Iridium(I)-Catalyzed Cycloisomerization of Enynes

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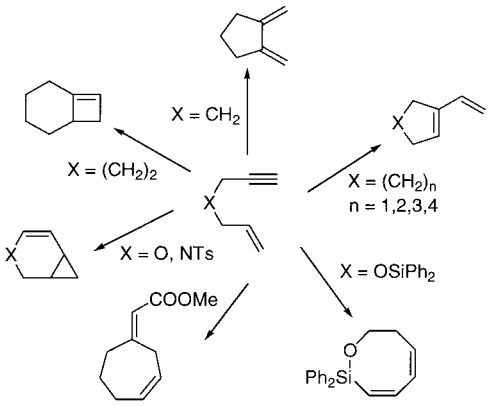
The development of new, efficient methods for the construction of ring systems from simple acyclic building blocks represents an important ongoing challenge for synthetic organic chemists.[1] One of the most extensively studied, recent approaches involves the transition-metal-catalyzed cycloisomerization of enynes.[2] A variety of such reactions have been developed thus far, and they can be classified into several types, depending on the type of transformation: (1) to cyclopentane derivatives containing an exo 1,3- or 1,4-diene unit,[3] (2) to bicyclo[4.2.0]-octene derivatives via a [2 + 2] cycloaddition,[4] (3) to bicyclo[4.1.0]heptene derivatives,[5] (4) to seven-membered cyclic alkenes,[6] (5) to eight-membered cyclic dienylsilane,[7] and (6) to 1-vinylcycloalkenes via skeletal reorganization.[8,9] The reaction course is complicated and depends on reaction variables, such as the structure of the substrates, the nature of the catalysts, additives, solvents, and as well as others. Because of these variables, it is clear that the examination of a variety of substrates and catalyst type is of important in terms of finding new types of cycloisomerization reactions of enynes. Although a variety of transition metals have been examined for their ability to catalyze cycloisomerizations, the Ir-catalyzed cycloisomerization of enynes has not been comprehensively examined. Recently, we found that simple transition-metal halides, such as $[RuCl_2(CO)_3]_2$ and $PtCl_2$, serve as effective catalysts for the skeletal reorganization of enynes to 1-vinylcycloalkenes in high product yields and a high selectivity (>98% isomeric purity in all cases).[9a,b,10] A characteristic feature of these catalytic systems is that they can be used with the enynes having a terminal acetylenic moiety. The latter are not suitable substrates for the other catalytic systems reported to date.[8] In the case of Ru(II) and Pt(II) catalyst systems, only skeletal reorganization occurred, and other types of cycloisomerization were not detected. In contrast, it was found that the reaction pattern for the Ir(I)-catalyzed reaction of enynes depends on both the structure of substrates and the nature of catalyst systems used. We wish to report herein on the Ir-catalyzed cycloisomerization of 1,6- and 1,7-enynes.

Scheme 1. Cycloisomerization of Enynes



The reaction of 1,6-enyne **1** was carried out under both CO and N_2, because we had previously observed that the presence of a CO ligand on the metal in the Ru(II)-catalyzed reaction appears to be effective in allowing the reaction to proceed.[9a] The treatment of 1,6-enyne **1** with 4 mol % $[IrCl(CO)_3]_n$ in toluene at 80 °C under an atmosphere of CO gave a skeletal reorganization product, 3-ethenyl-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (**2**), in 50% isolated yield (eq 1). The reaction was slow, and 2 days were required to complete the reaction. No byproducts were detected by GC and NMR, although the starting substrate **1** was completely consumed.[11] The reaction was more effective when conducted in an atmo-

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(1) For recent reviews on transition-metal-catalyzed cyclization, see: Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.

(2) A recent review on cycloisomerization of enynes, see: Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1.

(3) Pd: Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887. Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053. Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268. Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. S.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636. Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233. Wartenberg, F.-H.; Hellendahl, B.; Blechert, S. *Synlett* **1993**, 539. Trost, B. M.; Czeskis, B. A. *Tetrahedron Lett.* **1994**, *35*, 211. Co: 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. Ti: Sturla, S. J.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1976. Ru: Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 714. Paih, J. L.; Rodríguez, D. C.; Dérien, S.; Dixneuf, P. H. *Synlett* **2000**, 95. Nishida, M.; Adachi, N.; Onozuka, K.; Matsumura, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 9158. Rh: Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490. Cao, P.; Zhang, X. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4104.

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(6) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 9728.

