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Rhodium-Catalyzed Silylcarbocyclization (SiCaC) and Carbonylative Silylcarbocyclization (CO−SiCaC) Reactions of Enynes

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Abstract: The reaction of a 1,6-enyne with a hydrosilane catalyzed by $Rh(acac)(CO)_2$, $Rh_4(CO)_{12}$, or $Rh_2Co_2(CO)_{12}$ under ambient CO atmosphere or N_2 gives 2-methyl-1-silylmethylidene-2-cyclopentane or its heteroatom congener in excellent yield through silylcarbocycization (SiCaC) process. The same reaction, but in the presence of a phosphite such as $P(OEt)_3$ and $P(OPh)_3$ under 20 atm of CO, affords the corresponding 2-formylmethyl-1-silylmethylidene-2-cyclopentane or its heteroatom congener with excellent selectivity through carbonylative silylcarbocycization (CO−SiCaC) process. The SiCaC reaction has also been applied to a 1,6-enyne bearing a cyclohexenyl group as the alkene moiety and a 1,7-enyne system. The functionalized five- and six-membered ring systems obtained by these novel cyclization reactions serve as useful and versatile intermediates for the syntheses of natural and unnatural heterocyclic and carbocyclic compounds. Possible mechanisms for the SiCaC and CO−SiCaC reactions as well as unique features of these processes are discussed.

Introduction

Development of practical and effective cyclization reactions for the syntheses of carbocycles and heterocycles of medicinal interest or intermediates useful for functional materials has been the subject of extensive research. Among numerous annulation methods available to synthesize these compounds, the power and efficiency of transition metal-promoted carbocyclization processes[1] has been demonstrated in a number of elegant syntheses of complex molecules and natural products.[2] Recently, significant advances have been made in the transition metal-catalyzed carbocyclization reactions with the use of a stoichiometric amount of a reducing agent in the process. Hydrosilanes,[3] hydrostannanes,[4] borylsilanes,[5] borylstannanes,[6] disilanes,[7] distannanes,[7] and silastannanes[7] are among the commonly used reducing agents for these processes.[8] The resulting tandem addition/cyclization reactions are particularly useful for yielding functionalized carbocycles or heterocycles with concomitant incorporation of metal or heteroatom groups that are amenable for further synthetic manipulations.

In the course of our extensive research program to develop silicon-initiated carbometalation processes, silylformylation,[9,3b] silylcarbocyclization (SiCaC),[3a−d] silylcarbobicyclization (SiCaB),[10,3d] silylcyclocarbonylation (SiCCa),[11] and silylcarbotricyclization (SiCaT)[12] have been discovered. We have also reported the silylcarbocyclization-hydrosilylation (SiCaC−HS)

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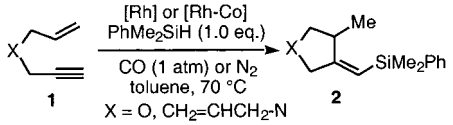
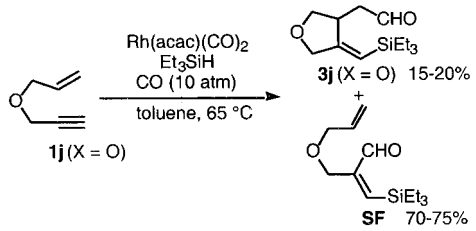
Scheme 1



Scheme 2



reaction of 1,6-enynes[3d] as well as the carbonylative carbotricyclization (CO−CaT) reaction of enediynes.[13]

The first silylcarbocyclization was discovered serendipitously during our detailed product analysis of the silylformylation of 1-hexyne catalyzed by Rh and Rh−Co carbonyl clusters, which gave dibutylcyclopentenone by incorporating two molecules of 1-hexyne, one molecule of hydrosilane, and one molecule of CO.[3a] Following up this discovery, we investigated the intramolecular version of this reaction using a couple of 1,6-enynes catalyzed by Rh and Rh−Co complexes, which led to the discovery of the novel silylcarbocyclization (SiCaC) reaction in 1992 (Scheme 1).[3a] When the SiCaC reaction of allyl propargyl ether with Et_3SiH catalyzed by $Rh(acac)(CO)_2$ was carried out under higher pressure of CO (10 atm), the first carbonylative SiCaC reaction (CO−SiCaC) took place to give the corresponding 3-*exo*-silylmethylidene-4-formylmethyl-tetrahydrofuran as minor product (15−20%) together with the simple silylformylation product (70−75%) (Scheme 2). Our discoveries of these two novel silicon-initiated carbocyclization reactions have spurred substantial interests in this field for the exploration of similar carbocyclization processes. We will describe here a full account of our study on the silylcarbocyclization (SiCaC) and carbonylative silylcarbocyclization (CO−SiCaC) reactions of 1,6-enynes and related systems.

Results and Discussion

Silylcarbocyclization (SiCaC) of 1,6-Enynes. The scope of the SiCaC reaction has been investigated systematically by looking at the key elements and reaction variables involved in this process. First, the efficacy of Rh and Rh−Co complexes as catalyst for this process was examined using 4,4-bis(carbethoxy)hept-6-en-1-yne (**1a**) as the 1,6-enyne substrate. Results are summarized in Table 1. As Table 1 shows, the reaction of **1a** with Me_2PhSiH (1.0 equiv) catalyzed by $Rh(acac)(CO)_2$ (1.0 mol %) in toluene at 70 °C under ambient pressure of CO for 18 h gives a 3:1 mixture of SiCaC product 4,4-bis(carbethoxy)-1-(*E*)-dimethylphenylsilylmethylidene-2-methylcyclopentane (**2a**) and CO−SiCaC product 4,4-bis(carbethoxy)-1-(*E*)-dimethylphenylsilylmethylidene-2-(formylmethyl)cyclopentane (**3a**) in 75% yield, accompanied by a small amount of hydrosilylation product (∼5%) (Table 1, entry 1). The use of $(^tBuNC)_4RhCo(CO)_4$, which is the best catalyst for intramolecular silylformylation of *ω*-siloxyalkynes,[9e] in xylene increased the overall yield of the carbocyclization products, but the product selectivity remains the same, that is, **2a**:**3a** = 3:1 (entry 2). However, the product selectivity is remarkably improved to 10:1 when the same reaction is carried out in hexane at 65 °C (entry 3). Thus, the efficacy of various rhodium catalysts has been examined in hexane. It is worth mentioning that the use of Rh and Rh−Co carbonyl clusters such as $Rh_4(CO)_{12}$[14] and $Rh_2Co_2(CO)_{12}$[15] allows the SiCaC reaction of **1a** to occur instantaneously at ambient temperature, yielding **2a** as almost exclusive product (entries 4−10). Increasing the hydrosilane ratio to **1a** from 1.0 to 1.5 or higher gives **2a** as essentially the sole product based on GC analysis (**2a**:**3a** ≥ 130:1) (entries 5, 6, 9). SiCaC product **2a** can be isolated in excellent yield through removal of solvent followed by simple flash chromatography on silica gel (entry 5). As expected, at higher dilution (0.13 vs 0.4 M), the CO concentration increases thereby somewhat decreasing the selectivity for **2a** to 60:1 (entry 7). The reaction can be carried out with catalyst loading as low as 0.05 mol % although these conditions require longer reaction time (8 h vs <1 min), and the product selectivity is reduced to 35:1 (entry 8). The reaction employing $Rh_2Co_2(CO)_{12}$ as catalyst proceeds under nitrogen atmosphere, giving **2a** as the single product (>1000:1, i.e., the limit of GC analysis) (entry 10).[16]

Next, a range of hydrosilanes was examined for their efficacy in the SiCaC reaction using **1a** as the substrate. Results are summarized in Table 2. As Table 2 shows, hydrosilanes possessing aryl groups such as Me_2PhSiH and $MePh_2SiH$ react with **1a** instantaneously to give **2a** in excellent isolated yields (entries 1, 2). Reactions with hydrosilanes containing alkoxy groups are equally rapid, giving complete conversion to the SiCaC products (entries 3−5). More sterically demanding Ph_3SiH also gives product **Ph_3Si-2a**, albeit higher temperature and longer reaction time are required (entry 6). However, less reactive and bulky trialkylhydrosilane, $^tBuMe_2SiH$, does not yield any SiCaC product (entry 7), but gives only a small amount

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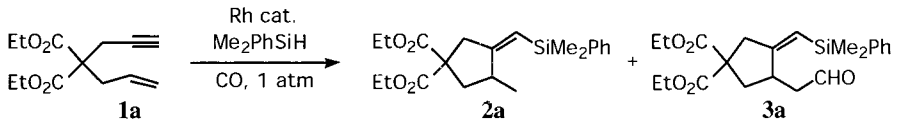
(16) The CO atmosphere appears to be necessary or at least preferred to stabilize the active catalyst species for most catalyst precursors, especially $Rh_4(CO)_{12}$. $Rh_2Co_2(CO)_{12}$ seems to be sufficiently stable under N_2 atmosphere to catalyze the SiCaC reactions. Nevertheless, unless the reactions are very fast, all catalysts decompose under N_2 during the reaction over a longer period of time.

Table 1. Rh-Catalyzed SiCaC Reaction of Enyne **1a**[a]

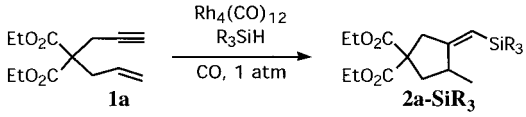


1a **2a** **3a**

entry	catalyst (mol %)	solvent	conc. (M)	Me_2PhSiH (equiv.)	temp (°C)	time	yield (%)[b]	ratio (**2a**:**3a**)[b]
1	$Rh(acac)(CO)_2$ (1.0)	toluene	0.4	1.0	70	18 h	75	3:1
2	$(^tBuNC)_4RhCo(CO)_4$ (1.0)	xylene	0.2	1.0	100	12 h	90	3:1
3	$Rh(acac)(CO)_2$ (1.0)	hexane	0.4	1.0	65	1.5 h	98	10:1
4	$Rh_4(CO)_{12}$ (0.5)	hexane	0.4	1.0	22	18 min	100	30:1
5	$Rh_4(CO)_{12}$ (0.5)	hexane	0.4	1.5	22	<1 min	99 (95)	130:1
6	$Rh_4(CO)_{12}$ (0.5)	hexane	0.4	2.0	22	<1 min	100	>150:1
7	$Rh_4(CO)_{12}$ (0.5)	hexane	0.13	1.5	22	<1 min	99	60:1
8	$Rh_4(CO)_{12}$ (0.05)	hexane	0.4	5.0	22	8 h	99	35:1
9	$Rh_2Co_2(CO)_{12}$ (0.5)	hexane	0.4	1.5	22	<1 min	100	138:1[c]
10	$Rh_2Co_2(CO)_{12}$ (0.5)	hexane	0.4	5.0	22	<1 min	100	>1000:1[c]

[a] Reactions were run on a 1 mmol scale. [b] Yields and ratios were determined by GC analysis. Isolated yields are in parentheses. [c] Reaction was run under nitrogen atmosphere.

