Cyclization/Hydrosilylation of Functionalized Diynes Catalyzed by a Cationic Rhodium Bis(phosphine) Complex

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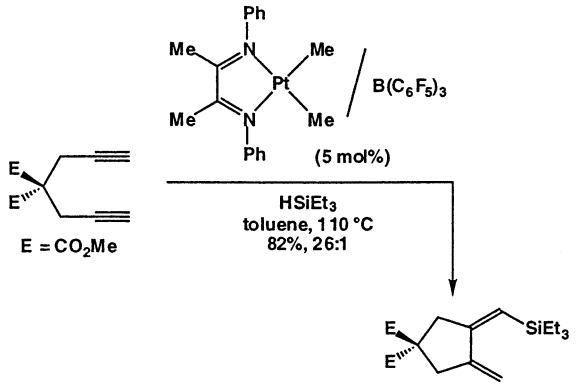
The cationic rhodium complex [Rh(BINAP)(COD)]$^+$ BF_4^- (**2**) [BINAP = (±)-2,2′-bis-(diphenylphosphino)binaphthyl] catalyzed the cyclization/hydrosilylation of 5,5-dicarbomethoxy-2,7-nonadiyne (**1**) and triethylsilane to form (*E*,*Z*)-1,1-dicarbomethoxy-3-ethylidene-4-(1-triethylsilylethylidene)cyclopentane (**3**) in 77% yield with ≥50:1 isomeric purity. A number of functionalized 1,6-diynes that possessed internal alkynes in addition to **1** underwent cyclization/hydrosilylation catalyzed by **2** to form silylated 1,2-dialkylidenecycloalkanes in moderate to good yield with high diastereoselectivity.

Introduction

Functionalized 1,2-dialkylidene cyclopentanes can be readily elaborated via [4+2] cycloaddition with dienophiles and are therefore useful intermediates in the synthesis of complex polycyclic compounds. One approach to the synthesis of 1,2-dialkylidene cycloalkanes is via the transition metal-catalyzed cyclization/addition of nonconjugated diynes employing hydrosilanes (Scheme 1),[1−6] hydrostannanes,[7] stannylsilanes,[8] borylsilanes,[9] borylstannanes,[10] and hydrogen equivalents as the stoichiometric reductant.[11] However, the cyclization/hydrosilylation of diynes, particularly 1,6-diynes, remains problematic, which is unfortunate given the versatility of the vinyl silyl group formed in these transformations.[12] For example, Ni(0)-catalyzed diyne cyclization/hydrosilylation is restricted to 1,7-diynes,[3] while cyclization/hydrosilylation of 1,6-diynes catalyzed by Wilkinson's catalyst suffers from limited substrate scope and low yields.[4] Rhodium carbonyl complexes also catalyze the cyclization/hydrosilylation of 1,6-diynes but form primarily disilylated monoalkylidenecyclopentanes and products of silylbicyclization.[5,6]

We have addressed the absence of a general and efficient catalyst for the cyclization/hydrosilylation of functionalized 1,6-diynes, through the development of a platinum-catalyzed procedure for the cyclization/hydrosilylation of functionalized 1,6-diynes that possess terminal alkynes.[1,2] For example, reaction of dimethyl dipropargylmalonate and triethylsilane catalyzed by a 1:1 mixture of [PhN=C(Me)C(Me)=NPh]$PtMe_2$ and $B(C_6F_5)_3$ led to the isolation of the corresponding silylated (*Z*)-1,2-dialkylidenecyclopentane in 82% yield with good selectivity (Scheme 1).[2] This procedure tolerated a number of functional groups and displayed good diastereoselectivity, but was generally restricted to diynes that possessed terminal alkynes. We therefore sought to ameliorate this limitation and here we report the cyclization/hydrosilylation of functionalized 1,6-diynes that possess internal alkynes catalyzed by a cationic rhodium bis(phosphine) complex.

Scheme 1



Results and Discussion

Cationic rhodium bis(phosphine) complexes are active catalysts for the hydrosilylation of functionalized alkynes[13] and catalyze a number of intramolecular C−C bond-forming processes.[14,15] For these reasons, we investigated the utility of cationic rhodium bis(phosphine) complexes as catalysts for diyne cyclization/hydrosilylation. Reaction of 5,5-dicarbomethoxy-2,7-nonadiyne (**1**) (0.08 M) with triethylsilane (0.17 M) and a catalytic

(1) Madine, J. W.; Wang, X.; Widenhoefer, R. A. *Org. Lett.* **2001**, *3*, 385.
(2) Wang, X.; Chakrapani, H.; Madine, J. W.; Keyerleber, M. A.; Widenhoefer, R. A. *J. Org. Chem.* **2002**, *67*, 2778.
(3) (a) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478. (b) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett* **1992**, 539.
(4) Muraoka, T.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 7325.
(5) Matsuda, I.; Eshibashi, H.; Ii, N. *Tetrahedron Lett.* **1995**, *36*, 241.
(6) (a) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 6690. (b) Ojima, I.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* **1994**, *59*, 7594. (c) Ojima, I.; Kass, D. F.; Zhu, J. *Organometallics* **1996**, *15*, 5191.
(7) Lautens, M.; Smith, N. D.; Ostrovsky, D. *J. Org. Chem.* **1997**, *62*, 8970.
(8) Greau, S.; Radetich, B. N.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **2000**, *122*, 8579.
(9) Onozawa, S.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229.
(10) Onozawa, S.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389.
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(12) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.
(13) (a) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045. (b) Takeuchi, R.; Ebata, I. *Organometallics* **1997**, *16*, 3707. (c) Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1777. (d) Takeuchim R.; Tanouchi, N. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2909.

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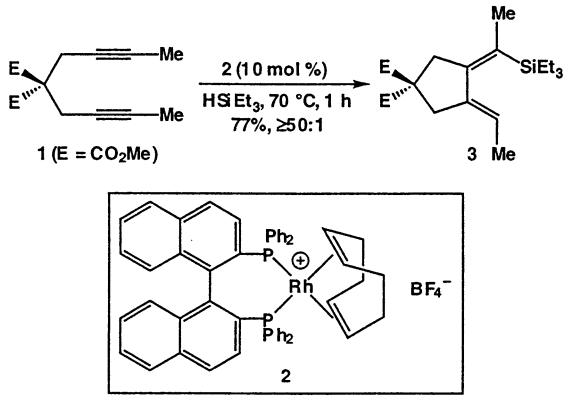
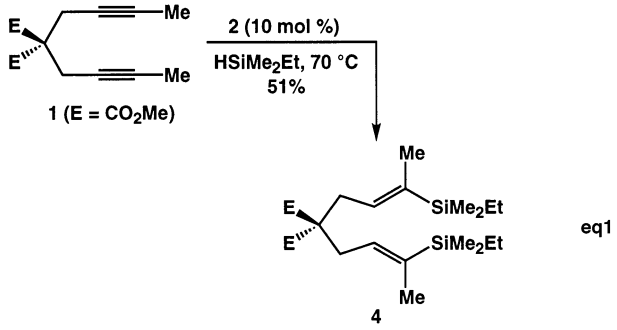
Scheme 2



amount of $[Rh(BINAP)(COD)]^+ BF_4^-$ (**2**) [BINAP = (±)-2,2′-bis(diphenylphosphino)binaphthyl] (10 mol %) at 70 °C for 1 h led to complete consumption of **1** and isolation of the silylated 1,2-dialkylidene cyclopentane **3** in 77% yield with ≥50:1 isomeric purity (Scheme 2). GCMS analysis of the crude reaction mixture also revealed the presence of a small quantity (≤5%) of a disilylated byproduct, which became more pronounced at higher silane concentration. Although an exhaustive survey of potential bis(phosphine) ligands was not performed, cationic rhodium complexes generated from achiral bis(phosphine) ligands such as bis(diphenylphosphino)ethane) were less effective than was **2**.[16]