(7) Kagoshima, H.; Hayashi, M.; Hashimoto, Y.; Saigo, K. *Organometallics* **1996**, *15*, 5439.

(8) Pd: (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647. (c) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850. (d) Trost, B. M.; Chang, V. K. *Synthesis* **1993**, 824. W: Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. Cr: Watanuki, S.; Ochifuji, N.; Mori, M. *Organometallics* **1994**, *13*, 4129. Ru: Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020. Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082. Mori, M.; Kitamura, T.; Sakakibara, N.; Sato, Y. *Org. Lett.* **2000**, *2*, 543. Ackermann, L.; Bruneau, C.; Dixneuf, P. H. *Synlett* **2001**, 397. Pt: See ref 5c.

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(10) Recently, Fürstner and Trost utilized our catalytic system for total synthesis. Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305. Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801.

(11) Small amounts of insoluble polymeric materials are formed in some cases, causing incomplete material balances.

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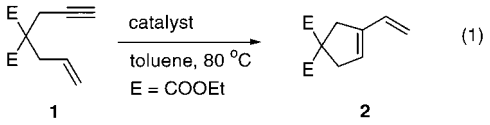


1 2 (1)

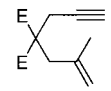
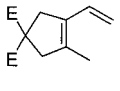
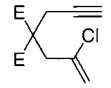
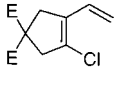
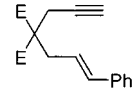
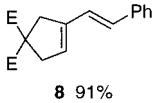
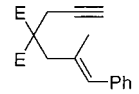
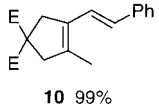
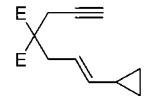
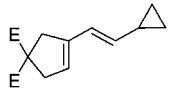
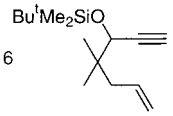
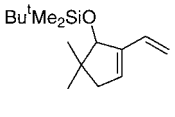
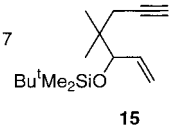
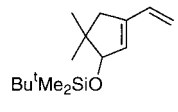
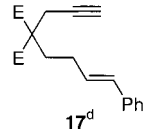
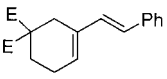
$[IrCl(CO)_3]_n$ CO	2 d	50%
$[IrCl(CO)_3]_n$ N_2	20 h	59%
$[IrCl(cod)]_2$ CO	12 h	51%
$[IrCl(cod)]_2$ N_2	6 h	0%

sphere of N_2, and a comparable yield was obtained after 20 h. In contrast to the CO ligand-coordinated iridium complex $[IrCl(CO)_3]_n$, $[IrCl(cod)]_2$ required an atmosphere of CO to show catalytic activity. No reaction took place when the reaction was carried out under N_2, as shown in eq 1. These results showed that Ir(I) catalysts also requires a CO ligand on the metals to show a catalytic activity probably due to the π-acidic character of the CO ligand, which confers more electrophilicity to the complex.

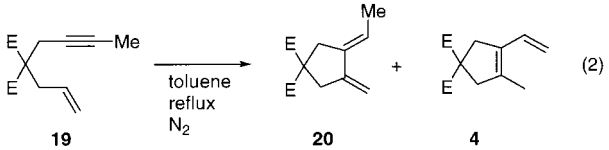
The reaction of a variety of 1,6-enynes and a 1,7-enyne was examined in the presence of $[IrCl(CO)_3]_n$ as the catalyst under N_2, and the results are summarized in Table 1. Apparently, the substitution of an alkyl or aryl group at an olefinic part acceraleted the reaction and increased the product yield. For example, after **3** and **7** were allowed to react for several hours, **4** and **8** were obtained in >90% yields (Table 1, entries 1 and 3), although the unsubstituted enyne **1** required 20 h to reach a yield of 59%. Phenyl-substituted enyne **7** underwent skeletal reorganization smoothly to give *trans*-1-styrylcyclopentene **8** (Table 1, entry 3). The reaction of **11** resulted in skeletal reorganization to give **12**, with the cyclopropane ring being intact (Table 1, entry 5).[12] Enynes having a *tert*-butyldimethylsiloxy group at the propargylic and allylic position, **13** and **15**, serve as suitable substrates for the skeletal reorganization (Table 1, entries 6 and 7).

