JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Rhodium-Catalyzed Enantioselective Cyclizations of γ-Alkynylaldehydes with Acyl Phosphonates: Ligand- and Substituent-Controlled C−P or C−H Bond Cleavage

Kengo Masuda,[†] Norifumi Sakiyama,[†] Rie Tanaka,[†] Keiichi Noguchi,[‡] and Ken Tanaka*[,†]

[†]Department of Applied Chemistry, Graduate School of Engineering, and [‡]Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

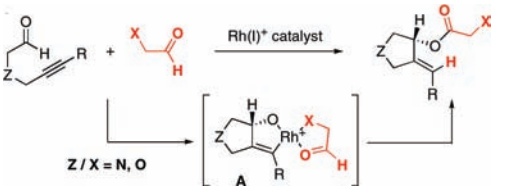
Supporting Information

ABSTRACT: It has been established that a cationic rhodium(I)/(*R*)-H_8-BINAP or (*R*)-Segphos complex catalyzes two modes of enantioselective cyclizations of γ-alkynylaldehydes with acyl phosphonates via C−P or C−H bond cleavage. The ligands of the Rh(I) complexes and the substitutents of both γ-alkynylaldehydes and acyl phosphonates control these two different pathways.

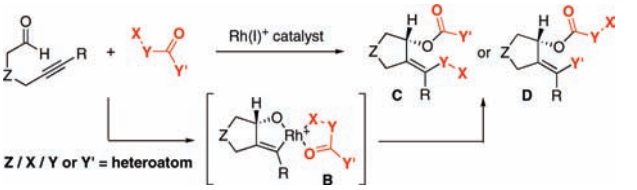
Transition-metal-catalyzed reductive coupling is a valuable strategy for regio- and stereocontrolled formation of C−C bonds.[1] A number of transition-metal-catalyzed intramolecular reductive cyclizations of γ-alkynylaldehydes have been developed for the stereoselective synthesis of cyclic allylic alcohols with a trisubstituted alkene component.[2−4] For these cyclizations, the combinations of nickel catalysts and organosilanes,[2c,f] and rhodium catalysts and dihydrogen,[3c] have been most frequently employed. Montgomery proposed that the Ni-catalyzed cyclization using organosilanes proceeds via σ-bond metathesis of the organosilane Si−H bond and the Ni−O bond of the oxanickelacyclopentene intermediate.[2c,f] Krische proposed that the Rh-catalyzed cyclization using dihydrogen proceeds via σ-bond metathesis of the dihydrogen H−H bond and the Rh−O bond of the oxarhodacyclopentene intermediate.[3c] Recently, our research group discovered the cationic Rh(I)/(*R*)-H_8-BINAP complex-catalyzed enantioselective reductive cyclization of γ-alkynylaldehydes with heteroatom-substituted acetaldehydes, leading to cyclic allylic esters with a trisubstituted alkene component (Scheme 1).[5] Mechanistic studies indicated that the reaction would proceed through oxarhodacyclopentene intermediate **A** with the chelating heteroatom-substituted acetaldehyde.[5]

We anticipated that reaction of the γ-alkynylaldehyde and a chelating carbonyl compound, possessing the heteroatom−carbonyl bond (Z/X/Y or Y′ = heteroatom), would furnish cyclization product **C** or **D** through cleavage of the heteroatom−carbonyl bond (C−Y or C−Y′ bond) in oxarhodacyclopentene intermediate **B** (Scheme 2). In this Communication, this hypothesis is embodied as the cationic Rh(I)/(*R*)-H_8-BINAP complex-catalyzed enantioselective cyclization of γ-alkynylaldehydes with acyl phosphonates, leading to cyclic allylic esters with a tetrasubstituted alkene component[6] through C−P bond cleavage. In addition, it was found that a cationic Rh(I)/(*R*)-Segphos complex catalyzes another enantioselective

Scheme 1



Scheme 2



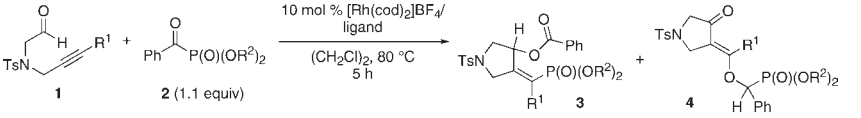
cyclization of γ-alkynylaldehydes with acyl phosphonates, which furnishes cyclic α,β-unsaturated ketones with a tetrasubstituted alkene component[6] through C−H bond cleavage.