The chemoselectivity of rhodium-catalyzed cyclization/hydrosilylation employing trialkylsilanes depended strongly on the steric bulk of the silane. For example, rhodium-catalyzed reaction of diyne **1** and $HSiMe_2Et$ employing the conditions used to synthesize **3** formed predominantly the disilylated uncyclized compound **4**, which was isolated in 51% yield as a single isomer by ^1H NMR spectroscopy (eq 1). Conversely, slow addition



eq1

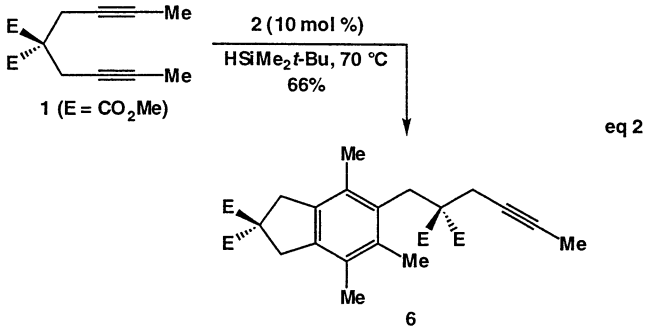
of $HSiMe_2Et$ to a mixture of **1** and a catalytic amount of **2** over 35 min formed predominantly (94% selectivity) the desired silylated 1,2-dialkylidenecyclopentane **5**, which was isolated in 56% yield (Table 1, entry 1). In contrast, reaction of **1** and $HSiMe_2t$-Bu catalyzed by **2** formed neither the desired dialkylidenecyclopentane nor the disilylated uncyclized product, but instead led to

Table 1. Cyclization/Hydrosilylation of Functionalized 1,6-diynes Catalyzed by $[Rh(BINAP)(COD)]^+ BF_4^-$ (2) in DCE at 70 °C

entry	diyne	silane	carbocycle	yield (%)	isomer ratio
1	E = CO_2Me	$HSiMe_2Et$	5	56	≥25:1[a]
2		$HSiMePh_2$	7	60	≥50:1[b]
3	R^1, R^2 = Et	$HSiEt_3$	12	56	≥25:1[a]
4	$R^1, R^2 = n$-C_5H_{11}		13	60	≥25:1[a]
5	R^1 = Me, R^2 = Et		14	65	15:1
6	R^1, R^2 = H		15	31	4:1[a]
7	R = Piv		16	72	≥50:1[b]
8	R = Ac		17	68	34:1
9	R = Me		18	70	≥50:1[b]
10	R = Bn		19	62	≥25:1[a]
11	R = Ph		20	73	≥50:1[b]
12	R = $CONMe_2$		21	70	≥50:1[b]
13			22	70	10:1
14			23	40	≥50:1[b]
15	E = CO_2Et		24	29	≥25:1[a]

[a] Single isomer detected by ^1H and ^{13}C NMR analysis. [b] Single isomer detected by GC analysis.

cyclotrimerization and formation of arene **6** in 66% isolated yield (eq 2); rhodium-catalyzed alkyne cyclotrimerization has previously been observed.[8,15,17]



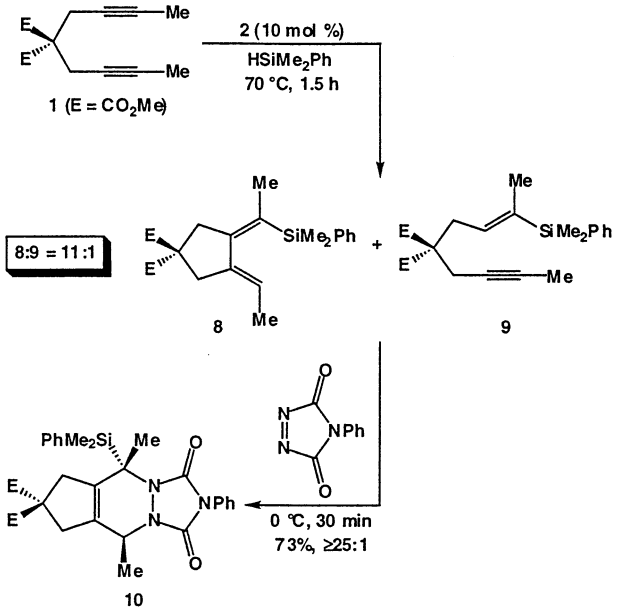
eq 2

(14) (a) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936. (b) Cao, P.; Wang, B.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 6490. (c) Barnhart, R. W.; Wang, X.; Noheda, P.; Bergens, S. H.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1994**, *116*, 1821.

(15) Matsuda, I.; Shibata, M. P.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, *28*, 3361.

(16) Reaction of **1** and $HSiEt_3$ catalyzed by $[Rh(DPPE)(COD)]^+ BF_4^-$ [DPPE = bis(diphenylphosphino)ethane] at 70 °C reached 70% completion after 2 h to form **3** in 21% GC yield. This reaction formed predominantly disilylated uncyclized material.

Scheme 3



Aryl and benzyl silanes also underwent efficient rhodium-catalyzed cyclization/hydrosilylation and reaction of **1** with methyldiphenylsilane catalyzed by **2** formed dialkylidene cyclopentane **7** in 60% yield with good diastereoselectivity (Table 1, entry 2). In comparison, rhodium-catalyzed cyclization/hydrosilylation of **1** with dimethylphenylsilane formed an inseparable 11:1 mixture of the desired 1,2-dialkylidene cyclopentane **8** and the silylated uncyclized isomer **9** in ~85% combined yield by GC analysis of the crude reaction mixture (Scheme 3). Treatment of the crude reaction mixture with 4-phenyl[1,2,4]triazole-3,5-dione at 0 °C for 30 min converted **8** to Diels−Alder adduct **10**, which was isolated in 73% yield (Scheme 3). Similarly, rhodium-catalyzed cyclization/hydrosilylation of **1** and benzyldimethylsilane followed by treatment with [1,2,4]triazole-3,5-dione gave tricyclic adduct **11** in 69% isolated yield (Table 2, entry 1).

A number of functionalized diynes underwent rhodium-catalyzed cyclization/hydrosilylation (Table 1) or rhodium-catalyzed cyclization/hydrosilylation coupled with [4+2] cycloaddition (Table 2) to form the corresponding carbocycles (**12**−**32**) in moderate to good yield with excellent stereoselectivity. For example, diynes substituted with methyl, ethyl, or *n*-pentyl groups underwent cyclization/hydrosilylation to form the corresponding dialkylidene cyclopentanes in good yield with good selectivity (Table 1, entries 1−5). Noteworthy was the highly regioselective rhodium-catalyzed cyclization/hydrosilylation of 5,5-dicarbomethoxy-2,7-decadiyne to form cyclopentane **14** in 65% yield as a 15:1 mixture of regioisomers (Table 1, entry 5). Efficient rhodium-catalyzed cyclization/hydrosilylation was restricted to diynes that possessed internal alkynes and this rhodium-catalyzed process therefore complements our platinum-catalyzed protocol.[1,2] For example, rhodium-catalyzed cyclization/hydrosilylation of dimethyl dipropargylmalonate formed cyclopentane **15** in only 31% yield as a 4:1 mixture of diastereomers (Table 1, entry 6).

(17) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1994**, *13*, 1081.

Rhodium-catalyzed diyne cyclization/hydrosilylation tolerated a number of functional groups including pivaloate, acetate, benzyloxy, carbamoyl, and acetal groups (Tables 1, entries 7−12). The presence of *gem*-dialkyl groups on the substrate backbone often facilitates transition metal-mediated or -catalyzed cyclization due to the Thorpe−Ingold effect.[18] However, *gem*-dialkyl substitution on the diyne was not required for efficient rhodium-catalyzed cyclization/hydrosilylation as reaction of di(2-butynyl)tosylamide and $HSiEt_3$ catalyzed by **2** formed pyrrolidine **22** in 70% yield (Table 1, entry 13). In comparison, rhodium-catalyzed cyclization/hydrosilylation of di(2-butynyl) ether formed tetrahydrofuran **23** in 40% yield (Table 1, entry 14). Rhodium-catalyzed cyclization/hydrosilylation of 1,7-diynes was less efficient than was cyclization/hydrosilylation of 1,6-diynes, and reaction of 5,5,6,6-tetracarboethoxy-2,8-decadiyne and $HSiEt_3$ catalyzed by **2** formed 1,2-dialkylidene cyclohexane **24** in 29% yield (Table 1, entry 15).