Table 2. Efficacy of Hydrosilanes in SiCaC Reaction of **1a**[a]



1a **2a-SiR$_3$**

entry	R_3SiH	temp (°C)	time	product	yield (%)[b]
1	Me_2PhSiH	22	<1 min	**2a**	95
2	$MePh_2SiH$	22	<1 min	**2a-SiMePh$_2$**	94
3	$(EtO)_2MeSiH$	22	<1 min	**2a-SiMe(OEt)$_2$**	>99
4	$(EtO)_3SiH$	22	<1 min	**2a-Si(OEt)$_3$**	99
5	$(MeO)_3SiH$	22	<1 min	**2a-Si(OMe)$_3$**	>99
6	Ph_3SiH	70	3 h	**2a-SiPh$_3$**	50
7	$^tBuMe_2SiH$	22	2 h	**2a-SiMe$_2$Bu^t**	0[c]

[a] Reactions were run on a 1 mmol scale using 1.5 equiv of silane at 0.4 M concentration in hexane under ambient pressure of CO. [b] Isolated yields. [c] Some hydrosilylation product formed.

of the hydrosilylation product. The use of hydrosilanes bearing aryl and alkoxy substituents is synthetically useful as the resulting vinylsilane moieties of the SiCaC products could be easily transformed into other functional groups via oxidation.[17]

As shown in Table 1, the optimal reaction conditions for the SiCaC reaction include the use of $Rh_4(CO)_{12}$ or $Rh_2Co_2(CO)_{12}$ clusters, 1.5 equiv of Me_2PhSiH at 0.4 M (or higher) concentration in hexane at room temperature and ambient pressure of CO or N_2. Thus, a variety of 1,6-enynes has been subjected to the optimal conditions for the SiCaC process to examine the scope of this reaction in terms of functional group tolerance. A 1,6-enyne bearing an internal acetylene moiety (**1k**) and a 1,7-enyne (**1l**) have also been empolyed. Results are summarized in Table 3.

As Table 3 shows, the SiCaC reaction is applicable to a range of substrates, allowing the rapid synthesis of highly functionalized *exo*-silylmethylenecyclopentane and pyrrolidine derivatives **2** in excellent isolated yields (entries 1−8). The reaction tolerates various functional groups including ester, ether, sulfonamide, and amine. The formation of product **2h** indicates that the Rh-catalyzed SiCaC reaction occurs exclusively at the 1,6-enyne moiety, but not at the 1,6-diene moiety (entry 8). Free hydroxyl groups are tolerated under the SiCaC reaction conditions albeit the yield of **2i** is somewhat lower than others (entry 9). The reaction of allyl propargyl ether (**1j**), in the presence of a Rh or Rh−Co cluster catalyst is found to be slow at ambient temperature. However, by running the reaction at 70 °C with the use of $Rh(acac)(CO)_2$ as the catalyst brings about a clean conversion of **1j** to SiCaC product **2j** (entry 10). Methyl substitution at the terminal alkyne carbon is also tolerated, although longer reaction time (3 h vs <1 min) is necessary to give **2k** in high yield (entry 11). The formation of a six-membered ring carbocycle is possible (entry 12) although it is less effective than the five-membered ring formation, as expected. Thus, the reaction of 4,4-bis(carbomethoxy)oct-7-en-1-yne (**1l**) at 70 °C for 1 h gives the SiCaC product **2l** in 34% yield, accompanied by hydrosilylation (21%) and silylformylation products (17%) (entry 12).

The attempted SiCaC reactions of enynes bearing a substituted alkene moiety, **1m** and **1n**, led exclusively to hydrosilylation or silylformylation or both of the alkyne moiety (Chart 1). However, the reaction of **4**, wherein the olefin substitution is constrained in a ring, with Me_2PhSiH catalyzed by $Rh(acac)(CO)_2$ at 50 °C resulted in the formation of bicyclo[4.3.0]nonene **6** in 84% isolated yield (Scheme 3). Bicyclic product **6** was found to possess cis ring juncture in the fused ring system on the basis of the unambiguous NOE experiments (See Experimental Section). The observed exclusive formation of the cis ring juncture is readily explained by taking into account the transition-state model of the carbometalation step (see TS-**5**). As TS-**5** clearly illustrates, only possible approach of β-silylvinyl−[Rh] moiety to the olefin moiety of cyclohexenyl group of **4** is to form the cis juncture as observed. This carbometalation also defines the stereochemical arrangement of the [Rh] moiety, which is anti (or trans) to the bridgehead hydrogen. Accordingly, the β-hydride elimination can take place only with one of the methylene hydrogen syn (or cis) to the [Rh] moiety. Diene **1o** also failed to undergo carbocyclization under the standard SiCaC reaction conditions (Chart 1).

Carbonylative Silylcarbocyclization (CO−SiCaC) of 1,6-Enynes. As mentioned in the Introduction, the very first Rh-catalyzed CO−SiCaC reaction of 1,6-diyne was discovered in these laboratories with **1j** as the substrate as a minor pathway in the SiCaC reaction.[3a] Since this reaction gives versatile intermediates for organic syntheses, systematic variation of reaction parameters was performed for the CO−SiCaC reaction of **1a**, which was selected as the standard substrate, to optimize the selectivity for the formation of product **3a**. While our study

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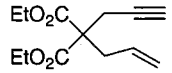
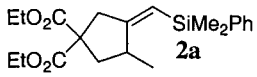
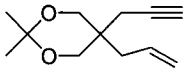
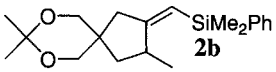
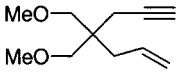
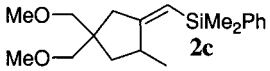
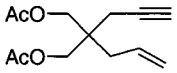
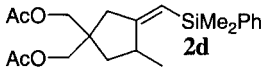
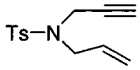
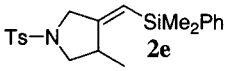
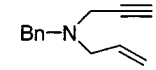
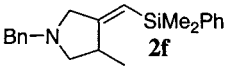
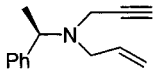
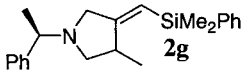
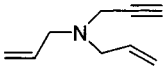
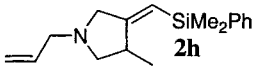
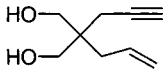
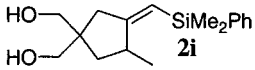
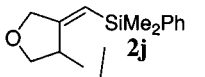
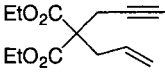
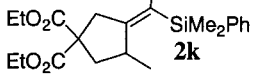
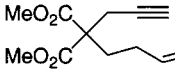
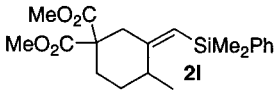
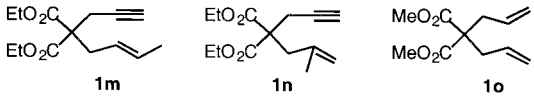
Table 3. Rhodium-Catalyzed SiCaC Reaction of Enynes[a]

entry	enyne		catalyst	atmos-phere	time	temp (°C)	product		yield (%)[b]
1		**1a**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2a**	95
2		**1b**	$Rh_2Co_2(CO)_{12}$	N_2	<1 min	22		**2b**	92
3		**1c**	$Rh_2Co_2(CO)_{12}$	N_2	15 min	22		**2c**	96
4		**1d**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2d**	90
5		**1e**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2e**	86
6		**1f**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2f**	83
7		**1g**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2g**	89
8		**1h**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2h**	74
9		**1i**	$Rh_4(CO)_{12}$	CO	<1 min	22		**2i**	52
10[c,d]		**1j**	$Rh(acac)(CO)_2$	CO	12 h	70		**2j**	82
11		**1k**	$Rh_4(CO)_{12}$	CO	3 h	22		**2k**	89
12[c]		**1l**	$Rh_4(CO)_{12}$	CO	1 h	70		**2l**	34

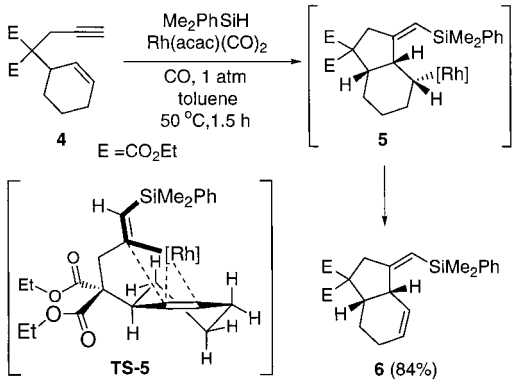
[a] Reactions were run on a 1 mmol scale using 0.5 mol% of rhodium cluster and 1.5 equiv of Me_2PhSiH at 0.4 M concentration in hexane under ambient pressure. [b] Isolated yields. [c] Reaction in toluene. [d] 1 mol% of catalyst used.

Chart 1. Substrates That Failed To Cyclize under SiCaC Conditions



1m **1n** **1o**

Scheme 3

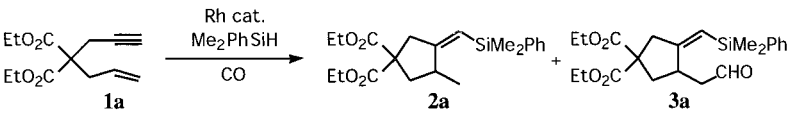


was in progress, Matsuda et al. reported a similar process, involving a silylformylation/carbocyclization process with the use of a hydrosilane and CO in the presence of a Rh catalyst.[18]

From the results shown in Table 1, we anticipated that the selectivity for CO−SiCaC product **3a** should be improved by running the reaction with 1 equiv of a hydrosilane in higher dilution of the Rh catalyst and a substrate, which should increase dissolved CO concentration and hence the formation of carbonylative SiCaC product **3a**. Results obtained under various conditions are summarized in Table 4. The reaction of **1a** with Me_2PhSiH (1.05 equiv) catalyzed by $Rh(acac)(CO)_2$ (1.0 mol %) at 0.2 M concentration in toluene at 50 °C and ambient pressure of CO for 3 h gives a 1:3 mixture of **3a** and **2a** in 78% yield (entry 1). Addition of PPh_3 or $P(OPh)_3$ as ligand to the reaction system reverses the product ratio, yielding **3a** as the major product (entries 2−5). It should be noted that the **3a**:**2a** ratio has reached 19:1 in 95% yield when 4 mol % of $P(OPh)_3$ is used. Another effort to improve the selectivity for **3a** is to increase CO pressure (entries 6−8). The reaction of **1a** at 70 °C and 20 atm of CO in 1,4-dioxane for 24 h favors the formation of **3a** over **2a** in a 5:1 ratio even without phosphite additive (entry 6). Lowering the substrate concentration from 0.1 to 0.02 M without phosphite additive affords **3a** predominantly (**3a**:**2a** = 8:1) (entry 7). However, only a slight improvement is observed by increasing the CO pressure from 20 to 30 atm (entry 8). These results imply that a combination of a ligand additive, low substrate concentration, higher tem-

(18) Fukuta, Y.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1999**, *40*, 4703.

