ORGANIC LETTERS

2003
Vol. 5, No. 26
4967−4970

Immobilized Cobalt/Rhodium Heterobimetallic Nanoparticle-Catalyzed Silylcarbocylization and Carbonylative Silylcarbocyclization of 1,6-Enynes

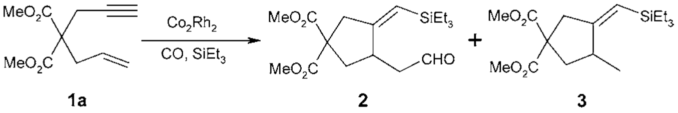
Kang Hyun Park, Il Gu Jung, So Yeon Kim, and Young Keun Chung*

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Korea

ykchung@plaza.snu.ac.kr

Received September 29, 2003

ABSTRACT



Reaction of 1,6-enynes with a hydrosilane in the presence of immobilized cobalt/rhodium bimetallic nanoparticles gives 2-methyl-1-silylmethylidene-2-cyclopentanes in the absence of carbon monoxide and 2-formylmethyl-1-silylmethylidene-2-cyclopentanes under 1 atm of carbon monoxide, respectively.

The development of efficient synthetic methods in the construction of carbocycles and heterocycles has been the subject of extensive study because of their relevance to medicine and functional materials.[1] Among numerous available methods, the transition-metal-mediated cyclization reaction has attracted much attention and become one of the most popular.[2] However, considerable effort is still being devoted to developing more efficient and practical methods for the synthesis of cyclic organic compounds from readily available starting materials. Recently, transition-metal-catalyzed cyclization/hydrosilylation reactions have become well developed.[3] Particularly, carbonylative silylcarbocyclization processes are useful because of the reactivity of the silylated carbocycles bearing an aldehyde group formed in these transformations. Unfortunately, the reaction conditions require high pressures (20−36 atm) of carbon monoxide.[3b,d] Such reaction conditions may limit the range of functional groups that are tolerated.

Recently, the chemistry of transition-metal nanoparticles has been rapidly developed[4] and their use has widened to many catalytic reactions including oxidation, hydrogenation, Pauson−Khand reactions, reductive Pauson−Khand reactions, etc.[5] Very recently, we found[6] that cobalt/rhodium nanoparticles (Co_2Rh_2) derived from $Co_2Rh_2(CO)_{12}$ were quite useful catalysts in Pauson−Khand-type reactions. While we were investigating the use of Co_2Rh_2 as a catalyst, we

---

[1] (a) Li, C.-L.; Liu, R.-S. *Chem. Rev.* **2000**, *100*, 3127. (b) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990. (c) *Cycloaddition Reactions in Carbohydrate Chemistry*; Giuliano, R. M. , Ed.; ACS Symposium Series 494; American Chemical Society: Washington, DC, 1992. (d) Thebtaranonth, C.; Thebtaranonth, Y. *Cyclization Reactions*; CRC Press: 1993. (e) Ali, B. E.; Alper, H. *Synlett* **2000**, 161.

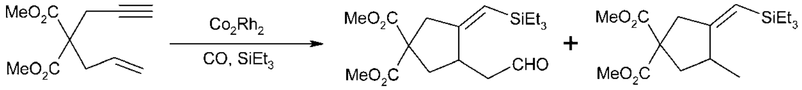
[2] (a) Fletcher, A. J.; Christie, S. D. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657. (b) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (c) Montgomery, J. *Acc. Chem. Res.* **2000**, *33*, 467. (d) Dell, C. P. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3873. (e) Tsuji, J. *Transition Metal Reagents and Catalysts*; John Wiley & Sons: New York, 2000. (f) Cacchi, S. *J. Organomet. Chem.* **1999**, *576*, 42. (g) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1. (h) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (i) Harvey, D. F.; Signo, D. M. *Chem. Rev.* **1996**, *96*, 271. (j) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (k) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635. (l) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813.

[3] (a) Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905. (b) Ojima, I.; Vu, A. T.; Lee, S.-Y.; McCullagh, J. V.; Moralee, A. C.; Fujiwara, M.; Hoang, T. H. *J. Am. Chem. Soc.* **2002**, *124*, 9164. (c) Ojima, I.; Moralee, A. C.; Vassar V. C. *Top. Catal.* **2002**, *19*, 89. (d) Muraoka, T.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 7325. (e) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478. (f) Molander, G. A.; Retsch, W. H. *J. Am. Chem. Soc.* **1997**, *119*, 8817.