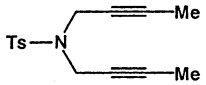
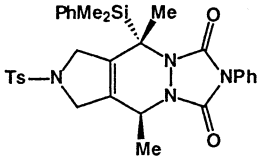
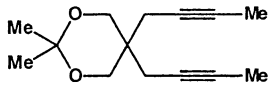
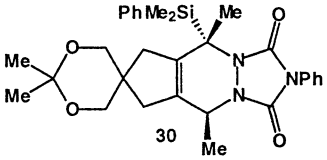
On the basis of the proposed mechanism for alkyne hydrosilylation catalyzed by cationic rhodium bis(phosphine) complexes,[13] we propose a mechanism for the rhodium-catalyzed cyclization/hydrosilylation of diyne **1** (Scheme 4). Oxidative addition of the H−Si bond of the silane to a cationic Rh(I) species could form the Rh(III) silyl hydride species **I**. Coordination and β-migratory insertion of one of the triple bonds of **1** into the Rh−Si bond of **I** (silylmetalation) could form the rhodium alkenyl hydride complex **II**. Coordination and subsequent β-migratory insertion of the pendant alkyne into the Rh−C bond of **II** could form the rhodium dienyl complex **III**. Formal C−H reductive elimination from **III** could release the silylated 1,2-dialkylidenecyclopentane **A** with the correct stereochemistry and regenerate the cationic Rh(I) complex **I** (Scheme 4). Alternatively, formal C−H reductive elimination from alkenyl hydride complex **II** would regenerate **I** and form the silylated uncyclized product **B**, which could undergo subsequent hydrosilylation to form the disilylated uncyclized product **C**.

A mechanism involving insertion of a C≡C bond of **1** into the Rh−H bond of **I** (hydrometalation) could also, in principle, account for the formation of cyclization/hydrosilylation product **C** and silylated uncyclized products **A** and **B** in the rhodium-catalyzed reaction of **1** with silanes. For example, hydrometalation of a C≡C bond of **1** with **I** could transfer the hydrogen atom to either the internal or external carbon atom of the alkyne to form rhodium alkenyl species **IV** or **V**, respectively (Scheme 5). Alkenyl species **IV** could undergo C−Si reductive elimination to form the silylated uncyclized products **B** and **C**, while **V** could undergo intramolecular carbometalation followed by C−Si reductive elimination to form the dialkylidenecyclopentane **A**. However, because neither **IV** nor **V** alone can account for the formation of both **A** and **B** + **C**, a mechanism involving hydrometalation requires formation of both **IV** and **V**, and requires that the **IV**:**V** ratio parallel the **B**+**C**:**A** ratio (Scheme 5).[19]

We can rule out a mechanism initiated by hydrometalation on the basis of the regioselectivity of alkyne

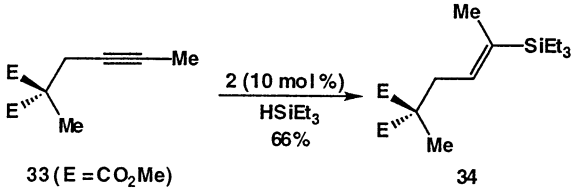
(18) (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 5, p 1037. (b) DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505. (c) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

Table 2. Cyclization/Hydrosilylation of Functionalized 1,6-Diynes Catalyzed by [Rh(BINAP)(COD)]$^+$ BF_4^- (2) in DCE at 70 °C Followed by [4+2] Cycloaddition with 4-Phenyl[1,2,4]triazole-3,5-dione at 0 °C for 30 min

entry	diyne	silane	carbocycle	yield (%)	isomer ratio
1	R = Me	$HSiMe_2Bn$	11	69	≥25:1[a]
2	R = Et	$HSiMe_2Ph$	25	54	≥25:1[a]
3	R = Piv		26	53	≥25:1[a]
4	R = Ac		27	45	≥25:1[a]
5	R = Me		28	58	≥25:1[a]
6			 29	45	≥25:1[a]
7			 30	45	≥25:1[a]
8	R = Ph		31	60	6:1[b]
9	R = $CONMe_2$		32	66	3:1[c]

[a] Single isomer detected by ^1H and ^{13}C NMR analysis. [b] Major isomer isolated in 45% yield. [c] Major isomer isolated in 40% yield.

hydrosilylation catalyzed by **2**. For example, reaction of diyne **1** and $HSiEt_3$ (1.7 M) catalyzed by **2** at 70 °C formed predominantly the dialkylidene cyclopentane **3** (Scheme 2), and therefore, conversion of **1** to **3** via the hydrometalation pathway would require predominant formation of rhodium alkenyl silyl intermediate **V** (Scheme 5). Conversely, conversion of **1** to **3** via the proposed silylmetalation pathway would proceed via rhodium alkenyl hydride intermediate **II** (Scheme 4). Although we cannot distinguish between the formation of intermediate **V** or **II** in the reaction of **1** with $HSiEt_3$ catalyzed by **2**, this information can be gleaned from the reaction of $HSiEt_3$ with dimethyl (2-butynyl)methylmalonate (**33**), which is sterically and electronically similar to diyne **1**, but which cannot undergo intramolecular carbometalation. Specifically, hydrosilylation of **33** via the hydrometalation pathway should deliver the silyl group to the internal C≡C carbon atom, while hydrosilylation of **33** via our proposed silylmetalation pathway should deliver the silyl group to the external C≡C carbon atom. Indeed, reaction of **33** with $HSiEt_3$ (1.7 M) catalyzed by **2** at 70 °C led to exclusive delivery of the silyl group to the external alkynyl carbon atom to form alkenyl silane **34** in 66% isolated yield (eq 3).

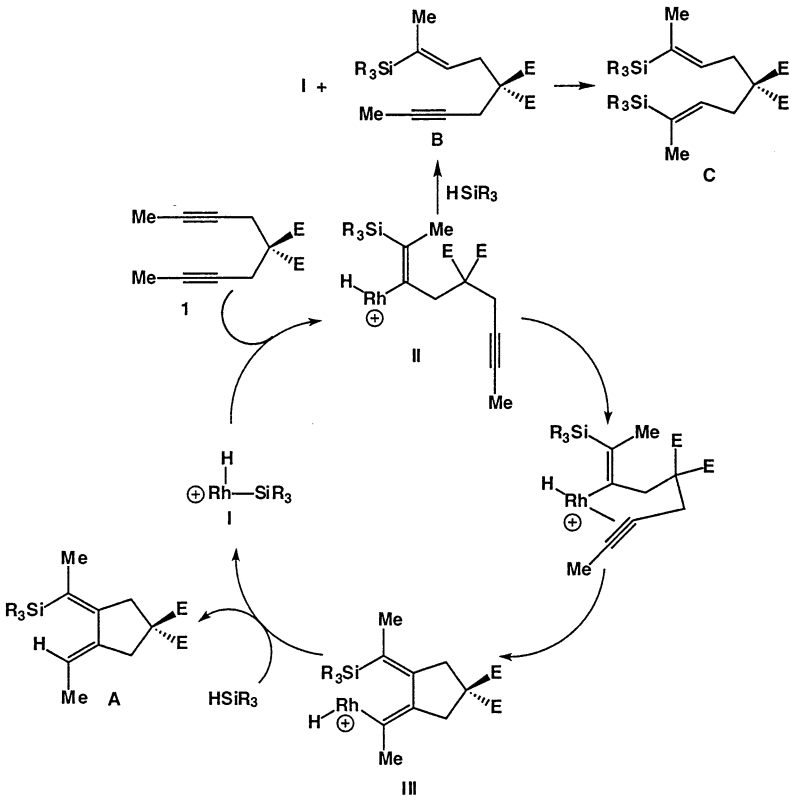


33 (E = CO_2Me) 34 eq 3

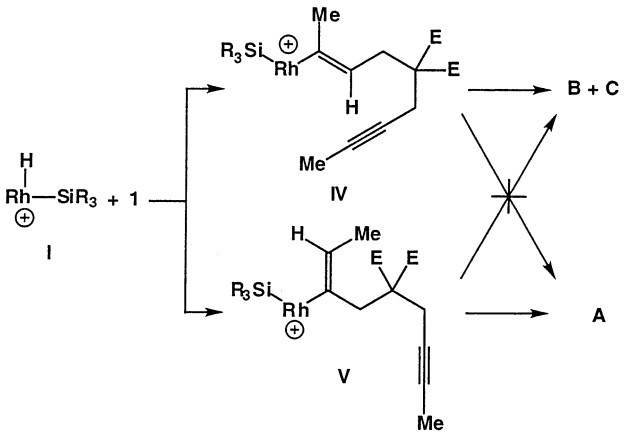
The ratio of silylated uncyclized:cyclization/hydrosilylation products (**B**+**C**:**A**) formed in the rhodium-catalyzed reaction of diynes with silanes depended on both the steric bulk and concentration of the silane. For

(19) A mechanism involving hydrometalation would also require that the **IV**:**V** ratio depend on silane concentration to account for the formation of disilylated uncyclized product **4** and cyclization/hydrosilylation product **5** in the reaction of **1** and $HSiMe_2Et$ catalyzed by **2** at high and low silane concentration, respectively.