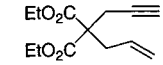
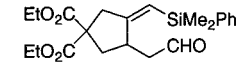
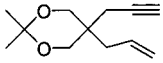
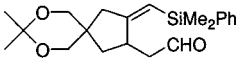
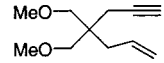
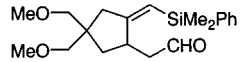
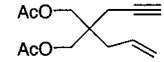
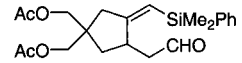
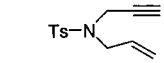
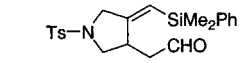
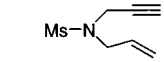
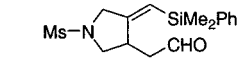
Table 4. Rhodium-Catalyzed CO−SiCaC Reaction of Enyne **1a**[a]



entry	catalyst	ligand (equiv/Rh)	solvent	conc (M)	CO (atm)	temp (°C)	time (h)	yield (%)[b]	ratio (**2a**:**3a**)[b]
1	$Rh(acac)(CO)_2$	none	toluene	0.2	1	50	3	78	3:1
2	$Rh(acac)(CO)_2$	PPh_3 (1)	toluene	0.2	1	50	7	87	1:1.5
3	$Rh(acac)(CO)_2$	PPh_3 (3)	toluene	0.2	1	50	18	98	1:3
4	$Rh(acac)(CO)_2$	$P(OPh)_3$ (2)	toluene	0.2	1	50	8	92	1:12
5	$Rh(acac)(CO)_2$	$P(OPh)_3$ (4)	toluene	0.2	1	50	14	95	1:19
6	$Rh(acac)(CO)_2$	none	1,4-dioxane	0.1	20	70	24	85	1:5
7	$Rh_4(CO)_{12}$	none	1,4-dioxane	0.02	20	70	24	86	1:8
8	$Rh_4(CO)_{12}$	none	1,4-dioxane	0.02	30	70	24	88	1:9
9	$Rh_4(CO)_{12}$	$P(OPh)_3$ (5)	1,4-dioxane	0.02	20	105	48	96(87)	1:39
10	$Rh_4(CO)_{12}$	$P(OEt)_3$ (3)	1,4-dioxane	0.02	20	105	48	98	1:50
11	$Rh_4(CO)_{12}$	$P(OEt)_3$ (5)	1,4-dioxane	0.02	20	105	48	99(91)	1:77

[a] Reactions were run on a 1 mmol scale using 1 mol% of $Rh(acac)(CO)_2$ or 0.5 mol% of $Rh_4(CO)_{12}$ and 1.05 equiv of Me_2PhSiH. [b] Yields and ratios were determined by GC analysis. Isolated yields of **3a** are in parentheses.

Table 5. Rh-Catalyzed CO−SiCaC Reaction of 1,6-Enynes[a]

entry	enyne		product		yield (%)[b]
1		**1a**		**3a**	91
2		**1b**		**3b**	89
3		**1c**		**3c**	83
4		**1d**		**3d**	91
5		**1e**		**3e**	85
6		**1p**		**3p**	56

[a] Reactions were run on a 1 mmol scale using 0.5 mol% of $Rh_4(CO)_{12}$, 1.05 equiv of Me_2PhSiH and 10 mol% of $P(OEt)_3$ at 0.02 M concentration in 1,4-dioxane under 20 atm of CO at 105 °C for 48 h. [b] Isolated yields.

perature, and sufficiently high CO pressure would maximize the selectivity for CO−SiCaC product. In fact, the reaction using $P(OPh)_3$ as ligand (5 equiv to Rh) and low substrate concentration (0.02 M) at 105 °C and 20 atm of CO for 48 h gives **3a** with very high selectivity (**3a**:**2a** = 39:1) in 96% yield (entry 9). Along this line of approach, the optimal conditions have been found, which consist of $Rh_4(CO)_{12}$ (0.5 mol %) and $P(OEt)_3$ (10 mol %; 5 equiv to Rh) at 105 °C and 20 atm of CO at 0.02 M substrate concentration in 1,4-dioxane. The reaction under the optimal conditions affords **3a** as essentially the sole product (**3a**:**2a** = 77:1 by GC analysis), which is isolated in 91% yield after removal of solvent followed by simple flash chromatography on silica gel (entry 11).

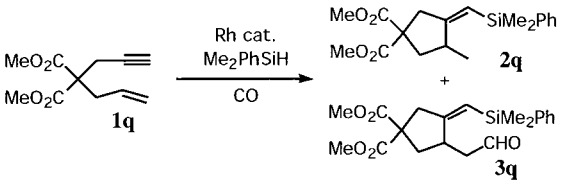
Next, various 1,6-enynes were subjected to the optimal CO−SiCaC reaction conditions mentioned above and the results are summarized in Table 5. The reaction of **1a** giving **3a** exclusively (vide supra) is listed as reference (entry 1). As Table 5 shows, the CO−SiCaC reaction provides an efficient route to highly functionalized *exo*-silylmethylene-cyclopentane and pyrrolidine derivatives **3** bearing a formylmethyl moiety at the C2 position. The reaction also tolerates a variety of functional groups, including ester, ketal, ether, and sulfonamide, to give CO−SiCaC products **3b**−**e** in high-to-excellent isolated yields after purification by flash column chromatography on silica gel (entries 2−5). The reaction of 4-methanesulfonyl-4-azahept-6-en-1-yne **1p**, bearing a sulfonamide group in the backbone, was not as clean as other cases, giving **3p** in 56% isolated yield (entry 6). To our surprise, under the CO−SiCaC reaction conditions, allyl(benzyl)propargylamine **1f** led to the exclusive formation of SiCaC product **2f**, accompanied by a small amount of hydrosilylation product.[19] A possible explanation for this result is discussed later in the Mechanism section (vide infra).

The optimal conditions mentioned above include high dilution of reactants, which is not advantageous in practical syntheses. Accordingly, we performed further optimization of the CO−SiCaC process and have indeed found a synthetically more favorable procedure. The improved procedure includes the freezing of the substrate solution in dioxane before addition of the catalyst and hydrosilane. The frozen reaction mixture is then placed in an autoclave and pressurized with 20 atm of CO. This "freeze and CO" protocol should prevent any reaction from occurring before the system is subjected to the high pressure of CO. Since the SiCaC product predominates at lower CO concentration (i.e., lower CO pressure or higher concentration of the substrate or both), this protocol should be able to block the SiCaC reaction by freezing the reaction to start until the whole reaction system is under high CO pressure and thus favors the formation of the CO−SiCaC product.

First, this protocol was examined using substrate **1q**, and the results are summarized in Table 6. As Table 6 shows, this protocol has a profound effect on the product selectivity. When the reaction was carried out without phosphite ligand at 70 °C and 20 atm of CO at 0.02 M concentration of **1q**, a high selectivity (1:27, i.e., 96.3%) is observed in favor of the formation of CO−SiCaC product **3q** (entry 1). However, the selectivity drops to 1:6 when the same reaction is run at 1.0 M concentration of **1q**, which is not surprising though (entry 2). When the reactions are carried out in the presence of $P(OEt)_3$ at 105 °C, high selectivities (1:26−1:45) are observed even at 0.2−1.0 M concentrations (entries 3−5). It is noteworthy that a practically useful high selectivity (1:26) is achieved even at 1.0 M concentration under these conditions (entry 5). These results clearly indicate that the "freeze and CO" protocol allows

(19) This rather peculiar phenomenon was also pointed out by Fukuta, Matsuda, and Itoh, but without any interpretation. See ref 18.

Table 6. Rhodium-Catalyzed CO-SiCaC Reaction of Enyne **1q** Using the "Freeze and CO" Protocol[a]



entry	conc (M)	ligand (equiv./Rh)	temp (°C)	time (h)	ratio (**2q:3q**)[b]
1	0.02	none	70	24	1:27
2	1.0	none	70	24	1:6
3	0.2	$P(OEt)_3$ (5)	105	48	1:45
4	0.5	$P(OEt)_3$ (5)	105	48	1:38
5	1.0	$P(OEt)_3$ (5)	105	48	1:26

[a] Reactions were run on 1 mmol scale using 0.5 mol% of $Rh_4(CO)_{12}$ and 1.05 equiv of Me_2PhSiH under 20 atm of CO. Yield was >98% by GC analysis for all cases. [b] Ratios were determined by GC analysis.

Table 7. CO−SiCaC Reaction of Enyne **1a** Using the "Freeze and CO" Protocol[a]

entry	conc (M)	ligand (equiv/Rh)	temp (°C)	time (h)	ratio (**2a:3a**)[b]
1	0.02	$P(OEt)_3$ (5)	105	48	1:125
2	0.2	$P(OEt)_3$ (5)	105	48	1:95
3	0.5	$P(OEt)_3$ (5)	105	48	1:65
4	1	$P(OEt)_3$ (5)	105	48	1:64

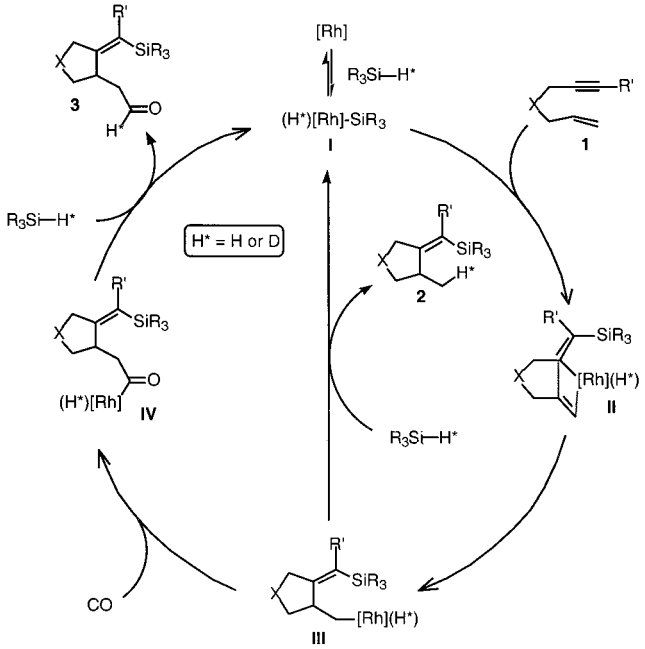
[a] Reactions were run on a 1 mmol scale using 0.5 mol% of $Rh_4(CO)_{12}$ and 1.05 equiv of Me_2PhSiH under 20 atm of CO. Yield was >98% by GC analysis for all cases. [b] Ratios were determined by GC analysis.

the CO−SiCaC reaction to be conducted at normal concentrations (i.e., not high dilution) without compromising the selectivity for the CO−SiCaC product.

Next, the "freeze and CO" with $P(OEt)_3$ protocol was applied to the reaction of **1a** for comparison with the results shown in Table 4, wherein the best selectivity for **3a** was 1:77 (i.e., 98.7%) (see Table 4, entry 11). The results are summarized in Table 7. As expected, the "freeze and CO" protocol increases the selectivity dramatically, for example, the best selectivity for the formation of **3a** with this protocol is 1:125 (i.e., 99.2%) (entry 1) as compared to 1:77 obtained earlier (vide supra). A high selectivity (1:64) is still achieved even at 1.0 M concentration (entry 4). Accordingly, it can be said that the ultimate optimal reaction conditions have been found for the CO−SiCaC reaction through this study.