[4] (a) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (b) Kralik, M.; Biffis, A. *J. Mol. Catal. A: Chem.* **2001**, *177*, 113. (c) Thomas, J. M.; Raja, R. *Chem. Record* **2001**, *1*, 448. (d) Rao, C. N. R.; Cheetham, A. K. *J. Mater. Chem.* **2001**, *11*, 2887. (e) Gai, P. L.; Roper, R.; White, M. G. *Curr. Opin. Solid St. Mater. Sci.* **2002**, *6*, 401.

10.1021/ol035895+ CCC: $25.00

Table 1. Co_2Rh_2-Catalyzed Silylcarbocyclization Reaction of 1,6-Enyne[a]



1a **2** **3** (1)

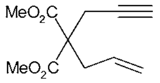
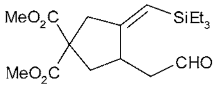
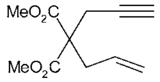
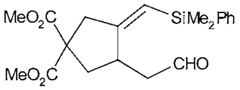
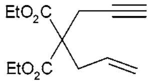
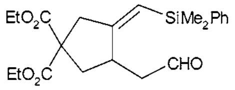
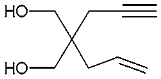
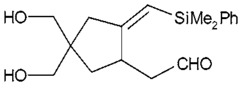
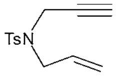
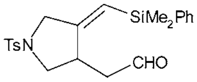
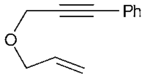
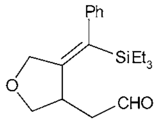
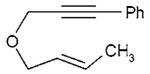
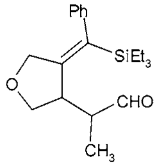
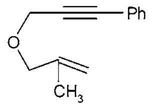
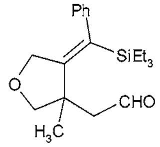
entry	catalyst	solvent	CO (atm)	temp (°C)	time (h)	yields (%)[b] 2	yields (%)[b] 3
1	Co_2Rh_2	toluene	1	65	12	54	41
2	Co_2Rh_2	toluene	5	65	12	96	
3	Co_2Rh_2	toluene	10	65	18	98	
4	Co_2Rh_2	1,4-dioxane	1	105	12	93	
5	Co_2Rh_2	hexane		22	2		90
6	recovered from # 4	1,4-dioxane	1	105	12	92	
7	recovered from # 6	1,4-dioxane	1	105	12	93	
8	recovered from # 7	1,4-dioxane	1	105	12	91	
9	recovered from # 8	1,4-dioxane	1	105	12	90	

[a] Reaction conditions: substrate (0.65 mmol) and catalyst (0.029 mmol). [b] Isolated yields.

found that Co_2Rh_2 catalyzed the silylcarbocyclization of 1,6-enynes to silylated carbocycles and carbonylative silylcarbocyclization of 1,6-enynes to silylated carbocycles bearing an aldehyde group under 1 atm of carbon monoxide. Here we report the use of cobalt/rhodium heterobimetallic nanoparticles in the catalytic silylcarbocyclization of enynes with and without carbon monoxide.

A toluene solution of **1a**, triethylsilane, and a catalytic amount of Co_2Rh_2 was heated for 18 h at 65 °C under 1 atm of CO (eq 1).[7] Chromatographic separation of the reaction products through silica gel gave two products, a carbonylative silylcarbocyclized product **2** and a silylcarbocyclized product **3** in 54 and 41% yields, respectively. Some variable factors were examined for exploring the optimal reaction conditions to obtain **2** or **3** as the sole product. The results are summarized in Table 1. As the pressure of CO increased to 5 atm in toluene solution at 65 °C (entry 2), **2** was obtained as the sole product in the dramatically increased yield of 96%. A further increase of CO pressure led to the isolation of **2** in 98% yield with no formation of **3** (entry 3). However, the use of high CO pressure is cumbersome with laboratory facilities. Thus, the use of 1 atm of CO is much preferred. When 1,4-dioxane was used as a reaction medium at 105 °C under 1 atm of CO (entry 4), a high yield (93%) of **2** was obtained. Interestingly, when the reaction was carried out in hexane at room temperature in the absence of carbon monoxide (entry 5), **3** was obtained as the sole product in 90% yield. Thus, we established the following preliminary reaction conditions: under 1 atm of CO, in 1,4-dioxane, at 105 °C, for 12 h for carbonylative silylcarbocyclization, and in hexane, at 22 °C, for 2 h for silylcarbocyclization.