Scheme 4



Scheme 5



example, under comparable conditions ([silane] = 1.0−1.7 M), rhodium-catalyzed reaction of **1** with $HSiEt_3$ formed predominantly the dialkylidene cyclopentane **3** (Scheme 2), while reaction of **1** with the sterically less hindered $HSiMe_2Et$ formed predominantly the disilylated uncyclized product **4** (eq 1). Conversely, slow addition of $HSiMe_2Et$ to a mixture of **1** and **2** formed predominantly the dialkylidene cyclopentane **5** (Table 1, entry 1). These observations are inconsistent with a mechanism involving direct C−H reductive elimination from rhodium alkenyl hydride species **II**,[20] and point to a mechanism involving silane-promoted C−H reductive elimination.[21] Silane-promoted reductive elimination of **II** could occur either via oxidative addition of the silane Si−H bond to generate the Rh(V) dihydro silyl intermediate **VI** that undergoes subsequent C−H reductive elimination (Scheme 6, path a) or via direct σ-bond metathesis of the Si−H bond of the silane with the Rh−C bond of **II** without formation of a discrete intermediate (Scheme 6, path b). Both the oxidative addition of silanes to neutral Rh(III) complexes to form Rh(V) complexes[22] and the silane-promoted C−H reductive elimination of Rh(III) alkyl hydride complexes have been documented.[23] Similarly, σ-bond metathesis of a Co−alkyl bond with the Si−H bond of a silane to form an alkane and a cobalt silyl compound has been forwarded as a pathway in olefin hydrosilylation catalyzed by cationic Co(III) complexes.[24]

In summary, the cationic rhodium complex $[Rh(BINAP)(COD)]^+ BF_4^-$ (**2**) catalyzes the cyclization/hydrosilylation of 1,6-diynes that possess internal alkynes to form silylated 1,2-dialkylidenecyclopentanes in moderate to good yield with high diastereoselectivity. The mechanism of rhodium-catalyzed cyclization/hydrosilylation likely involves initial silylmetalation of a C≡C bond of the diyne followed by intramolecular carbometalation and silane-promoted reductive elimination.

(20) We thank a reviewer for alerting our attention to this inconsistency.

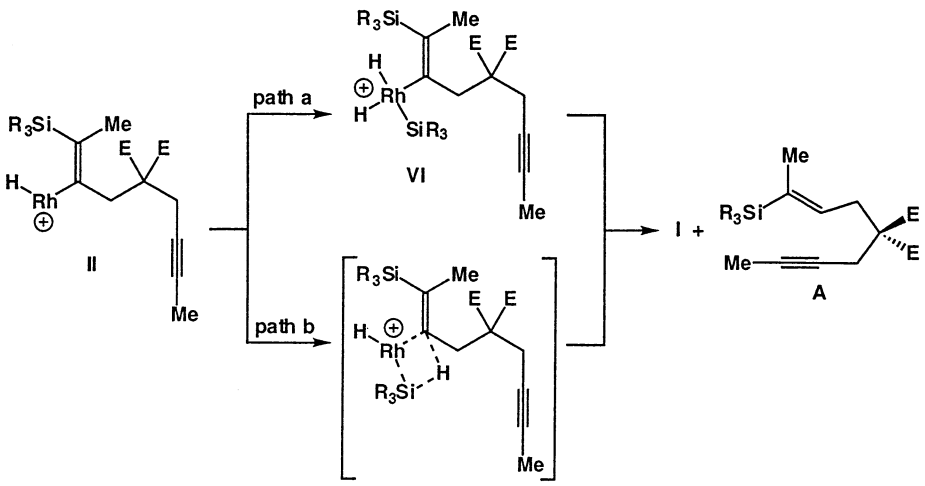
(21) The failure to obtain silylated products from the reaction of **1** with $HSiMe_2t$-Bu is presumably a result of the steric bulk of the silane. Sluggish oxidative addition of the Si−H bond of $HSiMe_2t$-Bu to rhodium due to unfavorable steric interaction may either preclude formation of the rhodium silyl hydride species **I** or prohibit reductive elimination from rhodium alkenyl intermediates **II** and **III**. In either case, cyclotrimerization presumably occurs in a reaction manifold separate from that which generates the silylated products.

(22) (a) Duckett, S. B.; Daddleton, D. M.; Jackson, S. A.; Peruttz, R. N.; Poliakoff, M.; Upmacis, R. K. *Organometallics* **1988**, *7*, 1526. (b) Duckett, S. B.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 28.

(23) (a) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (b) Nagashima, H.; Tatebe, K.; Ishibashi, T.; Nakaoka, A.; Sakakibara, J.; Itoh, K. *Organometallics* **1995**, *14*, 2868.

(24) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151.

Scheme 6



Experimental Section

General Methods. Catalytic reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained at 400 MHz for ^{1}H and at 100 MHz for ^{13}C in $CDCl_3$ at room temperature unless otherwise specified. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25-m poly(dimethylsiloxane) capillary column. Flash column chromatography was performed employing 200−400 mesh silica gel (EM) or ∼150 mesh neutral grade III alumina (Brockmann). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Silanes were used as received. CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. $[Rh(BINAP)(COD)]^+ BF_4^-$ (**2**) was prepared employing a published procedure.[25] The synthesis of diynes is described in the Supporting Information.

(*E*,*Z*)-1,1-Dicarbomethoxy-3-ethylidene-4-(1-triethylsilylethylidene)cyclopentane (3). A solution of $HSiEt_3$ (160 μL, 1.0 mmol), $[Rh(COD)(BINAP)]^+ BF_4^-$ (**2**) (46 mg, 0.050 mmol), and dimethyl 2,2-dibut-2-ynylmalonate (**1**) (118 mg, 0.50 mmol) in DCE (6.0 mL) was stirred at 70 °C for 1 h, cooled to room temperature, and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 50:1) gave **3** (135 mg, 77%) as a colorless oil. The stereochemistry of **3** was determined by ^{1}H−^{1}H NOESY analysis (Figure S1). Cross-peaks were observed between the vinylic hydrogen atom and the triethylsilyl methylene protons and between the vinylic methyl groups and the proximal ring methylene protons (Figure S1). TLC (hexanes−EtOAc = 10:1): R_f 0.32. ^{1}H NMR: δ 5.60 (tq, J = 2.0, 6.8 Hz, 1 H), 3.98 (s, 2 H), 3.97 (s, 2 H), 2.27 (d, J = 1.2 Hz, 2 H), 2.22 (t, J = 0.8 Hz, 2 H), 2.06 (s, 6 H), 1.68 (s, 3 H), 1.65 (d, J = 6.8 Hz, 3 H), 0.88 (t, J = 7.6 Hz, 9 H), 0.64 (dq, J = 0.8, 7.9 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 171.4, 152.0, 140.2, 125.6, 120.3, 67.4, 42.1, 37.9, 35.0, 21.2, 20.9, 15.0, 8.1, 5.0. IR (neat, cm^{-1}): 2952, 2910, 2878, 1742, 1373, 1226, 1035, 722. Anal. Calcd (found) for $C_{21}H_{36}O_4Si$: C, 66.27 (66.21); H, 9.53 (9.42).

Compounds **12**−**24** were synthesized using a procedure analogous to that used to synthesize **3**. Compounds **4** and **7** were synthesized using a procedure analogous to that used to synthesize **3** except that 0.6 mmol (1.0 M) silane was employed.

