JOC Article

Rhodium Complex-Catalyzed Cycloisomerization of Allenenes: Exo and Endo Cyclization Depending on the Auxiliary Ligands

Tatsuya Makino and Kenji Itoh*

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

itohk@apchem.nagoya-u.ac.jp

Received October 20, 2003

In the presence of a catalytic amount of a rhodium(I) complex, allenenes undergo cycloisomerization reactions resulting in the selective formation of *exo*-alkylidenecarbocycles and heterocycles. In the catalytic system of rhodium complexes with triaryl phosphites, cyclic 1,4- or 1,5-dienes are formed in good to excellent yields in the formal exo-cyclization mode via the metallacycle intermediate having an *exo*-alkylidene moiety. In this cycloisomerization, (*E*)- and (*Z*)-allenenes are transformed stereospecifically to the corresponding cyclic (*E*)- and (*Z*)-1,4-dienes, respectively. On the other hand, the reactions under carbon monoxide atmosphere exclusively afford seven-membered-ring products through an endo-mode cyclization. The unusual cyclization involves an allylic C−H activation process. The allenene bearing a silicon substituent at the olefinic terminus incorporates carbon monoxide to give the corresponding [2+2+1] cycloaddition product. This result apparently indicates that the catalysis of the rhodium complex is explained in terms of the oxidative cyclization of an allenene to furnish the key *exo*-alkylidene metallacycle intermediate at the first stage of the catalysis.

Introduction

Carbocycles and heterocycles are extremely important and basic skeletons in many biologically active natural products with several complex structures. Thus the development of effective methods for the construction of ring systems has been the subject of extensive investigation. Increasing social needs for environmentally friendly chemical processes call for the transition metal complex-catalyzed carbocyclization of alkynes and alkenes as valuable and powerful protocols for the preparation of a wide range of carbocycles or heterocycles with high efficiency and selectivity.[1] Above all, transition metal-catalyzed cycloisomerization reactions are atom economical and environmentally benign synthetic processes because there is no requirement of additional reactants excepting catalysts and solvents.[2,3] Especially, the active development of the catalytic cycloisomerization reaction of 1,*n*-enynes has been achieved, and various transition metal complexes have been reported to be efficient (Ti,[4] Ru,[5] Rh,[6] Ir,[7] Ni−Cr,[8] Pd,[9,10] and Pt[5g]). It was revealed that a stoichiometric amount of cobalt[11] and nickel[12] complexes promoted such enyne cycloisomerizations. Similarly, transition metal-catalyzed cycloisomerizations of 1,*n*-dienes have also been widely investigated (Sc,[13] Ti,[14] Zr,[15] Ta,[16] Ru,[17] Rh,[18] Ni,[19] and Pd[20]).

Though interesting and useful transformations of allenes had been known,[21] allenes still received less attention as a component for the catalytic formation of carbon−carbon multiple bonds compared with alkynes and alkenes. In the past decade, the transition metal-catalyzed reaction of allenes has been noticed as an important carbon−carbon and carbon−heteroatom bond-forming process, since it exhibited high chemo-, regio-, and stereoselectivity. In particular, several palladium complexes have been employed for a wide range of

* To whom correspondence should be addressed. Phone: +81-52-789-5112. Fax: +81-52-789-3205.

(1) (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (b) Negishi, E.; Copéret, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365−393. (c) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. *Chem. Rev.* **1996**, *96*, 635−662. (d) Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133−154. (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813−834. (f) Trost, B. M.; Toste, D. F.; Pinkerton, A. B. *Chem. Rev.* **2002**, *101*, 2067−2096.

(2) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1−16.

(3) For reviews on transition metal-catalyzed atom economical reactions, see: (a) Trost, B. M. *Science* **1991**, *254*, 1471−1477. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281. (c) Trost, B. M. *Chem. Eur. J.* **1998**, *4*, 2405−2412. (d) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695−705.

(4) Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976−1977.

(5) (a) Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158−9159. (b) Mori, M.; Kozawa, Y.; Nishida, M.; Kanamaru, M.; Onozuka, K.; Takimoto, M. *Org. Lett.* **2000**, *2*, 3245−3247. (c) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 9728−9729. (d) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714−715. (e) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025−5036. (f) Le Paih, J.; Rodríguez, D. C.; Dérien, S.; Dixneuf, P. H. *Synlett* **2000**, 95−97. (g) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511−10520.

(6) (a) Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490−6491. (b) Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 4104−4106. (c) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198−8199. (d) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457−3460. (e) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526−4529. (f) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198−8199. (g) Tong, X.; Zhang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2003**, *125*, 6370−6371.

(7) Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. *J. Org. Chem.* **2001**, *66*, 4433−4436.

(8) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268−5270.

10.1021/jo035551x CCC: $27.50
Published on Web 12/24/2003

transition metal catalysis of allenes.[22] There are generally two methodologies to approach the desired products. One is the addition of carbon or heteroatom nucleophiles to the allene moiety, which is activated by coordinative interaction with transition metal complexes.[22c−f] The other depends on carbometalation and oxidative cyclization of an allene functionality.[22d,e,23−26] Especially, a number of quests have been made for catalytic carbonylative cycloaddition reactions,[27] such as the intramolecular allenic Pauson−Khand reaction, i.e., the [2+2+1] cycloaddition of allenynes,[28−31] according to the latter concept.

Catalytic cycloisomerizations of allenes also have been under current investigation. For example, Brummond et

(9) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781−1783. (b) Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887−4890. (c) Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053−6054. (d) Trost, B. M.; Lee, D. C.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 651−654. (e) Trost, B. M.; Lee, D. C. *J. Org. Chem.* **1989**, *54*, 2271−2274. (f) Trost, B. M.; Edstrom, E. D.; Carter-Petillo, M. B. *J. Org. Chem.* **1989**, *54*, 4489−4490. (g) Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636−644. (h) Trost, B. M.; Pedregal, C. *J. Am. Chem. Soc.* **1992**, *114*, 7292−7294. (i) Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233−8236. (j) Trost, B. M.; Czeskis, B. A. *Tetrahedron Lett.* **1994**, *35*, 211−214. (k) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255−4267. (l) Trost, B. M.; Romero, D. L.; Rise, F. *J. Am. Chem. Soc.* **1994**, *116*, 4268−4278. (m) Goeke, A.; Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 662−663. (n) Yamada, H.; Aoyagi, S.; Kibayashi, C. *Tetrahedron Lett* **1997**, *38*, 3027−3030. (o) Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 249−253. (p) Hatano, M.; Mikami, K. *J. Mol. Catal. A* **2003**, *196*, 165−169. (q) Hatano, M.; Mikami, K. *J. Am. Chem. Soc.* **2003**, *125*, 4704−4705. (r) Hatano, M.; Yamanaka, M.; Mikami, K. *Eur. J. Org. Chem.* **2003**, 2552−2555.

(10) For applications to total syntheses of natural products, see: (a) Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586−4588. (b) Trost, B. M.; Jebaratnam, D. J. *Tetrahedron Lett.* **1987**, *28*, 1611−1614. (c) Trost, B. M.; Hipskind, P. A.; Chung, J. Y. L.; Chan, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1502−1504. (d) Trost, B. M.; Phan, L. T. *Tetrahedron Lett.* **1993**, *34*, 4735−4738. (e) Trost, B. M.; Krische, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 233−234. (f) Trost, B. M.; Li, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6625−6633. (g) Trost, B. M.; Krische, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 6131−6141. (h) Trost, B. M.; Haffner, C. D.; Jebaratnam, D. J.; Krische, M. J.; Thomas, A. P. *J. Am. Chem. Soc.* **1999**, *121*, 6183−6192. (i) Trost, B. M.; Corte, J. R.; Gudiksen, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3662−3664.

(11) (a) Llerena, D.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 7353−7356. (b) Buisine, O.; Aubert, C.; Malacria, M. *Chem. Eur. J.* **2001**, *7*, 3517−3525. (c) Kagoshima, H.; Hayashi, M.; Hashimoto, Y.; Saigo, K. *Organometallics* **1996**, *15*, 5439−5441. (d) Kraft, M. E.; Wilson, A. M.; Dasse, O. A.; Bonaga, L. V. R.; Cheung, Y. Y.; Fu, Z.; Shao, B.; Scott, I. L. *Tetrahedron Lett.* **1998**, *39*, 5911−5914. (e) Dolaine, R.; Gleason, J. L. *Org. Lett.* **2000**, *2*, 1753−1756. (f) Ajamian, A.; Gleason, J. L. *Org. Lett.* **2001**, *3*, 4161−4164.

(12) (a) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286−1288. (b) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539−546.

(13) (a) Bunel, E. E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976−978. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74−84. (c) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406−9407.

(14) (a) Akita, M.; Yasuda, H.; Nagasuna, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 554−558. (b) Lehmkuhl, H.; Tsien, Y.-L. *Chem. Ber.* **1983**, *116*, 2437−2446. (c) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Franwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630−8641. (d) Okamoto, S.; Livinghouse, T. *J. Am. Chem. Soc.* **2000**, *122*, 1223−1224. (e) Okamoto, S.; Livinghouse, T. *Organometallics* **2000**, *19*, 1449−1451.

(15) (a) Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 4715−4716. (b) Thiele, S.; Erker, G. *Ber./Recl.* **1997**, *130*, 201−207. (c) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492−2494. (d) Schweder, B.; Walther, D.; Döhler, T.; Klobes, O.; Görls, H. *J. Prakt. Chem.* **1999**, *341*, 736−747.

(16) (a) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315−1317. (b) Smith, G.; McLain, S. J.; Schrock, R. R. *J. Organomet. Chem.* **1980**, *202*, 269−277.

(17) (a) Yamamoto, Y.; Ohkoshi, N.; Itoh, K. *J. Org. Chem.* **1999**, *64*, 2178−2179. (b) Yamamoto, Y.; Nakagai, Y.; Ohkoshi, N.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6372−6380.

(18) (a) Bright, A.; Molone, J. F.; Nicholson, J. K.; Powell, J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1971**, 712−713. (b) Schmitz, E.; Urban, R.; Heuck, U.; Zimmermann, G.; Gründemann, E. *J. Prakt. Chem.* **1976**, *318*, 185−192. (c) Schmitz, E.; Heuck, U.; Habisch, D. *J. Prakt. Chem.* **1976**, *318*, 471−478. (d) Grigg, R.; Mitchell, T. R. B.; Ramasubbu, A. *J. Chem. Soc., Chem. Commun.* **1980**, 27−28. (e) Grigg, R.; Malone, J. F.; Mitchell, T. R. B.; Ramasubbu, A.; Scott, R. M. *J. Chem. Soc., Parkin Trans. 1* **1984**, 1745−1754.

(19) (a) Bodoganovic, B. *Adv. Organomet. Chem.* **1979**, *17*, 105−140. (b) Behr, A.; Freudenberg, U.; Keim, W. *J. Mol. Catal.* **1986**, *35*, 9−17. (c) Radetich, B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 8007−8008. (d) Walther, D.; Döhler, T.; Heubach, K.; Klobes, O.; Schweder, B.; Görls, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 923−932.