Table 2. Co_2Rh_2-Catalyzed Carbonylative Silylcarbocyclization of 1,6-Enynes[a]

entry	subtrate	product	yield (%)[b]
1			93
2			98
3			96
4			52
5			93
6			87
7			58
8			23

[a] Reaction conditions: an enyne substrate (0.20 g, 0.65 mmol), R_3SiH (3.25 mmol), and catalyst (10 mg, 0.029 mmol), 1,4-dioxane, 1 atm CO, 105 °C, 12 h. [b] Isolated yields.

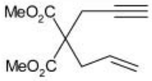
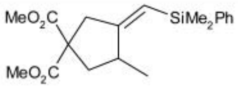
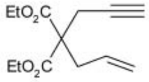
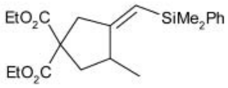
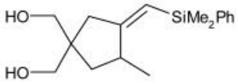
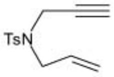
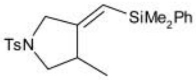
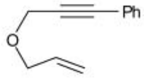
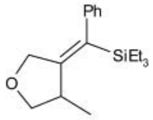
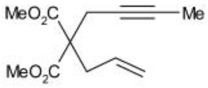
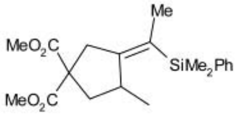
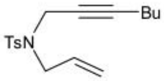
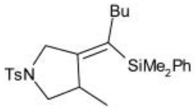
---

(5) (a) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc*. **2000**, *122*, 1243. (b) Lu, P.; Teranishi, T.; Asakura, K.; Miyake, M.; Toshima, N. *J. Phys. Chem. B* **1999**, *103*, 9673. (c) Kim, S.-W.; Son, S. U.; Lee, S. S.; Hyeon, T.; Chung, Y. K. *Chem. Commun*. **2001**, 2212. (d) Son, S. U.; Park, K. H.; Chung, Y. K. *Org. Lett*. **2002**, *4*, 3983. (e) Son, S. U.; Lee, S. I.; Chung, Y. K.; Kim, S.-W.; Hyeon, T. *Org. Lett*. **2002**, *4*, 277. (f) Park, K. H.; Son, S. U.; Chung, Y. K. *Chem. Commun*. **2003**, 1898. (g) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc*. **2002**, *124*, 4228. (h) Choi, K.-M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Lett*. **2003**, *32*, 180.

(6) Park, K. H.; Kim, S. Y.; Chung, Y. K. *Chem. Commun*. Submitted.

(7) An enyne substrate (0.20 g, 0.65 mmol), Et_3SiH (0.52 mL, 3.25 mmol), and catalyst (10 mg, 0.029 mmol) were dissolved in 10 mL of 1,4-dioxane$_2$. The resulting solution was heated to 105 °C for 12 h. Evaporation followed by chromatography on a silica gel column eluting with hexane/diethyl ether (v/v 10:1) gave a product and the catalyst.

Table 3. Co_2Rh_2-Catalyzed Silylcarbocyclization of 1,6-Enynes[a]

entry	subtrate	product	yield (%)[b]
1			95
2			97
3			83
4			90
5			91
6			87
7			92

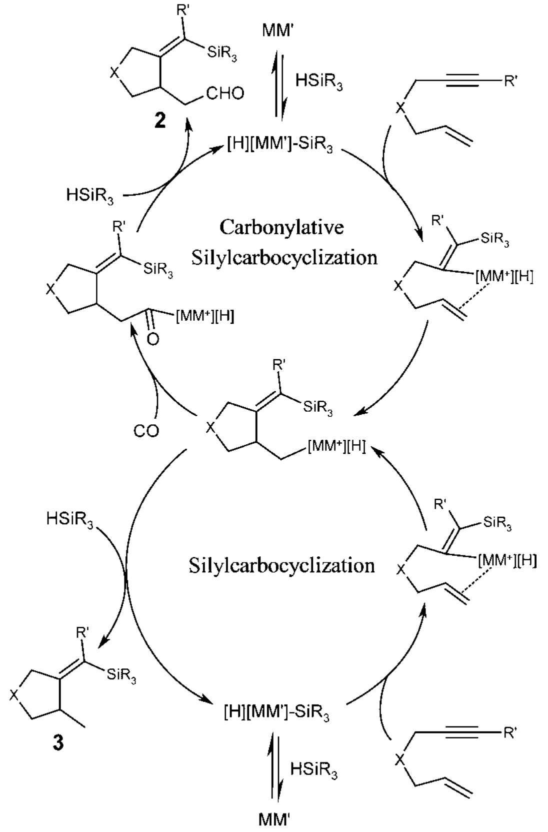
[a] Reaction conditions: an enyne substrate (0.20 g, 0.65 mmol), R_3SiH (3.25 mmol), and catalyst (10 mg, 0.029 mmol), hexane, 22 °C, 2 h. [b] Isolated yields.