Next, we examined the reaction of 1,6-enynes, which contained a substituent on the acetylenic carbon. The treatment of a methyl-substituted enyne **19** with $[IrCl(CO)_3]_n$ under the same reaction conditions as those in eq 1 resulted in no reaction. It was found that the addition of $AgClO_4$ improved the reaction slightly. Thus, the $[IrCl(cod)]_2$ (0.04 mmol)/$AgClO_4$ (0.08 mmol)-catalyzed reaction of **19** (1 mmol) under N_2 gave 1,2-alkylidenecyclopentane **20** in 24% yield (eq 2). We then examined the effects of additives, to obtain a cleaner reaction. As a result, it was found that the presence of tetramethylethylenediamine (tmeda) (0.08 mmol) leads to the formation of **20** as the main product in good yield (eq 2). On the other hand, the use of dppb (1,4-bis(diphenylphosphino)-butane) as the additive gave 1-vinylcyclopentene derivative **4** as a single product. The product **4** was apparently formed via a double-bond isomerization of the initial product, the 1,2-alkylidenecyclopentane **20**. A similar isomerization of 1,2-alkylidenecyclopentane to 1-vinylcyclopentenes has also been reported by Trost.[13] The catalytic systems investigated were not general and were applicable only to specific substrates. For example, propargyl allyl ethers, such as **23**, gave complex mixtures under these reaction conditions. We then investigated the

Table 1. Iridium(I)-Catalyzed Skeletal Reorganization of Enynes[a]

entry	enyne	time	product[b]
1	 **3**	2 h	 **4** 93%
2	 **5**	35 h	 **6** 38%
3	 **7**	3 h	 **8** 91%
4	 **9**	2 h	 **10** 99%
5	 **11**	12 h	 **12** 47%
6	 **13**	3 h	 **14** 83%
7	 **15**	3 h	 **16** 83% (80%)
8[c]	 **17**[d]	4 d	 **18** 54%

[a] Reaction conditions: enyne (1 mmol), $[IrCl(CO)_3]_n$ (0.04 mmol), toluene (5 mL), 80 °C under N_2. [b] All yields are isolated yields by column chromatography on silica gel. The number in parentheses indicates the purity of the isolated product. Parentheses are omitted when the product purity was in excess of 98%. [c] At 100 °C. [d] E/Z = 81/19 mixture.



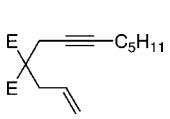
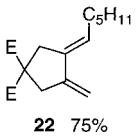
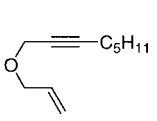
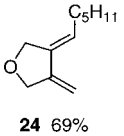
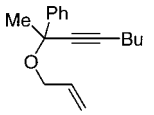
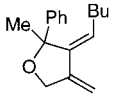
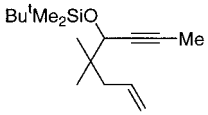
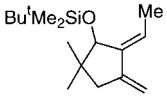
19 **20** **4** (2)

$[IrCl(cod)]_2/AgClO_4$	9 h	24% (100/0)
$[IrCl(cod)]_2/AgClO_4$ tmeda	5 h	64% (100/0)
$[IrCl(cod)]_2/AgClO_4$ dppb	3 h	83% (0/100)
$[IrCl(cod)]_2$/HOAc 80 °C	3 h	69% (89/11)

(12) The catalytic [5 + 2] cycloaddition of intramolecular yne-vinylcyclopropanes, related to **11**, is known. Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164. Trost, B. M.; Toste, F. D.; Shen, H. J. *Am. Chem. Soc.* **2000**, *122*, 2379.

(13) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255.

Table 2. Iridium(I)/HOAc-Catalyzed Cycloisomerization of 1,6-Enynes[a]

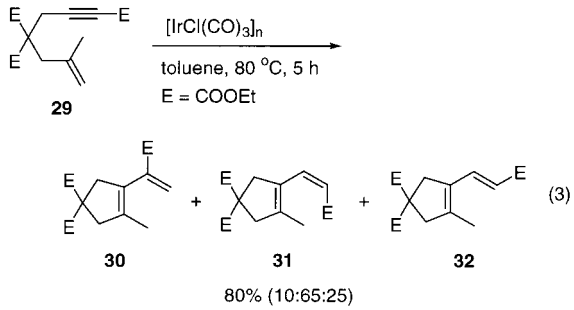
entry	enyne	time	product[b]
1	 **21**	6 h	 **22** 75%
2	 **23**	1 h	 **24** 69%
3[c]	 **25**	1 h	 **26** 92%
4	 **27**	7 h	 **28** 50%

[a] Reaction conditions: enyne (1 mmol), $[IrCl(cod)]_2$ (0.04 mmol), HOAc (0.16 mmol), toluene (5 mL), 80 °C under N_2. [b] All of yields are isolated yields by column chromatography on silica gel. [c] The reaction was run at 40 °C.

use of acetic acid as the additive because it is known to lead to the selective formation of 1,2-alkylidenecyclopentanes in the Pd- or Ru-catalyzed cycloisomerization of enynes.[14,15] In fact, it was found that the use of acetic acid as an additive afforded **20** in good yield.

