# Rhodium-Catalyzed Intramolecular Silylcarbotricyclization (SiCaT) of Triynes

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*Received May 5, 1998*

Transition metal-catalyzed cyclotrimerization of acetylenes has attracted considerable interest as a powerful method for construction of highly substituted and/or functionalized benzene derivatives and has found many applications to the syntheses of natural and unnatural products of interest.[2] We describe here a novel silicon-initiated intramolecular cyclotrimerization, i.e., "silylcarbotricyclization (SiCaT)", of dodec-1,6,11-triynes, tridec-1,6,12-triyne, and tetradec-1,7−13-triyne catalyzed by rhodium complexes, which proceeds through three consecutive carbometalations.

In the course of our studies on the silylcarbocyclization (SiCaC) reactions of alkenynes and alkynals (eq 1),[3,4] we have found that the alkyl-rhodium intermediate 2 (X = CH₂) can be further trapped by another alkyne moiety in alkenyne 4 to give bis-(methylenecyclopentyl) 6, stereospecifically (eq 2).[5] Although

$$
\text{(1)} \qquad \begin{array}{c} 1 \quad X = CH_2, O \\ Y = CH_2, C(CO_2Et)_2, O, NR \end{array}
$$

$$
\text{(2)}
$$
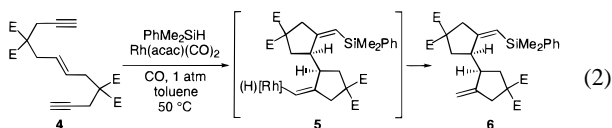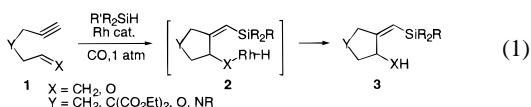
carbometalation of the vinylsilane moiety with the vinyl-[Rh] species in the same molecule to form the corresponding fused tricyclic skeleton is conceptually possible in this reaction, such a cyclization has not taken place. Instead, a simple reductive elimination occurred to give 6. This result may well be attributable to the rotational freedom about the bond connecting the two cyclopentyl units.

We anticipated that restricting this rotational freedom by introducing a carbon−carbon double bond would generate a rigid framework that would facilitate the subsequent carbometalation to realize the third carbocyclization, i.e., SiCaT reaction. This anticipation led us to investigate the cascade SiCaC reaction of dodec-1,6,11-triynes.[6] Representative results are summarized in Table 1.

(1) Visiting graduate student on leave from Faculty of Pharmaceutical Sciences, Hokkaido University, supported by the Japan Society for Promotion of Science Fellowship in 1997.

(2) For recent reviews on metal-catalyzed acetylene cyclotrimerizations, see: (a) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon/Elsevier Science: Kidlington, 1995; Vol. 12, p 741. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 539. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* 1996, 96, 49. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* 1996, 96, 635.

(3) (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.; Fracchiolla, D. A.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* 1994, 59, 7594. (d) Ojima, I.; Kass, D. F.; Zhu, J. *Organometallics* 1996, 15, 5191. (e) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* 1998, 120, 6690.

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(5) Ojima, I.; McCullagh, J. V.; Shay, W. R. *J. Organomet. Chem.* 1996, 521, 421.

(6) Doyle and Shanklin reported an unexpected cyclotrimerization of but-3-yn-2-one and methyl propynoate, giving the corresponding trisubstituted benzenes under silylformylation[9] conditions using Rh₂(pfb)₄ (pfb = perfluorobutyrate) and Et₃SiH under ambient pressure of CO. See ref 9m.

