technology Agency]JST (Japan)]. We thank Takasago International Corporation for the gift of segphos and H_8-binap, Umicore for generous support in supplying rhodium complexes, and Dr. Yu Shibata (Tokyo Institute of Technology) for assistance in the preparation of the manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201502505.

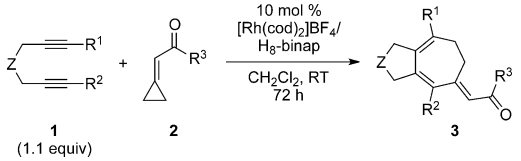
Table 1: Optimization of reaction conditions for the rhodium-catalyzed cycloaddition of **1a** with **2a**.[a]



Entry	Ligand	Catalyst [mol%]	*t* [h]	Yield [%][b] **3aa**	**4aa**
1	segphos	20	16	32	8
2	binap	20	16	60	8
3	H_8-binap	20	16	60	0
4	dppf	20	16	< 2	0
5[c]	dppe	20	16	0	0
6[d]	H_8-binap	10	72	50	0

[a] $[Rh(cod)_2]BF_4$ (0.040 mmol), ligand (0.040 mmol), **1a** (0.22 mmol), **2a** (0.20 mmol), and CH_2Cl_2 (2.0 mL) were used. To a CH_2Cl_2 solution of the rhodium catalyst and **2a** was added a CH_2Cl_2 solution of **1a**. [b] Yield of the isolated product. [c] $[Rh(nbd)_2]BF_4$ was used in place of $[Rh(cod)_2]BF_4$. [d] $[Rh(cod)_2]BF_4$ (0.020 mmol) and ligand (0.020 mmol) were used. binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, H_8-binap = 2,2′-bis(diphenyl-phospino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl, cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenyphosphino)ethane, dppf = 1,1′-bis-(di-phenylphosphino)ferrocene, Segphos = 5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole.

Table 2: Rhodium-catalyzed [3+2+2] cycloadditions of symmetrical 1,6-diynes (**1**) with cyclopropylidene compounds (**2**).[a]

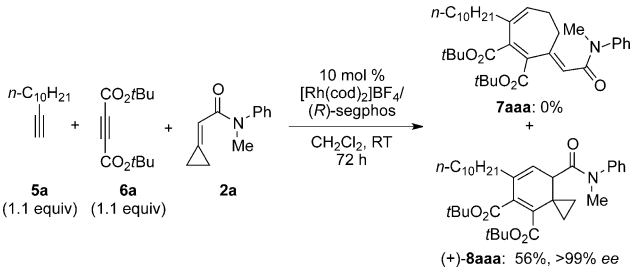


Entry	**1** (Z, R^1, R^2)	**2** (R^3)	**3**/Yield [%][b]
1	**1a** [$C(CO_2Me)_2$, Me, Me]	**2a** (NMePh)	**3aa**/50
2	**1b** (CAc_2, Me, Me)	**2a** (NMePh)	**3ba**/59
3	**1c** [$C(CH_2OBn)_2$, Me, Me]	**2a** (NMePh)	**3ca**/64
4	**1d** (NTs, Me, Me)	**2a** (NMePh)	**3da**/42
5	**1e** (O, Me, Me)	**2a** (NMePh)	**3ea**/54
6	**1f** [$C(CO_2Me)_2$, H, H]	**2a** (NMePh)	complex mixture
7	**1g** (O, Ph, Me)	**2a** (NMePh)	**3ga**/35
8	**1c** [$C(CH_2OBn)_2$, Me, Me]	**2b** (NMe_2)	**3cb**/57
9	**1a** [$C(CO_2Me)_2$, Me]	**2c** (OEt)	complex mixture

[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), (*S*)-H_8-binap (0.020 mmol), **1** (0.22 mmol), **2** (0.20 mmol), and CH_2Cl_2 (2.0 mL) were used. To a CH_2Cl_2 solution of the Rh catalyst and **2** was added a CH_2Cl_2 solution of **1**. [b] Yield of the isolated product. Ts = 4-toluenesulfonyl.