We first examined the reaction of tosylamide-linked γ-alkynylaldehyde **1a** and diethyl benzoyl phosphonate (**2a**) in the presence of the cationic Rh(I)/(*R*)-H_8-BINAP complex (10 mol %). Gratifyingly, the expected cyclization of **1a** with **2a** via C−P bond cleavage[7,8] proceeded at 80 °C to give cyclic allylic ester **3aa** in good yield with excellent ee (Table 1, entry 1). The effect of bisphosphine ligands (Figure 1) was then examined, which revealed that biaryl bisphosphine ligands are effective for this reaction and yields of **3aa** are linearly correlated with dihedral angles of ligands [dihedral angles,[9] H_8-BINAP > BINAP > Segphos; yields of **3aa**, H_8-BINAP > BINAP > Segphos] (entries 1−3), while non-biaryl bisphosphine ligands are totally ineffective (entries 4 and 5). Interestingly, the use of (*R*)-Segphos as a ligand furnished another cyclization product, cyclic α,β-unsaturated ketone **4aa**, via the aldehyde C−H bond cleavage in 24% yield with 98% ee (entry 3). The yield of **3** was significantly decreased and that of **4** was slightly increased by employing γ-alkynylaldehyde **1b**, possessing the *n*-butyl group at the alkyne terminus, instead of **1a** (entry 6). Importantly, the correlation between yields of products and dihedral angles of

Received: February 11, 2011
Published: April 18, 2011

dx.doi.org/10.1021/ja201337x | *J. Am. Chem. Soc.* 2011, 133, 6918–6921

Table 1. Effect of Ligands and Substituents of γ-Alkynylaldehydes 1 and Benzoyl Phosphonates 2



entry	1 (R^1)	2 (R^2)	ligand	3/% yield[a] (% ee)	4/% yield[a] (% ee)
1	**1a** (Me)	**2a** (Et)	(*R*)-H_8-BINAP	(+)-**3aa**/73 (>99)	**4aa**/0
2	**1a** (Me)	**2a** (Et)	(*R*)-BINAP	(+)-**3aa**/67 (>99)	**4aa**/7[b]
3	**1a** (Me)	**2a** (Et)	(*R*)-Segphos	(+)-**3aa**/55 (>99)	(−)-**4aa**/24 (98)
4[c]	**1a** (Me)	**2a** (Et)	(*S,S*)-DIOP	**3aa**/0	**4aa**/0
5[c,d]	**1a** (Me)	**2a** (Et)	(*S,S*)-Chiraphos	**3aa**/0	**4aa**/0
6	**1b** (*n*-Bu)	**2a** (Et)	(*R*)-H_8-BINAP	(+)-**3ba**/20 (>99)	(+)-**4ba**/26 (97)
7	**1b** (*n*-Bu)	**2a** (Et)	(*R*)-BINAP	(+)-**3ba**/13 (>99)	(+)-**4ba**/29 (97)
8	**1b** (*n*-Bu)	**2a** (Et)	(*R*)-Segphos	**3ba**/0	(+)-**4ba**/67 (99)
9	**1a** (Me)	**2b** (Me)	(*R*)-H_8-BINAP	(+)-**3ab**/73 (>99)	**4ab**/0
10	**1a** (Me)	**2c** (*i*-Pr)	(*R*)-H_8-BINAP	(+)-**3ac**/30 (>99)	**4ac**/10[b]
11	**1a** (Me)	**2c** (*i*-Pr)	(*R*)-Segphos	(+)-**3ac**/17 (>99)	(−)-**4ac**/60 (>99)
12	**1b** (*n*-Bu)	**2b** (Me)	(*R*)-H_8-BINAP	(+)-**3bb**/26 (>99)	**4bb**/11[b]
13	**1b** (*n*-Bu)	**2c** (*i*-Pr)	(*R*)-H_8-BINAP	**3bc**/0	(−)-**4bc**/36 (98)
14	**1b** (*n*-Bu)	**2c** (*i*-Pr)	(*R*)-Segphos	**3bc**/0	(−)-**4bc**/77 (>99)

[a] Isolated yield. [b] NMR yield. The product could not be isolated in a pure form. [c] For 16 h. [d] $[Rh(nbd)_2]BF_4$ was used.

ligands in the formation of ketone **4ba** is opposite to that in the formation of ester **3aa** [yields of **4ba**, H_8-BINAP < BINAP < Segphos] (entries 6−8). The effect of the alkoxy groups of benzoyl phosphonates was also examined (entries 9−14): the use of sterically less demanding dimethyl benzoyl phosphonate (**2b**) furnished the corresponding esters **3** as major products (entries 9 and 12); in contrast, the use of sterically demanding diisopropyl benzoyl phosphonate (**2c**) increased the yields of the corresponding ketones **4** (entries 10 and 13). The combined use of sterically demanding acyl phosphonate **2c** and (*R*)-Segphos, possessing the smallest dihedral angle, furnished ketones **4** in the highest yields (entries 11 and 14).

