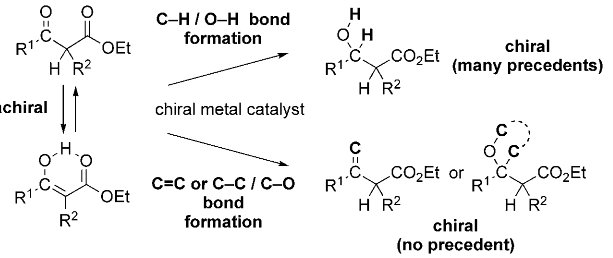
DOI: 10.1002/ange.201007727

Asymmetric Catalysis

Rhodium-Catalyzed Asymmetric Formal Olefination or Cycloaddition: 1,3-Dicarbonyl Compounds Reacting with 1,6-Diynes or 1,6-Enynes**

*Takeshi Suda, Keiichi Noguchi, and Ken Tanaka**

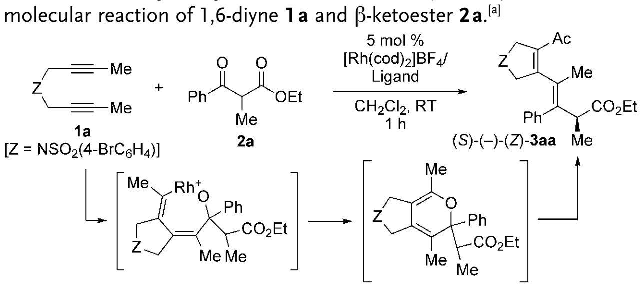
Transition-metal-catalyzed asymmetric hydrogenation of enolizable β-ketoesters leading to β-hydroxyesters is a useful method for the one-step construction of two consecutive stereocenters.[1–3] In this reaction, the ketone carbonyl group is enantioselectively reduced with hydrogen through C−H/O−H bond formation (Scheme 1). In contrast, asymmetric olefination or cycloaddition of the ketone carbonyl group of β-ketoesters through C=C or C−C/C−O bond formation would furnish chiral β,γ-unsaturated esters or β-alkoxyesters in a single step (Scheme 1).[4] Despite potential synthetic utility of such reactions, no report has been found in the literature to date. In 2007 our research group reported that a cationic rhodium(I)/H_8-binap complex[5,6] is a highly active and versatile catalyst for the [2+2+2] cycloaddition[7] of 1,2-dicarbonyl compounds with 1,6-diynes.[8–12] After this report, we succeeded using the cationic rhodium(I)/H_8-binap complex as a catalyst in the asymmetric [2+2+2] cycloaddition of 1,2-dicarbonyl compounds with 1,6-enynes, thereby constructing two stereocenters with high enantio- and diastereoselectivity.[13,14] We report herein the cationic rhodium(I)/H_8-binap or segphos complex as a catalyst for the asymmetric formal olefination and cycloaddition of 1,3-dicarbonyl compounds with 1,6-diynes and 1,6-enynes, respectively, which construct one or three stereocenters with high diastereo- and enantioselectivity.[15]



Scheme 1. Transition-metal-catalyzed asymmetric C−H/O−H versus C=C or C−C/C−O bond-forming reactions of enolizable β-ketoesters.

We first investigated the reaction of β-ketoester **2a** (1.1 equiv) with sulfonamide-linked 1,6-diyne **1a** in the presence of a cationic rhodium(I)/(*R*)-binap complex (5 mol%). Gratifyingly, the reaction proceeded at room temperature for only 1 hour to give α-methyl-β,γ-unsaturated ester **3aa** with moderate yield and enantioselectivity presumably through [2+2+2] cycloaddition and subsequent electrocyclic ring opening[16] (Table 1, entry 1). After screening biaryl bisphosphine ligands (entries 1–3), the use of (*R*)-segphos furnished **3aa** with the highest *ee* value, but the yield was still moderate (entry 3). The use of excess **2a** (2.0 equiv) in the reaction using (*R*)-segphos increased the product yield along with slight improvement of the product *ee* value (entry 4). Significant improvement of both the product yield and *ee* value using excess **2a** was observed in the reaction using (*R*)-H_8-binap, which furnished **3aa** with the highest yield and *ee* value (entry 5). The absolute configuration of the major