Mechanism. It is logical to hypothesize that the mechanism for the intramolecular silylcarbocyclization of enynes should be closely related to that of hydrosilylation and silylformylation of alkynes. Mechanistic studies performed in these laboratories and others have revealed that both hydrosilylation[20] and silylformylation[9a,f,s] share the same fundamental reaction sequence, which includes the initial formation of silyl−[M](H) species through the oxidative addition of a hydrosilane to a metal complex, followed by insertion of an alkyne into the Si−[M] bond of the silyl−[M](H) species to form the corresponding β-silylvinyl−[M](H) species. Subsequent hydrosilane-induced reductive elimination (hydride shift) gives a hydrosilylation product.[20] In the presence of CO, however, the insertion of CO into the β-silylvinyl−[M](H) complex takes place to form β-silylacryloyl−[M](H) species, followed by reductive elimination, yielding a silylformylation product.[9a,f,s]

Scheme 4. Proposed Mechanism for the SiCaC and CO−SiCaC Reactions



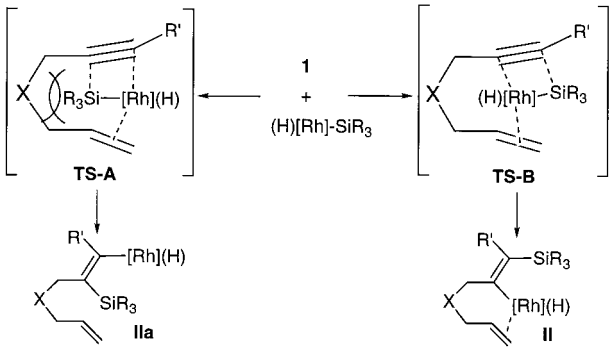
The most plausible mechanism for the silylcarbocyclization of enyne **1**, which can accommodate the formations of both SiCaC product **2** and CO−SiCaC product **3**, is proposed in Scheme 4 by taking into account the mechanisms for hydrosilylation and silylformylation mentioned above. As Scheme 4 illustrates, the silylcarbocyclization of enynes should begin with formation of the active catalyst species, silyl−[Rh] complex **I**, followed by insertion of the acetylene moiety of enyne **1** to generate β-silylvinlyl−[Rh] complex **II**. Coordination of the olefin moiety, followed by intramolecular carbometalation, leads to the formation of *exo*-methylenecyclopentylmethyl−[Rh] complex **III**. In the absence of CO or at very low concentration of CO, hydrosilane-promoted reductive elimination occurs to give SiCaC product **2** and regenerates silyl−[Rh] complex **I**. At higher CO concentration, migratory insertion of CO into the alkyl−[Rh] bond of **III** leads to the formation of acyl−[Rh] complex **IV**.[21] Subsequent hydrosilane-promoted reductive elimination affords CO−SiCaC product **3** and regenerates the active catalyst species **I**. A CO atmosphere is not essential for the SiCaC process as exemplified in Table 3 (entries 2 and 3). However, the use of a CO atmosphere appears to stabilize the active [Rh] catalyst species, especially when Rh and Rh−Co carbonyl clusters are used for a prolonged period of time.

It should be noted that the coordination of the alkene moiety to the [Rh] metal appears to have a very strong directing effect on the regioselective insertion of the alkyne moiety to the Si−[Rh] bond in the conversion of **I** to **II**. As Table 3 shows (entry 11), the reaction of **1k** bearing an internal alkyne moiety gives the SiCaC product **2k** in 89% isolated yield. Since a simple hydrosilylation of 2-alkyne, for example, 5,5-di(carbethoxy)-oct-2-yne, should give a mixture of 2-silylalkane and 3-silyl-

(20) (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chicheser, U.K., 1989; Vol. 2, p 1479. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (c) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 8, p 763.

(21) For reviews on migratory insertion of CO, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

Scheme 5



alkane, the insertion of the alkyne moiety of **2k** is expected to give a mixture of two regioisomeric β-silylvinyl−[Rh](H) complexes (**II** and its regioisomer **IIa**), but it is obvious that this is not happening. A simple molecular modeling inspection of the hypothetical four-centered transition states indicates (i) the transition state **TS-A** that leads to the formation of 3-silyl-2-alkenyl−[Rh] intermediate **IIa** is sterically quite strained when the alkene moiety is coordinating to the [Rh] metal and also cannot undergo intramolecular carbometalation (i.e., carbocyclization) due to extremely unfavorable geometry, and (ii) the transition state **TS-B** that leads to 2-silyl-3-alkenyl−[Rh] intermediate **II**, which is sterically much more favorable than the transition state **TS-A** and ready for the subsequent carbocyclization to give **III** (Scheme 5). Accordingly, it is clear that the chelate formation involving the alkene moiety plays a key role in the extremely regioselective addition of the Si−[M] species to the alkyne moiety of **1**, which leads to the formation of **II** and then **III** (See Scheme 4).

As mentioned above, the reaction of allyl(benzyl)propargylamine (**1h**) under the CO−SiCaC conditions ($P(OEt)_3$, 105 °C and 20 atm of CO) does not give any trace of the expected CO−SiCaC product **3h**, but only affords SiCaC product **2h**. This rather peculiar result can be explained by taking into account a very likely coordination of **1h** to the [Rh] metal of the intermediate **III** in a chelating manner using the π-acetylenic bond (or π-olefinic bond) as well as the basic nitrogen atom. This chelation evidently effectively blocks the migratory insertion of CO into the alkyl−[Rh] bond, which is essential for the formation of the acyl−[Rh] intermediate **IV**. The fact that this peculiar phenomenon is observed only for 1,6-enyne substrates with a trialkylamine moiety bearing a basic nitrogen strongly supports the proposed explanation.

As Scheme 4 shows, it is apparent that the migratory CO insertion to **III** and the hydrosilane-promoted reductive elimination of **2** from **III** are competing processes under the reaction conditions. Accordingly, higher CO pressures surely favor the CO insertion to form **IV**. However, higher pressures should also favor the CO insertion to **II**, which leads to the formation of a simple silylformylation product without carbocyclization.[3a] Thus, an appropriate modification of the [Rh] coordination sites is necessary to promote the CO insertion to **III**, but not to **II**. As Table 4 indicates, addition of a phosphite, especially $P(OEt)_3$, exerts an remarkable influence on the selectivity for CO−SiCaC (entries 9−11). It has been shown that phosphines and CO greatly enhance the rate of migratory CO insertion.[22] This is due to the fact that this process is reversible because of a free coordination site generated after the migration of the alkyl group to the vicinal CO ligand. Trapping of this vacant site by addition of an external ligand or CO thus suppresses the reversibility of the CO insertion.[22] As mentioned above, the CO−SiCaC process requires a delicate stereoelectronic balance of ligands on the active [Rh] species, in that the ligand(s) should stabilize the acyl−[Rh] intermediate **IV**, but should not impose too much steric hindrance for the approach of another molecule of a hydrosilane to promote reductive elimination as well as the coordination of an enyne to the Si−[Rh] sepecies **I**, forming **II**. The fact that PPh_3 possessing a better σ-donor property but a much larger cone angle than $P(OPh)_3$ or $P(OEt)_3$ is not a good ligand for this process (Table 4, entries 2 and 3) is a clear indication of the delicate stereoelectronic balance in the coordination sphere of the catalyst metal center and that phosphites, especially $P(OEt)_3$, are the appropriate ligands for the CO−SiCaC process. The reaction rate should be reduced when a strongly coordinating and bulky ligand is occupying a coordination site of the [Rh] catalyst species. This is consistent with the observation that more forced conditions are necessary for the CO−SiCaC reaction to proceed smoothly in the presence of a phosphtie ligand as compared to the SiCaC reaction. The observed marked efficiency of the "freeze and CO" protocol is also consistent with the discussion just mentioned above. Thus, the combination of $P(OEt)_3$ addition and the "freeze and CO" protocol can achieve extremely high CO−SiCaC selectivity without using high dilution conditions (Tables 6 and 7).

Conclusions

A full account of our study on the scope and limitation of unique SiCaC and CO−SiCaC reactions of enynes is described. The SiCaC and CO−SiCaC reactions provide rapid access to functionalized five-membered heterocyclic as well as carbocyclic ring systems from 1,6-enynes, which serve as useful and versatile intermediates for the syntheses of natural and unnatural compounds of biological interest or intermediates useful for functional materials. Either SiCaC products or CO−SiCaC products can be obtained with extremely high selectivity under the optimal conditions for each process. The SiCaC reaction is applicable to the 1,7-enyne system albeit the yield is lower. The most likely mechanism for these processes, which share key intermediate complexes in the catalytic cycle, is proposed.

Experimental Section

General Method. All experiments were performed under a nitrogen or CO atmosphere in oven-dried glassware using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova-600 (600 MHz ^1H, 150 MHz ^{13}C), Gemini-300 (300 MHz ^1H, 75 MHz ^{13}C), a General Electric QE-300 (300 MHz ^1H, 75 MHz ^{13}C), or a Bruker AC-250 (250 MHz ^1H, 62.5 MHz ^{13}C) spectrometer in deuterated solvents using residual protons ($CHCl_3$: 7.26 ppm ^1H, 77.0 ppm ^{13}C) as the internal reference unless otherwise stated. NMR solvents were dried over anhydrous K_2CO_3 or passed through a short column of activated alumina. Chemical shifts (δ) are given in parts per million downfield from tetramethylsilane (TMS). Infrared spectra were recorded on a Mattson Galaxy Series-3000 FTIR spectrometer using samples as neat oils or as KBr disks. Analytical gas chromatography was performed with a Hewlett-Packard 5890 Series II gas chromatograph (FID) with a Hewlett-Packard HP 3396A integrator using either a 15 m J&W DB-1, a 30 m J&W DB-17, or a 25 m 3% OV-101 capillary column. Elemental analyses were performed by

(22) Crabtree, R. H. In *The Organometallic Chemistry of the Transition Metals*, Wiley: New York, 1994; Chapter 7, p 161.

M-H-W Laboratories, Phoenix, Arizona. High-resolution mass spectrometric analyses were conducted at the Mass Spectrometry Facility of the University of California at Riverside. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel plates with F-254 indicator.

Materials. All solvents used as reaction media were distilled under nitrogen immediately before use; ether, THF, and toluene were distilled from Na/benzophenone ketyl, and CH_2Cl_2 was distilled from CaH_2. Carbon monoxide was purchased from Liquid Carbonic Specialty Gases, Oak Brook, Illinois, and passed through Drierite before use. Rh(acac)-$(CO)_2$, was provided by Mitsubishi Chemical Corporation and used as received. Rhodium clusters, $Rh_4(CO)_{12}$[14] and $Rh_2Co_2(CO)_{12}$,[15] were prepared according to literature methods. Hydrosilanes were purchased from Aldrich Chemical Co. and Gelest, Inc., distilled under nitrogen, and stored over activated molecular sieves 4 Å. Solvents for extraction and chromatography were reagent grade and used as received. All other reagents were purified by simple distillation or passing through a short column of activated alumina or silica gel. Silica gel used for chromatography, MN-Kieselgel 60, was purchased from Brinkman Instruments Inc.

Caution: Since carbon monoxide is a toxic gas, all reactions using carbon monoxide should be carried out with care in a hood with sufficient ventilation.

General Procedure for the Catalytic SiCaC Reaction. A typical procedure is described for the reaction of 4,4-bis(carbethoxy)hept-6-en-1-yne (**1a**). A reaction vessel equipped with a stirring bar and a CO inlet, was charged with $Rh_4(CO)_{12}$ (3.8 mg, 0.005 mol, 0.5 mol %). After purging the vessel with CO, hexane (1.0 mL) was added to dissolve the catalyst. Me_2PhSiH (68 mg, 0.5 mmol) was added via a syringe. After stirring for 5 min at ambient temperature, the reaction mixture was then cannulated into a 5-mL round-bottomed flask containing a solution of **1a** (238 mg, 1 mmol), Me_2PhSiH (138 mg, 1 mmol) in hexane (1.5 mL) via CO pressure without stirring. The resulting mixture was stirred for less than 1 min, and the reaction mixture was submitted to GC analysis. After the reaction was complete, all volatiles were removed under reduced pressure, and the crude product was purified by column chromatography on silica gel.