Thus, we explored the scope of the enantioselective cyclization of γ-alkynylaldehydes with acyl phosphonates via the C−P bond cleavage by using 10 mol % of the cationic Rh(I)/(*R*)-H_8-BINAP complex at 80 °C, as shown in Table 2. With respect to γ-alkynylaldehydes, **1c** and **1a**, possessing hydrogen and the methyl group, respectively, at the alkyne terminus reacted with **2a** to give the corresponding esters in good yields with excellent ee's (entries 1 and 2). On the other hand, aldehydes **1d**, **1b**, and **1e**, possessing sterically demanding ethyl, *n*-butyl, and phenyl groups, respectively, at the alkyne terminus, reacted with **2b** to give the corresponding esters in moderate to low yields (entries 3−5). Not only tosylamide-linked γ-alkynylaldehydes **1a**−**e** but also ether-linked γ-alkynylaldehyde **1f** could participate in this reaction by using excess **2a** (entry 6). With respect to acyl phosphonates, sterically and electronically diverse aryl groups could be employed for the carbonyl substituent to give the corresponding esters in good yields with excellent ee's (entries 7−11). Alkyl groups could also be employed for the carbonyl substituent to give the corresponding esters in good yields with excellent ee's (entries 12−14). The absolute configuration of (+)-**3ca** was unambiguously determined to be *S* by the anomalous dispersion method.

Reaction of γ-alkynylaldehyde **1e** and ketoester **5** instead of acyl phosphonate **2** was also examined under the same reaction conditions employed in Table 2, but an unidentified complex mixture of products was generated. At room temperature, the corresponding dimer **6**[S] was generated with high yield and ee (Scheme 3).[10]

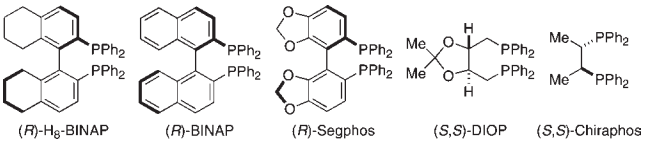
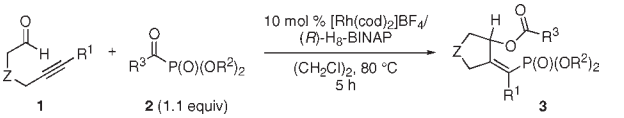


Figure 1. Structures of chiral bisphosphine ligands.

Table 2. Rh-Catalyzed Enantioselective Cyclization of 1 with 2 via C−P Bond Cleavage



entry	1 (Z, R^1)	2 (R^3, R^2)	3	yield (%)[a]	ee (%)
1	**1c** (NTs, H)	**2a** (Ph, Et)	(*S*)-(+)-**3ca**	64	>99
2	**1a** (NTs, Me)	**2a** (Ph, Et)	(+)-**3aa**	73	>99
3	**1d** (NTs, Et)	**2b** (Ph, Me)	(+)-**3db**	40	>99
4	**1b** (NTs, *n*-Bu)	**2b** (Ph, Me)	(+)-**3bb**	26	>99
5	**1e** (NTs, Ph)	**2b** (Ph, Me)	(+)-**3eb**	39	>99
6[b]	**1f** [O, $(CH_2)_3$Ph]	**2a** (Ph, Et)	(+)-**3fa**	33	>99
7	**1a** (NTs, Me)	**2d** (2-MeC_6H_4, Et)	(+)-**3ad**	67	>99
8	**1a** (NTs, Me)	**2e** (4-ClC_6H_4, Et)	(+)-**3ae**	71	>99
9	**1a** (NTs, Me)	**2f** (4-FC_6H_4, Et)	(+)-**3af**	65	>99
10	**1c** (NTs, H)	**2g** (4-$MeOC_6H_4$, Et)	(+)-**3cg**	65	>99
11	**1a** (NTs, Me)	**2g** (4-$MeOC_6H_4$, Et)	(+)-**3ag**	53	>99
12	**1a** (NTs, Me)	**2h** (Me, Et)	(+)-**3ah**	71	>99
13	**1a** (NTs, Me)	**2i** (Et, Et)	(+)-**3ai**	69	>99
14	**1a** (NTs, Me)	**2j** (*i*-Pr, Et)	(+)-**3aj**	72	>99