(20) (a) Grigg, R.; Mitchell, T. R. B.; Ramasubbu, A. *J. Chem. Soc., Chem. Commun.* **1979**, 669−670. (b) Heumann, A.; Moukhliss, M. *Synlett* **1998**, 1211−1212. (c) Widenhoefer, R. A.; Perch, N. S. *Org. Lett.* **1999**, *1*, 1103−1105. (d) Kisanga, P.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 10017−10026. (e) Kisanga, P.; Goj, L. A.; Widenhoefer, R. A. *J. Org. Chem.* **2001**, *66*, 635−637. (f) Goj, L. A.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 11133−11147. (g) Bray, K. L.; Fairlamb, I. J. S.; Lloyd-Jones, G. C. *Chem. Commun* **2001**, 187−188. (h) Bray, K. L.; Charmant, J. P. H.; Fairlamb, I. J. S.; Lloyd-Jones, G. C. *Chem. Eur. J.* **2001**, *7*, 4205−4215. (i) Oh, C. H.; Kim, J. D.; Han, J. W. *Chem. Lett.* **2001**, 1290−1291 and also see refs 18b,c,e and 19c.

(21) (a) Patai, S. *The Chemistry of Ketenes, Allenes and Related Compunds*; Wiley: Chichester, UK, 1980. (b) Landor, S. R. *The Chemistry of Allenes*; Academic Press: London, UK, 1982. (c) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (d) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805−2827. (e) Zimmer, R. *Synthesis* **1993**, 165−178. (f) Zimmer, R.; Khan, F. A. *J. Prakt. Chem.* **1996**, *338*, 92−94.

(22) (a) Grigg, R.; Sridharan, V. *Pure Appl. Chem.* **1998**, *338*, 1047−1057. (b) Lautens, M.; Rovis, T.; Smith, N. D.; Ostrovsky, D. *Pure Appl. Chem.* **1998**, *338*, 1059−1064. (c) Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199−207. (d) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067−3125. (e) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590−3593. (f) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12−21. (f) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701−712.

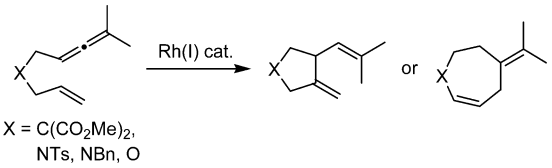
(23) For leading papers on the late transition metal-catalyzed carbocyclization in the past decade, see: Rh: (a) Kang, S.-K.; Hong, Y.-T.; Lee, J.-H.; Kim, W.-Y.; Lee, I.; Yu, C.-M. *Org. Lett.* **2003**, *5*, 2813−2816. Ni: (b) Montgomery, J.; Song, M. *Org. Lett.* **2002**, *4*, 4009−4011. (c) Kang, S.-K.; Yoon, S.-K. *Chem. Commun.* **2002**, 2634−2635. Pd: (d) Ma, S.; Negishi, E. *J. Org. Chem.* **1994**, *59*, 4730−4732. (e) Ma, S.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 6345−6357. (f) Doi, T.; Yanagisawa, A.; Nakanishi, S.; Yamamoto, K.; Takahashi, T. *J. Org. Chem.* **1996**, *61*, 2062−2063. (g) Doi, T.; Yanagisawa, A.; Yamamoto, K.; Takahashi, T. *Chem. Lett.* **1996**, 1085−1086. (h) Kang, S.-K.; Baik, T.-G.; Kulak, A. N.; Ha, Y.-H.; Lim, Y.; Park, J. *J. Am. Chem. Soc.* **2000**, *122*, 11529−11530. (i) Kang, S.-K.; Ha, Y.-H.; Ko, B.-S.; Lim, Y.; Jung, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 343−345. (j) Kang, S.-K.; Lee, S.-W.; Jung, J.; Lim, Y. *J. Org. Chem.* **2002**, *67*, 4376−4379. (k) Ha, Y.-H.; Kang, S.-K. *Org. Lett.* **2002**, *4*, 1143−1146. (l) Gai, X.; Grigg, R.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 1765−1766. (m) Löfstedt, J.; Franzén, J.; Bäckvall, J.-E. *J. Org. Chem.* **2001**, *66*, 8015−8025. (n) Franzén, J.; Löfstedt, J.; Dorange, I.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2002**, *124*, 11246−11247. (o) Franzén, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2003**, *125*, 6056−6057. (p) Löfstedt, J.; Närhi, K.; Dorange, I.; Bäckvall, J.-E. *J. Org. Chem.* **2003**, *68*, 7243−7248. (q) Shin, S.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2001**, *123*, 8416−8417. (r) Ohno, H.; Miyamura, K.; Takeoka, Y.; Tanaka, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 2647−2650 and references therein.

(24) For leading papers on early transition metal-mediated carbocyclization in recent years, see: (a) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 11295−11305. (b) Urabe, H.; Sato, F. *Tetrahedron Lett.* **1998**, *39*, 7329−7332. (c) Sato, F.; Urabe, H.; Okamoto, S. *Synlett* **2000**, 753−775 and references therein.

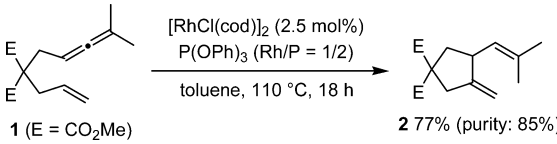
(25) For catalytic intramolecular cycloadditions, see the following. [3+2], Rh: (a) Hayashi, M.; Ohmatsu, T.; Meng, Y.-P.; Saigo, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 837−839. [4+2], Rh and Ni: (b) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843−1844. [5+2], Rh: (c) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 5348−5349. Wender and co-workers also applied the rhodium-catalyzed reaction to total syntheses of natural products, see: (d) Wender, P. A.; Fuji, M.; Husfeld, C. O.; Love, J. A. *Org. Lett.* **1999**, *1*, 137−139. (e) Wender, P. A.; Zhang, L. *Org. Lett.* **2000**, *2*, 2323−2326. (f) Wender, P. A.; Bi, F. C.; Gamber, G. G.; Gosselin, F.; Hubbard, R. D.; Scanio, M. J. C.; Sun, R.; Williams, T. J.; Zhang, L. *Pure Appl. Chem.* **2002**, *74*, 25−31. Cf. for the stoichiometric [2+2] cycloaddition with molybdenum complexes, see: (g) Shen, Q.; Hammond, G. B. *J. Am. Chem. Soc.* **2002**, *124*, 6534−6535.

al. and Shibata et al. quite recently reported independently that allenynes undergo catalytic cycloisomerization to afford cross-conjugated trienes in the presence of rhodium complexes.[32] Moreover, the transition metal-catalyzed cycloisomerization reaction of *allenenes* is also expected to be valuable.[33,34] Trost and co-workers reported pioneering studies with nickel−chromium[33a] and palladium[33b] catalysts. Recently, Kang et al. employed ruthenium catalysts in the cycloisomerization of allenenes to cyclic 1,3-dienes or 1,4-dienes.[33c]

SCHEME 1



SCHEME 2



Herein, we wish to report the rhodium(I)-catalyzed cycloisomerization of allenenes with high efficiency and selectivity by way of the participation of the internal allenic π-bond to generate corresponding carbocycles and heterocycles (Scheme 1).[35] It should be noted that the present cyclization proceeds via formal exo- or endo-mode cyclization pathways in striking dependence on the auxiliary ligands.

Results and Discussion

Cycloisomerization of Allenenes Leading to Five-Membered Rings. We first examined the reaction of allenene **1** in the presence of a catalytic amount of [RhCl(cod)]$_2$ (2.5 mol %, cod = 1,5-cyclooctadiene) and P(OPh)$_3$ (Rh/P = 1/2) in toluene at 110 °C and obtained an encouraging result, i.e., the cyclic 1,4-diene **2** processing the *exo*-methylene moiety was isolated in 77% yield with 85% purity as the cycloisomerization product (Scheme 2).[36] The rhodium complex was essential to this transformation; no reaction occurred without the rhodium catalyst under the identical conditions. To optimize reaction conditions, a series of experiments was undertaken with allenene **1** as a model substrate to find the best reaction conditions, e.g., solvents and catalysts (Table 1). The effect of additives will be discussed in detail later (vide infra). While the cycloisomerization proceeded in di-*n*-butyl ether, isolated yields and selectivity decreased to some extent (entry 2). Highly efficient conversions of **1** into **2** were observed in 1,4-dioxane and chlorobenzene (entries 3 and 4). Particularly, the former afforded the best result on both a product yield and selectivity. This result suggests that the coordination of the rhodium center to 1,4-dioxane gives a stabilizing

(26) For catalytic intermolecular cycloadditions, see the following. [2+2], Ni: (a) Saito, S.; Hirayama, K.; Kabuto, C.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10776−10780. [3+2], Pd: (b) Meguro, M.; Yamamoto. Y. *J. Org. Chem.* **1999**, *64*, 694−695. [2+2+2], Ni: (c) Shanmugasundaram, M.; Wu, M.-S.; Cheng, C.-H. *Org. Lett.* **2001**, *3*, 4233−4236. (d) Shanmugasundaram, M.; Wu, M.-S.; Jeganmohan, M.; Huang, C.-W.; Cheng, C.-H. *J. Org. Chem.* **2002**, *67*, 7724−7729. (e) Wu, M.-S.; Shanmugasundaram, M.; Cheng, C.-H. *Chem. Commun.* **2003**, 718−719. [4+2], Rh: (f) Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2248−2250. [4+2], Pd: (g) Siegel, H.; Hopf, H.; Germer, A.; Binger, P. *Chem. Ber.* **1978**, *111*, 3112−3118. (h) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7163−7164. (i) Murakami, M.; Minamida, R.; Itami, K.; Sawamura, M.; Ito, Y. *Chem. Commun.* **2000**, 2293−2294. [4+4], Pd: (j) Murakami, M.; Itami, K.; Ito, Y. *Synlett* **1999**, 951−953.

(27) [2+2+1], Ru: (a) Kang, S.-K.; Kim, K.-J.; Hong, Y.-T. *Angew. Chem., Int. Ed.* **2002**, *41*, 1584−1586. [4+1], Fe: (b) Eaton, B. E.; Rollman, B.; Kaduk, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 6245−6246. (c) Sigman, M. S.; Kerr, C. E.; Eaton, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 7545−7546. (d) Sigman, M. S.; Eaton, B. E. *J. Org. Chem.* **1994**, *59*, 7488−7491. (e) Sigman, M. S.; Eaton, B. E. *J. Am. Chem. Soc.* **1996**, *118*, 11783−11788. [4+1], Rh and Pt: (f) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2691−2694. (g) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11672−11673. (h) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 2950−2951. (i) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4130−4135. (j) Murakami, M.; Itami, K.; Ito, Y. *Organometallics* **1999**, *18*, 1326−1336. [4+1], Pd: (k) Mandai, T.; Tsuji, J.; Tsujiguchi, Y.; Saito, S. *J. Am. Chem. Soc.* **1993**, *115*, 5865−5866. (l) Darcel, C.; Bruneau, C.; Dixneuf, P. H. *Synlett* **1996**, 218−220. [5+1], Ir: (m) Murakami, M.; Itami, K.; Ubukata, M.; Tsuji, I.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 4−5. [4+4+1], Pd: (n) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 3418−3420.