4,4-Bis(carbethoxy)-1-(*Z*)-dimethylphenylsilylmethylidene-2-methylcyclopentane (2a): viscous colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.51); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 0.95 (d, J = 6.8 Hz, 3H, CH_3CH), 1.25 (t, J = 7.1 Hz, 6H, CH_3CH_2O), 1.85 (dd, J = 13.0 Hz, 3.5 Hz, 1H, CH_2CH), 2.35 (m, 1H, CH_2CHCH_3), 2.39 (dd, J = 13.0 Hz, 8.5 Hz, 1H, CH_2CH), 2.83 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 3.28 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 4.15 (q, J = 7.1 Hz, 4H, CH_3CH_2O), 5.50 (s br, 1H, C=CH), 7.33 (m, 3H, Ph-H), 7.51 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.88, −0.89, 14.25, 14.29, 22.50, 36.98, 42.01, 44.87, 58.73, 61.63, 61.66, 118.72, 127.97, 129.03, 133.97, 139.73, 165.11, 172.00, 172.24; IR (neat, cm^{-1}) 3048 (w), 2978 (m), 2933 (m), 2907 (w), 2872 (w), 1731 (s), 1625 (m), 1462 (w), 1449 (m), 1425 (m), 1389 (w), 1367 (m), 1268 (s), 1243 (s), 1177 (s), 1129 (m), 1111 (s), 1097 (s), 1065 (m), 1031 (m), 895 (w), 827 (m), 788 (m), 731 (m), 720 (s), 701 (s). Anal. Calcd for $C_{21}H_{30}O_4Si$: C, 67.34; H, 8.07. Found: C, 67.07; H, 7.83.

4,4-Bis(carbethoxy)-1-(*Z*)-methyldiphenylsilylmethylidene-2-methylcyclopentane (2a-SiMePh$_2$): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.49); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.66 (s, 3H, CH_3Si), 0.82 (d, J = 7.0 Hz, 3H, CH_3CH), 1.26 (t, J = 7.1 Hz, 6H, CH_3CH_2O), 1.85 (dd, J = 13.0 Hz, 3.5 Hz, 1H, CH_2CH), 2.57 (m, 1H, CH_2CHCH_3), 2.59 (dd, J = 13.0 Hz, 8.5 Hz, 1H, CH_2CH), 2.91 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 3.34 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 4.20 (q, J = 7.1 Hz, 2H, CH_3CH_2O), 4.21 (q, J = 7.1 Hz, 2H, CH_3CH_2O), 5.71 (s br, 1H, C=CH), 7.33 (m, 6H, Ph-H), 7.53 (m, 4H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.87, 14.23, 14.27, 22.16, 37.05, 42.01, 44.95, 58.62, 61.65, 61.68, 116.64, 127.97, 127.98, 129.28, 129.34, 134.82, 134.95, 137.47, 137.93, 166.83, 171.99, 172.29; IR (neat, cm^{-1}) 3069 (m), 3048 (w), 2979 (m), 2933 (m), 2907 (w), 2872 (w), 1731 (s), 1625 (m), 1462 (w), 1447 (m), 1428 (m), 1389 (w), 1367 (m), 1268 (s), 1244 (s), 1178 (s), 1129 (m), 1109 (s), 1097 (s), 1067 (m), 1031 (m), 862 (w), 827 (m), 788 (m), 737 (m), 720 (s), 701 (s). Anal. Calcd for $C_{26}H_{32}O_4Si$: C, 71.52; H, 7.39. Found: C, 71.63; H, 7.18.

4,4-Bis(carbethoxy)-1-(*Z*)-triphenylsilylmethylidene-2-methylcyclopentane (2a-SiPh$_3$): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.34); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (d, J = 7.1 Hz, 3H, CH_3CH), 1.23 (t, J = 7.2 Hz, 3H, CH_3CH_2O), 1.24 (t, J = 7.2 Hz, 3H, CH_3CH_2O), 1.79 (dd, J = 13.2 Hz, 4.8 Hz, 1H, CH_2CH), 2.33 (m, 1H, CH_2CHCH_3), 2.95 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 3.40 (d, J = 16.4 Hz, 1H, $CH_2C{=}C$), 4.18 (m, 4H, CH_3CH_2O), 5.93 (s br, 1H, C=CH), 7.33 (m, 9H, Ph-H), 7.53 (m, 6H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.20, 14.26, 21.75, 37.13, 41.93, 45.15, 58.43, 61.78, 114.63, 127.98, 129.55, 135.57, 136.04, 168.28, 172.00, 172.30; IR (neat, cm^{-1}) 3067 (m), 3048 (m), 2979 (s), 2934 (m), 2907 (m), 2871 (w), 1961 (w), 1892 (w), 1824 (w), 1728 (s), 1623 (m), 1588 (w), 1567 (w), 1483 (m), 1461 (m), 1446 (m), 1367 (m), 1267 (s), 1243 (s), 1177 (s), 1129 (s), 1108 (s), 1066 (s), 1030 (m), 998 (m), 918 (w), 904 (w), 861 (m), 820 (m), 791 (w), 742 (s), 704 (s). Anal. Calcd for $C_{26}H_{32}O_4Si$: C, 74.66; H, 6.89. Found: C, 74.74; H, 6.75.

4,4-Bis(carbethoxy)-1-(*Z*)-methyldiethoxysilylmethylidene-2-methylcyclopentane (2a-SiMe(OEt)$_2$): viscous, colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 3H, CH_3Si), 1.15 (m, 6H, CH_3CH_2OSi), 1.23 (t, J = 7.1 Hz, 6H, $CH_3CH_2O_2C$), 1.88 (dd, J = 13.4 Hz, 5.8 Hz, 1H, CH_2CH), 2.65 (dd, J = 13.4 Hz, 8.2 Hz, 1H, CH_2CH), 2.80 (d, J = 16.5 Hz, 1H, $CH_2C{=}C$), 2.84 (m, 1H, CH_2CHCH_3), 3.40 (td, J = 2.0 Hz, 16.5 Hz, 1H, $CH_2C{=}C$), 3.80 (m, 4H, CH_3CH_2OSi), 4.18 (m, 4H, $CH_3CH_2O_2C$), 5.25 (s br, 1H, C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.77, 14.22, 18.50, 18.54, 22.01, 37.36, 42.22, 44.72, 58.27, 58.71, 61.61, 61.69, 115.25, 167.64, 171.89, 172.21; IR (neat, cm^{-1}) 2975 (m), 2929 (m), 2907 (m), 2878 (m), 1732 (s), 1629 (w), 1447 (w), 1390 (m), 1367 (w), 1244 (s), 1166 (m), 1102 (s), 1080 (s), 1035 (m), 952 (m), 838 (m), 825 (m), 762 (m). Anal. Calcd for $C_{18}H_{32}O_6Si$: C, 58.03; H, 8.66. Found: C, 57.81; H, 8.57.

4,4-Bis(carbethoxy)-1-(*Z*)-trimethoxysilylmethylidene-2-methylcyclopentane (2a-Si(OMe)$_3$): viscous, colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J = 7.1 Hz, 3H, CH_3CH), 1.21 (q, J = 7.2 Hz, 3H, CH_3CH_2O), 1.88 (dd, J = 13.5 Hz, 6.0 Hz, 1H, CH_2CH), 2.67 (ddd, J = 13.5 Hz, 8.2 Hz, 1.1 Hz, 1H, CH_2CH), 2.82 (m, 1H, CH_2CHCH_3), 2.84 (d, J = 16.8 Hz, 1H, $CH_2C{=}C$), 3.24 (td, J = 2.2 Hz, 16.8 Hz, 1H, $CH_2C{=}C$), 3.52 (s, 9H, CH_3OSi), 4.16 (m, 4H, CH_3CH_2O), 5.17 (d br, J = 1.6 Hz, 1H, C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.20, 21.78, 37.73, 42.16, 44.76, 50.48, 58.76, 61.64, 61.71, 109.07, 171.00, 171.75, 172.04; IR (neat, cm^{-1}) 2977 (s), 2943 (s), 2873 (m), 2840 (s), 2022 (w), 2000 (w), 1895 (w), 1738 (s), 1628 (m), 1574 (w), 1566 (w), 1538 (w), 1474 (m), 1453 (m), 1390 (w), 1367 (m), 1271 (s), 1244 (s), 1191 (s), 1091 (s), 1033 (m), 920 (w), 903 (w), 856 (m), 842 (m), 822 (s), 804 (s), 754 (m), 722 (w). Anal. Calcd for $C_{16}H_{28}O_7Si$: C, 53.31; H, 7.83. Found: C, 53.06; H, 7.62.

4,4-Bis(carbethoxy)-1-(*Z*)-triethoxysilylmethylidene-2-methylcyclopentane (2a-Si(OEt)$_3$): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 3/1, R_f = 0.57); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, J = 7.1 Hz, 3H, CH_3CH), 1.21 (t, J = 7.1 Hz, 9H, CH_3CH_2OSi), 1.23 (m, 6H, $CH_3CH_2O_2C$), 1.91 (dd, J = 13.4 Hz, 6.0 Hz, 1H, CH_2CH), 2.69 (ddd, J = 13.4 Hz, 7.9 Hz, 1.1 Hz, 1H, CH_2CH), 2.84 (d, J = 16.5 Hz, 1H, $CH_2C{=}C$), 2.94 (m, 1H, CH_2CHCH_3), 3.27 (td, J = 2.2 Hz, 16.5 Hz, 1H, $CH_2C{=}C$), 3.80 (q J = 7.1 Hz, 6H, CH_3CH_2OSi), 4.17 (m, 4H, $CH_3CH_2O_2C$), 5.21 (d br, J = 2.2 Hz, 1H, C=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.22, 18.38, 21.92, 37.58, 42.15, 44.74, 58.44, 58.76, 61.60, 61.69, 110.73, 169.94, 171.82, 172.17; IR (neat, cm^{-1}) 2976 (s), 2929 (m), 2886 (m), 1734 (s), 1630 (w), 1462 (w), 1446 (m), 1390 (m), 1367 (m), 1283 (m), 1271 (m), 1243 (s), 1168 (s), 1100 (s), 1080 (s), 1036 (m), 960 (s), 862 (w), 854 (w), 836 (m),

811 (m), 780 (m), 718 (w). Anal. Calcd for $C_{19}H_{34}O_7Si$: C, 56.69; H, 8.51. Found: C, 56.48; H, 8.66.