[a] Isolated yield. [b] **2a**, 2.5 equiv.

dx.doi.org/10.1021/ja201337x |*J. Am. Chem. Soc.* 2011, 133, 6918–6921

Scheme 3

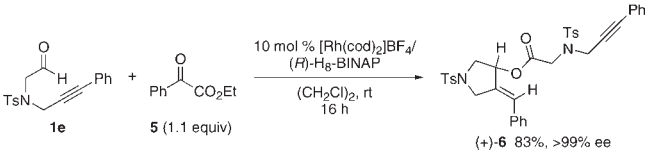
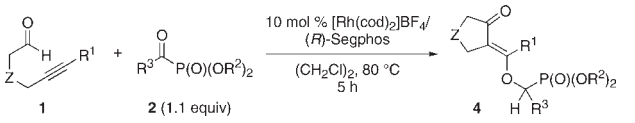


Table 3. Rh-Catalyzed Enantioselective Cyclization of 1 with 2 via C−H Bond Cleavage



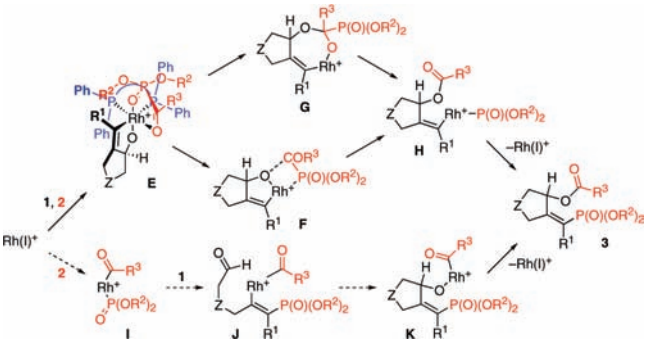
entry	1 (Z, R^1)	2 (R^3, R^2)	4	yield (%)[a]	ee (%)
1	**1c** (NTs, H)	**2c** (Ph, *i*-Pr)	**4cc**	0	–
2	**1a** (NTs, Me)	**2c** (Ph, *i*-Pr)	(−)-**4ac**	60	>99
3	**1d** (NTs, Et)	**2c** (Ph, *i*-Pr)	(−)-**4dc**	74	>99
4	**1b** (NTs, *n*-Bu)	**2c** (Ph, *i*-Pr)	(*R*)-(−)-**4bc**	77	>99
5	**1e** (NTs, Ph)	**2c** (Ph, *i*-Pr)	(+)-**4ec**	50	94
6	**1f** [O, $(CH_2)_3$Ph]	**2c** (Ph, *i*-Pr)	**4fc**	0	–
7	**1b** (NTs, *n*-Bu)	**2a** (Ph, Et)	(+)-**4ba**	67	99
8	**1b** (NTs, *n*-Bu)	**2d** (2-MeC_6H_4, Et)	(−)-**4bd**	39	99
9	**1b** (NTs, *n*-Bu)	**2e** (4-ClC_6H_4, Et)	(−)-**4be**	60	99
10	**1b** (NTs, *n*-Bu)	**2f** (4-FC_6H_4, Et)	(−)-**4bf**	52	99
11	**1b** (NTs, *n*-Bu)	**2g** (4-MeOC_6H_4, Et)	**4bg**	0	–
12	**1b** (NTs, *n*-Bu)	**2h** (Me, Et)	**4bh**	0	–

[a] Isolated yield.