This catalytic system was applicable to substrates that contain an alkyl group at the acetylenic carbon and no substituents at the olefinic portion (Table 2). In all cases, further double bond isomerization products, such as **4**, were not observed. The replacement of a methyl group by a pentyl group gave **22** with a high selectivity (Table 2, entry 1). The reaction of propargyl allyl ether **23** gave **24** in 69% yield (Table 2, entry 2). As both Grigg[16] and Trost[17] reported, the products produced from propargyl allyl ethers are unstable, but a substitution at the propargyl position confers stability on the product. In fact, the substrate **25** gave **26** in 92% yield (Table 2, entry 3). Substrate **25** is sufficiently reactive to react even at 0 °C (11 h, 87% yield). The decrease in the amount of the loading catalyst (0.01 mmol) at 40 °C had no effect on the efficiency of the reaction and gave **26** in 86% yield after 5 h. The role of acetic acid is the generation of an H−Ir species, and the reaction mechanism for the formation of 1,2-dialkylidenecyclopentanes involves (1) hydrometalation of the H−Ir species to alkynes, (2) carbometalation, and (3) β-hydride elimination, as has been proposed by Trost[14] and Dixneuf.[15]

Substitution with an electron-withdrawing group gave a mixture of three skeletal reorganization products in the presence of $[IrCl(CO)_3]_n$, as has already observed for the $PtCl_2$-catalyzed reaction (eq 3).[9b]



In summary, an iridium complex also catalyzes the cycloisomerization of enynes. The reaction patterns depend on the structure of the substrates and the nature of the catalyst systems. On the basis of the results obtained here and of the recently published results,[9,18] it would be expected that new type of transformation could be explored through the interaction of alkynes and electrophilic transition metal complexes.

Experimental Section

Iridium complexes, $[IrCl(CO)_3]_n$ and $[IrCl(cod)]_2$, were purchased from Strem Chemicals and used without purification. Products **2**, **4**, **6**, **8**, **10**, **14**, **16**, and **18** have already been reported in our previous reports.[9a,b] Product **26** is a known compound.[15] Toluene was distilled over CaH_2.

Typical Procedure for $[IrCl(CO)_3]_n$-Catalyzed Skeletal Reorganization of Enynes: 3-Ethenyl-3-cyclopentene-1,1-dicarboxylic Acid Diethyl Ester (2). To a suspension of $[IrCl(CO)_3]_n$ (12.5 mg, 0.04 mmol) in toluene (1 mL) were added (2-propenyl)(2-propynyl)propanedioic acid diethyl ester (**1**) (238.3 mg, 1.00 mmol) and toluene (4 mL), and the resulting mixture was stirred at 80 °C under N_2 for 20 h. After being to room temperature, the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10/1, R_f = 0.23) to give 3-ethenyl-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (**2**) (140.6 mg, 59%) as a colorless oil.

Typical Procedure for $[IrCl(cod)]_2$/HOAc-Catalyzed Cycloisomerization of Enynes: (*E*)-3-Hexene-4-methylenecyclopentane-1,1-dicarboxylic Acid Diethyl Ester (22). To a solution of $[IrCl(cod)]_2$ (6.3 mg, 0.0094 mmol) and HOAc (2.3 μL, 0.04 mmol) in toluene (0.5 mL) were added 2-octynyl-2-propenylpropanedioic acid diethyl ester (**21**) (77.4 mg, 0.25 mmol) and toluene (0.75 mL), and the resulting mixture was stirred at 80 °C for 6 h. After being cooled to room temperature, the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5/1, R_f = 0.41) to give (*E*)-3-hexylidene-4-methylenecyclopentane-1,1-dicarboxylic acid diethyl ester (**22**) (58 mg, 75%) as colorless oil.