2-(*Z*)-Dimethylphenylmethylidene-3,8,8-trimethyl-7,9-dioxaspiro-[4,5]decane (2b): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 15/1, R_f = 0.49); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 3H, CH_3Si), 0.38 (s, 3H, CH_3Si), 0.97 (d, J = 7.1 Hz, 3H, CH_3CH), 1.13 (dd, J = 13.7 Hz, 5.5 Hz, 1H, CH_2CH), 1.42 (s, 6H, $(CH_3)_2C$), 1.83 (dd, J = 13.7 Hz, 8.5 Hz, 1H, CH_2CH), 2.51 (m, 3H, CH_2C=C and CH_2CHCH_3), 3.52 (s, 2H, OCH_2C), 3.64 (d, J = 11.2 Hz, 1H, OCH_2C), 3.72 (d, J = 11.2 Hz, 1H, OCH_2C), 5.52 (s br, 1H, C=CH), 7.33 (m, 3H, Ph-H), 7.53 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.74, −0.60, 22.61, 23.60, 25.46, 35.97, 40.11, 41.31, 45.03, 68.14, 70.24, 97.96, 119.00, 127.91, 128.97, 133.89, 140.03, 167.09; IR (neat, cm^{-1}) 3068 (m), 3048 (w), 2991 (m), 2954 (s), 2856 (m), 1626 (m), 1453 (m), 1428 (m), 1382 (m), 1369 (m), 1346 (w), 1247 (s), 1200 (s), 1155 (m), 1114 (s), 1069 (s), 1043 (m), 1033 (m), 934 (m), 917 (w), 845 (s), 834 (s), 786 (m), 770 (m), 731 (s), 701 (s). Anal. Calcd for $C_{20}H_{30}O_2Si$: C, 72.67; H, 9.15. Found: C, 72.46; H, 9.02.

4,4-Bis(methoxymethyl)-1-(*Z*)-dimethylphenylsilylmethylidene-2-methylcyclopentane (2c): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 35/1, R_f = 0.37); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.36 (s, 3H, CH_3Si), 0.38 (s, 3H, CH_3Si), 0.98 (d, J = 6.7 Hz, 3H, CH_3CH), 1.24 (dd, J = 13.5 Hz, 5.5 Hz, 1H, CH_2CH), 1.80 (dd, J = 13.5 Hz, 8.5 Hz, 1H, CH_2CH), 2.18 (d, J = 15.4 Hz, 1H, CH_2C=C), 2.50 (d, J = 15.4 Hz, 1H, CH_2C=C), 2.53 (m, 1H, CH_2CHCH_3), 3.14 (m, 2H, OCH_2C), 3.30 (m, 2H, OCH_2C), 3.34 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 5.46 (s br, 1H, C=CH), 7.35 (m, 3H, Ph-H), 7.55 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.62, −0.53, 23.65, 36.40, 40.27, 43.88, 46.05, 59.47, 59.51, 75.46, 77.67, 117.73, 127.86, 128.90, 133.92, 140.34, 168.62; IR (neat, cm^{-1}) 3068 (m), 3049 (w), 3018 (w), 2954 (m), 2923 (m), 2874 (s), 2825 (m), 2808 (m), 1626 (m), 1476 (w), 1457 (m), 1427 (m), 1390 (w), 1248 (m), 1198 (m), 1166 (m), 1154 (m), 1110 (s), 966 (m), 846 (s), 834 (s), 788 (m), 770 (m), 729 (m), 700 (m). Anal. Calcd for $C_{19}H_{30}O_2Si$: C, 71.64; H, 9.49. Found: C, 71.52; H, 9.25.

4,4-Bis(acetoxymethyl)-1-(*Z*)-dimethylphenylsilylmethylidene-2-methyl-cyclopentane (2d): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.31); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.37 (s, 3H, CH_3Si), 0.38 (s, 3H, CH_3Si), 0.99 (d, J = 7.1 Hz, 3H, CH_3CH), 1.27 (dd, J = 13.5 Hz, 5.5 Hz, 1H, CH_2CH), 1.86 (dd, J = 13.5 Hz, 8.2 Hz, 1H, CH_2CH), 2.06 (s, 6H, CH_3CO), 2.22 (d, J = 15.3 Hz, 1H, CH_2C=C), 2.58 (d, J = 15.3 Hz, 1H, CH_2C=C), 2.56 (m, 1H, CH_2CHCH_3), 3.84 (d, J = 11.0 Hz, 1H, OCH_2C), 3.93 (d, J = 11.0 Hz, 1H, OCH_2C), 4.03 (s, 1H, OCH_2C), 4.04 (s, 1H, OCH_2C), 5.51 (s br, 1H, C=CH), 7.35 (m, 3H, Ph-H), 7.54 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.80, −0.72, 21.02, 21.05, 23.47, 36.05, 40.20, 43.67, 44.09, 66.13, 68.24, 119.31, 127.92, 128.99, 133.87, 139.82, 186.20, 171.17, 171.23; IR (neat, cm^{-1}) 3018 (w), 2956 (m), 2895 (w), 2870 (w), 1744 (s), 1628 (w), 1467 (w), 1428 (m), 1379 (m), 1366 (m), 1246 (s), 1112 (m), 1037 (s), 844 (m), 837 (m), 805 (m), 786 (w), 772 (w), 732 (m), 702 (m). Anal. Calcd for $C_{21}H_{30}O_4Si$: C, 67.34; H, 8.07. Found: C, 67.58; H, 7.89.

1-(4-Toluenesulfonyl)-3-(*E*)-dimethylphenylsilylmethylidene-4-methylpyrrolidine (2e): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.40); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 0.93 (d, J = 7.1 Hz, 3H, CH_3CH), 2.44 (s, 3H, CH_3Ph), 2.64 (m, 1H, CH_2CHCH_3), 3.09 (dd, J = 13.5 Hz, 5.5 Hz, 1H, CH_2CH), 3.18 (dd, J = 9.4 Hz, 1.3 Hz, 1H, CH_2CH), 3.61 (dd, J = 14.3 Hz, 1.6 Hz, 1H, CH_2C=C), 4.06 (d, J = 14.3 Hz, 1H, CH_2C=C), 5.46 (s br, 1H, C=CH), 7.33 (m, 5H, Ph-H), 7.46 (m, 2H, Ph-H), 7.70 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.18, −1.03, 20.80, 21.70, 37.49, 54.00, 55.61, 119.18, 127.95, 128.02, 129.30, 129.79, 133.09, 133.78, 138.71, 143.68, 159.29; IR (neat, cm^{-1}) 3068 (w), 3047 (w), 2960 (m), 2929 (m), 2898 (m), 2871 (m), 1635 (m), 1598 (m), 1494 (w), 1427 (m), 1405 (m), 1375 (m), 1347 (s), 1306 (m), 1290 (m), 1249 (m), 1183 (m), 1166 (s), 1095 (s), 1112 (s), 1095 (s), 1042 (s), 1017 (m), 834 (s), 819 (s), 775 (m), 732 (s), 702 (s). Anal. Calcd for $C_{21}H_{27}NO_2SSi$: C, 65.41; H, 7.06; N, 3.63. Found: C, 65.25; H, 6.83; N, 3.50.

1-Benzyl-3-(*E*)-dimethylphenylsilylmethylidene-4-methylpyrrolidine (2f): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.30); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.39 (s, 3H, CH_3Si), 0.40 (s, 3H, CH_3Si), 1.07 (d, J = 6.9 Hz, 3H, CH_3CH), 2.41 (dd, J = 8.2 Hz, 3.0 Hz, 1H, CH_2CH), 2.66 (m, 1H, CH_2CHCH_3), 2.72 (dd, J = 8.2 Hz, 6.6 Hz, 1H, CH_2CH), 3.10 (dd, J = 13.7 Hz, 1.6 Hz, 1H, CH_2C=), 3.41 (d, J = 13.7 Hz, 1H, CH_2C=C), 3.60 (s, 2H, NCH_2Ph), 5.47 (d br, J = 1.6 Hz, 1H, C=CH), 7.25−7.37 (m, 8H, Ph-H), 7.55 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.82, −0.78, 21.57, 37.31, 60.66, 62.76, 63.01, 116.05, 127.11, 127.91, 128.41, 128.93, 129.00, 133.98, 139.20, 139.91, 165.19; IR (neat, cm^{-1}) 3066 (m), 3026 (w), 2957 (s), 2927 (m), 2871 (m), 2786 (m), 1688 (m), 1633 (m), 1452 (m), 1427 (m), 1373 (w), 1340 (m), 1299 (m), 1249 (s), 1153 (m), 1140 (m), 1113 (s), 882 (w), 832 (s), 797 (s), 773 (m), 730 (s), 699 (s). Anal. Calcd for $C_{21}H_{27}NSi$: C, 78.44; H, 8.46; N, 4.36. Found: C, 78.35; H, 8.33; N, 4.33.

***(S)*-1-(1-Phenylethyl)-3-(*E*)-dimethylphenylsilylmethylidene-4-methylpyrrolidine (2 g):** viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.33); ^{1}H NMR (300 MHz, $CDCl_3$) δ [0.37 (s, CH_3Si), 0.42 (s, CH_3Si), (1:1.2), 6H], 1.04 (d, J = 6.0 Hz, 3H, CH_3CH), [1.35 (d, J = 2.1 Hz), 1.36 (d, J = 2.1 Hz), (1:1.2), 3H, $CH_3C(H)Ph$], [2.24 (d, J = 5.7 Hz), 2.43 (dd, J = 7.2 Hz, 11.2 Hz), (1:1.2), 1H, CH_2CH], 2.65 (m, 1H, CH_2CHCH_3), 2.67 (m, 1H, CH_2-CH), [3.03 (d, J = 14.1 Hz), 3.15 (d, J = 14.1 Hz), (1:1.2), 1H, CH_2C=], 3.17 (m, 1H, $(CH_3)PhCH$), [3.24 (d, J = 14.1 Hz), 3.48 (d, J = 14.1 Hz), (1:1.2), 1H, CH_2C=], [5.43 (s, br), 5.46 (s, br), (1:1.2), 1H, C=CH], 7.25−7.37 (m, 8H, Ph-H), 7.56 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.81, −0.78, [21.54, 21.68, (1:1.2)], [23.22, 23.28, (1:1.2)], [37.17, 37.26, (1:1.2)], [61.40, 61.76, (1:1.2)], [61.96, 62.40, (1:1.2)], [65.98, 66.01, (1:1.2)], [115.76, 115.84, (1:1.2)], 127.04, 127.37, 127.89, [128.46, 128.50, (1:1.2)], 128.98, 133.98, 139.98, [145.73, 145.74, (1:1.15)], 165.32; IR (neat, cm^{-1}) 3066 (m), 3050 (m), 3024 (m), 2969 (s), 2930 (m), 2901 (m), 2871 (m), 2777 (m), 1631 (m), 1492 (w), 1451 (m), 1492 (w), 1451 (m), 1427 (m), 1371 (m), 1316 (w), 1308 (w), 1248 (m), 1157 (m), 1112 (m), 862 (m), 832 (s), 800 (m), 765 (m), 729 (s), 700 (m). Anal. Calcd for $C_{22}H_{29}NSi$: C, 78.75; H, 8.71; N, 4.17. Found: C, 78.53; H, 8.52; N, 4.07.