We subsequently explored the scope of the enantioselective cyclization of γ-alkynylaldehydes with acyl phosphonates via the aldehyde C−H bond cleavage by using 10 mol % of the cationic Rh(I)/(*R*)-Segphos complex at 80 °C as shown in Table 3. With respect to γ-alkynylaldehydes, the reaction of sterically less demanding terminal γ-alkynylaldehyde **1c** and **2c** failed to furnish the corresponding ketone (entry 1). On the other hand, internal γ-alkynylaldehydes **1a**, **1d**, **1b**, and **1e** reacted with **2c** to give the corresponding ketones in moderate to good yields with high ee's (entries 2−5). Unfortunately, the reaction of ether-linked γ-alkynylaldehyde **1f** and **2c** led to an unidentified complex mixture of products (entry 6). With respect to acyl phosphonates, not only phenyl (**2a**, entry 7) but also sterically demanding *o*-tolyl (**2d**, entry 8) and electron-deficient aryl-substituted acyl phosphonates (**2e** and **2f**, entries 9 and 10) reacted with **1b** to give the corresponding ketones in moderate to good yields with high ee's. However, electron-rich aryl- and alkyl-substituted acyl phosphonates (**2g** and **2h**, entries 11 and 12) could not participate in this reaction. The absolute configuration of (−)-**4bc** was unambiguously determined to be *R* by hydrolysis to the known chiral secondary alcohol, (*R*)-(+)-(hydroxyphenylmethyl)phosphonic acid diisopropyl ester [(*R*)-(+)-**7**].[11]

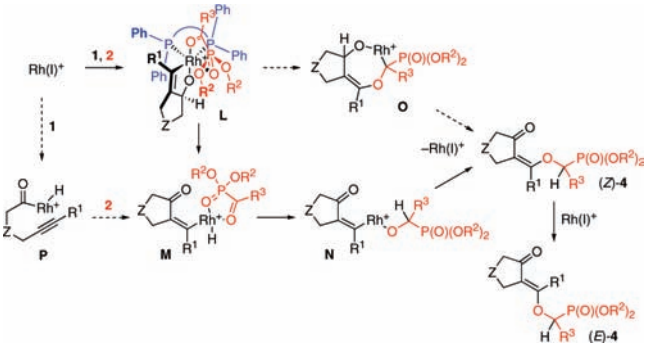
Scheme 4 depicts possible mechanisms for the formation of ester **3**. γ-Alkynylaldehyde **1** reacts with the Rh(I) catalyst, affording oxarhodacyclopentene **E** with chelating acyl phosphonate **2**. σ-Bond metathesis of the C−P bond and the Rh−O bond in intermediate **F** or carbonyl insertion[12] into the Rh−O bond to generate dioxarhodacycle **G**[13] followed by β-phosphorus elimination affords intermediate **H**, which undergoes reductive elimination to afford ester **3**.

Scheme 4. Possible Mechanism for Formation of 3[a]



[a] Bisphosphine ligand is omitted for clarity except in intermediate **E**.

Scheme 5. Possible Mechanism for Formation of 4[a]



[a] Bisphosphine ligand is omitted for clarity except in intermediate **L**.

Alternatively, activation of the C−P bond of **2** with the Rh(I) catalyst[7,8] affords intermediate **I**, which reacts with **1** to afford intermediate **K** through intermediate **J**. Subsequent reductive elimination of Rh affords ester **3**. No productive reaction was observed under the reaction conditions when substrate **1** was replaced with a simple alkyne or a simple aldehyde. This result suggests that the sequence involving intermediates **E** and **H** is most likely, since both the aldehyde and alkyne must be present for reaction to occur.

Scheme 5 depicts possible mechanisms for the formation of ketone **4**. γ-Alkynylaldehyde **1** reacts with the Rh(I) catalyst, affording oxarhodacyclopentene **L** with chelating acyl phosphonate **2**. We believe that coordination mode of **2** to Rh in this intermediate **L** is opposite to that in intermediate **E**, which would furnish ester **3**. β-Hydride elimination to generate intermediate **M** followed by insertion of the carbonyl group of **2** affords intermediate **N**, which undergoes reductive elimination to afford (*Z*)-**4**. Subsequent double bond isomerization with the cationic Rh(I) catalyst[14] affords (*E*)-**4**. Electron-rich aryl- and alkyl-substituted acyl phosphonates (**2g** and **2h**) failed to react with **1b**, presumably due to low reactivity toward the carbonyl insertion into the less polar Rh−H bond of intermediate **M** compared with the Rh−O bond of intermediate **E**.