(28) Ti: (a) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 9450−9451. (b) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5881−5898. Rh: (c) Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, *624*, 73−87. (d) Brummond, K. M.; Still, P. C.; Rickards, B.; Geib, S. J. *Tetrahedron Lett.* **2002**, *43*, 3735−3738. (e) Brummond, K. M.; Chen, H.; Fisher, K. D.; Kerekes, A. D.; Rickards, B.; Still, P. C.; Geib, S. J. *Org. Lett.* **2002**, *4*, 1931−1934. (f) Brummond, K. M.; Gao, D. *Org. Lett.* **2003**, *5*, 3491−3494. (g) Mukai, C.; Nomura, I.; Yamanishi, K.; Hanaoka, M. *Org. Lett.* **2002**, *4*, 1755−1758. (h) Mukai, C.; Nomura, I.; Kitagaki, S. *J. Org. Chem.* **2002**, *68*, 1376−1385. Ir: (i) Shibata, T.; Kadowaki, S.; Hirase, M.; Kadowaki, S.; Takagi, K. *Synlett* **2003**, 268−270.

(29) For transition metal-promoted [2+2+1] cycloaddition of allenynes, see the following. Mo, Co, and Zr: (a) Kent, J. L.; Wan, H.; Brummond, K. M. *Tetrahedron Lett.* **1995**, *36*, 2407−2410. (b) Brummond, K. M.; Wan, H. *Tetrahedron Lett.* **1998**, *39*, 931−934. (c) Brummond, K. M.; Wan, H.; Kent, J. L. *J. Org. Chem.* **1998**, *63*, 6535−6545. (d) Brummond, K. M.; Kerekes, A. D.; Wan, H. *J. Org. Chem.* **2002**, *67*, 5156−5163. Co: (e) Ahmar, M.; Locatelli, C.; Colombier, D.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5281−5284. Brummond and co-workers applied the molybdenum-mediated reaction to total syntheses of natural products, see: (f) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087−5088. (g) Brummond, K. M.; Lu, J.; Peterson, J. *J. Am. Chem. Soc.* **2000**, *122*, 4915−4920.

(30) It was also disclosed that a stoichiometric amount of the cobalt complex promoted the intermolecular allenic Pauson−Khand reaction, see: (a) Ahmar, M.; Antras, F.; Cazes, B. *Tetrahedron Lett.* **1995**, *36*, 4417−4420. (b) Ahmar, M.; Chabanis, O.; Gauthier, J.; Cazes, B. *Tetrahedron Lett.* **1997**, *38*, 5277−5280.

(31) For recent reviews on Pauson−Khand reactions, see: (a) Geis, O.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911−914. (b) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297−341. (c) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263−3283. (d) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657−1668. (e) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1800−1810.

(32) (a) Brummond, K. M.; Chen, H.; Sill, P.; You, L. *J. Am. Chem. Soc.* **2002**, *124*, 15186−15187. (b) Shibata, T.; Takesue, Y.; Kadowaki, S.; Takagi, K. *Synlett* **2003**, 268−270. Cf. for the cobalt-mediated cycloisomerization of allenynes, see: (c) Llerena, D.; Aubert, C.; Malacria, M. *Tetrahedron Lett* **1996**, *37*, 7027−7030.

(33) (a) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 5231−5233. (b) Trost, B. M.; Matsuda, K. *J. Am. Chem. Soc.* **1988**, *110*, 5233−5235. (c) Kang, S.-K.; Ko, B.-S.; Lee, D.-M. *Tetrahedron Lett.* **2002**, *43*, 6693−6696.

(34) Previously, Trost et al. investigated the related ruthenium-catalyzed intermolecular couplings of allenes and alkenes derived from vinyl ketones to provide 1,3-dienes, see: (a) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 4068−4069. (b) Trost, B. M.; Pinkerton, A. B.; Kremzow, D. *J. Am. Chem. Soc.* **2001**, *123*, 12466−12476.

(35) For a preliminary communication, see: Makino, T.; Itoh, K. *Tetrahedron Lett.* **2003**, *44*, 6335−6338.

(36) The conversion and the purity were determined by GC analysis of the reaction mixture and the isolated product **2**, respectively. The recovered allenene **1** was included in the impurity.

TABLE 1. Effect of Solvents and Catalysts on Cycloisomerization of Allenene 1[a]

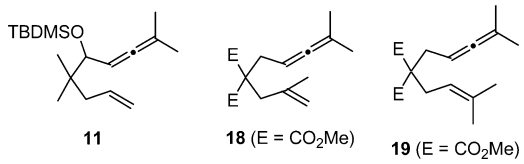
entry	catalyst (mol %)	solvent	time (h)	yield (%)[b]	purity (%)[c]
1	$[RhCl(cod)]_2$ (2.5)	toluene	18	77	85
2	$[RhCl(cod)]_2$ (2.5)	*n*-Bu_2O	18	62	74
3	$[RhCl(cod)]_2$ (2.5)	1,4-dioxane	12	92	95
4	$[RhCl(cod)]_2$ (2.5)	PhCl	14	81	90
5	$[RhCl(cod)]_2$ (2.5)	DMF	24	26	53
6	$[RhCl(coe_2)]_2$ (2.5)	1,4-dioxane	12	77	89
7	$[RhCl(CO)_2]_2$ (2.5)	1,4-dioxane	14	87	90
8	$[Rh(cod)_2]PF_6$ (5)	1,4-dioxane	24	87	85
9	$Rh(acac)(CO)_2$ (5)	1,4-dioxane	24	31	59

[a] All reactions were carried out with Rh complexes and $P(OPh)_3$ (Rh/P = 1/2) at 110 °C (bath temperature) under Ar atmosphere. [b] Isolated yield. [c] Determined by GC analyses.

effect on the catalytic active species. On the other hand, *N*,*N*-dimethylformamide (DMF) was an improper solvent and a large quantity of undesirable isomers and oligomers were formed (entry 5). In addition to $[RhCl(cod)]_2$, other rhodium(I) complexes bearing bridged chloride ligands such as $[RhCl(coe)_2]_2$ (coe = cyclooctene) and $[RhCl(CO)_2]_2$ were also effective catalysts (entries 6 and 7). A cationic complex $[Rh(cod)_2]PF_6$ was also acceptable (entry 8), whereas $Rh(acac)(CO)_2$ (acac = acetylacetonato) resulted in a striking decrease in the isolated yield and the purity of **2** (entry 9). Furthermore, other rhodium complexes, a rhodium(0) complex $Rh_4(CO)_{12}$ and a rhodium(III) complex $[Cp^*RhCl_2]_2$, provided no expected product **2** but a complex mixture of unidentified oligomers. A rhodium(II) complex $[Rh(OAc)_2]_2$ exhibited no catalytic activity. The above observation indicates that 1,4-dioxane and $[RhCl(cod)]_2$ are the best choice of solvent and catalyst combination, respectively. It is notable that the analogous iridium(I) complex $[IrCl(cod)]_2$ also furnished the cycloisomerization product **2** under identical conditions despite much lower efficiency and selectivity (51% yield with 82% purity).

The results obtained for other allenenes under the optimum conditions are shown in Table 2. Further investigations revealed that the more bulky phosphite ligand P(O-*o*-tol)$_3$ improved the selectivity of cycloisomerizations to raise the purity of the cyclization products (entry 1). The reaction of the barbituric acid derivative **3** provided a spiro-ring product **4** (entry 2). Allenene **5** derived from tosylamide cycloisomerized favorably to afford pyrrolidine derivative **6** despite somewhat low selectivity (entry 3),[37] whereas the benzylamine derivative **7**, which contains a more electron-rich nitrogen atom, resulted in a significant decrease in the yield of the desired product **8** (entry 4). Similarly, the oxygen-tethered allenene **9** gave the tetrahydrofuran derivative **10** in poor yield concomitant with inseparable isomers (entry 5). In both reactions, unidentified oligomers were formed. We presumed that the strong coordination of electron-rich heteroatoms of **7** and **9** forced the orientation of the allene and the alkene in an anti conformation, which was unsuitable for the desirable cyclizations. Unfortunately, allenene **11**, which has a bulky substituent, *tert*-butyldimethylsilyloxy, hardly underwent cycloisomerization, resulting in the recovery of starting material (Chart 1). There might have been steric interaction between the *tert*-butyldimethylsilyloxy group and the coordinated phosphite ligands to retard the requisite coordination of the rhodium center to **11** for cyclization. We then investigated the influence of substituents at the alkene moiety of allenenes. The (*E*)-allenenes ***E*-12** bearing a trimethylsilyl group at the alkene terminus were subjected to smooth cycloisomerization to provide only the corresponding (*E*)-1,4-dienes ***E*-13** (entry 6). In a similar manner, the phenyl-substituted (*E*)-allenenes ***E*-14** were exclusively converted into ***E*-15** (entry 7). On the other hand, the cyclization of its stereoisomer ***Z*-14** (*E*/*Z* = 1/56.2) achieved the selective formation of the corresponding cyclic product ***Z*-15** in excellent yield (*E*/*Z* = 1/21.9, entry 8). These results indicate that the present cycloisomerization proceeds with high stereospecificity. The respective stereochemistry of ***E*-13**, ***E*-15**, and ***Z*-15** was unambiguously confirmed by the observation of appreciable NOE correlations as depicted in Figure 1.

CHART 1



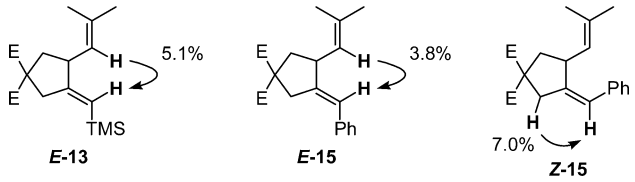


FIGURE 1. NOE correlations for ***E*-13**, ***E*-15**, and ***Z*-15**.

