Palladium-Catalyzed Ring-Opening Cyclization/ Hydrosilylation of 1-Cyclopropyl-1,6-heptadienes to Form (*E*)-1-Butenyl Cyclopentanes

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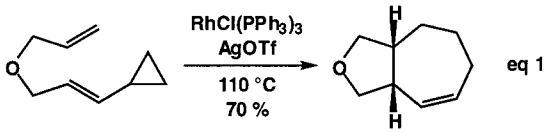
Reaction of 4,4-dicarbomethoxy-1-cyclopropyl-1,6-heptadiene (**3**) and $HSiMe_2OSiPh_2t$-Bu catalyzed by a 1:1 mixture of (phen)Pd(Me)Cl (**2**) (phen = 1,10-phenanthroline) and $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$] in CH_2Cl_2 at 0 °C for 12 h formed (*E*)-*trans*-3-(1-butenyl)-4-(3-*tert*-butyl-1,1-dimethyl-3,3-diphenyldisiloxymethyl)-1,1-dicarbomethoxycyclopentane (**4**) in 93% isolated yield as a 25:1 mixture of isomers. Reaction of 4,4-dicarbomethoxy-1-cyclobutyl-1,6-heptadiene (**12a**) and $HSiMe_2OSiPh_2t$-Bu (0.13 M) catalyzed by **2**/$NaBAr_4$ formed a 1.9:1 mixture of 1-pentenyl- (**13a**) and cyclobutylmethyl- (**14a**) cyclopentanes in 73% combined yield.

Introduction

Vinylcyclopropanes are versatile synthetic intermediates that undergo thermal isomerization under forcing conditions to form 1,3-dienes and/or cyclopentenes.[1] In comparison, photolytic or acid-catalyzed isomerization of vinylcyclopropanes occurs at considerably lower temperatures.[1] Vinylcyclopropanes also undergo isomerization in the presence of transition metal complexes under mild conditions. For example, $PdCl_2(CH_3CN)_2$ reacts with vinylcyclopropanes at room temperature to form π-allyl palladium complexes resulting from net addition of Pd−Cl across the cyclopropyl C−C bond.[2] Ni(0),[3] Rh(I),[4] and Pt(II)[5] complexes catalyze the ring-opening isomerization of vinylcyclopropanes to form predominantly 1,3-dienes. Conversely, vinylcyclopropanes that possess an additional double bond undergo Ni(0)-,[6] Rh(I)-,[7] and Pd(0)-catalyzed[8] ring-expanding isomerization to form cyclopentenes. Related to these processes are the Ru-catalyzed [5+2] cycloaddition of vinylcyclopropanes with alkynes[9] and the Rh-catalyzed [5+2] cycloaddition of vinylcyclopropanes with alkenes,[10] alkynes,[11] and allenes (eq 1).[12]



eq 1

We have recently reported the cyclization/hydrosilylation of functionalized dienes catalyzed by cationic palladium phenanthroline[13] and pyridine−oxazoline complexes.[14] For example, reaction of dimethyl diallylmalonate and dimethylphenylsilane catalyzed by [(phen)Pd(Me)OEt_2]$^+BAr_4^-$ [phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$] (5 mol %) in CH_2Cl_2 at 0 °C gave the silylated carbocycle **1** in 93% as a 53:1 mixture of diastereomers (Scheme 1).[13a] Given the established reactivity of vinylcyclopropanes toward transition metal complexes, we considered that a 1-cyclopropyl-1,6-heptadiene might undergo palladium-catalyzed cyclization/hydrosilylation to form products resulting from ring-opening of the cyclopropyl group. Here we report that 1-cyclopropyl-1,6-heptadienes undergo ring-opening cyclization/hydrosilylation to form (*E*)-(1-butenyl)cyclopentanes.