**Table 1.** SiCaT Reactions of Triynes 7 Catalyzed by Rh and Rh−Co Complexes[a]

| Entry | 7 | Cat. | R₃SiH (equiv.) | °C | h | Yield[b] (%) | Product ratio[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 8 | 9 | 10 |
| 1 | 7a | A | PhMe₂SiH(2) | 70 | 24 | 94(82) | 40(42) | 40(42) | 20(16) |
| 2 | 7a | B | PhMe₂SiH(1.2) | 70 | 24 | 87 | 55 | 37 | 8 |
| 3 | 7a | C | PhMe₂SiH(1.2) | 70 | 24 | 86 | 54 | 41 | 5 |
| 4 | 7a | D | PhMe₂SiH(2) | 22 | 34 | 95 | 85 | 10 | 5 |
| 5 | 7a | D | PhMe₂SiH(5) | 22 | 23 | 94 | 70 | 23 | 7 |
| 6 | 7a | E | PhMe₂SiH(2) | 22 | 34 | 100 | 86 | 10 | 4 |
| 7 | 7a | D | (EtO)₂MeSiH(2) | 22 | 20 | 97(81) | 84(84) | 16(16) | 0 |
| 8 | 7a | D | (EtO)₃SiH(2) | 22 | 18 | 88(73) | 89(89) | 11(11) | 0 |
| 9 | 7a | D | Et₃SiH (2) | 22 | 46 | 90(77) | 90(100) | 10(0) | 0 |
| 10 | 7a | D | ᵗBuMe₂SiH(2) | 22 | 60 | 80(70) | 93(100) | 7(0) | 0 |
| 11 | 7a | D | Ph₂MeSiH(2) | 22 | 43 | 95(85) | 88(88) | 12(12) | 0 |
| 12 | 7a | D | Ph₃SiH(2) | 22 | 55 | 57(50) | 93(100) | 7(0) | 0 |
| 13 | 7b | D | PhMe₂SiH(2) | 22 | 60 | 90(71) | 88(100) | 12(0) | 0 |
| 14 | 7c | D | PhMe₂SiH(2) | 22 | 35 | 75(69) | 92(92) | 8(8) | 0 |
| 15 | 7d | D | PhMe₂SiH(2) | 22 | 38 | 94(76) | 91(100) | 9(0) | 0 |
| 16[c] | 7e | A | PhMe₂SiH(1) | 70 | 24 | 89(71) | 12(9) | 88(91) | 0 |
| 17[c] | 7e | A | PhMe₂SiH(1) | 22 | 24 | 98(83) | 13(12) | 87(88) | 0 |
| 18[c] | 7e | D | PhMe₂SiH(2) | 22 | 11 | 99 | 15 | 85 | 0 |
| 19 | 7f | A | PhMe₂SiH(1) | 50 | 10 | (54) | 0 | (100) | 0 |
| 20 | 7f | A | PhMe₂SiH(1) | 22 | 24 | 77(70) | 0 | 100(100) | 0 |
| 21 | 7f | D | PhMe₂SiH(1) | 22 | 7 | 92 | 0 | 100 | 0 |
| 22 | 7g | A | PhMe₂SiH(1) | 60 | 21 | 57(50) | 0 | 100(100) | 0 |
| 23 | 7g | A | PhMe₂SiH(1) | 22 | 24 | 64(53) | 17(15) | 83(85) | 0 |
| 24 | 7g | D | PhMe₂SiH(1) | 22 | 0.5 | 75 | 24 | 76 | 0 |

a: X = C(CO₂Et)₂
b: X = C(OCH₂CH₂O) (cyclic)
c: X = C(CH₂OMe)₂
d: X = C(CH₂OBn)₂
e: X = N-Ts
f: X = N-Bn
g: X = O

[a] Reactions were run with triyne 7 (0.33-0.5 mmol scales) and Rh catalyst (0.5-1 mol%) in toluene under CO atmosphere unless otherwise noted. Catalyst A = Rh(acac)(CO)₂, B = [Rh(NBD)Cl]₂, C = [Rh(COD)Cl]₂, D = Rh₄(CO)₁₂, E = Rh₂Co₂(CO)₁₂. [b] Yields and product ratios were determined by ¹H NMR analyses using mesitylene as the external standard. Isolated yields and product ratios are in parentheses. [c] Reaction was run in toluene/1,4-dioxane mix solvent (1/1).

The reaction of triyne 7a (0.5 mmol) with PhMe₂SiH (1.0 mmol) catalyzed by Rh(acac)(CO)₂ (1 mol %) in toluene (6 mL) under carbon monoxide atmosphere[7] at 70 °C for 24 h afforded tetrahydro-*as*-indacenes, 8a and 9a, as the major products and bis(silylmethylcyclopentenyl) 10a as the minor product in 94% yield (8a:9a:10a = 2:2:1) (Table 1, entry 1). The efficacy of various rhodium catalysts was also examined. The use of rhodium dimers such as [Rh(NBD)Cl]₂ and [Rh(COD)Cl]₂ (entries 2−3) gives substantially higher selectivity in the formation of SiCaT products, 8a and 9a. The use of rhodium and rhodium−cobalt clusters such as Rh₄(CO)₁₂ and Rh₂Co₂(CO)₁₂[8] enables the SiCaT reaction of 7a to take place at 22 °C, giving 8a as the predominant product (entries 4−6). It should be noted that the use of 5 equiv of PhMe₂SiH in the Rh₄(CO)₁₂-catalyzed reaction rather decreases the relative yield of 8a (entry 5). A number of other hydrosilanes are also effective for this reaction (entries 7−12), providing 8a predominantly. Reactions with reactive hydrosilanes such as (EtO)₂MeSiH and (EtO)₃SiH (entries 7−8) occur much faster than those with alkyl and arylsilanes such as Et₃SiH, t-BuMe₂SiH, and

(7) CO atmosphere appears to be necessary to stabilize the active catalyst species. Reactions under N₂ were sluggish and gave lower yields.