Table 1: Screening of ligands for rhodium-catalyzed asymmetric intermolecular reaction of 1,6-diyne **1a** and β-ketoester **2a**.[a]



Entry	Ligand	**2a** [equiv]	Yield [%][b] (*E*/*Z*)	*ee* [%][c]
1	(*R*)-binap	1.1	69 (1:7)	61 (*S*)
2	(*R*)-H_8-binap	1.1	66 (1:7)	70 (*S*)
3	(*R*)-segphos	1.1	61 (1:5)	92 (*S*)
4	(*R*)-segphos	2.0	83 (1:6)	94 (*S*)
5	(*R*)-H_8-binap	2.0	97 (1:7)	96 (*S*)

[a] In all entries, complete conversions of **1a** were observed. [b] Yield of isolated product. [c] The *ee* value and absolute configuration of a major olefin geometric isomer. (*R*)-binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, (*R*)-H_8-binap = (*R*)-2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl, cod = 1,5-cyclooctadiene, (*R*)-segphos = (*R*)-5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole.

[*] T. Suda, Prof. Dr. K. Tanaka
Department of Applied Chemistry, Graduate School of Engineering
Tokyo University of Agriculture and Technology
Koganei, Tokyo 184-8588 (Japan)
Fax: (+81) 42-388-7037
E-mail: tanaka-k@cc.tuat.ac.jp
Homepage: http://www.tuat.ac.jp/~tanaka-k/
Prof. Dr. K. Noguchi
Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588 (Japan)

[**] This work was supported partly by Grants-in-Aid for Scientific Research (Nos. 20675002 and 20·8746) from MEXT (Japan). We are grateful to Takasago International Corporation for the gift of H_8-binap, segphos, and xyl-segphos, and Umicore for generous support in supplying a rhodium complex.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007727.

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product (−)-(*Z*)-**3aa** was determined to be *S* by derivatization into the known (*R*)-2-benzoyl-1-propanol.[17]