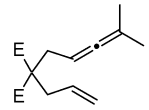
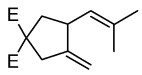
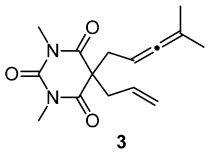
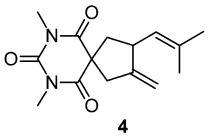
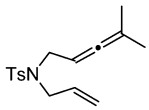
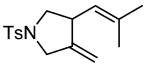
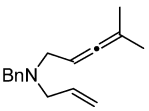
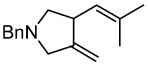
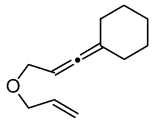
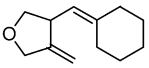
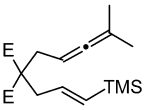
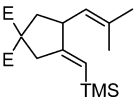
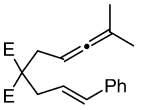
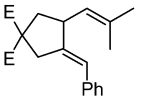
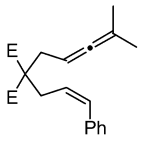
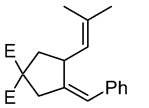
Interestingly, the analogous allenene **16** with a methyl group at the terminal position of the alkene moiety showed characteristic behavior (Table 3). In contrast to the cycloisomerizations described above, the reaction of allenene **16** (*E*/*Z* = 3/1) exclusively afforded cyclic 1,5-diene **17** instead of the 1,4-diene as a mixture of diastereomers with preferential formation of the cis isomer (cis/trans = 2.8/1, entry 1). The phosphite P(O-*o*-$PhC_6H_4)_3$, more bulky than P(O-*o*-tol)$_3$, was not effective in the improvement of the stereoselectivity (entry 2). The fact that a similar distribution of diastereomers was obtained in the reaction of ***E*-16** apparently indicates that there is no correlation between the geometry of the alkene moiety in **16** and the stereochemistry of cyclic 1,5-diene **17** (entry 3). The stereochemistry of **17** was assigned on the basis of the value of the H−H coupling constant between a pair of the protons at the ring junctures (J = 7.5 Hz). Furthermore, Figure 2 compares the ^{13}C NMR spectral data for the major product and that for the minor product, that is, the signal for the carbon neighboring the stereocenter appears at a higher field by steric compression of a gauche interaction in the cis isomer relative to the trans isomer in ^{13}C NMR spectra.[38]

The attempted cyclization of an allenene with a *gem*-disubstituted alkene such as **18** completely failed and the

(37) Almost pure **6** was readily obtained by recrystallization from ethyl acetate/*n*-hexane.

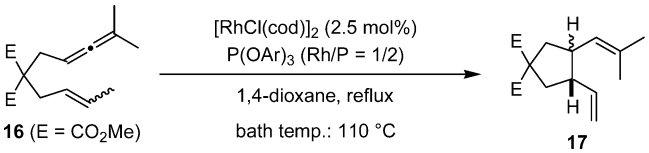
(38) Siverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998.

TABLE 2. Rh-Catalyzed Cycloisomerization of Allenenes[a]

entry	allenene	product	cat. amount (mol%)	time (h)	yield (%)[b]	purity (%)[c]
1	 **1**	 **2**	2.5	18	92	99
2	 **3**	 **4**	5	24	94	95
3	 **5**	 **6**	2.5	3	93	86
4	 **7**	 **8**	5	24	28	97
5	 **9**	 **10**	5	24	32	84
6	 **12**	 **13**	5	24	94	92
7	 ***E*-14**	 ***E*-15**	5	24	97	96
8	 (*E*/*Z* = 1/56.2) ***Z*-14**	 (*E*/*Z* = 1/21.9) ***Z*-15**	5	24	96	92

[a] All reactions were carried out with $[RhCl(cod)]_2$ and $P(O\text{-}o\text{-}tol)_3$ (Rh/P = 1/2) in 1,4-dioxane at 110 °C (bath temperature) under Ar atmosphere. E = CO_2Me. [b] Isolated yield. [c] Determined by GC analyses.

TABLE 3. Cycloisomerizations of Allenene 16



16 (E = CO_2Me) **17**

entry	*E*/*Z* ratio of **16**	$P(OAr)_3$	time (h)	yield (%)[a]	purity (%)[b]	cis/trans ratio of **17**[b]
1	3/1	$P(O\text{-}o\text{-}tol)_3$	20	90	87	2.8/1
2	3/1	$P(O\text{-}o\text{-}PhC_6H_4)_3$	24	93	93	3/1
3	30/1	$P(O\text{-}o\text{-}PhC_6H_4)_3$	24	91	91	2.8/1

[a] Isolated yield. [b] Determined by GC analyses.

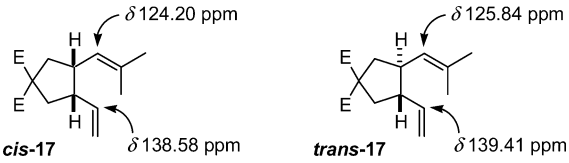
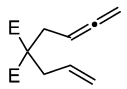
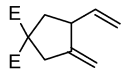
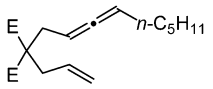
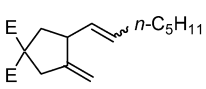
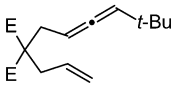
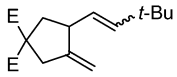


FIGURE 2. Selected data for ^{13}C NMR spectra of *cis*- and *trans*-**17**.

starting material remained intact (Chart 1). This suggests that the existence of a hydrogen atom at the internal olefinic position is necessary to cycloisomerization leading to 1,5-dienes (vide infra). Allenene **19** containing a trisubstituted alkene also resulted in no reaction due to the inhibition of its coordination by the steric congestion of the alkene moiety (Chart 1).

Furthermore, we explored the tolerance of the allenic moiety toward these catalytic cyclizations (Table 4). Even allenene **20**, possessing the parent allenyl moiety, readily underwent cycloisomerization despite the low yield of the corresponding product **21** (entry 1). The employment of $P(O\text{-}o\text{-}PhC_6H_4)_3$ improved both the yield and the purity

TABLE 4. Effect of Substituents at the Allene Moiety[a]

entry	allenene	product	cat. amount (mol%)	$P(OAr)_3$	time (h)	yield (%)[b]	purity (%)[c]	*E*/*Z* ratio[c]
1	 **20**	 **21**	2.5	P(O-*o*-tol)$_3$	3	41	92	–
2	**20**	**21**	2.5	P(O-*o*-PhC$_6$H$_4$)$_3$	3	52	95	–
3	 **22**	 **23**	2.5	P(O-*o*-tol)$_3$	12	78	>99	2.6/1
4	**22**	**23**	2.5	P(O-*o*-PhC$_6$H$_4$)$_3$	24	64	93	5.4/1
5	 **24**	 **25**	7.5	P(O-*o*-tol)$_3$	24	87	98	1.5/1
6	**24**	**25**	7.5	P(O-*o*-PhC$_6$H$_4$)$_3$	24	91	99	8.3/1

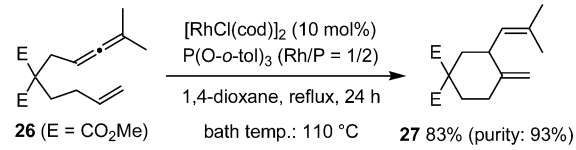
[a] All reactions were carried out with $[RhCl(cod)]_2$ and $P(OAr)_3$ (Rh/P = 1/2) in 1,4-dioxane at 110 °C (bath temperature) under Ar atmosphere. E = CO_2Me. [b] Isolated yield. [c] Determined by GC analyses.

of **21** (entry 2). We assumed that the steric vacancy of the allene moiety promoted side reactions such as a catalytic dimerization of allenes.[39] The reaction of **22** with only one alkyl substituent at the allenic terminus provided the cyclic 1,4-diene **23** as an *E*/*Z* mixture with predominant formation of the *E* isomer (*E*/*Z* = 2.6/1, entry 3). The geometry was accurately determined by the values of the H−H coupling constants of vinylic protons (***E*-23**: J = 15.3 Hz; ***Z*-23**: J = 10.8 Hz). The change of the ligand to P(O-*o*-PhC$_6$H$_4$)$_3$ somewhat improved the stereoselectivity (*E*/*Z* = 5.4/1, entry 4). In the cyclization of **24**, which has the more bulky *tert*-butyl group, the stereoselectivity lowered in comparison with the case of **22** (*E*/*Z* = 1.5/1, entry 5), whereas the reaction with P(O-*o*-PhC$_6$H$_4$)$_3$ enhanced the *E*/*Z* ratio of **25** up to 8.3/1 (entry 6). Each geometric isomer of **25** was unambiguously determined in a similar manner (***E*-25**: J = 15.5 Hz; ***Z*-25**: J = 11.5 Hz).

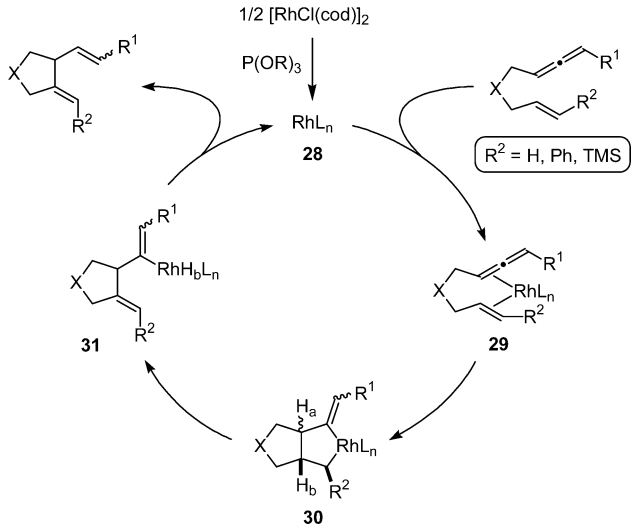
It is noteworthy that the cycloisomerization of even one carbon homologated allenene such as **26** selectively provided the corresponding *exo*-methylenecyclohexane **27** without the undesirable isomerization of the C−C double bonds while high loading of the rhodium catalyst was necessary for complete consumption of **26** (Scheme 3).

It is particularly important that no hydride sources were required for the present cycloisomerizations. As a consequence, the cyclization should proceed via a metallacycle intermediate generated by an oxidative cyclization mechanism[33b] rather than via hydrometalation of metal-hydride species followed by a sequence of carbometalation and β-hydrogen elimination.[33a,c] A plausible

SCHEME 3



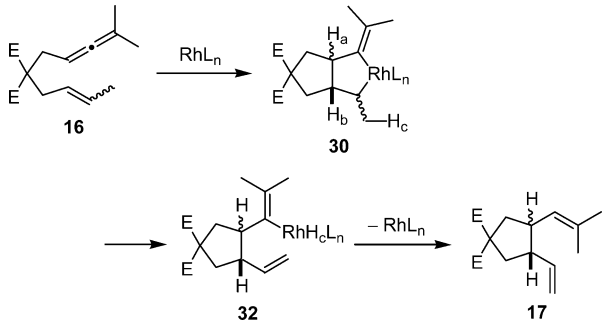
SCHEME 4



mechanism for the rhodium-catalyzed cycloisomerization of allenenes is shown in Scheme 4. The initial step is the coordination of the allenene with a mononuclear rhodium(I) phosphite complex, which was generated by the reaction of $[RhCl(cod)]_2$ with 2 equiv of triaryl phosphites in situ, at the internal allenic π-bond to lead to the formation of complex **29**.[40] Subsequently, the oxidative cyclization gave rhodacyclopentane(III) **30** possessing the

(39) For recent examples, see the following. Pd: (a) Arisawa, M.; Sugihara, T.; Yamaguchi, M. *Chem. Commun.* **1998**, 2615−2616. (b) Oh, C. H.; Yoo, H. S.; Jung, S. H. *Chem. Lett.* **2001**, 1288−1289.