(*E*,*E*)-Dimethyl 2,2-Bis[3-(ethyldimethylsilyl)-2-butenyl]malonate (4). Colorless oil, 51%. TLC (hexanes−EtOAc = 10:1): R_f 0.56. ^{1}H NMR: δ 5.50 (tq, J = 7.0, 2.0 Hz, 2 H), 3.68 (s, 6 H), 2.68 (d, J = 7.2 Hz, 4 H), 1.62 (d, J = 1.6 Hz, 6 H), 0.87 (t, J = 8.0 Hz, 6 H), 0.50 (q, J = 8.0 Hz, 4 H), −0.02 (s, 12 H). ^{13}C{^{1}H} NMR: δ 172.1, 140.1, 132.7, 57.8, 52.6, 31.4, 15.1, 7.7, 6.6, −4.1. HRMS calcd (found) for $C_{21}H_{40}O_4Si_2$ (M^+): 412.2465 (412.2466).

(*E*,*Z*)-1,1-Dicarbomethoxy-3-ethylidene-4-(1-ethyldimethylsilylethylidene)cyclopentane (5). Ethyldimethylsilane (85 μL, 0.6 mmol) was added dropwise over 35 min to a solution of **1** (118 mg, 0.50 mmol) and **2** (46 mg, 0.050 mmol) in DCE (6.0 mL) at 70 °C. Concentration of the solution and chromatography of the residue (Al_2O_3; hexanes−EtOAc = 50:1) gave **5** (90 mg, 56%) as a colorless oil. TLC (hexanes−EtOAc = 10:1): R_f 0.44. ^{1}H NMR: δ 5.55 (tq, J = 2.2, 6.8 Hz, 1 H), 3.72 (s, 3 H), 2.98 (d, J = 1.2 Hz, 2 H), 2.90 (s, 2 H), 1.71 (s, 3 H), 1.69 (d, J = 7.2 Hz, 3 H), 0.68 (t, J = 7.8 Hz, 9 H), 0.61 (q, J = 7.6 Hz, 6 H), 0.07 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.7, 149.8, 139.1, 127.2, 120.8, 57.0, 53.1, 39.5, 36.9, 20.5, 15.0, 8.6, 7.9, −1.6. IR (neat, cm^{-1}): 2952, 1738, 1434, 1263, 1199, 1162, 1059, 827, 772. Anal. Calcd (found) for $C_{17}H_{28}O_4Si$: C, 62.92 (62.78); H, 8.70 (8.57).

2,2-Dicarbomethoxy-5-(2,2-dicarbomethoxy-4-hexynyl)-4,6,7-trimethylindan (6). Reaction of $HSiMe_2t$-Bu (42 μL, 0.30 mmol), **1** (59 mg, 0.25 mmol), and **2** (23 mg, 0.025 mmol) in DCE (3.0 mL) at 70 °C for 1 h followed by concentration of the solution and chromatography of the residue (SiO_2; hexanes−EtOAc = 50:1 → 5:1) gave **6** (39 mg, 66%) as a colorless oil. TLC (hexanes−EtOAc = 2:1): R_f 0.51. ^{1}H NMR: δ 3.74 (s, 6 H), 3.60 (s, 2 H), 3.58 (s, 6 H), 3.55 (s, 2 H), 3.51 (s, 2 H), 3.70 (q, J = 2.4 Hz, 2 H), 2.20 (s, 3 H), 2.18 (s, 3 H), 2.12 (s, 3 H), 1.78 (t, J = 2.4 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 172.8, 171.5, 137.3, 136.5, 136.1, 132.8, 131.5, 130.0, 79.3, 74.8, 59.4, 59.3, 53.3, 52.8, 41.0, 40.8, 31.7, 25.3, 17.6, 17.4, 17.2, 3.9. HRMS calcd (found) for $C_{26}H_{32}O_8$ (M^+): 472.2097 (472.2094).

(*E*,*Z*)-1,1-Dicarbomethoxy-3-ethylidene-4-(1-methyldiphenylsilylethylidene)cyclopentane (7). Colorless oil, 60%. TLC (hexanes−EtOAc = 10:1): R_f 0.25. ^{1}H NMR: δ 7.46−7.30 (m, 10 H), 5.30 (tq, J = 11.5, 2.0 Hz, 1 H), 3.75 (s, 3 H), 3.10 (d, J = 0.8 Hz, 2 H), 2.80 (s, 2 H), 1.74 (s, 3 H), 1.20 (d, J = 6.8 Hz, 3 H), 0.60 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.7, 152.8, 138.1, 137.7, 135.1, 132.6, 129.1, 128.0, 123.1, 57.0, 53.2, 39.9, 36.9, 31.6, 14.5, −1.5. IR (neat, cm^{-1}): 2951, 1735, 1428, 1262, 1201, 1164, 1110, 1064, 792, 728, 701. Anal. Calcd (found) for $C_{26}H_{30}O_4Si$: C, 71.85 (71.47); H, 6.96 (6.62).

Compounds 9 and 10. A solution of **1** (118 mg, 0.50 mmol), **2** (46 mg, 0.050 mmol), and $HSiMe_2Ph$ (85 μL, 0.6 mmol) in DCE (6.0 mL) was heated at 70 °C for 1.5 h and cooled to 0 °C. 4-Phenyl[1,2,4]triazole-3,5-dione (88, mg, 0.50 mmol) was added to the reaction mixture and the resulting solution was stirred at 0 °C for 30 min and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 5:1) gave **10** (198 mg, 73%) as a white solid and **9** (10 mg, 5%),

(25) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.

which was obtained in insufficient quantities to determine its physical nature. Compounds **11** and **24**−**31** were synthesized employing an analogous procedure.

For 9: TLC (hexanes−EtOAc = 2:1): R_f 0.77. ^{1}H NMR: δ 7.45−7.32 (m, 5 H), 5.58 (qt, J = 1.6, 7.2, Hz, 1 H), 3.69 (s, 6 H), 2.89 (d, J = 7.2 Hz, 2 H), 2.73 (q, J = 2.4 Hz, 3 H), 1.75 (t, J = 2.4 Hz, 3 H), 1.70 (d, J = 0.8 Hz, 3 H), 0.31 (s, 6 H). ^{13}C{^{1}H} NMR: δ 171.0, 140.1, 138.4, 134.3, 134.0, 129.2, 128.0, 79.1, 73.9, 57.6, 52.9, 31.3, 23.5, 15.2, 3.8, −3.2.

For 10: Mp 122−124 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.45. ^{1}H NMR: δ 7.50−7.30 (m, 10 H), 4.37 (q, J = 6.4 Hz, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.10−2.84 (m, 4 H), 1.88 (s, 3 H), 1.23 (d, J = 6.4 Hz, 3 H), 0.48 (s, 3 H), 0.42 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.1, 172.0, 152.8, 151.9, 135.5, 134.9, 134.7, 131.6, 130.3, 129.4, 129.2, 128.2, 128.1, 125.7, 58.2, 58.1, 40.9, 40.8, 20.8, 15.9, −2.2, −2.8. IR (neat, cm^{-1}): 2989, 2953, 1712, 1504, 1415, 1262, 1201, 1073, 812, 705. Anal. Calcd (found) for $C_{29}H_{33}N_3O_6Si$: C, 63.60 (63.45); H, 6.07 (5.93).

Compound 11. White solid, 69%. Mp 123−125 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.39. ^{1}H NMR: δ 7.50−6.96 (m, 10 H), 4.54 (q, J = 6.0 Hz, 1 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.22−3.03 (m, 4 H), 2.24 (d, J = 13.6 Hz, 1 H), 2.17 (d, J = 13.6 Hz, 1 H), 1.92 (s, 3 H), 1.32 (d, J = 6.4 Hz, 3 H), 0.06 (s, 3 H), 0.03 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.1, 171.9, 153.0, 152.6, 138.5, 135.0, 131.5, 129.6, 129.5, 128.8, 128.6, 128.5, 126.0, 124.8, 58.5, 58.3, 53.5, 52.0, 40.9, 40.8, 24.7, 20.4, 15.8, −3.3. IR (neat, cm^{-1}): 2959, 1735, 1710, 1599, 1413, 1262, 1202, 1167, 1073, 815, 765. Anal. Calcd (found) for $C_{30}H_{35}N_3O_6Si$: C, 64.15 (63.96); H, 6.28 (6.13).