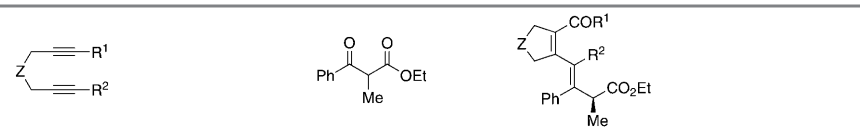
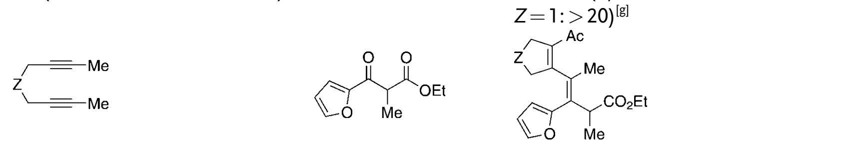
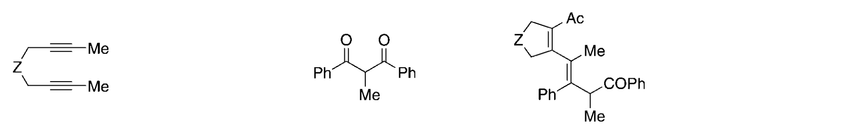
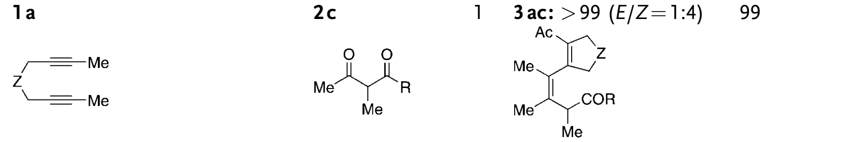
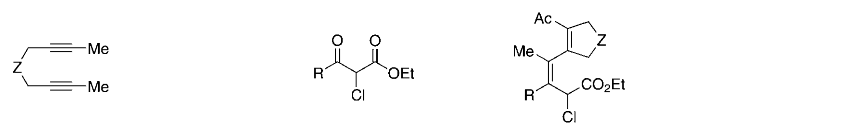
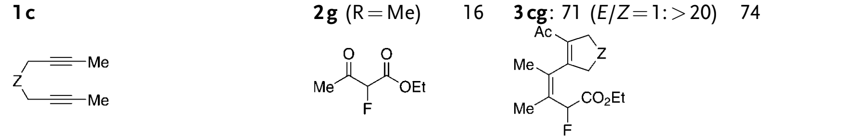
The generality of the asymmetric intermolecular formal olefination of 1,3-dicarbonyl compounds with 1,6-diynes was then examined by using the cationic rhodium(I)/(*R*)-H_8-binap complex as a catalyst at room temperature (Table 2).[16] With respect to 1,6-diynes, a variety of symmetrical and unsymmetrical internal 1,6-diynes (**1a**–**e**; entries 1–5) could be employed for this reaction, although a moderate *ee* value was observed in the case of **1c** (entry 3) and slow additions were required in cases of **1d** and **1e** (entries 4 and 5). With respect to 1,3-dicarbonyl compounds, both aryl-substituted β-ketoesters **2a** and **2b** (entries 1 and 6) and 1,3-diketone **2c** (entry 7) reacted with **1a** to give the formal olefination products with high yields and *ee* values. However, the reactions of both methyl-substituted β-ketoester **2d** (entry 8) and 1,3-diketone **2e** (entry 9) with **1a** proceeded in lower yields because of the formation of the homo-[2+2+2]-cycloaddition products of **1a**, although the *ee* values were high. The formation of chloro- or fluoro-substituted stereocenters (entries 10–13) other than methyl-substituted ones was also possible, although the lower enantioselectivity was observed.

Next, the asymmetric [2+2+2] cycloaddition of β-ketoester **2a** with sulfonamide-linked 1,6-enyne **4** was attempted, and was expected to furnish the bicyclic chiral ester **5** possessing three stereocenters (Scheme 2). However, no reaction was observed at room temperature, and the homo-[2+2+2] cycloaddition of 1,6-enyne **4** proceeded at 80 °C.

Thus, an asymmetric intramolecular [2+2+2] cycloaddition of a β-ketoester with a 1,6-enyne was investigated as shown in Table 3.[18] Fortunately, the reaction of substrate **6a**, in which the 1,6-enyne and α-methyl-β-ketoester moieties are connected with a benzene ring, in the presence of the cationic rhodium(I)/(*S*)-binap complex (10 mol %) proceeded at 80 °C to give the desired cycloaddition product **7a** in good yield with excellent diastereoselectivity, although the enantioselectivity was moderate (entry 1). After screening biaryl bisphosphine ligands (entries 1–3), the use of (*S*)-segphos furnished **7a** with the highest yield and *ee* value (entry 3). As increasing the steric bulk on the phosphorus [(*S*)-xyl-segphos] decreased both the yield and *ee* value (entry 4), (*S*)-segphos was selected as the best ligand.