1-(Prop-2-enyl)-3-(*E*)-dimethylphenylsilylmethylidene-4-methylpyrrolidine (2h): viscous colorless liquid; TLC (silica gel, hexanes/EtOAc = 2/1, R_f = 0.49); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.38 (s, 6H, CH_3Si), 1.05 (d, J = 6.8 Hz, 3H, CH_3CH), 2.37 (dd, J = 8.4 Hz, 3.4 Hz, 1H, CH_2CH), 2.66 (m, 1H, CH_2CHCH_3), 2.75 (dd, J = 8.4, 6.6 Hz, 1H, CH_2CH), 3.07 (d, J = 6.6 Hz, 2H, NCH_2CH=CH_2), 3.11 (dd, J = 13.7 Hz, 1.8 Hz, 1H, CH_2C=), 3.38 (d, J = 13.7 Hz, 1H, CHC=), 5.10 (dd, J = 10.2 Hz, 1.9 Hz, 1H, HC=CH_2), 5.20 (ddd, J = 17.1 Hz, 2.3 Hz, 1.6 Hz, 1H, HC=CH_2), 5.50 (dd, J = 3.5 Hz, 1.9 Hz, 1H, C=CH(Si)), 5.91 (tdd, J = 6.3 Hz, 17.1 Hz, 10.2 Hz, 1H, HC=CH_2), 7.34 (m, 3H, Ph-H), 7.55 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.99, −0.92, 21.37, 37.06, 59.45, 62.79, 62.93, 116.32, 117.20, 128.00, 129.11, 134.09, 135.99, 139.93, 165.03; IR (neat, cm^{-1}) 3068 (w), 3049 (w), 3008 (w), 2998 (w), 2958 (s), 2928 (s), 2907 (m), 2871 (m), 2784 (m), 1633 (m), 1472 (w), 1449 (w), 1427 (m), 1372 (w), 1338 (m), 1300 (m), 1248 (s), 1155 (m), 1113 (s), 995 (m), 919 (m), 884 (w), 842 (s), 832 (s), 798 (m), 772 (m), 729 (s), 700 (s). Anal. Calcd for $C_{17}H_{25}NSi$: C, 75.21; H, 9.28; N, 5.15. Found: C, 75.40; H, 9.07; N, 4.91.

4,4-Bis(hydroxymethyl)-1-(*Z*)-dimethylphenylsilylmethylidene-2-methylcyclopentane (2i): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 1/2, R_f = 0.23); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.37 (s, 3H, CH_3Si), 0.38 (s, 3H, CH_3Si), 0.99 (d, J = 6.8 Hz, 3H, CH_3CH), 1.17 (dd, J = 13.4 Hz, 5.2 Hz, 1H, CH_2CH), 1.82 (ddd, J = 13.4 Hz, 8.5 Hz, 1.1 Hz, 1H, CH_2CH), 2.29 (d, J = 15.4 Hz, 1H, CH_2C=C), 2.37 (s br, 2H, OH), 2.48 (td, J = 1.9 Hz, 15.4 Hz, 1H, CH_2C=C),

2.55 (m, 1H, CH_2CHCH_3), 3.53 (s, 2H, CH_2OH), 3.70 (s, 2H, CH_2-OH), 5.51 (s, br, 1H, C═CH), 7.35 (m, 3H, Ph-H), 7.54 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.73, −0.63, 23.61, 36.16, 39.88, 43.36, 46.71, 68.46, 71.62, 118.62, 127.90, 128.96, 133.87, 140.06, 167.40; IR (neat, cm^{-1}) 3350 (s), 3341 (s), 2953.8 (s), 2928 (s), 2870 (s), 1626 (m), 1457 (w), 1427 (m), 1247 (m), 1112 (s), 1023 (m), 843 (s), 834 (s), 798 (m), 776 (m), 730 (m), 700 (m). Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9,02. Found: C, 70.09; H, 8.87.

3-(*E*)-Dimethylphenylsilylmethylidene-4-methyltetrahydrofuran (2j): viscous colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.43); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.38 (s, 3H, CH_3Si), 0.39 (s, 3H, CH_3Si), 1.01 (d, J = 6.9 Hz, 3H, CH_3CH), 2.64 (m, 1H, CH_2CHCH_3), 3.62 (dd, J = 8.2 Hz, 1.9 Hz, 1H, CH_2CH), 3.82 (dd, J = 8.2, 5.5 Hz, 1H, CH_2CH), 4.17 (dd, J = 13.7 Hz, 1.9 Hz, 1H, CH_2C═), 4.44 (dd, J = 1.2, 13.7 Hz, 1H, CH_2C═), 5.46 (s br, 1H, C═CH), 7.32 (m, 3H, Ph-H), 7.56 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.74, −0.62, 20.65, 38.41, 73.71, 77.85, 115.31, 128.34, 129.41, 134.16, 139.66, 164.38. Anal. Calcd for $C_{14}H_{20}OSi$ C, 72.36; H, 8.67. Found: C, 72.37; H, 8.52.

4,4-Bis(carbethoxy)-1-(*Z*)-(1-dimethylphenylsilylethylidene)-2-methylcyclopentane (2k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.38 (s, 6H), 0.86 (d, J = 7.5 Hz, 3H), 1.24 (m, 6H), 1.67 (m, 3H), 2.01 (m, 1H), 2.47 (m, 1H), 2.76 (m, 1H), 2.94 (d, J = 17.5 Hz, 1H), 3.16 (d, J = 17.5 Hz, 1H), 4.19 (m, 4H), 7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −0.88, 14.05, 19.50, 22.84, 37.46, 38.49, 41.16, 58.38, 61.47, 123.76, 127.70, 128.73, 133.83, 140.00, 157.64, 173.00. IR (neat) 3068 (w), 3049 (w), 2977 (w), 1730 (s), 1625 (m), 1250 (s), 1185 (m), 1109 (m), 823 (m). Anal. Calcd for $C_{22}H_{32}O_4Si$ C, 68.00; H, 8.30. Found: C, 68.22; H, 8.06.

5,5-Bis(carbomethoxy)-1-(*Z*)-methyldiphenylsilylmethylidene-2-methylcyclohexane (2l): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.49); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.32 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 1.01 (d, J = 7.1 Hz, 3H, CH_3-CH), 1.42 (d br, J = 13.7 Hz, 1H, $CH_2CH_2CHCH_3$), 1.70 (ddt, J = 4.2 Hz, 4.4 Hz, 13.7 Hz, 1H, $CH_2CH_2CHCH_3$), 1.91 (dt, J = 4.1 Hz, 13.7 Hz, 1H, $CH_2CH_2CHCH_3$), 2.18 (d br, J = 13.7 Hz, 1H, CH_2CH_2-$CHCH_3$), 2.60 (m, 1H, $CH_2CH_2CHCH_3$), 2.74 (d, J = 13.8 Hz, 1H, CH_2C═C), 2.85 (d, J = 13.8 Hz, 1H, CH_2C═C), 3.73 (s, 6H, CH_3-OCO), 5.40 (s, br, 1H, C═CH), 7.34 (m, 3H, Ph-H), 7.50 (m, 2H, Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.83, −0.49, 18.46, 25.84, 29.65, 35.34, 39.59, 52.48, 52.92, 57.77, 123.28, 127.87, 128.96, 133.85, 140.01, 159.32, 170.95, 172.60; IR (neat, cm^{-1}) 3069 (w), 3048 (w), 2998 (w), 2954 (s), 2869 (w), 1737 (s), 1616 (m), 1457 (M), 1430 (m), 1319 (m), 1284 (m), 1248 (s), 1223 (s), 1213 (s), 1194 (m), 1176 (s), 1155 (m), 1134 (m), 1113 (m), 1063 (m), 1028 (m), 878 (w), 853 (m), 836 (s), 793 (m), 773 (m), 731 (m), 701 (m). Anal. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83. Found: C, 66.54; H, 7.82.

9-(*Z*)-Dimethylphenylsilylmethylidene-7,7-bis(carbethoxy)bicyclo-[4.3.0]non-2-ene (6): ^{1}H NMR (600 MHz) δ 0.35 (3H, s), 0.38 (3H, s), 1.18−1.28 (7H, m), 1.42 (1 H, m), 1.84−1.91 (1H, m), 1.92−2.00 (1H, m), 2.73 (1H, d, J = 16.2 Hz), 2.93 (1H, ddd, J = 12.6, 7.8, 4.8 Hz), 3.20 (1H, m), 3.43 (1H, dt, J = 16.2, 2.4 Hz), 4.10−4.28 (4H, m), 5.56 (1H, s), 5.61 (1H, m), 5.64 (1H, m), 7.34 (3H, m), 7.52 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.0, −0.6, 14.1, 22.3, 23.3, 42.3, 43.3, 61.3, 61.4, 62.6, 119.3, 126.8, 127.8, 128.2, 128.9, 133.8, 161.4, 169.8, 171.4; IR (neat, cm^{-1}) 3036 (w), 2955 (s), 2331 (m), 1731 (s), 1625 (m), 1443 (m), 1361 (m), 1249 (s), 832 (s), 732 (m). Anal. Calcd for $C_{24}H_{32}O_4Si$ C, 69.87; H, 7.82. Found: C, 69.79; H, 7.91.

The structure of **6** was determined on the basis of 2D NMR analyses (COSY and HETCOR) as well as 1D difference NOE experiments (see Supporting Information). The 1D difference NOE experiments unambiguously established the cis ring juncture and *Z* geometry of $PhMe_2$-Si-methylidene moiety at the C-9 position in that strong NOE was observed between H−C(1) and H−C(5), but no NOE was observed between H−C(1) and the vinyl proton of the 9-silyl-*exo*-methylene moiety. Similar results on the NOE experiments of closely related 9-*exo*-methylenebicyclo[4.3.0]nonene[23a,b]or nonan-2-one[23c] systems have been reported, which further support our assignments of the stereochemistry of **6**.

General Procedure for the Catalytic CO−SiCaC Reaction. A typical procedure is described for the reaction of **1a**. A reaction vessel equipped with a stirring bar and a CO inlet, was charged with $Rh_4(CO)_{12}$ (3.8 mg, 0.005 mmol, 0.5 mol %). After purging the vessel with CO, 1,4-dioxane (2 mL) was added to dissolve the catalyst. After stirring for 5 min at ambient temperature, $P(OEt)_3$ (17 mg, 0.10 mmol; 5 equiv to Rh) in 1,4-dioxane (2 mL) was added via a syringe, and the mixture was stirred for an additional 10 min. The color of the solution turned from bright red to dark red during this period. The resulting catalyst solution was then cannulated into a 100-mL round-bottomed flask containing a solution of **1a** (238 mg, 1 mmol), Me_2PhSiH (145 mg, 1.05 mmol) in 1,4-dioxane (50 mL) via CO pressure without stirring. The resulting mixture was placed in a 300-mL stainless steel autoclave, pressurized with CO gas (20 atm) and then heated to 105 °C with stirring for 48 h. After releasing CO, the reaction mixture was submitted to GC analysis. All volatiles were removed under reduced pressure and the crude product was purified by silica gel column chromatography using hexanes/EtOAc (15/1) as eluant.

General Procedure for the "Freeze and CO" Protocol for the CO−SiCaC Reaction. A Schlenk-type flask containing $Rh_4(CO)_{12}$ (3.8 mg, 0.005 mmol) and a stirring bar was purged with CO, and 1,4-dioxane (2.0 mL) was added to dissolve the catalyst. After stirring for 5 min at ambient temperature, $P(OEt)_3$ (17 mg, 0.10 mmol) in dioxane (1.0 mL) was added via syringe. The catalyst solution was stirred for an additional 10 min and cannulated into a reaction flask containing an enyne (1.0 mmol) in dioxane (2.0 mL), which had been purged with CO and frozen by submerging in liquid nitrogen under CO. Me_2PhSiH in dioxane (1.0 mL) was added via syringe and the reaction flask placed into a 300-mL stainless steel autoclave that had been purged with CO. Then, the autoclave was charged with CO (20 atm) and heated at 105 °C for 48 h. The autoclave was cooled to 0 °C and the pressure released to take out the reaction flask. Then, the reaction mixture was subjected to GC analysis.