Alternatively, insertion of the carbonyl group of **2** into the Rh−C bond of intermediate **L** to generate dioxarhodacycle **P** followed by β-hydride elimination and reductive elimination would also afford (*Z*)-**4**. In addition, activation of the aldehyde C−H bond of **1** to generate intermediate **P** followed by

dx.doi.org/10.1021/ja201337x | *J. Am. Chem. Soc.* 2011, 133, 6918–6921

carborhodation would also furnish intermediate **M**. However, these mechanisms are unlikely because they involve an unusual attack of the (alkenyl)rhodium carbon at the carbonyl oxygen and hydrorhodation not carborhodation which is common in the hydroacylation of alkynylaldehydes.[15,16]

The ligand- and substituent-controlled formation of ester **3** or ketone **4** might be explained as follows, although the precise mechanism cannot be determined at the present stage. Increasing the steric bulk of R^1 of **1** and/or R^2 of **2** would favor the formation of intermediate **L** over intermediate **E** due to steric repulsion between substituents R^1 and R^2. Use of the biaryl bisphosphine ligand with the small dihedral angle increases the steric repulsion between R^1 of **1** and the equatorial phenyl group of the ligand, which would also favor the formation of sterically less demanding intermediate **L** over intermediate **E**.

In conclusion, it has been established that a cationic Rh(I)/(*R*)-H_8-BINAP or (*R*)-Segphos complex catalyzes two unprecedented modes of cyclizations of heteroatom-linked γ-alkynylaldehydes with acyl phosphonates via C−P or C−H bond cleavage with outstanding enantioselectivity. These two different reaction pathways depend on the dihedral angles of the ligands and the substitutents on both γ-alkynylaldehydes and acyl phosphonates. Future studies will focus on elucidating the reaction mechanism and expanding the reaction scope to include chelating carbonyl compounds possessing a variety of heteroatom−carbonyl bonds.

■ ASSOCIATED CONTENT

Supporting Information. Procedures, characterization data, and X-ray crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
tanaka-k@cc.tuat.ac.jp

■ ACKNOWLEDGMENT

This work was supported partly by Grants-in-Aid for Scientific Research (Nos. 20675002 and 23105512) from MEXT, Japan. We deeply appreciate Takasago International Corp. for the gift of H_8-BINAP and Segphos, Umicore for generous support in supplying a rhodium complex, and reviewers for valuable suggestions regarding the reaction mechanism.

■ REFERENCES

(1) Reviews: (a) Montgomery, J. *Acc. Chem. Res.* **2000**, *33*, 467. (b) Ikeda, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 5120. (c) Montgomery, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 3890. (d) Jang, H.-Y.; Krische, M. J. *Acc. Chem. Res.* **2004**, *37*, 653.(e) Fujiwara, M.; Ojima, I. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005; p 129. (f) Montgomery, J.; Sormunen, G. J. *Top. Curr. Chem.* **2007**, *279*, 1. (g) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217. (h) Skucas, E.; Ngai, M.-Y.; Komanduri, V.; Krische, M. J. *Acc. Chem. Res.* **2007**, *40*, 1394. (i) Moslin, R. M.; Miller-Moslin, K.; Jamison, T. F. *Chem. Commun.* **2007**, 4441. (j) Jeganmohan, M.; Cheng, C. H. *Chem. Eur. J.* **2008**, *14*, 10876.

(2) Ni-catalyzed reactions: (a) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065. (b) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 6098. (c) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **2000**, *122*, 6950. (d) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698. (e) Knapp-Reed, B.; Mahandru, G. M.; Montgomery, J. *J. Am. Chem. Soc.* **2005**, *127*, 13156.(f) Baxter, R. D.; Montgomery, J. *J. Am. Chem. Soc.* **2011**, *133*, 5728.

(3) Rh-catalyzed reactions: (a) Ojima, I.; Tzamarioudaki, M.; Tsai, C.-Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643. (b) Bennacer, B.; Fujiwara, M.; Lee, S.-Y.; Ojima, I. *J. Am. Chem. Soc.* **2005**, *127*, 17756. (c) Rhee, J. U.; Krische, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 10674. (d) Rhee, J. U.; Jones, R. A.; Krische, M. J. *Synthesis* **2007**, 3427.

(4) Ru-catalyzed reaction: (a) Patman, R. L.; Chaulagain, M. R.; Williams, V. M.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 2066. Ti-catalyzed reaction: (b) Crowe, W. E.; Rachita, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6787.

(5) Tanaka, R.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* **2010**, *132*, 1238.