The generality of this asymmetric intramolecular [2+2+2] cycloaddition of 1,3-dicarbonyl compounds with 1,6-enynes was then examined by using the cationic rhodium(I)/(*S*)-segphos complex as a catalyst at 80 °C (Table 4). With respect to the 1,3-dicarbonyl moieties, both acetyl (**6a**; entry 1) and benzoyl esters (**6b**; entry 2) could

Table 2: Rhodium-catalyzed asymmetric intermolecular formal olefination of 1,3-dicarbonyl compounds with 1,6-diynes.[a]

Entry	1	2	*t* [h]	Yield [%][b]	*ee* [%][c]
					
1	**1a** (Z = NSO_2Ar,[d] $R^1 = R^2$ = Me)	**2a**	1	(*S*)-**3aa**: 97 (*E*/*Z* = 1:7)	96
2	**1b** (Z = NTs, $R^1 = R^2$ = Me)	**2a**	1	**3ba**: 95 (*E*/*Z* = 1:8)	95
3[e]	**1c** (Z = $C(CO_2Bn)_2$, $R^1 = R^2$ = Me)	**2a**	16	**3ca**: 72 (*E*/*Z* = 1:7)	59
4[f]	**1d** (Z = NTs, $R^1 = R^2$ = Et)	**2a**	3	**3da**: 24 (*E*/*Z* = 1:>20)	99
5[f]	**1e** (Z = NTs, R^1 = Ph, R^2 = Me)	**2a**	16	**3ea**: 62 (*E*/*Z* = 1:>20)[g]	99
					
6	**1a**	**2b**	1	**3ab**: 89 (*E*/*Z* = 1:1)	95 (*E*), 95 (*Z*)
					
7	**1a**	**2c**	1	**3ac**: >99 (*E*/*Z* = 1:4)	99
					
8	**1a**	**2d** (R = OEt)	1	**3ad**: 38 (*E*/*Z* = 1:6)	94
9	**1a**	**2e** (R = Me)	16	**3ae**: 54 (*E*/*Z* = 1:2)	94 (*E*), 93 (*Z*)
					
10	**1a**	**2f** (R = Ph)	1	**3af**: 96 (*E*/*Z* = 1:3)	79
11	**1a**	**2g** (R = Me)	1	**3ag**: 50 (*E*/*Z* = 1:>20)	84
12[e]	**1c**	**2g** (R = Me)	16	**3cg**: 71 (*E*/*Z* = 1:>20)	74
					
13[e]	**1c**	**2h**	16	**3ch**: 65 (*E*/*Z* = 1:10)	67

[a] Reactions conditions: $[Rh(cod)_2]BF_4$ (5 mol %), (*R*)-H_8-binap (5 mol %), **1a**–**e** (1 equiv), **2a**–**h** (2 equiv) in CH_2Cl_2 at room temperature. Structure of the major olefin geometry isomer was described. [b] Yield of isolated product. [c] The *ee* value of the major olefin geometric isomer. [d] Ar = 4-BrC_6H_4. [e] Ligand: (*S*)-segphos (entry 3). Ligand: (*R*)-segphos (entries 12 and 13). [f] **1** was added to **2a** and the Rh catalyst over 2 h. [g] The regioisomer was generated in approximately 10 %, although this compound could not be isolated in a pure form. Bn = benzyl, Ts = 4-toluenesulfonyl.

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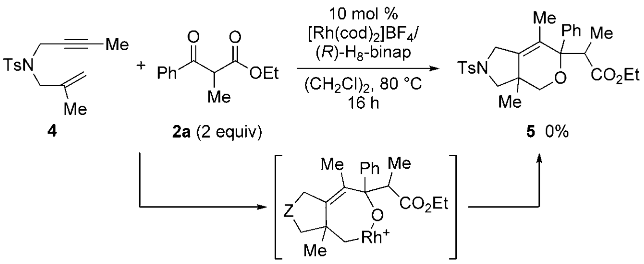
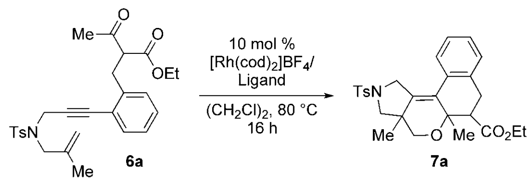


Scheme 2. Rhodium-catalyzed intermolecular reaction of 1,6-enyne **4** and β-ketoester **2a**.