(*E*,*Z*)-1,1-Dicarbomethoxy-3-propylidene-4-(1-triethylsilylpropylidene)cyclopentane (12). Colorless oil, 56%. TLC (hexanes−EtOAc = 10:1): R_f 0.45. ^{1}H NMR: δ 5.59 (tt, J = 7.6, 2.0 Hz, 1 H), 3.71 (s, 3 H), 3.03 (s, 3 H), 2.90 (d, J = 1.6 Hz, 2 H), 2.12 (q, J = 7.6 Hz, 2 H), 2.08 (pentet, J = 7.6 Hz, 2 H), 1.01 (t, J = 7.8 Hz, 3 H), 0.92 (t, J = 7.8 Hz, 3 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.67 (q, J = 7.6 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 172.6, 150.4, 138.0, 132.8, 127.8, 57.1, 53.1, 38.9, 36.6, 27.2, 23.0, 14.6, 14.0, 8.1, 5.2. IR (neat, cm^{-1}): 2956, 2873, 1739, 1254, 726. Anal. Calcd (found) for $C_{21}H_{36}O_4Si$: C, 66.27 (66.41); H, 9.53 (9.59).

(*E*,*Z*)-1,1-Dicarbomethoxy-3-hexylidene-4-(1-triethylsilylhexylidene)cyclopentane (13). Colorless oil, 60%. TLC (hexanes−EtOAc = 10:1): R_f 0.54. ^{1}H NMR: δ 5.60 (t, J = 7.4 Hz, 1 H), 3.71 (s, 6 H), 3.02 (s, 2 H), 2.90 (s, 2 H), 2.07 (t, J = 7.2 Hz, 2 H), 2.05 (q, J = 7.2 Hz, 2 H), 1.42−1.27 (m, 12 H), 0.89 (t, J = 6.4 Hz, 6 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.66 (q, J = 7.8 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 172.6, 150.5, 138.3, 131.4, 126.4, 57.1, 53.1, 39.2, 36.8, 34.7, 32.7, 32.1, 30.0, 29.9, 29.2, 23.0, 22.9, 14.5, 14.4, 8.2, 5.2. IR (neat, cm^{-1}): 2953, 2867, 1739, 1258, 1199, 1161, 726. Anal. Calcd (found) for $C_{27}H_{48}O_4Si$: C, 69.78 (70.06); H, 10.41 (10.55).

(*E*,*Z*)-1,1-Dicarbomethoxy-3-propylidene-4-[1-(triethylsilyl)ethylidene]cyclopentane (14). Colorless oil, 65%. TLC (hexanes−EtOAc = 10:1): R_f 0.50. ^{1}H NMR: δ 5.54 (tt, J = 2.0, 7.4 Hz, 1 H), 3.71 (s, 6 H), 2.98 (d, J = 1.2 Hz, 2 H), 2.91 (s, 2 H), 2.07 (quintet, J = 7.6 Hz, 2 H), 1.71 (s, 3 H), 1.00 (t, J = 7.6 Hz, 3 H), 0.87 (t, J = 8.0 Hz, 9 H), 0.65 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 172.6, 150.6, 137.9, 127.6, 125.5, 57.0, 53.1, 39.5, 37.0, 23.0, 20.8, 14.1, 8.0, 4.9. IR (neat, cm^{-1}): 2953, 2873, 1739, 1434, 1257, 1200, 1162, 1065, 1106, 726. Anal. Calcd (found) for $C_{20}H_{34}O_4Si$: C, 65.53 (65.43); H, 9.35 (9.45).

(*E*,*Z*)-3-Ethylidene-1,1-bis(trimethylacetoxymethyl)-4-(1-triethylsilylethylidene)cyclopentane (16). Colorless oil, 72%. TLC (hexanes−EtOAc = 10:1): R_f 0.62. ^{1}H NMR: δ 5.60 (tq, J = 2.1, 6.9 Hz, 1 H), 3.98 (d, J = 11.2 Hz, 2 H), 3.94 (d, J = 10.8 Hz, 2 H), 2.28 (d, J = 1.2 Hz, 2 H), 2.24 (s, 2 H), 1.68 (s, 3 H), 1.65 (d, J = 6.8 Hz, 3 H), 1.20 (s, 18 H), 0.89 (t, J = 7.6 Hz, 9 H), 0.65 (q, J = 7.6 Hz, 6 H).^{13}C{^{1}H} NMR: δ 178.6, 152.2, 140.3, 125.5, 120.3, 67.2, 42.6, 39.3, 37.6, 34.9, 27.5, 20.8, 15.0, 8.1, 5.0. IR (neat, cm^{-1}): 2957, 2808, 2877, 1732, 1478, 1282, 1145, 1001, 723. Anal. Calcd (found) for $C_{27}H_{48}O_4Si$: C, 69.78 (69.66); H, 10.41 (10.09).

(*E*,*Z*)-1,1-Bis(acetoxymethyl)-3-ethylidene-4-(1-triethylsilylethylidene)cyclopentane (17). Colorless oil, 68%. TLC (hexanes−EtOAc = 10:1): R_f 0.23. ^{1}H NMR: δ 5.60 (tq, J = 2.0, 6.8 Hz, 1 H), 3.98 (s, 2 H), 3.97 (s, 2 H), 2.27 (d, J = 1.2 Hz, 2 H), 2.22 (t, J = 0.8 Hz, 2 H), 2.06 (s, 6 H), 1.68 (s, 3 H), 1.65 (d, J = 6.8 Hz, 3 H), 0.88 (t, J = 7.6 Hz, 9 H), 0.64 (dq, J = 0.8, 7.9 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 171.4, 152.0, 140.2, 125.6, 120.3, 67.4, 42.1, 37.9, 35.0, 21.2, 20.9, 15.0, 8.1, 5.0. IR (neat, cm^{-1}): 2952, 2910, 2878, 1742, 1373, 1226, 1035, 722. Anal. Calcd (found) for $C_{21}H_{36}O_4Si$: C, 66.27 (66.21); H, 9.53 (9.42).

(*E*,*Z*)-3-Ethylidene-1,1-dimethoxymethyl-4-(1-triethylsilylethylidene)cyclopentane (18). Colorless oil, 70%. TLC (hexanes−EtOAc = 10:1): R_f 0.64. ^{1}H NMR: δ 5.56 (tq, J = 2.2, 6.8 Hz, 1 H), 3.34 (s, 6 H), 3.24 (s, 4 H), 2.22 (d, J = 1.2 Hz, 2 H), 2.17 (t, J = 1.6 Hz, 2 H), 1.68 (s, 3 H), 1.65 (d, J = 6.8 Hz, 3 H), 0.89 (t, J = 7.6 Hz, 9 H), 0.65 (q, J = 7.8 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 153.8, 141.6, 124.3, 119.4, 76.6, 59.6, 43.9, 38.2, 35.1, 20.8, 14.9, 8.1, 5.0. IR (neat, cm^{-1}): 2950, 2873, 1457, 1198, 1111, 1005, 726. Anal. Calcd (found) for $C_{19}H_{36}O_2Si$: C, 70.31 (70.13); H, 11.18 (11.20).

(*E*,*Z*)-1,1-Dibenzyloxymethyl-3-ethylidene-4-(1-triethylsilylethylidene)cyclopentane (19). Colorless oil, 62%. TLC (hexanes−EtOAc = 10:1): R_f 0.47. ^{1}H NMR: δ 7.30−7.23 (m, 10 H), 5.53 (q, J = 6.8 Hz, 1 H), 4.49 (s, 4 H), 3.37 (s, 4 H), 2.26 (s, 2 H), 2.21 (s, 2 H), 1.66 (s, 3 H), 1.62 (d, J = 7.2 Hz, 3 H), 0.86 (t, J = 8.0 Hz, 9 H), 0.62 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 154.0, 141.7, 139.3, 128.6, 127.8, 127.7, 124.2, 119.3, 74.1, 73.6, 44.2, 38.4, 35.2, 20.9, 15.0, 8.1, 5.0. IR (neat, cm^{-1}): 3377, 2953, 2873, 1720, 1453, 1361, 1272, 1097, 1026, 736, 698. Anal. Calcd (found) for $C_{31}H_{44}O_2Si$: C, 78.10 (78.01); H, 9.30 (9.14).