Results and Discussion

We began our study employing the known cyclopropyl diene **3** and the bulky disiloxane $HSiMe_2OTBDPS$ (TBDPS = $SiPh_2t$-Bu), which has been successfully employed in asymmetric diene cyclization/hydrosilylation.[14c] The active cationic palladium catalyst was generated in situ from mixtures of (phen)Pd(Me)Cl (**2**)

(1) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev*. **1988**, *17*, 229.
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(5) Doyle, M. R.; van Leusen, D. *J. Org. Che*m. **1982**, *47*, 5326.
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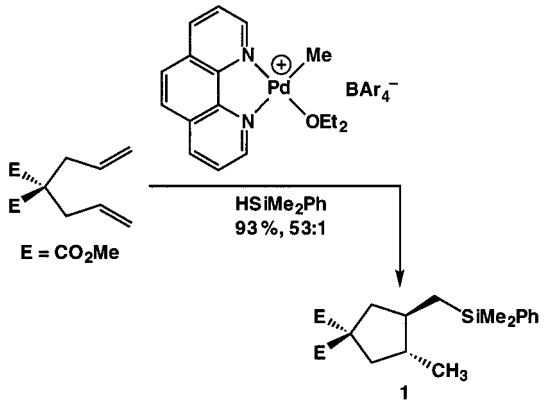
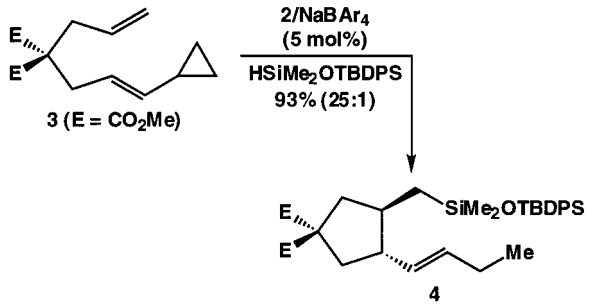
Scheme 1



Scheme 2



and $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$]. Reaction of **3** and $HSiMe_2OTBDPS$ catalyzed by **2**/$NaBAr_4$ (5 mol %) in CH_2Cl_2 at 0 °C for 12 h led to complete consumption of the diene. Concentration of the solution and chromatography of the residue gave the (*E*)-(1-butenyl)cyclopentane **4** in 93% yield as a 25:1 mixture of isomers (Scheme 2).[15] The expected trans stereochemistry of ring closure was indicated by the upfield doublet of doublets at δ 0.31 (J = 3.6, 14.8 Hz) in the ^{1}H NMR spectrum corresponding to one of the diastereotopic protons on the exocyclic silyl methylene group.[16] The *E*-stereochemistry of the exocyclic butenyl group was established by the large (J = 15.2 Hz) coupling constant of the alkenyl protons.

Cyclopropyl diene **3** also reacted with triethylsilane and benzyldimethylsilane to form the (*E*)-(1-butenyl)-cyclopentanes **5** and **6**, respectively, although both the yield and diastereoselectivity of ring-opening cyclization/hydrosilylation were diminished relative to **4** (Table 1, entries 1 and 2). Reaction of **3** with $DSiEt_3$ led to the isolation of **5**-d_1 in 78% yield as a 13:1 mixture of isomers (Table 1, entry 3). ^{13}C NMR analysis of **5**-d_1 revealed exclusive incorporation of deuterium into the terminal methyl group of the butenyl chain.[17] Cyclopropyl dienes that possessed homoallylic pivaloate ester (**7**) or acetoxy (**8**) groups also underwent ring-opening cyclization/hydrosilylation to form the corresponding (*E*)-(1-butenyl)cyclopentanes **9**−**11** with good diastereoselectivity (Table 1, entries 4−6).

Although a cyclobutyl ring possesses only slightly less strain (∼1 kcal/mol) than does a cyclopropyl ring, extension of ring-opening cyclization/hydrosilylation to 1-cyclobutyl-1,6-heptadienes was only partially successful. For example, reaction of the malonate-derived cyclobutyl diene **12a** and $HSiMe_2OTBDPS$ (0.13 M) led to the isolation of a 2:1 mixture of ring-opened (**13a**) and cyclobutylmethyl (**14a**) products in 73% combined yield (Scheme 3). Cyclization/hydrosilylation of **12a** employing a 7-fold higher silane concentration (1.0 M) formed a 1:3 mixture of **13a**:**14a** in 87% isolated yield (Scheme 3). Cyclization/hydrosilylation of the pivaloate-substituted cyclobutyl diene **12b** with $HSiMe_2OTBDPS$ (0.30 M) also formed mixtures of ring opened (**13b**) and cyclobutylmethyl (**14b**) products (Scheme 3).