SCHEME 5



exo-alkylidene moiety. Then, metallacycle **30** undergoes selective elimination of the *β*-hydrogen atom at the bridgehead position derived from vinylic hydrogen (H_b) to give a hydride vinyl complex **31**, which spontaneously induces reductive elimination to furnish the 1,4-diene product. Presumably, the elimination of the *β*-hydrogen derived from the allenic hydrogen (H_a) is disfavored due to the existence of the sp^2 carbon at the α position of the metallacycle intermediate **30**, because the Rh−C−C−H_a moiety cannot take the coplanar conformation required for such a *β*-hydrogen elimination.

The stereospecificity, as shown in the cycloisomerization of allenenes **12** and **14**, is attributed to a coplanar arrangement of Rh−C−C−H_b in the abstraction step of the *β*-hydrogen H_b. The specific generation of 1,5-diene **17** from methyl-substituted allenene **16** is explained by a mechanism depicted in Scheme 5. In rhodacycle **30**, H_c of the methyl group is more feasible for smooth *β*-hydrogen elimination than H_b at the ring juncture. Considering that the kinetic product *cis*-**17** formed predominantly in each reaction of **16** as shown in Table 3, the oxidative cyclization seems to be rate determining.

Next, we will discuss the stereoselectivity in the cyclizations of allenenes **22** and **24** having only one alkyl substituent at the allenic terminus (Table 4). As illustrated in Scheme 6, the formation of the *Z* isomer is anticipated to be more favorable with respect to the steric repulsion between the substituent R and the rhodium moiety. Nevertheless, the formation of the less favored *E* isomer took place preferentially over the *Z* isomer in both cases in **22** and **24**.[41] It is remarkable that the more bulky ligand P(O-*o*-PhC_6H_4)$_3$ promoted the formation of the *E* isomer. In striking contrast to this, excellent stereoselection was achieved in the [4+1] cycloaddition of vinylallenes[27f,j] and the [5+2] cycloaddition of allenevinylcyclopropanes,[25c] which might proceed via analogous mechanisms. The reason for the predominant formation of the sterically disfavored *E* isomer is not clear currently; however, steric repulsion may not be as significant in the allenene complex intermediate *syn*-**29**.

It should be noted that the analogous 1,6-diene **33** never reacted and remained intact under identical conditions (Scheme 7). This observation indicates that the allene moiety plays a key role in the cycloisomerization reaction.[42] The central sp carbon of the allene moiety causes characteristic reactivity toward oxidative cyclization to give metallacycle **30**.

Cycloisomerization of Allenenes Leading to Seven-Membered Rings. During the quests for the optimization of conditions of the cycloisomerization of allenene **1**, Wilkinson complex Rh$Cl(PPh_3)_3$ was found to cause a drastic change in the reaction pathway, i.e., the unexpected seven-membered-ring product **34** was obtained as the major product via an unusual endo-mode cyclization albeit in low isolated yield (Scheme 8).[43] This result apparently indicates that the mode of cyclizations depends on the electronic and steric nature of the ancillary ligands. Thus, the effect of ligands on formation of a seven-membered ring was immediately investigated. Although a full range of phosphine ligands, including bidentate phosphines, was examined, the desirable product **34** was obtained only in moderate yields along with unidentified isomers. Further studies revealed that the carbonyl complex $[RhCl(CO)_2]_2$ behaved as an effective catalyst leading to exclusive formation of **34** in 70% yield without additives (Scheme 9), whereas a similar reaction with $[RhCl(cod)]_2$ afforded **34** in poor yield (33%). This result implies that the carbonyl ligands on the rhodium center are quite important to the selective endo-mode cyclization.[44] Strong support for this presumption is that the identical reaction *under a carbon monoxide atmosphere* raised the yield of **34** to 80% (Scheme 9). Similarly, the tosylamide derivatives **5** underwent very rapid cyclization to give cyclic enamide **35** in 82% yield. It is also noteworthy that allenene **18**, which was an improper substrate for formation of five-membered rings, smoothly affords the corresponding seven-membered-ring **36** in 91% yield (Scheme 10). Unfortunately, other allenenes such as **3**, **7**, **9**, **14**, and **22** did not induce these endo-mode cyclizations.

Two plausible mechanisms for the formation of seven-membered rings are shown in Scheme 11. Path a involves a sequence of an allylic C−H activation and carbometalation with the central carbon atom of the allene followed by reductive elimination.[43] The other path is triggered by intramolecular nucleophilic attack of the alkene moiety to the coordinated allene in **38** (path b). The validity of path b was, however, discarded by the following experiments. Attempts to capture cationic intermediate **38** with D_2O or EtOD[45] completely failed to produce the expected hydroxy- or ethoxy-substituted products, and only furnished the ordinal seven-membered-ring product. In addition, no reaction occurred in the presence of other electrophilic transition metal catalysts such as Pt(II), which is widely known as an effective catalyst for

(40) In the case of the rhodium-catalyzed cycloisomerization of allenynes, the allene moiety coordinates to the rhodium(I) center at the external allenic *π*-bond to form the metallacycle intermediate, see refs 32a,b.

(41) No isomerization of the *Z* isomer to the more thermodynamically stable *E* isomer was observed under the reaction conditions.

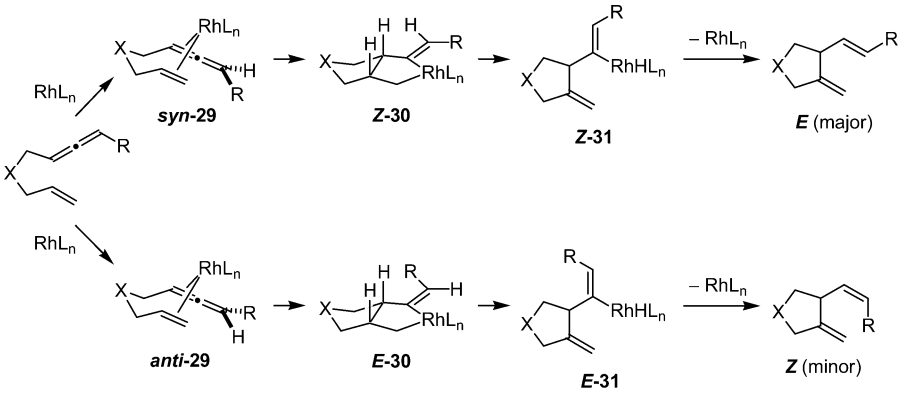
(42) Similar observations were reported in the rhodium- and platinum-catalyzed [4+1] cycloaddition of vinylallenes and the iridium-catalyzed [5+1] cycloaddition of allenylcyclopropanes, see refs 27f,j,k.

(43) Recently, Trost et al. reported the formation of *exo*-alkylidenecycloheptenes by the ruthenium-catalyzed cycloisomerization of 1,6-enynes, see refs 5c,e.

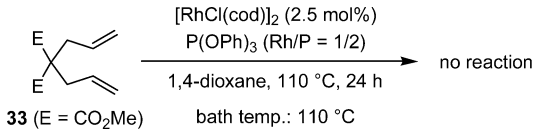
(44) Under a carbon monoxide atmosphere, even $[RhCl(cod)]_2$ behaved as an effective catalyst to give **34** in 74% yield.

(45) (a) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11549−11550. (b) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511−10520.

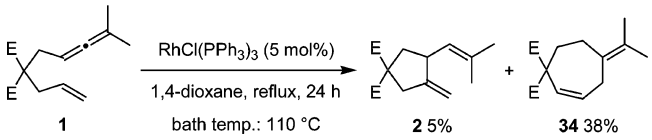
SCHEME 6



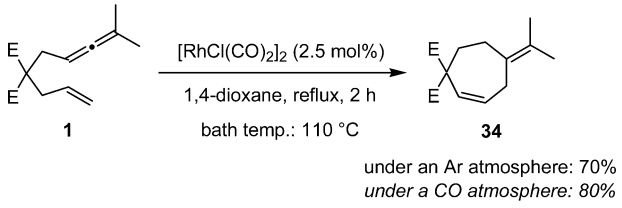
SCHEME 7



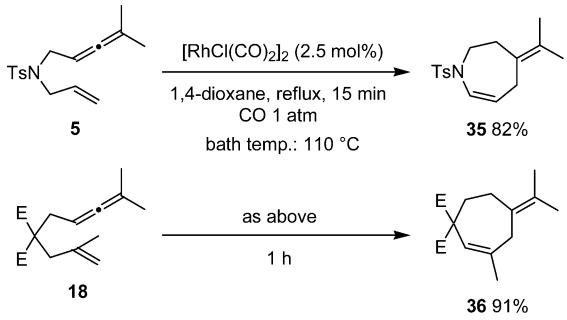
SCHEME 8



SCHEME 9

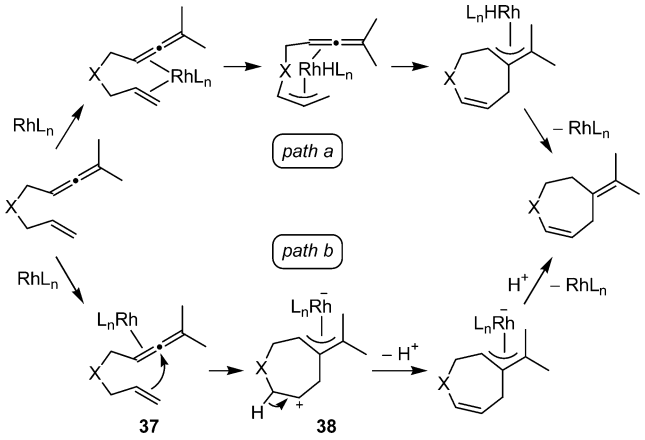


SCHEME 10

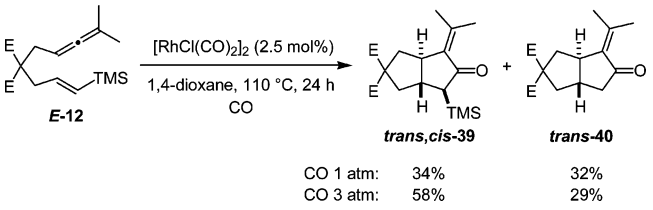


analogous cyclization of enynes.[45b,46] Unfortunately, we cannot currently give a sufficient account of the unfitness of several allenenes for the endo-mode cyclizations even employing the mechanism depicted in Scheme 11. The substituents might retard the appropriate conformation required for the allylic C−H activation. Needless to say,

SCHEME 11



SCHEME 12



the possibility of another reaction pathway cannot be completely excluded.

In striking contrast to the above, a similar reaction of trimethylsilyl-substituted allenene ***E*-12** incorporated carbon monoxide to afford the unprecedented [2+2+1] cycloaddition product *trans,cis*-**39** concomitant with its desilylation product *trans*-**40**[47] as a single stereoisomer, respectively (Scheme 12).[48] A higher CO pressure improved the efficiency of incorporation of carbon monoxide.[49] The formation of [2+2+1] cycloaddition products *trans,cis*-**39** and *trans*-**40** is ascribed to the enhanced stabilization of the metallacycle intermediate **30** in Scheme 4 by the silicon substituent at an α position to the rhodium(III) metal. We presume that the rate-determining CO insertion into metallacycle **30** allows

(46) (a) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901−903. (b) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305−8314. (c) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785−6786. (d) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863−11869. (e) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704−3709.

