Asymmetric Catalysis

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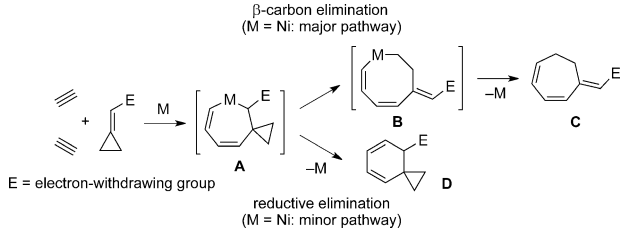
Rhodium-Catalyzed [3+2+2] and [2+2+2] Cycloadditions of Two Alkynes with Cyclopropylideneacetamides**

*Tomoka Yoshida, Yuki Tajima, Masayuki Kobayashi, Koji Masutomi, Keiichi Noguchi, and Ken Tanaka**

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-

[*] T. Yoshida, Y. Tajima, M. Kobayashi, Prof. Dr. K. Tanaka
Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology
Koganei, Tokyo 184-8588 (Japan)
K. Masutomi, Prof. Dr. K. Tanaka
Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152-8550 (Japan)
E-mail: ktanaka@apc.titech.ac.jp
Homepage: http://www.apc.titech.ac.jp/~ktanaka/
Prof. Dr. K. Noguchi
Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588 (Japan)
Prof. Dr. K. Tanaka
Japan Science and Technology Agency (JST), ACT-C
4-1-8 Honcho, Kawaguchi, Saitama, 332-0012 (Japan)

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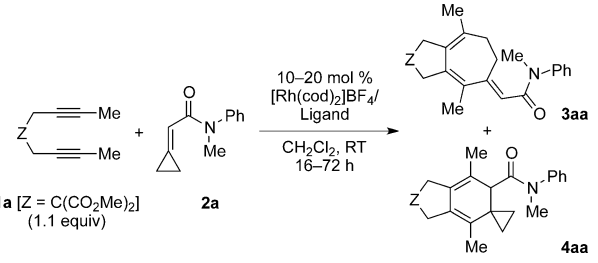
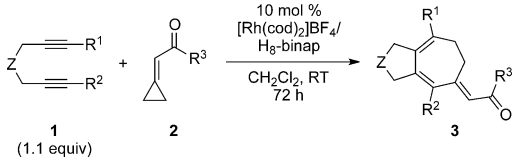
Table 1: Optimization of reaction conditions for the rhodium-catalyzed cycloaddition of **1a** with **2a**.[a]



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]

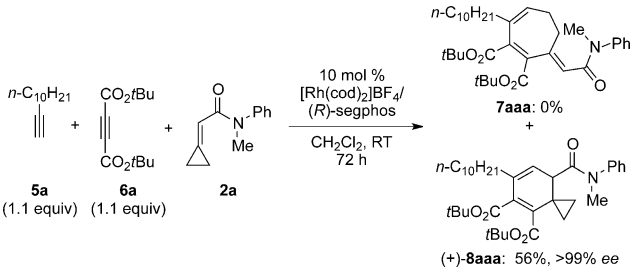


Entry	**1** (Z, R^1, R^2)	**2** (R^3)	**3**/Yield [%][b]
1	**1a** [$C(CO_2Me)_2$, Me, Me]	**2a** (NMePh)	**3aa**/50
2	**1b** (CAc_2, Me, Me)	**2a** (NMePh)	**3ba**/59
3	**1c** [$C(CH_2OBn)_2$, Me, Me]	**2a** (NMePh)	**3ca**/64
4	**1d** (NTs, Me, Me)	**2a** (NMePh)	**3da**/42
5	**1e** (O, Me, Me)	**2a** (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).

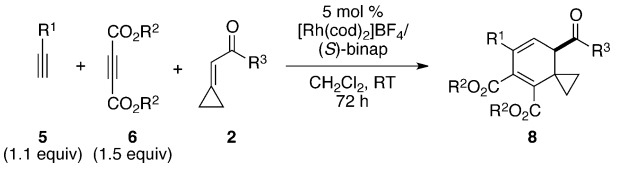
Our research group recently reported the cationic rhodium(I)-complex-catalyzed linear cross-trimerization of terminal alkynes, acetylenedicarboxylates, and acrylamides leading to substituted trienes, presumably through β-hydrogen elimination from rhodacycle intermediates.[12] We anticipated that the 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]



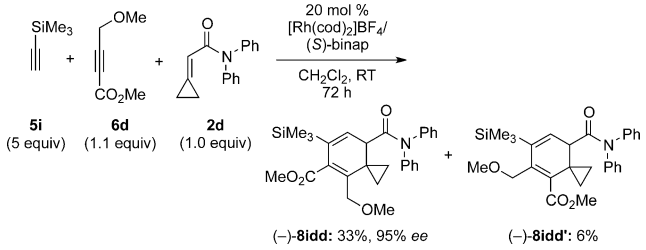
5 (1.1 equiv) **6** (1.5 equiv) **2** **8**

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.

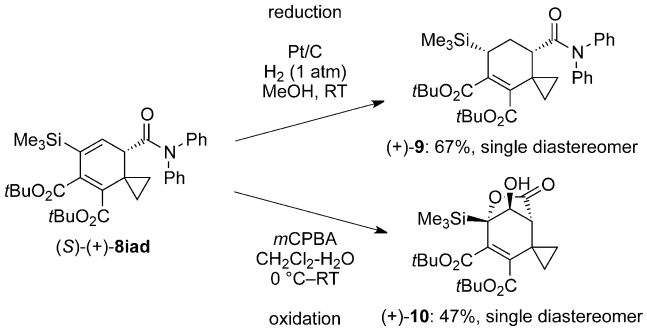
(−)-**8kad** was determined by an X-ray crystallographic analysis.[14]

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**.

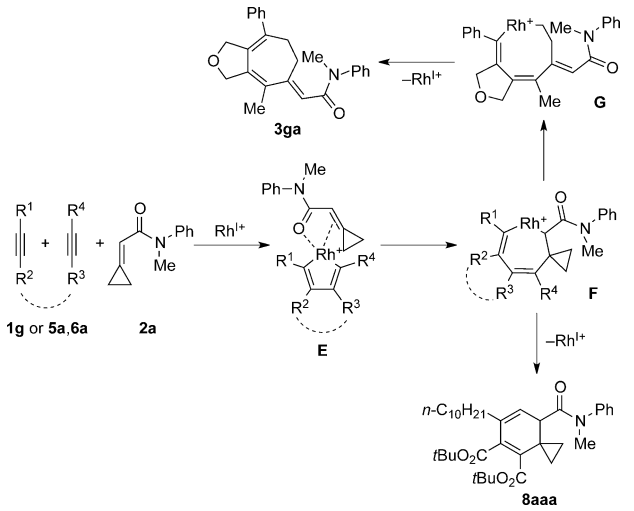
Reductive and oxidative transformation of the reaction product was briefly examined as shown in Scheme 4. Hydrogenation of (+)-**8iad** with Pt/C afforded the cyclohexene (+)-**9** in good yield as a single diastereomer. In contrast, oxidation of (+)-**8iad** with *m*CPBA afforded the lactone (+)-**10** 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

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