Asymmetric cyclization/hydrosilylation of functionalized 1,6-dienes catalyzed by a 1:1 mixture of the palladium pyridine−oxazoline complex (N−N)Pd(Me)-Cl [N−N = (*R*)-4-(*i*-Pr)-2-(2-pyridinyl)-2-oxazoline] (**2a**) and $NaBAr_4$ formed silylated cyclopentanes in good yield with up to 95% ee.[14] Because asymmetric cyclization/hydrosilylation tolerated olefinic substitution, we have also explored asymmetric ring-opening cyclization/hydrosilylation. To this end, reaction of **3**, $HSiMe_2$-OTBDPS, and a catalytic 1:1 mixture of **2a** and $NaBAr_4$ (10 mol %) at 0 °C for 12 h formed **4** in 69% yield as a single diastereomer with moderate enantiomeric excess (Scheme 4).

The formation of ring-opened products in the cyclization/hydrosilylation of strained 1-cycloalkyl-1,6-heptadienes is in accord with our proposed mechanism for palladium-catalyzed cyclization/hydrosilylation.[13a,b] For example, initial silylpalladation of the less hindered olefin of **3** by the palladium silyl intermediate **I** followed by intramolecular carbometalation would form the cyclopropylmethyl palladium intermediate **II** (Scheme 5). β-Elimination of a cyclopropyl methylene group would then form the palladium 3-butenyl complex **III**. Silylative cleavage of the Pd−C bond of **III** with $HSiEt_3$ would release **5** with regeneration of **I**. A possible mechanism involving silylative cleavage of the Pd−C bond of **II** followed by ring opening is precluded by the exclusive incorporation of deuterium into the terminal methyl group of **5**-d_1 formed in the reaction of **3** with $DSiEt_3$.

β-Elimination of alkyl groups not activated by ring strain has been observed only in the case of highly electrophilic alkyl d^0-metallocene complexes.[18,19] Conversely, β-alkyl elimination occurs readily in cyclobutylmethyl complexes of both early and late transition metals.[20−22] For example, halide abstraction from the cyclobutylmethylplatinum complex $(PMe_3)_2Pt(Cl)CH_2C(Me)CH_2CH_2CH_2$ with $AgBF_4$ at −78 °C led to β-alkyl elimination and formation of the platinum chelate complex $\{(PMe_3)_2Pt[\eta^1,\eta^2\text{-}CH_2CH_2CH_2C(Me)=CH_2]\}^+$-

(15) The crude reaction mixture contained several minor isomers that together accounted for ≤10% of the reaction mixture, all but one of which were removed via chromatography. The identity of these isomers remains unknown.

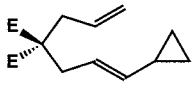
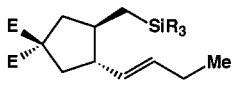
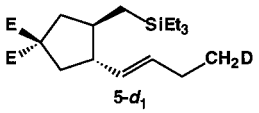
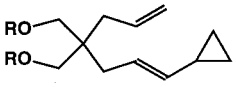
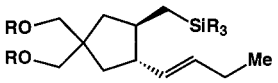
(16) This doublet of doublets is shifted downfield to ca. δ 0.85 in the corresponding cis-ring fused isomers: Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348.

(17) Exclusive formation of a terminal CH_2D group in **5**-d_1 was established by the 1:1:1 triplet at δ 13.8 (t, J_{CD} = 19 Hz) and the absence of a singlet corresponding to a terminal CH_3 group in the ^{13}C NMR spectrum.

(18) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 6472. (b) Horton, A. D. *Organometallics* **1996**, *15*, 2675. (c) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424. (d) Hajela, S.; Bercaw, J. E.; *Organometallics* **1994**, *13*, 1147.