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*Communications to the Editor*

*J. Am. Chem. Soc., Vol. 121, No. 13, 1999* 3231

**Scheme 1**
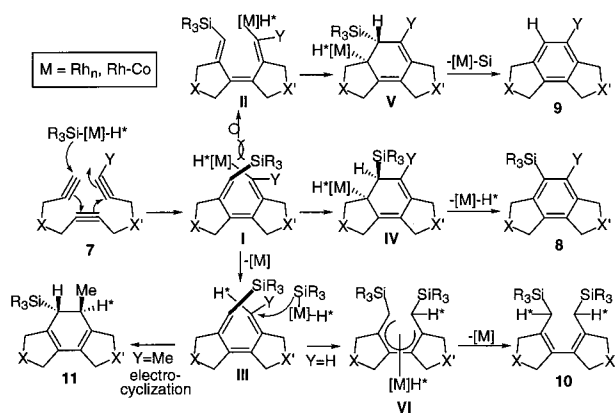


Ph$_2$MeSiH (entries 9−11). The reaction with bulky Ph$_3$SiH also takes place, albeit in lower yield (entry 12).
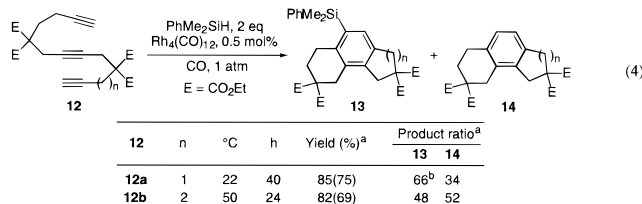
The SiCaT reaction is also applicable to substrates containing dioxane and ether functionalities (entries 13−15), yielding silylated product **8** selectively. For triynes with heteroatoms in the backbones, **7e−g**, the reactions catalyzed by Rh(acac)(CO)$_2$ proceed much faster than that of **7a** at 22 °C, giving predominantly tetrahydroindacenes **9e−g** accompanied by none or a small amount of 4-silyl-2,7-bisaza(or oxa)tetrahydroindacenes **8e−g** in good to excellent total yields (entries 17, 20, and 23). Reactions of **7e−g** at 22 °C (entries 17−18, 20−21, and 23−24) give higher yields than those run at higher temperatures (entries 16, 19, and 22). Note that the formation of 4-silyl-2,7-dioxa-tetrahydroin-dacene **8g** is only observed when the reaction of **7g** was run at 22 °C (entry 23−24). These results have important implications on the mechanism of the SiCaT reaction (vide infra). The use of Rh$_4$(CO)$_{12}$ in the reaction of **7g** slightly enhances the formation of silylated product **8g** (entry 24).

The reaction of **7h**, in which one of the terminal alkyne moieties is substituted with a methyl group, catalyzed by Rh$_4$(CO)$_{12}$ (0.5 mol %) proceeded cleanly at 22 °C to give 4-methyl-5-silyltetra-hydroindacene **8h**, 4-methyltetrahydroindacene **9h** and 4-methyl-5-silylhexahydroindacene **11** in quantitative yield by $^1$H NMR analysis (eq 3). The formation of **8h** and **11** clearly indicates that



(3)
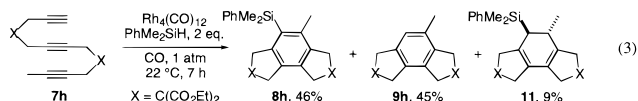
the reaction is initiated from the less hindered acetylene terminus of **7h**.

The formation of products with different ring sizes is also realized for the SiCaT reaction (eq 4). The reaction of **12a**



(4)

| 12 | n | °C | h | Yield (%)$^a$ | Product ratio$^a$ | |
|---|---|---|---|---|---|---|
| | | | | | 13 | 14 |
| 12a | 1 | 22 | 40 | 85(75) | 66$^b$ | 34 |
| 12b | 2 | 50 | 24 | 82(69) | 48 | 52 |

$^a$Yields and product ratios were determined by $^1$H NMR analyses using mesitylene as the external standard. Isolated yields and product ratios are in parentheses. $^b$Mixture of two regioisomers.

catalyzed by Rh$_4$(CO)$_{12}$ gives mainly the silylated product **13a** as a 1:1 mixture of two regioisomers (56%), along with nonsi-lylated product **14a** (29%). For **12b**, the reaction does not occur at room temperature but at 50 °C gives a 1:1 mixture of **13b** and **14b** in 82% total yield.