(47) Desilylation of α-silyl ketone *trans,cis*-**39** might proceed via the corresponding enol silyl ether under thermal or catalytic condition to provide *trans*-**40**, see: Matsuda, I.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215−3218.

(48) The stereochemistry for both *trans,cis*-**39** and *trans*-**40** was estimated from the NOESY spectra, respectively.

(49) More increase of CO pressure inhibited incorporation of carbon monoxide to give undesirable isomers.

excellent stereoselection in the [2+2+1] cycloaddition to furnish thermodynamically stable isomers *trans*,*cis*-**39** and *trans*-**40** exclusively.

Conclusion

We have found that rhodium(I) triaryl phosphite complexes effectively catalyzed cycloisomerization of allenenes to produce a variety of carbocycles and heterocycles. In the present transformation, the ligands played a key role and dominated the cyclization mode. For example, the reaction of triaryl phosphites exclusively afforded five-membered rings in the formal exo-cyclic mode via a metallacycle intermediate with an *exo*-alkylidene moiety. On the other hand, the reaction under a carbon monoxide atmosphere resulted in the selective formation of seven-membered rings by way of an allylic C−H activation process. We also found that the similar reaction of the allenene bearing a silicon substituent gave the [2+2+1] cycloaddition product as the result of incorporation of carbon monoxide.

Experimental Section

General Procedure for Rhodium(I)-Catalyzed Cycloisomerization of Allenenes with Triaryl Phosphite Ligands. To a oven-dried Schlenk flask containing $[RhCl(cod)]_2$[50] (3.1 mg, 0.063 mmol) was added a solution of $P(O\text{-}o\text{-}tol)_3$[51] (9.4 mg, 0.027 mmol) in 1,4-dioxane (1 mL). Then a solution of dimethyl 2-(4-methyl-2,3-pentadienyl)-2-(2-propenyl)malonate (**1**) (62.1 mg, 0.25 mmol) in 1,4-dioxane (1.5 mL) was added to the reaction vessel. The mixture was stirred at 110 °C for 18 h under an Ar atmosphere. After the solution was cooled to room temperature, the volatile materials were removed in vacuo. The residue was subjected to silica gel flash column chromatography (eluent: *n*-hexane/ethyl acetate = 20/1) to afford dimethyl 3-methylene-4-(2-methyl-1-propenyl)-cyclopentane-1,1-dicarboxylate (**2**) (56.9 mg, 92%) as a colorless oil. The gas chromatographic analysis of the isolated product revealed that **2** was contained in 99% purity.

Dimethyl 3-Methylene-4-(2-methyl-1-propenyl)cyclopentane-1,1-dicarboxylate (2). Colorless oil; R_f 0.54 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 889 (m), 1072 (m), 1173 (m), 1199 (m), 1269 (s), 1376 (w), 1435 (m), 1657 (w), 1737 (vs), 2954 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.64 (d, J = 1.5 Hz, 3H), 1.73 (d, J = 1.5 Hz, 3H), 1.86 (dd, J = 11.5, 13.0 Hz, 1H), 2.54 (ddd, J = 1.3, 7.5, 13.0 Hz, 1H), 2.95 (ddt, J = 2.3, 2.3, 17.0 Hz, 1H), 3.08 (d, J = 17.0 Hz, 1H), 3.32−3.37 (m, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 4.72−4.74 (m, 1H), 4.88−4.89 (m, 1H), 4.95−4.97 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 25.6, 40.0, 40.8, 42.4, 52.7, 52.8, 58.3, 106.9, 125.6, 133.6, 151.3, 172.1, 172.4 ppm; MS (FAB) *m*/*z* (rel intensity, %) 193 (79), 253 (MH^+, 100); HRMS (FAB) calcd for $C_{14}H_{20}O_4$ 252.1362; found 252.1329.

7,8-Dimethyl-2-methylene-3-(2-methyl-1-propenyl)-7,9-diazaspiro[4.5]decane-6,8,10-trione (4). Pale yellow viscous oil; R_f 0.33 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 844 (w), 891 (m), 968 (w), 1004 (w), 1053 (m), 1095 (m), 1148 (w), 1284 (m), 1298 (m), 1326 (m), 1377 (s), 1418 (s), 1455 (s), 1685 (vs), 1747 (m), 2928 (m), 2966 (m), 3078 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.66 (d, J = 1.5 Hz, 3H), 1.75 (d, J = 1.3 Hz, 3H), 2.03 (dd, J = 11.0, 12.5 Hz, 1H), 2.31 (dd, J = 8.5, 12.5 Hz, 1H), 2.98 (d, J = 16.5 Hz, 1H), 3.05 (ddt, J = 2.3, 2.3, 16.5 Hz, 1H), 3.31 (s, 3H), 3.32 (s, 3H), 3.68−3.75 (m, 1H), 4.80 (ddd, J = 2.0, 2.3, 2.3 Hz, 1H), 4.93 (d, J = 2.0 Hz, 1H), 5.01 (ddd, J = 1.3, 1.5, 9.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.2, 25.7, 28.8, 29.0, 42.2, 43.0, 45.2, 55.1, 106.9, 124.6, 134.5, 151.25, 151.34, 172.1, 172.5 ppm; MS (FAB) *m*/*z* (rel intensity, %) 169 (98), 221 (100), 277 (MH^+, 100); HRMS (FAB) calcd for $C_{15}H_{20}N_2O_3$ 276.1474, found 276.1455.

3-Methylene-4-(2-methyl-1-propenyl)-1-(4-methylbenznesulfonyl)pyrrolidine (6). White solid; R_f 0.38 (*n*-hexane/ethyl acetate = 5/1); mp 110−111 °C; IR ($CHCl_3$) ν 815 (m), 900 (m), 1058 (m), 1095 (s), 1161 (vs), 1209 (m), 1345 (s), 1454 (w), 1598 (w), 1666 (w), 2855 (w), 2917 (w), 2974 (w), 3029 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.69 (s, 3H), 2.43 (s, 3H), 2.62 (dd, J = 8.9, 9.0 Hz, 1H), 3.41 (ddd, J = 8.4, 8.7, 9.0 Hz, 1H), 3.63 (dd, J = 8.4, 9.0 Hz, 1H), 3.65 (ddt, J = 2.0, 2.0, 14.3 Hz, 1H), 4.04 (dd, J = 1.3, 14.3 Hz, 1H), 4.75−4.77 (m, 1H), 4.77−4.80 (m, 1H), 4.86−4.88 (m, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 21.5, 25.6, 42.5, 51.8, 53.5, 107.1, 121.7, 127.8, 129.6, 132.7, 136.0, 143.6, 147.5 ppm; MS (FAB) *m*/*z* (rel intensity, %) 292 (MH^+, 100); HRMS (FAB) calcd for $C_{16}H_{21}O_2NS$ 291.1293, found 291.1327.

1-Benzyl-3-methylene-4-(2-methyl-1-propenyl)pyrrolidine (8). Colorless oil; R_f 0.42 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 881 (s), 973 (w), 1028 (w), 1074 (w), 1126 (m), 1300 (m), 1333 (w), 1374 (m), 1453 (s), 1495 (m), 1663 (m), 2785 (vs), 2912 (vs), 2966 (s), 3028 (m), 3063 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.67 (d, J = 1.5 Hz, 3H), 1.73 (d, J = 1.5 Hz, 3H), 2.16 (dd, J = 8.8, 9.5 Hz, 1H), 3.01 (br d, J = 13.8 Hz, 1H), 3.09 (dd, J = 7.5, 8.8 Hz, 1H), 3.53−3.60 (m, 1H), 3.57 (d, J = 13.8 Hz, 1H), 3.60 (d, J = 12.5 Hz, 1H), 3.71 (d, J = 12.5 Hz, 1H), 4.75−4.77 (m, 1H), 4.87−4.89 (m, 1H), 5.00−5.04 (m, 1H), 7.25−7.28 (m, 1H), 7.31−7.38 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 25.7, 42.9, 58.9, 60.5, 105.5, 124.7, 127.2, 128.3, 129.0, 133.8, 138.1, 151.6 ppm; MS (FAB) *m*/*z* (rel intensity, %) 91 (100), 228 (MH^+, 36); HRMS (FAB) calcd for $C_{16}H_{21}N$ 227.1674, found 227.1665.

3-Cyclohexylidenemethyl-4-methylenetetrahydrofuran (10). Colorless oil; R_f 0.41 (*n*-hexane/ethyl acetate = 10/1); R (neat) ν 849 (w), 887 (m), 930 (m), 967 (w), 1071 (m), 1180 (w), 1232 (w), 1343 (w), 1446 (m), 1665 (w), 1726 (w), 2851 (s), 2927 (vs), 3076 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.48−1.61 (m, 6H), 2.08−2.17 (m, 4H), 3.38 (dd, J = 8.0, 9.5 Hz, 1H), 3.51−3.59 (m, 1H), 4.08 (dd, J = 8.0, 8.0 Hz, 1H), 4.29 (dtt, J = 2.0, 2.0, 13.4 Hz, 1H), 4.44 (dtt, J = 1.3, 2.4, 13.4 Hz, 1H), 4.85 (ddd, J = 2.0, 2.4, 3.0 Hz, 1H), 4.89−4.93 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 28.3, 28.7, 29.3, 37.3, 42.9, 71.4, 74.0, 104.0, 118.9, 143.3, 151.9 ppm; MS (FAB) *m*/*z* (rel intensity, %) 81 (95), 91 (100), 139 (61), 179 (MH^+, 47); HRMS (FAB) calcd for $C_{12}H_{19}O$ (MH^+) 179.1436, found 179.1416.

Dimethyl (*E*)-3-(2-Methyl-1-propenyl)-4-(trimethylsilyl)methylenecyclopentane-1,1-dicarboxylate (*E*-13). Colorless oil; R_f 0.54 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 840 (s), 959 (m), 1000 (m), 1062 (m), 1100 (m), 1174 (s), 1200 (s), 1249 (s), 1377 (m), 1434 (s), 1625 (m), 1738 (vs), 2953 (vs), 3474 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.62 (d, J = 1.5 Hz, 3H), 1.70 (d, J = 1.5 Hz, 3H), 1.81 (dd, J = 11.8, 12.9 Hz, 1H), 2.52 (ddd, J = 1.8, 7.8, 12.9 Hz, 1H), 2.90 (ddd, J = 2.5, 2.5, 17.3 Hz, 1H), 3.08 (ddd, J = 2.5, 2.5, 17.3 Hz, 1H), 3.28−3.34 (m, 1H), 3.72 (s, 3H), 3.74 (s, 3H), 4.90 (d of sept, J = 1.5, 9.0 Hz, 1H), 5.20 (ddd, J = 2.0, 2.5, 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.4, 18.1, 25.7, 39.9, 40.1, 45.1, 52.7, 52.8, 58.6, 120.4, 126.0, 133.8, 159.8, 172.2, 172.3 ppm; MS (FAB) *m*/*z* (rel intensity, %) 73 (100), 133 (74), 325 (MH^+); HRMS (FAB) calcd for $C_{17}H_{29}O_4Si$ (MH^+) 325.1835, found 325.1762.