propylideneacetamides was examined as shown in Table 2. With respect to 1,6-diynes, not only quaternary carbon-linked 1,6-diynes (**1a–c**) but also tosylamide- (**1d**) and oxygen-linked (**1e**) 1,6-diynes, possessing the methyl groups at the alkyne termini, reacted with **2a** to give the cycloheptadienes **3aa–ea** in moderate to good yields (entries 1–5). However, the use of the terminal 1,6-diyne **1f** led to a complex mixture of products (entry 6). The reaction of the unsymmetrical 1,6-diyne **1g** and **2a** afforded the cycloheptadiene single regioisomer **3ga** (entry 7). With respect to cyclopropylideneacetamides, not only *N*-methyl-*N*-phenyl (**2a**) but also *N*,*N*-dimethyl (**2b**) amides could be employed (entry 8). However, the reaction of **1a** and the cyclopropylideneacetate **2c** led to a complex mixture of products (entry 9).

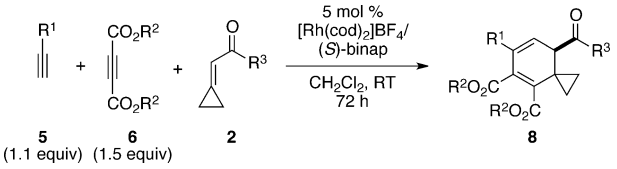
Our research group recently reported the cationic rhodium(I)-complex-catalyzed linear cross-trimerization of terminal alkynes, acetylenedicarboxylates, and acrylamides leading to substituted trienes, presumably through β-hydrogen elimination from rhodacycle intermediates.[12] We anticipated that the use of cyclopropylideneacetamides in place of acrylamides would afford either [3+2+2] or [2+2+2] cycloaddition products as a result of the absence of a β-hydrogen atom. Thus, we next examined the reaction of 1-dodecyne (**5a**), di-*tert*-butyl acetylenedicarboxylate (**6a**), and **2a** in the presence of cationic rhodium(I)/biaryl bisphosphine complexes. We were pleased to find that not the [3+2+2] cycloaddition (**7aaa**) but the [2+2+2] cycloaddition of **5a**, **6a**, and **2a** proceeded using rhodium(I)/(*R*)-segphos (10 mol%) to give the spiro-cyclohexadiene **8aaa** in moderate yield with a perfect *ee* value (Scheme 2).



Scheme 2. Rhodium-catalyzed enantioselective [2+2+2] cycloaddition of **5a**, **6a**, and **2a**.

Optimization of reaction conditions[13] revealed that the use of (*S*)-binap as a ligand and increasing the amount **6a** (1.5 equiv) afforded **8aaa** in the highest yield; the catalyst loading could be reduced to 5 mol%. The reaction scope is shown in Table 3. With respect to acetylenedicarboxylates, not only di-*tert*-butyl (**6a**) but also diethyl (**6b**) and dimethyl (**6c**) acetylenedicarboxylates could be employed (entries 1–3), but a higher catalyst loading (10 mol%) was required for **6c**. With respect to cyclopropylideneacetamides, the use of *N*,*N*-dimethyl (**2b**) and *N*,*N*-diphenyl (**2d**) amides (entries 4 and 5) afforded the corresponding spiro-cyclohexadienes in yields lower than that of **2a** (entry 1). With respect to terminal alkynes, alkyl-, alkenyl-, and aryl-substituted alkynes (**5a–h**) could be employed (entries 1–12), but the use of sterically demanding cyclohexyl (**5c**), cyclohexenyl (**5d**), and aryl (**5e–h**) acetylenes required higher catalyst loadings (10–20 mol%). Interestingly, trimethylsilylacetylene (**5i**) reacted with **2d** (entry 14) in a higher yield than with **2a** (entry 13).[11a] Benzyldimethyl (**5j**) and triethyl (**5k**) silylacetylenes also reacted with **2d** in high yields (entries 15 and 16). However, the use of **2c** significantly lowered the product yield (entry 17). Importantly, excellent *ee* values (96–>99%) were observed in all entries. The absolute configuration of

Table 3: Rhodium-catalyzed enantioselective [2+2+2] cycloadditions of **5**, **6**, and **2**.[a]