Table 3: Screening of ligands for rhodium-catalyzed asymmetric intramolecular reaction of **6a**.



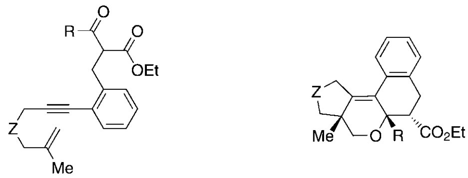
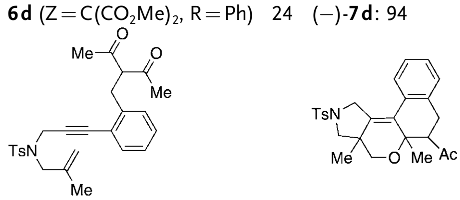
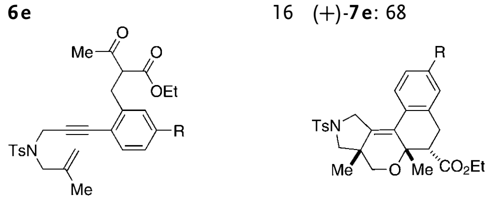
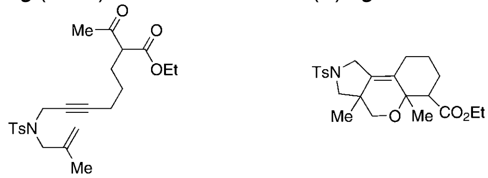
Entry	Ligand	Conv. [%][a]	Yield [%][b]	*ee* [%]
1	(*S*)-binap	90	72	61 (+)
2	(*S*)-H_8-binap	100	87	45 (+)
3	(*S*)-segphos	100	94	86 (+)
4	(*S*)-xyl-segphos	59	43	60 (+)

[a] Determined by ^{1}H NMR analysis. [b] Yield of isolated product. xyl-segphos = 5,5′-bis[di(3,5-dimethylphenyl)phosphino]-4,4′-bi-1,3-benzodioxole.

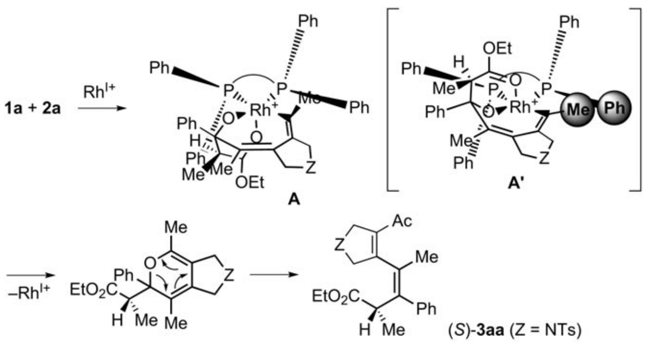
equally be employed to give tetracyclic esters **7a** and **7b**, respectively in high yields with good *ee* values. This observation is in sharp contrast to the reactions of entries 1 and 8 in Table 2 that exhibited significantly different reactivity. Not only β-ketoesters but also 1,3-diketone **6e** could participate in this reaction, although the product yield decreased (entry 5). With respect to the 1,6-enyne moieties, not only sulfonamide-linked 1,6-enynes but also malonate-linked 1,6-enynes **6c** and **6d** could be employed (entries 3 and 4). With respect to the tethers between the 1,6-enyne and 2-methylene-1,3-dicarbonyl moieties, not only the phenyl group but also the methoxyphenyl (**6f**; entry 6) and chlorophenyl (**6g**; entry 7) groups could be employed to give tetracyclic esters **7f** and **7g**, respectively, in high yields with good *ee* values. Furthermore, tricyclic ester **7h** could also be obtained with high *ee* value, although a high catalyst loading was required (entry 8). Importantly, the present asymmetric intramolecular [2+2+2] cycloaddition of 1,3-dicarbonyl compounds with 1,6-enynes is highly diastereoselective. Other diastereomers were detected in at least less than 5% yields by ^{1}H NMR analysis of the crude reaction mixture.