Dimethyl (*E*)-3-Benzylidene-4-(2-methyl-1-propenyl)-cyclopentane-1,1-dicarboxylate (*E*-15). Colorless oil; R_f 0.46 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 836 (w), 872 (w), 915 (w), 961 (w), 1063 (m), 1108 (w), 1157 (m), 1200 (s), 1267 (s), 1376 (w), 1434 (m), 1492 (w), 1598 (w), 1736 (vs), 2916 (m), 2952 (m), 3023 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.72 (d, J = 1.0 Hz, 3H), 1.81 (d, J = 1.0 Hz, 3H), 1.87 (dd,

(50) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218−220.
(51) (a) Kosolapoff, G. M. *Organophosphorus Compounds*; Wiley: New York, 1950. (b) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley: New York, 1973; Vol. 5.

J = 12.5, 12.8 Hz, 1H), 2.60 (ddd, J = 1.5, 7.0, 12.8 Hz, 1H), 3.23 (ddd, J = 2.5, 2.5, 18.0 Hz, 1H), 3.42 (d, J = 18.0 Hz, 1H), 3.55−3.60 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 5.05−5.07 (m, 1H), 6.13 (dt, J = 2.5, 5.0 Hz, 1H), 7.17−7.21 (m, 1H), 7.29−7.34 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.2, 25.7, 38.6, 40.1, 44.2, 52.7, 52.8, 59.1, 122.7, 125.7, 126.1, 128.2, 134.1, 137.8, 144.2, 172.0, 172.2 ppm; MS (FAB) m/z (rel intensity, %) 91 (100), 165 (53), 268 (46), 328 (M^+, 77); HRMS (FAB) calcd for $C_{20}H_{24}O_4$ 328.1675, found 328.1657.

Dimethyl (*Z*)-3-Benzylidene-4-(2-methyl-1-propenyl)-cyclopentane-1,1-dicarboxylate (*Z*-15). Colorless oil; R_f 0.52 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 698 (m), 755 (m), 840 (w), 891 (w), 916 (w), 965 (w), 1066 (m), 1110 (m), 1202 (s), 1255 (s), 1376 (m), 1434 (s), 1495 (m), 1598 (w), 1731 (vs), 2952 (s), 3023 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, J = 1.5 Hz, 3H), 1.65 (d, J = 1.0 Hz, 3H), 1.99 (dd, J = 6.8, 13.2 Hz, 1H), 2.79 (ddd, J = 1.6, 8.4, 13.2 Hz, 1H), 3.02 (ddd, J = 1.5, 1.5, 16.0 Hz, 1H), 3.31 (ddd, J = 2.3, 2.5, 16.0 Hz, 1H), 3.64−3.70 (m, 1H), 3.736 (s, 3H), 3.737 (s, 3H), 4.94−4.97 (m, 1H), 6.38−6.40 (m, 1H), 7.12−7.25 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.0, 25.3, 39.6, 42.0, 43.5, 52.68, 52.74, 58.1, 123.7, 126.1, 126.9, 127.7, 128.6, 131.8, 137.1, 144.5, 172.0, 172.1 ppm; MS (FAB) m/z (rel intensity, %) 91 (100), 153 (53), 213 (40), 268 (35), 328 (M^+, 100). HRMS (FAB) calcd for $C_{20}H_{24}O_4$ 328.1675, found 328.1700.

Dimethyl 3-(2-Methyl-1-propenyl)-4-vinylcyclopentane-1,1-dicarboxylate (17). Colorless oil; R_f 0.53 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 859 (w), 915 (m), 995 (m), 1097 (m), 1165 (s), 1197 (s), 1254 (vs), 1377 (m), 1435 (s), 1640 (w), 1732 (vs), 2927 (m), 2952 (s), 3076 (w), 3472 (w) cm^{-1}; MS (FAB) m/z (rel intensity, %) 207 (96), 235 (60), 267 (MH^+, 100); HRMS (FAB) calcd for $C_{15}H_{23}O_4$ (MH^+) 267.1596, found 267.1556. Cis (major): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 (d, J = 2.0 Hz, 3H), 1.66 (d, J = 2.0 Hz, 3H), 2.04 (dd, J = 7.5, 13.8 Hz, 1H), 2.24 (dd, J = 7.8, 13.5 Hz, 1H), 2.42 (dd, J = 7.4, 13.5 Hz, 1H), 2.45 (dd, J = 7.3, 13.8 Hz, 1H), 2.70 (dddd, J = 7.4, 7.5, 7.5, 7.8 Hz, 1H), 2.95 (dddd, J = 7.3, 7.5, 7.5, 9.0 Hz, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 4.89−5.00 (m, 3H), 5.70 (ddd, J = 9.0, 10.5, 17.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 25.8, 38.9, 40.2, 41.6, 47.2, 52.7, 52.8, 59.0, 114.9, 124.2, 132.8, 138.6, 172.9, 173.3 ppm. Trans (minor), additional signals: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, J = 2.3 Hz, 3H), 1.67 (d, J = 2.3 Hz, 3H), 1.99 (dd, J = 10.5, 13.8 Hz, 1H), 2.51 (dd, J = 7.8, 13.5 Hz, 1H), 2.54 (dd, J = 7.0, 10.5 Hz, 3H), 5.65 (ddd, J = 7.3, 10.3, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.4, 25.7, 39.8, 40.9, 44.6, 50.5, 58.2, 114.8, 125.8, 133.5, 139.4, 173.0, 173.1 ppm.

Dimethyl 3-Methylene-4-vinylcyclopentane-1,1-dicarboxylate (21). Colorless oil; R_f 0.45 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 821 (w), 892 (m), 918 (m), 992 (w), 1015 (w), 1072 (m), 1109 (w), 1169 (m), 1200 (m), 1269 (m), 1435 (m), 1640 (w), 1658 (w), 1737 (vs), 2953 (m), 2982 (w), 3078 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (dd, J = 11.0 13.0 Hz, 1H), 2.57 (ddd, J = 1.5, 7.5, 13.0 Hz, 1H), 2.94 (ddt, J = 2.3, 2.3, 17.0 Hz, 1H), 3.07 (br d, J = 17.0 Hz, 1H), 3.12−3.18 (m, 1H), 3.72 (s, 3H), 3.74 (s, 3H), 4.82 (q, J = 2.3 Hz, 1H), 4.98 (q, J = 2.3 Hz, 1H), 5.05−5.09 (m, 2H), 5.63 (ddd, J = 8.0, 9.5, 17.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.25, 40.27, 47.6, 52.75, 52.82, 58.5, 108.1, 116.1, 139.0, 150.3, 172.0, 172.1 ppm; MS (FAB) m/z (rel intensity, %) 199 (100), 226 (MH_2^+, 19); HRMS (FAB) calcd for $C_{12}H_{17}O_4$ (MH^+) 225.1127, found 225.1106.

Dimethyl 3-(1-Heptenyl)-4-methylenecyclopentane-1,1-dicarboxylate (23). Colorless oil; R_f 0.50 (*n*-hexane/ethyl acetate = 5/1); IR ($CHCl_3$) ν 890 (m), 968 (w), 1073 (m), 1163 (s), 1200 (s), 1269 (s), 1434 (m), 1656 (w), 1737 (vs), 2855 (m), 2926 (s), 2954 (s) cm^{-1}; MS (FAB) m/z (rel intensity, %) 235 (100), 295 (MH^+, 92); HRMS (FAB) calcd for $C_{17}H_{26}O_4$ 294.1831, found 294.1843. *E* (major): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.23−1.38 (m, 6H), 1.95 (dd, J = 11.3, 13.3 Hz, 1H), 1.98−2.05 (m, 2H), 2.53 (ddd, J = 1.5, 7.6, 12.8 Hz, 1H), 2.92 (ddt, J = 2.3, 2.5, 16.8 Hz, 1H), 3.06 (br d, J = 16.8 Hz, 1H), 3.06−3.11 (m, 1H), 3.71 (s, 3H), 3.73 (s, 3H), 4.78−4.79 (m, 1H), 4.93−4.94 (m, 1H), 5.21 (ddt, J = 1.4, 8.3, 15.3 Hz, 1H), 5.47 (dt, J = 7.0, 15.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 22.47, 29.1, 31.3, 32.4, 40.2, 40.8, 46.7, 52.69, 52.75, 58.3, 107.6, 130.4, 132.8, 151.2, 172.1, 172.2 ppm. *Z* (minor): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.23−1.38 (m, 6H), 1.89 (dd, J = 11.5, 13.0 Hz, 1H), 1.98−2.05 (m, 2H), 2.54 (ddd, J = 1.5, 7.5, 13.0 Hz, 1H), 2.95 (ddt, J = 2.3, 2.4, 17.8 Hz, 1H), 3.08 (br d, J = 17.8 Hz, 1H), 3.42−3.48 (m, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.75−4.76 (m, 1H), 4.90−4.91 (m, 1H), 5.17 (ddt, J = 1.6, 8.9, 10.8 Hz, 1H), 5.50 (ddt, J = 1.0, 7.5, 10.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.00, 22.48, 27.4, 29.5, 31.4, 40.1, 40.9, 41.5, 52.72, 52.78, 58.4, 107.3, 130.2, 131.8, 150.9, 172.0, 172.3 ppm.

Dimethyl 3-(3,3-Dimethyl-1-butenyl-4-methylenecyclopentane-1,1-dicarboxylate (25). Colorless oil; R_f 0.52 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 890 (m), 972 (m), 1009 (w), 1072 (m), 1108 (w), 1157 (m), 1173 (m), 1200 (s), 1230 (s), 1252 (s), 1269 (s), 1362 (m), 1435 (m), 1657 (w), 1737 (vs), 2867 (m), 2904 (m), 2954 (s), 3077 (w) cm^{-1}; MS (FAB) m/z (rel intensity, %) 161 (100), 221 (100), 281 (MH^+, 100); HRMS (FAB) calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1678. *E* (major): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.96 (dd, J = 11.3, 12.8 Hz, 1H), 2.55 (ddd, J = 1.5, 7.5, 12.8 Hz, 1H), 2.93 (dddd, J = 2.0, 2.5, 2.5, 17.0 Hz, 1H), 3.03−3.10 (m, 2H), 3.72 (s, 3H), 3.74 (s, 3H), 4.77 (dddd, J = 0.8, 2.0, 2.5, 2.5 Hz, 1H), 4.93−4.95 (m, 1H), 5.12 (dd, J = 8.0, 15.5 Hz, 1H), 5.51 (dd, J = 1.0, 15.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 32.9, 40.2, 40.9, 46.7, 52.69, 52.8, 58.3, 107.5, 125.1, 143.8, 151.4, 172.1, 172.26 ppm. *Z* (minor) additional signals: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 9H), 1.84 (dd, J = 11.8, 12.8 Hz, 1H), 2.57 (ddd, J = 1.0, 7.5, 12.8 Hz, 1H), 2.99 (dddd, J = 2.0, 2.3, 2.5, 17.0 Hz, 1H), 3.03−3.09 (m, 2H), 3.72 (s, 3H), 3.75 (s, 3H), 4.81 (dddd, J = 0.8, 2.3, 2.5, 2.5 Hz, 1H), 4.93−4.95 (m, 1H), 4.97 (dd, J = 10.0, 11.5 Hz, 1H), 5.50 (dd, J = 1.0, 11.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.5, 33.0, 40.0, 41.3, 42.6, 52.73, 107.6, 129.0, 141.8, 151.0, 172.0, 172.31 ppm.