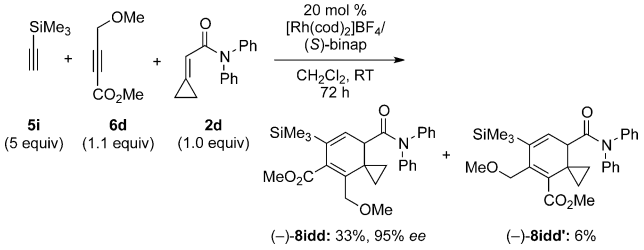


Entry	**5** (R^1)	**6** (R^2)	**2** (R^3)	**8**/Yield%[b] (% *ee*)
1	**5a** (*n*-$C_{10}H_{21}$)	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8aaa**/76 (>99)
2	**5a** (*n*-$C_{10}H_{21}$)	**6b** (Et)	**2a** (NMePh)	(−)-**8aba**/62 (99)
3[c]	**5a** (*n*-$C_{10}H_{21}$)	**6c** (Me)	**2a** (NMePh)	(−)-**8aca**/76 (>99)
4	**5a** (*n*-$C_{10}H_{21}$)	**6a** (*t*Bu)	**2b** (NMe_2)	(−)-**8aab**/50 (99)
5	**5a** (*n*-$C_{10}H_{21}$)	**6a** (*t*Bu)	**2d** (NPh_2)	(−)-**8aad**/59 (>99)
6	**5b** [$(CH_2)_2$Ph]	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8baa**/57 (99)
7[c]	**5c** (Cy)	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8caa**/74 (>99)
8[c]	**5d** (1-cyclohexenyl)	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8daa**/64 (>99)
9[c]	**5e** (Ph)	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8eaa**/65 (>99)
10[d,e]	**5f** (4-BrC_6H_4)	**6a** (*t*Bu)	**2a** (NMePh)	(+)-**8faa**/68 (>99)
11[d,e]	**5g** (4-$F_3CC_6H_4$)	**6a** (*t*Bu)	**2a** (NMePh)	(+)-**8gaa**/55 (99)
12[d,e]	**5h** (4-$MeOC_6H_4$)	**6a** (*t*Bu)	**2a** (NMePh)	(+)-**8haa**/42 (>99)[h]
13	**5i** ($SiMe_3$)	**6a** (*t*Bu)	**2a** (NMePh)	(−)-**8iaa**/73 (98)
14[f]	**5i** ($SiMe_3$)	**6a** (*t*Bu)	**2d** (NPh_2)	(*R*)-(−)-**8iad**/85 (>99)
15[g]	**5j** ($SiBnMe_2$)	**6a** (*t*Bu)	**2d** (NPh_2)	(−)-**8jad**/85 (>99)
16[c]	**5k** ($SiEt_3$)	**6a** (*t*Bu)	**2d** (NPh_2)	(*R*)-(−)-**8kad**/81 (>99)
17[f]	**5i** ($SiMe_3$)	**6a** (*t*Bu)	**2c** (OEt)	(−)-**8iac**/31 (96)

[a] $[Rh(cod)_2]BF_4$ (0.010 mmol), (*S*)-binap (0.010 mmol), **5** (0.22 mmol), **6** (0.30 mmol), **2** (0.20 mmol), and CH_2Cl_2 (2.0 mL) were used. To a CH_2Cl_2 solution of the rhodium catalyst was added CH_2Cl_2 solutions of **2**, **6**, and **5** in this order. [b] Yield of the isolated product based on **2**. [c] Catalyst: 10 mol%. [d] Catalyst: 20 mol%. [e] (*R*)-binap was used. [f] For 16 h. [g] For 24 h. [h] A regioisomeric product was also generated in ca. 10% yield. See the Supporting Information.