The most plausible mechanism for the SiCaT reaction that can accommodate all of the observed results is proposed in Scheme 1. As illustrated, the reaction proceeds through a silicon-initiated$^9$

cascade carbometalations to form the common intermediate **I**. Subsequent carbocyclization followed by $\beta$-hydride elimination leads to the formation of the normal SiCaT product **8**. Alterna-tively, **I** can undergo Z−E isomerization$^{10}$ to generate intermediate **II**. High reaction temperatures and the presence of heteroatoms in the substrate's backbones enhance the Z−E isomerization. The carbocyclization of **II** then yields intermediate **V**, in which the metal and the C-4 hydrogen are trans to each other, precluding the occurrence of $\beta$-hydride elimination. Thus, $\beta$-silyl elimination takes place instead to give nonsilylated SiCaT product **9**.$^{11}$ In the presence of excess hydrosilane, reductive elimination occurs to generate conjugated triene **III**. The fate of the triene **III** is governed by the substituent Y. When Y is a hydrogen, highly regioselective 1,6-hydrosilylation$^{3e}$ of **III** occurs to give **10**, while **III** undergoes a disrotatory electrocyclic reaction to yield **11** when Y is a methyl group. The steric hindrance caused by the *exo*-methyl group can be ascribed to the suppression of 1,6-hydro-silylation (see eq 3).

The observed high selectivity for the formation of **8** in reactions employing rhodium clusters as catalyst precursors may be attributed to the generation of a highly active catalyst species, probably a dinuclear complex. The highly active Rh−Co mixed dinuclear species has been proposed and characterized under the silylformylation conditions in these laboratories.$^{9a,f}$

Although various metal-catalyzed acetylene [2 + 2 + 2] cyclotrimerizations are known,$^2$ the SiCaT reaction is unique in that the reaction is initiated by Si-[M] species and proceeds in a cascade manner. The SiCaT reaction provides rapid access to functionalized tricyclic skeletons including those of 5−6−6 and 6−6−6 ring systems. Further studies on the scope of the SiCaT reaction and its applications to organic synthesis are actively underway.

**Supporting Information Available:** Experimental procedures, spec-tral data for all new compounds **7a−c**, **7e**, **8−14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9815529

(9) Examples of silicon-initiated reactions are SiCaC (see ref 3−5) and silylformylation reactions. For silylformylation reaction, see: (a) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (b) Ojima, I.; Donovan, R. J.; Ingallina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423. (c) Eguchi, M.; Zeng, Q.; Korda, A.; Ojima, I. *Tetrahedron Lett.* **1993**, *34*, 915. (d) Ojima, I.; Donovan, R. J.; Eguchi, M.; Shay, W. R.; Ingallina, P.; Korda, A.; Zeng, Q. *Tetrahedron* **1993**, *49*, 5431. (e) Ojima, I.; Vidal, E.; Tzamarioudaki, M.; Matsuda, I. *J. Am. Chem. Soc.* **1995**, *117*, 6797. (f) Ojima, I.; Li, Z.; Donovan, R. J.; Ingallina, P. *Inorg. Chim. Acta* **1998**, *270*, 279. (g) Ojima, I.; Li, Z. In *Catalysis by Di- and Polynuclear Metal Complexes*; Adams, R. A., Cotton. F. A., Eds.; John Wiley & Sons: Chichester, 1998; Chapter 9, pp 307−343. For contributions from other laboratories, see: (h) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (i) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. (j) Matsuda, I.; Sakakibara, J.; Nagashima, H.; *Tetrahedron Lett.* **1991**, *32*, 7431. (k) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, *33*, 5799. (l) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (m) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1994**, *13*, 1081. (n) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059. (o) Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1586. (p) Monteil, F.; Matsuda, I.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4419. (q) Leighton, J. L.; Chapman, E. *J. Am. Chem. Soc.* **1997**, *119*, 12416. (r) Matsuda, I.; Fukuta, Y.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327. (s) Maruoka, T.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 7325.

(10) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (b) R. Tanke; R. H. Crabtree *J. Am. Chem. Soc.*, **1990**, *112*, 7984−7989.

(11) Metallacycles may also be proposed as intermediates for the formation of **9**. However, control experiments clearly indicate the necessity of a hydrosilane to promote SiCaT reaction, i.e., in absence of a hydrosilane reaction gives only small amount of **9**.