4,4-Bis(carbethoxy)-1-(*Z*)-dimethylphenylsilylmethylidene-2-formylmethylcyclopentane (3a): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.23); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 3H, CH_3Si), 0.35 (s, 3H, CH_3Si), 1.24 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.25 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.92 (dd, J = 13.7 Hz, 4.9 Hz, 1H, CH_2CH), 2.32 (m, 2H, CH_2CHO), 2.66 (dd, J = 13.7 Hz, 8.2 Hz, 1H, CH_2CH), 2.90 (d, J = 16.5 Hz, 1H, CH_2C═C), 2.98 (m, 1H, CH_2CHCH_2), 3.19 (dt, J = 16.5 Hz, 2.2 Hz, 1H, CH_2C═C), 4.18 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 4.19 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 5.61 (s br, 1H, C═CH), 7.35 (m, 3H, Ph-H), 7.51 (m, 2H, Ph-H), 9.38 (d, J = 1.1 Hz, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.29, −0.94, 14.18, 14.24, 36.42, 39.66, 44.96, 50.17, 58.65, 61.74, 61.85, 120.58, 128.16, 129.39, 133.97, 139.07, 161.86, 171.55, 172.09, 200.71; IR (neat, cm^{-1}) 3069 (w), 3049 (m), 2980 (s), 2959 (s), 2905 (m), 2821 (w), 2721 (w), 1729 (s), 1629 (m), 1463 (m), 1446 (m), 1428 (s), 1405 (m), 1390 (m), 1366 (m0, 1281 (s), 1248 (s), 1186 (s), 1162 (s), 1111 (s), 1096 (s), 1082 (s), 1064 (s), 1029 (m), 905 (w), 836 (s), 784 (m), 733 (s), 702 (s). Anal. Calcd for $C_{22}H_{30}O_5Si$: C, 65.64; H, 7.51; Found: C, 65.45; H, 7.36.

2-(*Z*)-Dimethylphenylsilylethylidene-8,8-dimethyl-3-formylmethyl-7,9-dioxaspriro[4,5]decane (3b): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.21); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 6H, CH_3Si), 1.05 (dd, J = 13.7 Hz, 6.1 Hz, 1H, CH_2CH), 1.38 (s, 6H, CH_3C), 1.89 (dd, J = 13.7 Hz, 8.3 Hz, 1H, CH_2CH), 2.25 (m, 2H, CH_2CHO), 2.35 (d, J = 15.9 Hz, 1H, CH_2C═C), 2.53 (d, J = 15.9 Hz, 1H, CH_2C═C), 2.80 (m, 1H, CH_2CHCH_2), 3.57 (m, 4H,

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OCH_2C), 5.61 (s br, 1H, C=CH), 7.32 (m, 3H, Ph-H), 7.49 (m, 2H, Ph-H), 9.33 (d, J = 1.1 Hz, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.37, −1.16, 22.02, 25.48, 35.02, 38.90, 40.27, 45.33, 51.35, 67.37, 69.56, 97.88, 120.88, 127.95, 129.14, 133.70, 139.05, 163.48, 200.82; IR (neat, cm^{-1}) 3069 (m), 3048 (m), 2992 (s), 2952 (s), 2858 (s), 2717 (m), 2360 (m), 2342 (w), 1723 (s), 1626 (m), 1477 (w), 1453 (m), 1428 (m), 1405 (m), 1383 (s), 1371 (s), 1347 (m), 1304 (m), 1249 (s), 1198 (s), 1156 (m), 1110 (s), 1061 (s), 1033 (m), 998 (w), 932 (m), 919 (m), 834 (s), 731 (s), 701 (s). Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.57; H, 8.54.

4,4-Bis(carbomethoxy)-1-(*Z*)-dimethylphenylsilylmethylidene-2-formylmethylcyclopentane (3c): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.20); ^1H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 1.26 (dd, J = 14.0 Hz, 5.3 Hz, 1H, CH_2CH), 1.82 (dd, J = 14.0 Hz, 9.0 Hz, 1H, CH_2CH), 2.19 (d, J = 15.6 Hz, 1H, CH_2C=C), 2.34 (m, 2H, CH_2CHO), 2.49 (d br, J = 15.6 Hz, 1H, CH_2C=C), 2.84 (m, 1H, CH_2CHCH_2), 3.10 (s, 1H, OCH_2C), 3.11 (s, 1H, OCH_2C), 3.24 (s, 2H, OCH_2C), 3.29 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 5.54 (s br, 1H, C=CH), 7.32 (m, 3H, Ph-H), 7.49 (m, 2H, Ph-H), 9.37 (d, J = 1.1 Hz, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.32, −1.04, 35.79, 37.39, 43.61, 46.14, 51.15, 59.14, 59.25, 75.40, 76.83, 119.29, 127.84, 129.00, 133.69, 139.35, 165.23, 201.31; IR (neat, cm^{-1}) 3068 (m), 3048 (m), 2953 (s), 2925 (s), 2886 (s), 2880 (s), 2826 (m), 2720 (w), 1724 (s), 1626 (m), 1475 (m), 1458 (m), 1450 (m), 1428 (m), 1404 (m), 1389 (m), 1339 (w), 1302 (w), 1250 (s), 1198 (m), 1167 (m), 1113 (s), 998 (w), 966 (m), 879 (m), 837 (s), 784 (m), 732 (s), 701 (s). Anal. Calcd for $C_{20}H_{30}O_3Si$: C, 69.32; H, 8.73. Found: C, 69.05; H, 8.54.

4,4-Bis(acetoxymethyl)-1-(*Z*)-dimethylphenylsilylmethylidene-2-formylmethylcyclopentane (3d): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.15); ^1H NMR (300 MHz, $CDCl_3$) δ 0.34 (s, 3H, CH_3Si), 0.36 (s, 3H, CH_3Si), 1.25 (dd, J = 14.0 Hz, 6.1 Hz, 1H, CH_2CH), 1.95 (m, 2H, CH_2CHO), 2.03 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.23 (d, J = 16.2 Hz, 1H, CH_2C=C), 2.31 (d, J = 6.1 Hz, 1H, CH_2CH), 2.50 (d, J = 16.2 Hz, 1H, CH_2C=C), 2.86 (m, 1H, CH_2CHCH_2), 3.90 (m, 4H, $COOCH_2C$), 5.59 (s br, 1H, C=CH), 7.33 (m, 3H, Ph-H), 7.49 (m, 2H, Ph-H), 9.34 (s, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.49, −1.14, 20.80, 20.84, 35.27, 37.88, 43.89, 44.23, 51.13, 65.67, 67.65, 121.00, 128.00, 129.20, 133.72, 138.92, 162.82, 170.90, 170.99, 200.59; IR (neat, cm^{-1}) 3068 (m), 3048 (m), 3008 (w), 2999 (m), 2955 (m), 2894 (m), 2831 (m), 2722 (w), 1742 (s), 1627 (m), 1466 (m), 1428 (m), 1380 (m), 1366 (m), 1247 (s), 1234 (s), 1113 (m), 1039 (m), 998 (w), 983 (m), 903 (m), 838 (s), 786 (m), 734 (m), 702 (m). Anal. Calcd for $C_{22}H_{30}O_5Si$: C, 65.64; H, 7.51. Found: C, 65.39; H, 7.44.

1-(4-Toluenesulfonyl)-3-(*E*)-dimethylphenylsilylmethylidene-4-formylmethylpyrrolidine (3e): viscous colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.15); ^1H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 3H, CH_3Si), 0.31 (s, 3H, CH_3Si), 1.99 (d, J = 19.0 Hz, 1H, CH_2CH), 2.42 (s, 6H, Ph-CH_3), 2.50 (dd, J = 19.0 Hz, 10.7 Hz, 1H, CH_2CH), 2.97 (m, 2H, CH_2CHO), 2.23 (m, 1H, CH_2CHCH_2), 3.50 (dd, J = 14.6 Hz, 1.9 Hz, 1H, CH_2C=C), 3.50 (d, J = 14.6 Hz, 1H, CH_2C=C), 5.53 (s, 1H, C=CH), 7.32 (m, 5H, Ph-H), 7.49 (m, 2H, Ph-H), 7.64 (m, 2H, Ph-H), 9.36 (s, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.91, −1.53, 21.54, 36.55, 48.02, 53.48, 53.84, 120.98, 127.84, 128.09, 129.42, 129.70, 132.42, 133.68, 138.04, 143.77, 156.44, 199.42; IR (neat, cm^{-1}) 3067 (w), 3048 (w), 3018 (w), 3006 (w), 2999 (w), 2954 (m), 2922 (w), 2897 (w), 2854 (w), 1721 (s), 1635 (m), 1597 (w), 1494 (w), 1476 (w), 1453 (w), 1427 (m), 1403 (m), 1347 (s), 1305 (m), 1291 (w), 1251 (m), 1220 (w), 1184 (m), 1165 (s), 1113 (s), 1093 (s), 1042 (m), 1017 (m), 997 (w), 967 (w), 832 (s), 703 (s). Anal. Calcd for $C_{22}H_{27}NO_3SSi$: C, 63.89; H, 6.58, N, 3.39; S, 7.75. Found: C, 63.70; H, 6,59; N, 3.36; S, 7.71.

1-Methanesulfonyl-3-(*E*)-dimethylphenylsilylmethylidene-4-formylmethylpyrrolidine (3p): viscous, colorless liquid; TLC (silica gel, hexanes/EtOAc = 5/1, R_f = 0.15); ^1H NMR (300 MHz, $CDCl_3$) δ 0.36 (s, 3H, CH_3Si), 0.38 (s, 3H, CH_3Si), 2.05 (dd, J = 18.4 Hz, 1.9 Hz, 1H, CH_2CH), 2.61 (dd, J = 18.4 Hz, 11.0 Hz, 1H, CH_2CH), 2.79 (s, 3H, CH_3-SO_2), 3.09 (m, 1H, CH_2CHCH_2), 3.24 (m, 2H, CH_2CHO), 3.74 (dd, J = 14.8 Hz, 1.9 Hz, 1H, CH_2C=C), 4.10 (d br, J = 14.8 Hz, 1H, CH_2C=C), 5.63 (s br, 1H, C=CH), 7.32 (m, 3H, Ph-H), 7.47 (m, 2H, Ph-H), 9.40 (s, 1H, CHO); ^{13}C NMR (75 MHz, $CDCl_3$) δ -1.96, −1.56, 34.80, 36.88, 47.67, 53.17, 53.58, 121.38, 128.06, 129.39, 133.64, 137.94, 156.21, 199.34; IR (neat, cm^{-1}) 3068 (m), 3048 (m), 3013 (w), 2953 (m), 2897 (m), 2855 (m), 2727 (w), 1721 (s), 1685 (w), 1637 (m), 1479 (w), 1458 (w), 1427 (m), 1407 (m), 1387 (m), 1335 (s), 1251 (s), 1221 (w), 1158 (s), 1112 (s), 1092 (m), 1050 (s), 998 (m), 960 (m), 835 (s), 787 (m), 772 (m), 738 (s), 703 (s). Anal. Calcd for $C_{16}H_{23}NO_3SSi$: C, 56.94; H, 6.87; N, 4.15; S, 9.50. Found: C, 56.72; H, 6.97; N, 3.96; S, 9.31.

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Supporting Information Available: Synthesis, spectral data for all enynes **1a**−**1q** and **4** as well as NOE experiments for elucidation of the structure of **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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