(*E*,*Z*)-1-Carbomethoxy-3-ethylidene-1-phenyl-4-(1-triethylsilylethylidene)cyclopentane (20). Colorless oil, 73%. TLC (hexanes−EtOAc = 10:1): R_f 0.62. ^{1}H NMR: δ 7.40−7.24 (m, 5 H), 5.63 (q, J = 6.8 Hz, 1 H), 3.62 (s, 3 H), 3.57 (d, J = 16.0 Hz, 1 H), 3.50 (d, J = 14.0 Hz, 1 H), 2.72 (d, J = 16.0 Hz, 1 H), 2.64 (d, J = 14.0 Hz, 1 H), 1.80 (s, 3 H), 1.74 (d, J = 6.8 Hz, 3 H), 0.90 (t, J = 7.8 Hz, 9 H), 0.68 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 176.2, 152.1, 143.6, 140.3, 128.7, 127.2, 126.9, 124.8, 119.6, 55.2, 52.8, 42.5, 39.3, 20.9, 14.9, 8.0, 4.9. IR (neat, cm^{-1}): 2950, 2916, 2873, 1732, 1600, 1166, 728, 967. Anal. Calcd (found) for $C_{23}H_{34}O_2Si$: C, 74.54 (74.54); H, 9.25 (9.70).

(*E*,*Z*)-1-Carbomethoxy-3-ethylidene-1-dimethycarbamoyl-4-(1-triethylsilylethylidene)cyclopentane (21). Colorless oil, 70%. TLC (hexanes−EtOAc = 2:1): R_f 0.42. ^{1}H NMR: δ 5.56 (q, J = 6.8 Hz, 1 H), 3.72 (s, 3 H), 3.08−2.79 (m, 4 H), 2.95 (s, 3 H), 2.87 (s, 3 H), 1.70 (s, 3 H), 1.68 (d, J = 7.2 Hz, 3 H), 0.87 (t, J = 7.6 Hz, 9 H), 0.63 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 174.8, 170.9, 150.9, 139.5, 124.8, 119.8, 55.9, 53.1, 10.0, 37.8, 37.2, 20.6, 14.8, 8.0, 4.9. IR (neat, cm^{-1}): 2950, 1735, 1650, 1386, 725. Anal. Calcd (found) for $C_{20}H_{35}NO_3Si$: C, 65.71 (65.59); H, 9.65 (9.52).

(*Z*,*E*)-3-Ethylidene-1-(toluene-4-sulfonyl)-4-(1-triethylsilylethylidene)pyrrolidine (22). Pale yellow oil, 70%. TLC (hexanes−EtOAc = 10:1): R_f 0.36. ^{1}H NMR: δ 7.72 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 5.61 (tq, J = 2.0, 7.2 Hz, 1 H), 3.95 (s, 2 H), 3.94 (s, 2 H), 2.42 (s, 3 H), 1.67 (s, 3 H), 1.64 (d, J = 7.2 Hz, 3 H), 0.83 (t, J = 7.6 Hz, 9 H), 0.61 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 145.9, 143.8, 135.4, 134.0, 130.0, 128.0, 121.2, 52.5, 50.3, 21.7, 21.0, 15.2, 7.9, 4.5. IR (neat, cm^{-1}): 2951, 2867, 1597, 1458, 1349, 1163, 1098, 811, 727, 664. Anal. Calcd (found) for $C_{21}H_{33}NO_2SSi$: C, 64.40 (64.28); H, 8.49 (8.38).

(*Z*,*E*)-Triethyl-[1-(4-ethylidene-3-dihydrofuranylidene)-ethyl]silane (23). Pale yellow oil, 40%. TLC (hexanes−EtOAc = 10:1): R_f 0.57. ^{1}H NMR: δ 5.73 (q, J = 6.8 Hz, 1 H), 4.47 (d, J = 1.2 Hz, 2 H), 4.46 (s, 2 H), 1.70 (s, 3 H), 1.69 (d, J = 6.8 Hz, 3 H), 0.92 (t, J = 7.6 Hz, 9 H), 0.71 (q, J = 7.6 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 149.0, 138.1, 124.7, 118.9, 72.6, 70.5, 20.9,

15.4, 8.0, 4.4. IR (neat, cm^{-1}): 2952, 2873, 1458, 1072, 809, 731. Anal. Calcd (found) for $C_{14}H_{26}OSi$: C, 70.52 (70.37); H, 10.99 (10.83).

(*E*,*Z*)-1,1,2,2-Tetracarboethoxy-4-ethylidene-5-(1-triethylsilylethylene)cyclohexane (24). Colorless oil, 29%. TLC (hexanes−EtOAc = 2:1): R_f 0.75. ^{1}H NMR: δ 5.40 (q, J = 6.8 Hz, 1 H), 4.21−4.16 (m, 8 H), 2.96 (s, 4 H), 1.68 (s, 3 H), 1.60 (d, J = 6.8 Hz, 3 H), 1.26 (t, J = 7.2 Hz, 6 H), 1.25 (t, J = 7.2 Hz, 6 H), 0.87 (t, J = 8.0 Hz, 9 H), 0.55 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 148.5, 137.3, 129.0, 124.2, 61.9, 61.8, 81.0, 59.7, 35.0, 32.3, 18.6, 14.2, 13.6, 8.1, 5.2. IR (neat, cm^{-1}): 2959, 2910, 2880, 1737, 1366, 1197, 1096, 1042, 865, 728. Anal. Calcd (found) for $C_{28}H_{46}O_8Si$: C, 62.42 (62.31); H, 8.61 (8.47).

Compound 25. White solid, 54%. Mp 135−137. TLC (hexanes−EtOAc = 2:1): R_f 0.48. ^{1}H NMR: δ 7.48−7.31 (m, 10 H), 5.34 (s, 3 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.10−2.91 (m, 5 H), 2.24 (qdd, J = 5.2, 7.6, 14.8 Hz, 1 H), 1.74 (qd, J = 7.2, 14.4 Hz, 1 H), 1.61 (qdd, J = 3.2, 5.6, 8.0 Hz, 1 H), 0.91 (t, J = 7.0 Hz, 3 H), 0.73 (t, J = 7.4 Hz, 3 H), 0.45 (s, 3 H), 0.43 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.3, 172.0, 151.1, 151.0, 135.5, 134.6, 131.7, 130.2, 129.2, 129.0, 128.2, 128.1, 125.7, 62.2, 58.1, 55.4, 53.4, 41.3, 40.8, 25.3, 22.8, 8.8, 8.6, −2.4, −3.0. IR (neat, cm^{-1}): 2959, 1735, 1706, 1503, 1413, 1261, 1199, 1071. Anal. Calcd (found) for $C_{31}H_{37}N_3O_6Si$: C, 64.67 (64.82); H, 6.48 (6.56).

Compound 26. White solid, 53% yield. Mp 178−180 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.63. ^{1}H NMR: δ 7.49−7.32 (m, 10 H), 4.38 (q, J = 6.0 Hz, 1 H), 3.98 (s, 2 H), 3.82 (d, J = 10.8 Hz, 1 H), 3.62 (d, J = 11.2 Hz, 1 H), 2.39 (d, J = 16.4 Hz, 1 H), 2.26 (d, J = 17.2 Hz, 1 H), 2.11 (d, J = 16.0 Hz, 1 H), 1.91 (d, J = 16.0 Hz, 1 H), 1.88 (s, 3 H), 1.25 (d, J = 6.4 Hz, 3 H), 1.21 (s, 3 H), 1.17 (s, 3 H), 0.48 (s, 3 H), 0.44 (s, 3 H). ^{13}C{^{1}H} NMR: δ 178.5, 178.4, 153.0, 152.2, 135.9, 135.8, 134.6, 131.6, 130.4, 129.8, 129.3, 128.4, 128.3, 125.8, 67.1, 66.9, 58.1, 51.8, 44.5, 39.5, 39.3, 39.2, 38.9, 27.6, 27.5, 21.3, 16.0, −1.9, −2.8. IR (neat, cm^{-1}): 2983, 1710, 1411, 1281, 1144. Anal. Calcd (found) for $C_{37}H_{49}N_3O_6Si$: C, 67.34 (67.22); H, 7.48 (7.22).