Possible mechanisms for the selective formation of (*S*)-**3aa** and (3a*R*,5a*R*,6*R*)-**7b** using (*R*)-H_8-binap and (*S*)-segphos ligands are shown in Schemes 3 and 5, respectively, although the precise mechanisms cannot be concluded at the present stage. The reaction of **1a** and **2a** with the cationic rhodium(I)/(*R*)-H_8-binap complex furnishes intermediate **A** through coordination of the ester carbonyl group to rhodium.

Table 4: Rhodium-catalyzed asymmetric intramolecular cycloaddition of 1,3-dicarbonyl compounds with 1,6-enynes.[a]

Entry	6	*t* [h]	Yield [%][b]	*ee* [%]
				
1	**6a** (Z = NTs, R = Me)	16	(+)-**7a**: 94,	86
2	**6b** (Z = NTs, R = Ph)	16	(3a*R*,5a*R*,6*R*)-(−)-**7b**[c]: 95	87
3	**6c** (Z = C(CO_2Me)$_2$, R = Me)	16	(−)-**7c**: 98	88
4	**6d** (Z = C(CO_2Me)$_2$, R = Ph)	24	(−)-**7d**: 94	74
				
5[d]	**6e**	16	(+)-**7e**: 68	85
				
6	**6f** (R = OMe)	16	(+)-**7f**: 80	80
7	**6g** (R = Cl)	16	(+)-**7g**[c]: 90	84
				
8[e]	**6h**	24	(+)-**7h**: 59	92

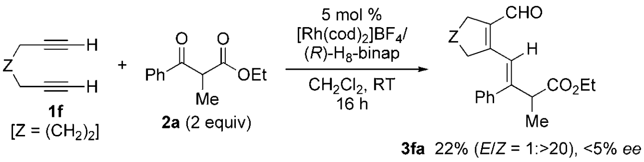
[a] Reaction conditions: [Rh(cod)$_2$]BF_4 (10 mol%), (*S*)-segphos (10 mol%), **6a–h** in (CH_2Cl)$_2$, 80°C. [b] Yield of isolated product. [c] The relative and absolute configuration of (−)-**7b** was determined to be 3a*R*,5a*R*,6*R* by the X-ray crystallographic analysis of the corresponding 4-bromobenzoyl ester (−)-**8**.[17,19] The relative configuration of (±)-**7g** was also confirmed by the X-ray crystallographic analysis of the corresponding 4-bromobenzoyl ester (±)-**9**.[17,19] [d] Ligand: (*S*)-binap. [e] Catalyst: 20 mol%.



Scheme 3. Possible mechanism for cationic rhodium(I)/(*R*)-H_8-binap-catalyzed selective formation of (*S*)-**3aa**.

Reductive elimination of rhodium and subsequent electrocyclic ring-opening furnishes (*S*)-**3aa**. The formation of intermediate **A′**, which would furnish (*R*)-**3aa**, is unfavorable because of the steric interaction between the equatorial phenyl group on the phosphorus atom of (*R*)-H_8-binap and the methyl group derived from **1a**.