To check the recyclability, Co_2Rh_2 catalyst was separated and reused several times for the carbonylative silylcarbocyclization reaction. The results shown in Table 1 confirm that the catalyst maintained its high activity even after being recycled five times.

The scope of the carbonylative silylcarbocyclization reaction has been investigated, and the results are summarized in Table 2. All terminal 1,6-enynes bridged by carbon, nitrogen, or oxygen atoms were good substrates. They gave the expected 2-formylmethyl-1-silylmethylidene-2-cyclopentanes and their heteroatom congeners in high yields (up to 98%). A 1,6-enyne bearing an internal acetylene moiety has also been employed (entry 6); the expected product was obtained in 87% yield. The reaction tolerates various functional groups, including ester, ether, and sulfonamide. We also tested enynes having a substituted alkene moiety, which were known to be inactive under Ojima's silylcarbocyclization reaction conditions.[3b] The expected products were obtained in 58 and 23% yields, respectively (entries 7 and 8). The relatively lower yields are presumably due to the steric hindrance of the methyl group.

We next screened the 1,6-enyne for the silylcarbocyclization reaction (Table 3). All terminal 1,6-enynes bridged by carbon, nitrogen, or oxygen atoms and 1,6-enynes having internal alkynes were good substrates. The expected *exo*-silylmethylenecyclopentanes or their heteroatom congeners were obtained in high yields (83−97%). We also tested enynes having a substituted alkene moiety under our reaction conditions. In contrast to the carbonylative silylcarbocyclization, they were inactive under our reaction conditions.

Scheme 1



Ojima and his group are pioneers[8] in this research field and have been in the forefront of the study of silylcarbocyclization and carbonylative silylcarbocyclization of 1,6-enynes.[3b,c] According to their reports,[3b] their optimal reaction conditions for silylcarbocyclization were quite mild, but those for the carbonylative silylcarbocyclization seemed to be cumbersome. Thus, compared to the previous studies,[3b,d] our reaction conditions for carbonylative silylcarbocyclization reaction are much milder and simpler to achieve. Moreover, our catalyst can be recycled many times without losing catalytic activity.

Ojima et al.[3b] proposed a plausible reaction mechanism. Recently, silylcarbocyclization of 1,6-enynes catalyzed by a cationic rhodium bis(phosphine) complex was reported by Widenhoefer et al.[9] They also proposed a working reaction mechanism that was almost the same as that proposed by Ojima et al. We expect that a plausible reaction mechanism will follow those of other studies (Scheme 1).

---

[8] (a) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580. (b) Ojima, I.; Tzamarioudaki, M.; Tsai, C.-Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643. (c) Ojima, I.; McCullagh, J. V.; Shay, W. R. *J. Organomet. Chem.* **1996**, *521*, 421. (d) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 3805.

[9] Chakrapani, H.; Liu, C.; Widenhoefer, R. A. *Org. Lett.* **2003**, *5*, 157.

In conclusion, we have demonstrated that immobilized cobalt−rhodium bimetallic nanoparticles are quite useful catalysts in the silylcarbocyclization reaction and carbonylative silylcarbocyclization reaction of 1,6-enynes. A judicious choice of the reaction conditions allows the reaction pathway to be controlled to give 2-methyl-1-silylmethylidene-2-cyclopentane or 2-formylmethyl-1-silylmethylidene-2-cyclopentane as the sole product. Some substrates known to be inactive in homogeneous catalysis can be carbonylatively silylcarbocyclized in reasonable yields. This method has several advantages such as reusability, mild reaction conditions, and no requirement for additives.

Acknowledgment. This work was supported by the Ministry of Science and Technology of Korea through Research Center for Nanocatalysis, one of the National Science Programs for Key Nanotechnology.

Supporting Information Available: Detailed experimental procedures of CO_2Rh_2 and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL035895+