(*E*)-3-(2-Cyclopropylethenyl)-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (12): colorless liquid; bp 75−80 °C/2 mmHg; R_f 0.41 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 0.39−0.44 (m, 2 H), 0.73−0.80 (m, 2 H), 1.25 (t, J = 7.1 Hz, 6 H), 1.36−1.48 (m, 1 H), 3.05 (s, 4 H), 4.19 (q, J = 7.1 Hz, 4 H), 5.07−5.16 (dd, J = 15.5, 8.9 Hz, 1 H), 5.40 (s, 1 H), 6.26 (d, J = 15.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 7.4, 14.1, 14.3, 39.7, 40.6, 58.8, 61.5, 123.0, 123.4, 136.0, 139.2, 171.9; IR (neat) 1732; MS (rel intensity) 278 (M^+, 23), 131 (100). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.79; H, 7.98.

(*E*)-3-Ethylidene-4-methylenecyclopentane-1,1-dicarboxylic acid diethyl ester (20): colorless oil; bp 100−110 °C/

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2.0 mmHg; R_f 0.14 (hexane/EtOAc = 15/1); ^{1}H NMR ($CDCl_3$) δ 1.25 (td, J = 7.3, 0.7 Hz, 6 H), 1.72 (d, J = 6.9 Hz, 3 H), 2.97 (s, 2 H), 3.00 (s, 2 H), 4.19 (qd, J = 7.3, 0.7 Hz, 4 H), 4.80 (s, 1 H), 5.23 (s, 1 H), 5.89−5.99 (qt, J = 6.9, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.9, 37.4, 41.4, 57.5, 61.5, 102.3, 116.5, 136.8, 145.1, 171.2; IR (neat) 1734; MS (rel intensity) 252 (M^+, 7), 105 (100); exact mass calcd for $C_{14}H_{20}O_4$ 252.1362, found 252.1363.

(*E*)-3-Hexylidene-4-methylenecyclopentane-1,1-dicarboxylic acid diethyl ester (22): colorless liquid; bp 80−85 °C/1.2 mmHg; R_f 0.41 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 6 H), 1.29−1.45 (m, 6 H), 2.08 (q, J = 7.3 Hz, 2 H), 2.97 (brs, 2 H), 3.00 (t, J = 2.0 Hz), 4.19 (q, J = 7.1 Hz, 4 H), 4.81 (s, 1 H), 5.25 (t, J = 2.3 Hz, 1 H), 5.88 (tt, J = 7.3, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.0, 29.6, 31.6, 37.6, 41.4, 57.7, 61.5, 102.4, 122.5, 135.8, 145.2, 171.2; IR (neat) 1736; MS (rel intensity) 309 (M^+, 11), 91 (100). Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.91; H, 9.45.

(*Z*)-Dihydro-3-hexylidene-4-methylene-3(2*H*)-furan (24): colorless liquid; bp 60−70 °C/20 mmHg; R_f 0.52 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3 H), 1.27−1.47 (c, 6 H), 2.01 (q, J = 7.6 Hz), 4.45 (brs, 2 H), 4.47 (brs, 2 H), 4.81 (s, 1 H), 5.28 (s, 1 H), 5.86 (tt, J = 7.6, 2.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.9, 29.7, 31.5, 70.7, 72.9, 99.6, 120.4, 136.0, 144.7; IR (neat) 1668, 1639; MS (rel intensity) 166 (M^+, 12), 95 (100); exact mass calcd for $C_{11}H_{18}O$ 166.1358, found 166.1360.

(*Z*)-[(2,2-Dimethyl-4-methylene-5-ethylidenecyclopentyl)oxy](1,1-dimethylethyl)dimethylsilane (28): colorless liquid; bp 50−60 °C/1.5 mmHg; R_f 0.83 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.09 (s, 3 H), 0.76 (s, 3 H), 0.87 (s, 9 H), 1.06 (s, 3 H), 1.82 (d, J = 7.3 Hz, 3 H), 1.99 (d, J = 15.7 Hz, 1 H), 2.49 (d, J = 15.7 Hz, 1 H), 4.10 (s, 1 H), 4.73 (s, 1 H), 5.21 (s, 1 H), 5.92 (q, J = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.3, −4.1, 15.5, 18.4, 22.8, 25.6, 25.9, 40.9, 44.3, 79.2, 102.1, 118.4, 144.1, 148.3; IR (neat) 1670, 1636; MS (relative intensity) 266 (M^+, 11), 209 (100). Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 72.04; H, 11.51.

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Supporting Information Available: Full characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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