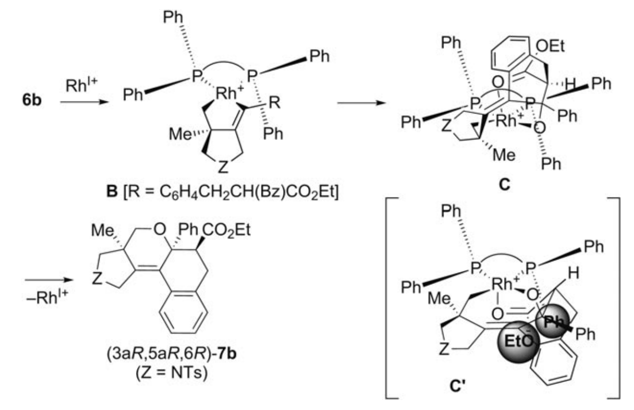
Indeed, the reactions of sterically more demanding internal diynes **1d**,**e** and **2a** furnished products **3da** and **3ea**, respectively, with higher *ee* values than **3ba** (Table 2, entries 4 and 5 versus entry 2). In contrast, the reaction of sterically less demanding terminal diyne **1e**[20] and **2a** furnished almost racemic product **3fa** (Scheme 4).



Scheme 4. Rhodium-catalyzed asymmetric intramolecular cycloaddition of 1,3-dicarbonyl compound with 1,6-diyne.

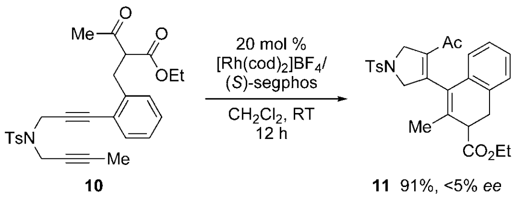
As shown in Scheme 5, the reaction of **6b** with the cationic rhodium(I)/(*S*)-segphos complex furnishes intermediate **B**, in which one chiral center is constructed enantioselectively. Indeed, this observed enantioface selection is consistent with our previously reported rhodium-catalyzed asymmetric intermolecular [2+2+2] cycloaddition of 1,2-dicarbonyl compounds with 1,6-enynes.[13] Subsequent ketone carbonyl group insertion and coordination of the ester carbonyl group to rhodium are able to furnish two intermediates, **C** and **C′**, in which two additional chiral centers are constructed diastereoselectively. However, the formation of the intermediate **C′**, which furnishes (3a*R*,5a*S*,6*S*)-**7b**, would be unfavorable because of the steric interaction between the axial phenyl group on the phosphorus atom of (*S*)-segphos and the ethoxy group derived from **6b**. Thus, reductive elimination of rhodium from the intermediate **C** furnishes (3a*R*,5a*R*,6*R*)-**7b**.

Importantly, the opposite absolute configurations of the tertiary stereocenter, α to the carbonyl group, were observed



Scheme 5. Possible mechanism for cationic rhodium(I)/(*S*)-segphos-catalyzed selective formation of (3a*R*,5a*R*,6*R*)-**7b**.

between the intermolecular reaction of 1,3-dicarbonyl compounds with 1,6-diynes and the intramolecular reaction of 1,3-dicarbonyl compounds with 1,6-enynes. Thus for comparison, the intramolecular reaction of a 1,3-dicarbonyl compound with a 1,6-diyne, not a 1,6-enyne, was examined. Interestingly, the reaction of substrate **10** proceeded to give almost racemic product **11**, although the product yield was high (Scheme 6).



Scheme 6. Rhodium-catalyzed intramolecular cycloaddition of 1,3-dicarbonyl compound with 1,6-diyne.

In conclusion, we have developed the cationic rhodium(I)/(*R*)-H_8-binap complex as a catalyst for the asymmetric intermolecular formal olefination of enolizable 1,3-dicarbonyl compounds with 1,6-diynes by [2+2+2] cycloaddition and subsequent electrocyclic ring opening. The asymmetric intramolecular [2+2+2] cycloaddition of 1,3-dicarbonyl compounds with 1,6-enynes was also accomplished by using a cationic rhodium(I)/(*S*)-segphos complex as a catalyst. Future work will focus on the synthetic application of this methodology.[21]

Received: December 9, 2010
Revised: February 28, 2011
Published online: April 7, 2011

Keywords: asymmetric catalysis · cycloaddition · enynes · olefination · rhodium

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