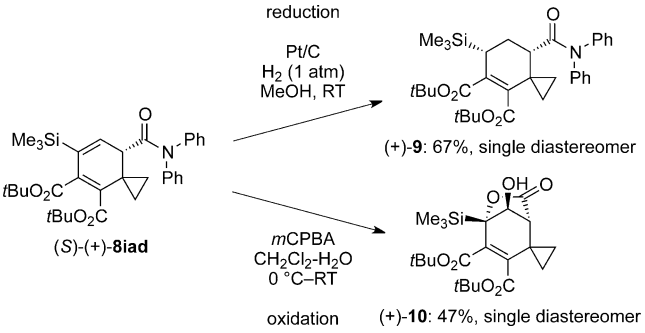
(−)-**8kad** was determined by an X-ray crystallographic analysis.[14]

The reaction of the unsymmetrical acetylenecarboxylate **6d**, possessing the methoxymethyl at the alkyne terminus, **5i**, and **2d** afforded the spiro-cyclohexadiene **8idd** in low yield with a high *ee* value along with a small amount of the regioisomer **8idd′** (Scheme 3).



Scheme 3. Rhodium-catalyzed enantioselective [2+2+2] cycloaddition of **5i**, **6d**, and **2d**.

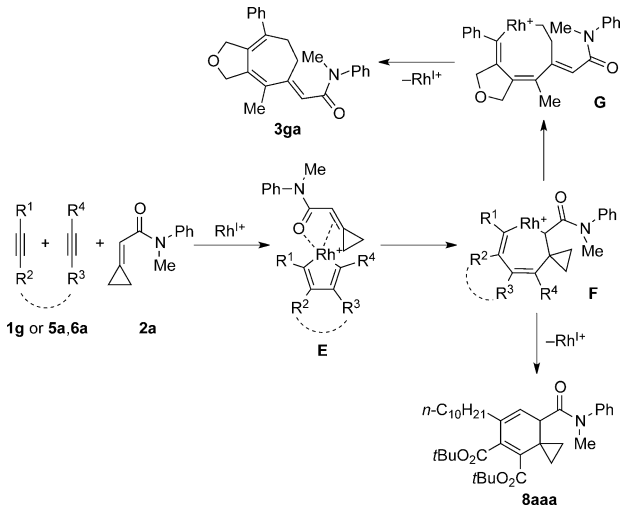
Reductive and oxidative transformation of the reaction product was briefly examined as shown in Scheme 4. Hydrogenation of (+)-**8iad** with Pt/C afforded the cyclohexene (+)-**9** in good yield as a single diastereomer. In contrast, oxidation of (+)-**8iad** with *m*CPBA afforded the lactone (+)-**10** in moderate yield as a single diastereomer, presumably through epoxidation followed by ring opening with the carbonyl oxygen atom.[15] The relative and absolute configurations of (+)-**10** were determined by an X-ray crystallographic analysis.[14]



Scheme 4. Reductive and oxidative transformation of **8iad**. *m*CPBA = *m*-chloroperbenzoic acid.

Possible reaction pathways for the chemo- and regioselective formation of **3ga** and **8aaa** are shown in Scheme 5. The diyne **1g** or the two alkynes **5a** and **6a** react with **2a** and rhodium to generate the intermediate **E**. Regioselective insertion of **2a** into **A** generates the intermediate **F**.[16] When **F** is generated from **1g**, β-carbon elimination affords the intermediate **G** and subsequent reductive elimination furnishes **3ga**. When **F** is generated from **5a** and **6a**, direct reductive elimination from **F** proceeds to give **8aaa**. Although the precise mechanism is not clear at the present stage, difference of steric or electronic nature in **F** may determine the reaction pathway.

In conclusion, we have established that a cationic rhodium(I)/H_8-binap complex catalyzes the [3+2+2] cycloaddition of 1,6-diynes with cyclopropylideneacetamides to produce cycloheptadiene derivatives. To the contrary, a cationic



Scheme 5. Possible mechanism for formation of **3ga** and **8aaa**.

rhodium(I)/(*S*)-binap complex catalyzes the enantioselective [2+2+2] cycloaddition of terminal alkynes, acetylenedicarboxylates, and cyclopropylideneacetamides to produce spirocyclohexadiene derivatives. Future work will focus on elucidation of the precise mechanism and further exploration of the cationic rhodium(I) complex-catalyzed cycloaddition reactions involving cyclopropylidene compounds.

Keywords: asymmetric catalysis · cycloaddition · heterocycles · rhodium · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 8241–8244
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Received: March 18, 2015
Published online: June 1, 2015