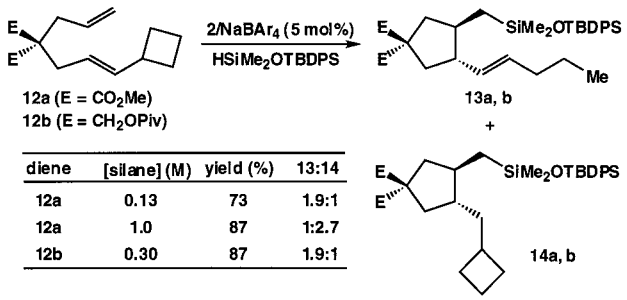
(19) β-Phenyl elimination from $[(dmpe)Pd(PMe_3)CH_2CMe_2Ph]^+BAr_4^-$ [dmpe = $Me_2PCH_2CH_2PMe_2$; Ar = 3,5-$C_6H_3(CF_3)_2$] at 60 °C for 24 h to form $[(dmpe)Pd(PMe_3)Ph]^+BAr_4^-$ has been recently reported: Cámpora, J.; Gutiérrez-Puebla, E.; López, J. A.; Monge, A.; Palma, P.; del Río, D.; Carmona, E. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3641.

Table 1. Ring-Opening Cyclization/Hydrosilylation of 1-Cyclopropyl-1,6-heptadienes Catalyzed by a 1:1 Mixture of (phen)Pd(Me)Cl (2) and $NaBAr_4$ (5 mol %) in CH_2Cl_2 at 0 °C

entry	diene	silane	carbocycle	yield (%)[a]	isomer ratio[b]
					
1	3 (E = CO_2Me)	$HSiEt_3$	5	69	11:1
2		$HSiMe_2Bn$	6	54	10:1
3		$DSiEt_3$	 5-d_1	78	13:1
					
4	7 (R = Piv)	$HSiEt_3$	9	58	23:1
5		$HSiMe_2OTBDPS$	10	78	32:1
6	8 (R = Ac)		11	83	>50:1

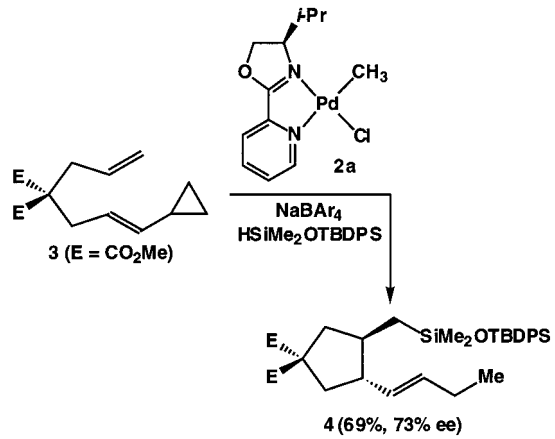
[a] Yields refer to isolated material of >95% purity. [b] Isomer ratio determined by GC analysis of the purified reaction mixture.

Scheme 3



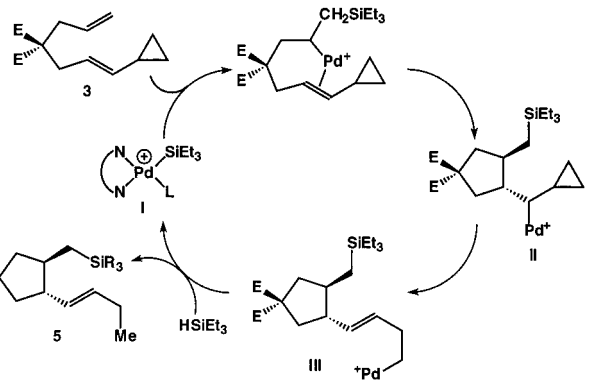
diene	[silane] (M)	yield (%)	13:14
12a	0.13	73	1.9:1
12a	1.0	87	1:2.7
12b	0.30	87	1.9:1

Scheme 4



BF_4^-.[20] Similarly, reaction of the yttrocene hydride dimer $(Cp^*_2YH)_2$ with methylenecyclobutane at −78 °C formed the 4-pentenylyttrium chelate complex $Cp^*_2Y(\eta^1,\eta^2\text{-}CH_2CH_2CH_2CH{=}CH_2)$ as the exclusive product, presumably via β-alkyl elimination from the initially formed cyclobutylmethylyttrium complex $Cp^*_2YCH_2CHCH_2CH_2CH_2$.[21]

Scheme 5



The predominant formation of the *E*-olefin in the ring-opening cyclization/hydrosilylation of strained 1-cycloalkyl-1,6-dienes is consistent with selective β-alkyl elimination from the more stable rotamer of **II**. Because β-elimination requires a syn-coplanar arrangement of the transition metal and the eliminating atom, β-alkyl elimination must occur from one of two possible rotamers, **IIa** and **IIb** (Scheme 6). Rotamer **IIa** should be favored relative to **IIb** due to the unfavorable steric interaction between the cyclopropyl and cyclopentyl groups in **IIb** that is avoided in **IIa**. Since the syn-coplanar arrangement of the eliminating groups is maintained in the transition state, the relative energies of rotamers **IIa** and **IIb** should be reflected in the respective transition states, leading to preferential β-alkyl elimination from **IIa** and predominant formation of (*E*)-**III** (Scheme 6).