Compound 27. Pale yellow oil, 45%. TLC (hexanes−EtOAc = 2:1): R_f 0.36. ^{1}H NMR: δ 7.49−7.31 (m, 10 H), 4.36 (q, J = 5.6 Hz, 1 H), 4.01 (d, J = 10.8 Hz, 1 H), 3.97 (d, J = 11.2 Hz, 1 H), 3.84 (d, J = 11.2 Hz, 1 H), 3.73 (d, J = 11.2 Hz, 1 H), 2.34 (d, J = 16.4 Hz, 1 H), 2.22 (d, J = 17.2 Hz, 1 H), 2.14 (d, J = 17.2 Hz, 1 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.94 (d, J = 17.6 Hz, 1 H), 1.88 (s, 3 H), 1.25 (d, J = 6.8 Hz, 3 H), 0.48 (s, 3 H), 0.44 (s, 3 H). ^{13}C{^{1}H} NMR: δ 171.3, 171.1, 153.0, 152.2, 135.9, 135.6, 134.6, 131.6, 130.3, 129.8, 129.3, 128.3, 125.8, 67.4, 67.0, 58.1, 51.7, 44.1, 39.7, 39.0, 21.2, 21.1, 16.0, −2.0, −2.7. IR (neat, cm^{-1}): 2971, 1740, 1708, 1502, 1412, 1229, 1037, 811. Anal. Calcd (found) for $C_{31}H_{37}N_3O_6Si$: C, 64.67 (64.49); H, 6.48 (6.39).

Compound 28. Colorless oil, 58%. TLC (hexanes−EtOAc = 2:1): R_f 0.57. ^{1}H NMR: δ 7.51−7.26 (m, 10 H), 4.34 (q, J = 6.4 Hz, 1 H), 3.34 (s, 3 H), 3.33 (s, 3 H), 3.27 (s, 2 H), 3.11 (d, J = 8.8 Hz, 1 H), 3.06 (d, J = 8.8 Hz, 1 H), 2.28 (d, J = 17.6 Hz, 1 H), 2.24 (d, J = 17.2 Hz, 1 H), 2.09 (d, J = 17.2 Hz, 1 H), 2.01 (d, J = 16.4 Hz, 1 H), 1.87 (s, 3 H), 1.23 (d, J = 6.4 Hz, 3 H), 0.46 (s, 3 H), 0.45 (s, 3 H). ^{13}C{^{1}H} NMR: δ 152.9, 152.2, 136.1, 135.6, 134.7, 131.7, 130.1, 129.9, 129.2, 128.2, 125.8, 76.7, 76.3, 59.6, 59.4, 58.2, 51.9, 46.1, 39.7, 39.0, 21.3, 16.0, −2.0, −2.5. IR (neat, cm^{-1}): 2965, 1762, 1708, 1410, 1110. Anal. Calcd (found) for $C_{29}H_{37}N_3O_4Si$: C, 67.02 (66.86); H, 7.18 (7.06).

Compound 29. White solid, 45%. Mp 173−176 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.42. ^{1}H NMR: δ 7.72−7.25 (m, 14 H), 4.25 (q, J = 5.2 Hz, 1 H), 4.17 (ddd, J = 2.8, 5.4, 12.8 Hz, 1 H), 4.11−3.99 (m, 2 H), 3.81 (tdd J = 2.8, 5.2, 13.2 Hz, 1 H), 2.47 (s, 3 H), 1.82 (s, 3 H), 1.17 (d, J = 6.4 Hz, 3 H), 0.38 (s, 3 H), 0.36 (s, 3 H). ^{13}C{^{1}H} NMR: δ 152.9, 151.8, 144.4, 134.8, 134.4, 134.1, 133.8, 131.3, 130.5, 129.3, 128.4, 128.3, 127.9, 127.4, 125.7, 57.3, 54.9, 54.5, 50.0, 21.9, 20.8, 16.2, −2.3, −3.2. IR (neat, cm^{-1}): 1763, 1708, 1502, 1412, 1347, 1164, 811, 668. Anal. Calcd (found) for $C_{31}H_{34}N_4O_4SSi$: C, 63.45 (63.59); H, 5.84 (5.79).

Compound 30. White solid, 45%. Mp 59−61 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.44. ^{1}H NMR: δ 7.49−7.31 (m, 10 H), 4.36 (q, J = 6.4 Hz, 1 H), 3.66 (d, J = 11.6 Hz, 1 H), 3.62 (d, J = 11.6 Hz, 1 H), 3.41 (d, J = 11.2 Hz, 1 H), 3.37 (d, J = 11.2 Hz, 1 H), 2.38−2.17 (m, 4 H), 1.88 (s, 3 H), 1.41 (s, 6 H), 1.25 (d, J = 6.4 Hz, 3 H), 0.48 (s, 3 H), 0.43 (s, 3 H). ^{13}C{^{1}H} NMR: δ 153.0, 152.2, 136.0, 135.4, 134.6, 131.6, 130.2, 130.0, 129.3, 128.2, 125.8, 98.2, 69.4, 69.1, 58.1, 51.9, 40.8, 40.1, 39.7, 25.0, 23.2, 21.3, 16.0, −2.0, −2.7. IR (neat, cm^{-1}): 2998, 2928, 1769, 1708, 1411. Anal. Calcd (found) for $C_{30}H_{37}N_3O_4Si$: C, 67.77 (67.65); H, 7.01 (6.96).

Compound 31. White solid, 45% as a single diastereomer. Mp 79−82 °C. TLC (hexanes−EtOAc = 2:1): R_f 0.57. ^{1}H NMR: δ 7.45−7.20 (m, 15 H), 4.39 (q, J = 6.0 Hz, 1 H), 3.65 (s, 3 H), 3.46 (d, J = 16.0 Hz, 1 H), 3.38 (d, J = 16.0 Hz, 1 H), 2.89 (d, J = 17.2 Hz, 1 H), 2.84 (d, J = 16.8 Hz, 1 H), 1.84 (s, 3 H), 1.17 (s, 3 H), 0.47 (s, 3 H), 0.39 (s, 3 H). ^{13}C{^{1}H} NMR: δ 176.0, 152.7, 152.0, 142.9, 135.7, 135.5, 134.7, 131.6, 131.0, 130.2, 129.2, 128.9, 128.2, 128.1, 127.5, 126.9, 125.6, 58.2, 57.4, 53.1, 51.9, 43.1, 43.0, 20.8, 15.8, −2.3, −2.6. IR (neat, cm^{-1}): 2977, 2953, 1764, 1503, 1268, 911, 701, 647. Anal. Calcd (found) for $C_{33}H_{35}N_3O_4Si$: C, 70.06 (70.09); H, 6.24 (6.31).

Compound 32. Pale yellow solid, 40% as a single diastereomer. Mp 184−187 °C. TLC (hexanes−EtOAc = 1:2): R_f 0.55. ^{1}H NMR: δ 7.51−7.26 (m, 10 H), 4.37 (q, J = 6.4 Hz, 1 H), 3.76 (s, 3 H), 3.21 (d, J = 16.4 Hz, 1 H), 3.02 (s, 3 H), 2.99 (partially obscured, 2 H), 2.88 (d, J = 16.4 Hz, 1 H), 2.73 (s, 3 H), 1.90 (s, 3 H), 1.25 (d, J = 6.4 Hz, 3 H), 0.47 (s, 3 H), 0.44 (s, 3 H). ^{13}C{^{1}H} NMR: δ 174.3, 170.0, 152.8, 151.8, 135.9, 134.7, 134.3, 131.6, 130.1, 129.2, 129.1, 128.2, 128.1, 125.7, 58.1, 57.1, 53.4, 42.4, 41.7, 37.3, 20.8, 16.0, −2.2, −3.0. IR (neat, cm^{-1}): 2953, 1762, 1708, 1650, 1400, 1261, 812, 737. Anal. Calcd (found) for $C_{30}H_{36}N_4O_5Si$: C, 64.26 (63.97); H, 6.47 (6.39).

Dimethyl Methyl-2-[3-(triethylsilyl)allyl]malonate (34). Colorless oil, 66% yield. TLC (hexanes−EtOAc = 10:1): R_f 0.45. ^{1}H NMR: δ 5.53 (qt, J = 1.6, 7.2 Hz, 1 H), 3.70 (s, 6 H), 2.70 (d, J = 7.2 Hz, 2 H), 1.65 (d, J = 2.0 Hz, 3 H), 1.39 (s, 3 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.55 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 172.9, 138.2, 133.8, 54.0, 52.7, 34.5, 20.2, 15.5, 7.7, 2.8. IR (neat, cm^{-1}): 2952, 2913, 2875, 1737, 1457, 1377, 1291, 1243, 1203, 1150, 1112. HRMS Calcd (found) for $C_{16}H_{31}O_4Si$ (MH^+): 315.1983 (315.1992).

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for new diynes, and the ^{1}H−^{1}H NOESY spectrum of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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