(6) Transition-metal-catalyzed syntheses of cyclic allylic alcohols with tetrasubstituted alkene component via alkylative or arylative cyclizations of γ-alkynylaldehydes have been reported. Ni: (a) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065. (b) Ni, Y.; Amarasinghe, K. K. D.; Montgomery, J. *Org. Lett.* **2002**, *4*, 1743. (c) Patel, S. J.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1364. (d) Patel, S. J.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3941. Rh: (e) Shintani, R.; Okamoto, K.; Otomaru, Y.; Ueyama, K.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, *127*, 54. (f) Miura, T.; Shimada, M.; Murakami, M. *Synlett* **2005**, 667. (g) Matsuda, T.; Makino, M.; Murakami, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4608. (h) Miura, T.; Shimada, M.; Murakami, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7598. (i) Miura, T.; Shimada, M.; Murakami, M. *Tetrahedron* **2007**, *63*, 6131. Pd: (j) Tsukamoto, H.; Ueno, T.; Kondo, Y. *J. Am. Chem. Soc.* **2006**, *128*, 1406. Fe: (k) Hojo, M.; Murakami, Y.; Aihara, H.; Sakuragi, R.; Baba, Y.; Hosomi, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 621. Mn: (l) Tang, J.; Okada, K.; Shinokubo, H.; Oshima, K. *Tetrahedron* **1997**, *53*, 5061. (m) Yorimitsu, H.; Tang, J.; Okada, K.; Shinokubo, H.; Oshima, K. *Chem. Lett.* **1998**, 11.

(7) Sm-mediated three-component coupling of acyl phosphonates and two carbonyl compounds via direct C−P bond activation: (a) Takaki, K.; Itono, Y.; Nagafuji, A.; Naito, Y.; Shishido, T.; Takehira, K.; Makioka, Y.; Taniguchi, Y.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 475. Cleavage of the C−P bond of acyl phosphonates by Yb and Sm: (b) Taniguchi, Y.; Fujii, N.; Takaki, K.; Fujiwara, Y. *J. Organomet. Chem.* **1995**, *491*, 173.

(8) In the Rh-catalyzed hydrogenation of acyl phosphonates, the cleavage of the C−P bond is predominant over the desired reduction of the carbonyl group: Goulioukina, N. S.; Bondarenko, G. N.; Bogdanov, A. V.; Gavrilov, K. N.; Beletskaya, I. P. *Eur. J. Org. Chem.* **2009**, 510.

(9) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405.

(10) We reported that the cationic Rh(I)/H_8-BINAP complex can catalyze enantio- and diastereoselective [2+2+2] cycloaddition of 1,6-enynes with ketoesters: Tanaka, K.; Otake, Y.; Sagae, H.; Noguchi, K.; Hirano, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 1312.

(11) Nakanishi, K.; Kotani, S.; Sugiura, M.; Nakajima, M. *Tetrahedron* **2008**, *64*, 6415.

(12) Cationic Rh(I) complex-catalyzed [2+2+2] and [4+2] cycloadditions involving acyl phosphonates: (a) Tanaka, K.; Tanaka, R.; Nishida, G.; Hirano, M. *Synlett* **2008**, 2017. (b) Tanaka, K.; Tanaka, R.; Nishida, G.; Noguchi, K.; Hirano, M. *Chem. Lett.* **2008**, *37*, 934.

(13) Alternatively, the formation of intermediate **G** via the coupling of Rh with **1** and **2** to generate dioxarhodacycle followed by alkyne insertion cannot be excluded. Ni-catalyzed Tishchenko reactions presumably through dioxanickelacycles: (a) Ogoshi, S.; Hoshimoto, Y.; Ohashi, M. *Chem. Commun.* **2010**, *46*, 3354. (b) Hoshimoto, Y.; Ohashi, M.; Ogoshi, S. *J. Am. Chem. Soc.* **2011**, *133*, 4668.

(14) Cationic Rh(I) complex-catalyzed *E*/*Z* isomerization of α,β-unsaturated carbonyl compounds: Tanaka, K.; Shoji, T.; Hirano, M. *Eur. J. Org. Chem.* **2007**, 2687.

(15) Cationic Rh(I)/BINAP complex-catalyzed intramolecular hydroacylation (and subsequent olefin isomerization) of methylene-linked γ-alkynylaldehydes: Takeishi, K.; Sugishima, K.; Sasaki, K.; Tanaka, K. *Chem. Eur. J.* **2004**, *10*, 5681.

(16) Review of transition-metal-catalyzed hydroacylation: Willis, M. C. *Chem. Rev.* **2010**, *110*, 725.