Dimethyl 4-Methylene-3-(2-methyl-1-propenyl)cyclohexane-1,1-dicarboxylate (27). Colorless oil; R_f 0.54 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 846 (w), 896 (m), 1011 (w), 1067 (m), 1087 (m), 1159 (s), 1202 (s), 1244 (s), 1292 (m), 1376 (w), 1435 (m), 1646 (m), 1732 (vs), 2952 (s), 3081 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (dd, J = 13.0, 13.0 Hz, 1H), 1.58 (d, J = 1.0 Hz, 3H), 1.73 (d, J = 1.0 Hz, 3H), 1.77 (ddd, J = 4.3, 13.4, 13.4 Hz, 1H), 2.09−2.16 (m, 1H), 2.32−2.42 (m, 3H), 2.96−3.01 (m, 1H), 3.67 (s, 3H), 3.77 (s, 3H), 4.63 (dd, J = 1.5, 2.0 Hz, 1H), 4.69 (dd, J = 1.5, 2.0 Hz, 1H), 5.04−5.07 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.9, 25.7, 32.0, 32.3, 38.1, 38.8, 52.5, 52.6, 55.1, 107.3, 125.3, 133.3, 148.3, 171.5, 172.2 ppm; MS (FAB) m/z (rel intensity, %) 147 (100), 207 (100), 267 (MH^+, 100); HRMS (FAB) calcd for $C_{15}H_{23}O_4$ (MH^+) 267.1596, found 267.1621.

General Procedure for Rhodium(I)-Catalyzed Cycloisomerization of Allenenes under a Carbon Monoxide Atmosphere. To a oven-dried Schlenk flask containing $[RhCl(CO)_2]_2$[52] (2.7 mg, 0.013 mmol) was added 1,4-dioxane (1 mL). Then a solution of dimethyl 2-(4-methyl-2,3-pentadienyl)-2-(2-propenyl)malonate (**1**) (70.6 mg, 0.28 mmol) in 1,4-dioxane (1.5 mL) was added to the reaction vessel. The system was charged with CO gas and the resultant mixture was stirred at 110 °C for 2 h under a CO atmosphere. After the solution was cooled to room temperature, the volatile materials were removed in vacuo. The residue was subjected to silica gel flash column chromatography (eluent; *n*-hexane/ethyl acetate = 20/1) to afford dimethyl 5-isopropylidene-2-cycloheptene-1,1-dicarboxylate (**34**) (59.4 mg, 80%) as a colorless oil.

Dimethyl 5-Isopropylidene-2-cycloheptene-1,1-dicarboxylate (34). Colorless oil; R_f 0.45 (*n*-hexane/ethyl acetate

(52) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211−214.

= 5/1); IR (neat) ν 807 (m), 1066 (s), 1229 (vs), 1373 (m), 1434 (s), 1737 (vs), 2952 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.60 (s, 3H), 2.39 (br s, 4H), 2.85 (d, J = 6.3 Hz, 2H), 3.70 (s, 6H), 5.64 (dt, J = 1.5, 10.8 Hz, 1H), 5.95 (dt, J = 6.3, 10.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.0, 20.3, 27.9, 30.3, 30.6, 52.7, 60.2, 124.8, 126.4, 128.5, 131.8, 171.4 ppm; MS (FAB) *m*/*z* (rel intensity, %) 192 (83), 253 (MH^+, 100). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.51; H, 8.01.

4-Isopropylidene-1-(4-methylbenzenesulfonyl)-2,3,4,5-tetrahydro-*1H*-azepine (35). Colorless oil; R_f 0.43 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 816 (m), 845 (w), 918 (m), 980 (w), 1018 (m), 1050 (s), 1092 (s), 1163 (vs), 1209 (w), 1291 (m), 1306 (m), 1339 (vs), 1398 (m), 1449 (m), 1494 (w), 1597 (m), 1648 (m), 2920 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.55 (s, 3H), 2.40−2.45 (m, 2H), 2.41 (s, 3H), 2.82 (d, J = 5.9 Hz, 2H), 3.70−3.73 (m, 2H), 5.01 (dt, J = 5.9, 8.9 Hz, 1H), 6.41 (dt, J = 1.5, 8.9 Hz, 1H), 7.27−7.28 (m, 2H), 7.65−7.68 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.8, 20.3, 21.4, 28.2, 32.2, 47.1, 111.7, 125.8, 126.7, 127.5, 127.9, 129.5, 137.0, 143.2 ppm; MS (FAB) *m*/*z* (rel intensity, %) 292 (MH^+, 100); HRMS (FAB) calcd for $C_{16}H_{21}NO_2S$ 291.1293, found 291.1286.

Dimethyl 5-Isopropylidene-3-methyl-2-cycloheptene-1,1-dicarboxylate (36). Colorless oil; R_f 0.42 (*n*-hexane/ethyl acetate = 5/1); IR (neat) ν 649 (w), 692 (w), 746 (w), 824 (m), 908 (w), 938 (w), 984 (w), 1021 (m), 1067 (m), 1118 (m), 1246 (vs), 1339 (w), 1374 (m), 1434 (s), 1736 (vs), 2727 (w), 2857 (m), 2952 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.62 (s, 3H), 1.84 (d, J = 1.3 Hz, 3H), 2.33−2.36 (m, 2H), 2.37−2.40 (m, 2H), 2.80 (s, 2H), 3.69 (s, 6H), 5.37 (d, J = 1.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.0, 20.4, 27.1, 27.9, 30.6, 35.5, 52.6, 59.5, 120.2, 125.0, 128.0, 140.6, 171.8 ppm; MS (FAB) *m*/*z* (rel intensity, %) 147 (84), 207 (82), 266 (M^+, 100); HRMS (FAB) calcd for $C_{15}H_{23}O_4$ (MH^+) 267.1596, found 267.1597.

General Procedure for Rhodium(I)-Catalyzed [2+2+1] Cycloaddition of Allenenes under Carbon Monoxide Pressure. A glass tube (27 mm in diameter) placed in a 100 mL stainless steel autoclave was charged with dimethyl (*E*)-2-(4-methyl-2,3-pentadienyl)-2-[3-(trimethylsilyl)-2-propenyl]-malonate (***E*-12**) (84.1 mg, 0.26 mmol), $[RhCl(CO)_2]_2$ (2.5 mg, 0.0064 mmol), and 1,4-dioxane (2.5 mL). After the reactor was flushed with 3 atm of CO three times, it was pressurized with CO to 3 atm. The contents were stirred at 110 °C for 24 h and cooled to room temperature. After excess CO was purged, the volatile materials were removed in vacuo. The residue was subjected to silica gel flash column chromatography (eluent: *n*-hexane/ethyl acetate = 30/1) to afford *trans*,*cis*-dimethyl 4-isopropylidene-5-oxo-6-(trimethylsilyl)hexahydropentalene-2,2-dicarboxylate (*trans*,*cis*-**39**) (52.7 mg, 58%) as colorless crystals, followed by *trans*-dimethyl 4-isopropylidene-5-oxo-hexahydropentalene-2,2-dicarboxylate (*trans*-**40**) (20.8 mg, 29%).

***trans*,*cis*-Dimethyl 4-Isopropylidene-5-oxo-6-(trimethylsilyl)hexahydropentalene-2,2-dicarboxylate (*trans*,*cis*-39).** Colorless crystal; mp 130−131 °C; R_f 0.43 (*n*-hexane/ethyl acetate = 5/1); IR ($CHCl_3$) ν 843 (m), 1014 (w), 1067 (w), 1155 (m), 1250 (s), 1268 (s), 1368 (w), 1436 (m), 1636 (m), 1697 (m), 1729 (vs), 2954 (m), 3023 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.58 (d, J = 13.0 Hz, 1H), 1.60−1.68 (m, 1H), 1.74 (dd, J = 12.0, 12.2 Hz, 1H), 1.85 (d, J = 2.3 Hz, 3H), 1.97 (dd, J = 12.4, 12.5 Hz, 1H), 2.09 (d, J = 2.3 Hz, 3H), 2.31−2.38 (m, 1H), 2.66 (dd, J = 5.3, 12.2 Hz, 1H), 2.96 (dd, J = 5.8, 12.4 Hz, 1H), 3.737 (s, 3H), 3.739 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ −2.2, 20.6, 23.7, 37.3, 37.3, 46.1, 47.9, 52.85, 52.86, 54.5, 61.8, 134.3, 143.3, 172.68, 172.70, 209.7 ppm; MS (FAB) *m*/*z* (rel intensity, %) 337 (100), 351 (53, $M - H^+$). Anal. Calcd for $C_{18}H_{28}O_5Si$: C, 61.33; H, 8.01. Found: C, 61.06; H, 7.75.

***trans*-Dimethyl 4-Isopropylidene-5-oxohexahydropentalene-2,2-dicarboxylate (*trans*-40).** Colorless oil; R_f 0.36 (*n*-hexane/ethyl acetate = 3/1); IR (neat) ν 822 (w), 837 (w), 902 (w), 936 (w), 967 (w), 1036 (m), 1065 (m), 1088 (m), 1198 (s), 1263 (s), 1369 (m), 1435 (s), 1624 (s), 1703 (vs), 1731 (vs), 2952 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.87 (d, J = 1.0 Hz, 3H), 1.92 (dd, J = 8.5, 13.5 Hz, 1H), 1.97 (dd, J = 7.8, 13.0 Hz, 1H), 2.20 (d, J = 1.5 Hz, 3H), 2.21 (dd, J = 5.0, 18.5 Hz, 1H), 2.58 (dd, J = 10.0, 18.5 Hz, 1H), 2.64 (ddd, J = 1.5, 7.8, 13.0 Hz, 1H), 2.59−2.73 (m, 1H), 2.88 (ddd, J = 1.5, 8.5, 13.5 Hz, 1H), 3.40−3.46 (m, 1H), 3.70 (s, 3H), 3.76 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 24.5, 34.7, 41.07, 41.08, 44.6, 45.4, 52.7, 52.8, 61.6, 135.0, 149.7, 171.7, 172.2, 206.4 ppm; MS (FAB) *m*/*z* (rel intensity, %) 217 (62), 249 (54), 281 (100, M^+); HRMS (FAB) calcd for $C_{15}H_{20}O_5$ 280.1336, found 280.1311.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research and the 21st Century COE Program "Nature-Guided Materials Processing" of the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We also gratefully acknowledge Dr. Kozo Matsumoto, Mr. Haruhisa Choushi, and Mr. Shin-ichi Komai at Nagoya University for the mass spectral measurements, and the Microanalytical Center of Kyoto University for the elemental analyses measurements.

Supporting Information Available: General experimental methods, detailed experimental procedures, and characterization data for all allenenes, related references and notes, and ^1H and ^{13}C NMR spectra for all cyclization products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035551X