In summary, 1-cyclopropyl-1,6-heptadienes undergo palladium-catalyzed ring-opening cyclization/hydrosilylation to form (*E*)-1-butenylcyclopentanes in good yield with good diastereoselectivity. In comparison, palladium-catalyzed cyclization/hydrosilylation of 1-cyclobutyl-1,6-heptadienes forms mixtures of ring-opened and cyclobutylmethyl products. Both the formation of the ring-opened products and the predominant formation of the *E*-olefin in the cyclization/hydrosilylation of strained 1-cycloalkyl-1,6-heptadienes are in accord with

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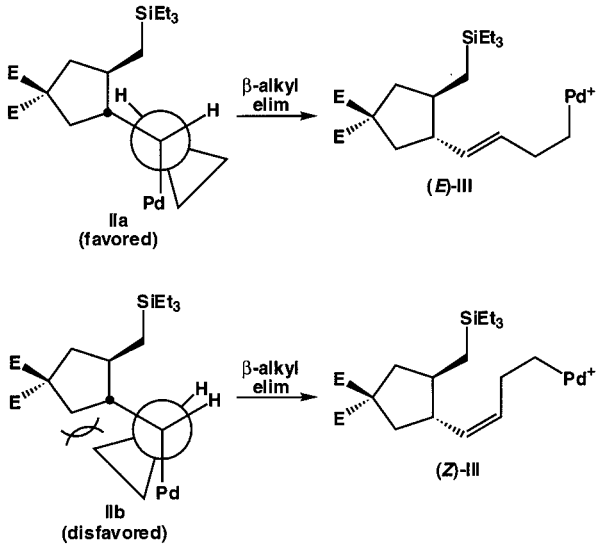
(21) Casey, C. P.; Hallenbeck, S. L.; Pollock, D. W.; Landis, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 9770.
(22) (a) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (b) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392.

Scheme 6



our previously proposed mechanism for palladium-catalyzed cyclization/hydrosilylation.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR were obtained on a Varian spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Routine gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Flash chromatography was performed employing 200−400 mesh Si gel (EM). Silver nitrate impregnated Si gel (20 wt %) was prepared according to a published procedure.[23] Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Methylene chloride and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Diene **3** was synthesized using a literature procedure;[24] the syntheses of remaining dienes are included in the Supporting Information. The enantiomeric excess of **4** formed in the reaction of **3** and $HSiMe_2OTBDPS$ catalyzed by **2a**/$NaBAr_4$ was determined by ^{1}H NMR spectroscopy employing $Eu(hfc)_3$ as a chiral shift reagent. Peaks corresponding to the enantiomeric pair were identified from analysis of *rac*-**4**.

(*E*)-*trans*-3-(1-Butenyl)-4-(3-*tert*-butyl-1,1-dimethyl-3,3-diphenyldisiloxymethyl)-1,1-dicarbomethoxycyclopentane (4). Diene **3**, CH_2Cl_2 (5 mL), and $HSiMe_2OTBDPS$ (0.60 g, 1.9 mmol) were added sequentially to a mixture of **2** (8 mg, 0.025 mmol) and $NaBAr_4$ (22 mg, 0.025 mmol) at 0 °C, and the resulting solution was stirred for 12 h. Solvent was evaporated under vacuum, and the residue was chromatographed (SiO_2; hexanes−ether = 9:1) to give **4** (260 mg, 93%) as a 25:1 mixture of isomers. ^{1}H NMR: δ 7.58−7.61 (m, 4 H), 7.24−7.39 (m, 6 H), 5.46 (td, J = 6.4, 15.2 Hz, 1 H), 5.02 (tdd, J = 1.6, 7.2, 15.2 Hz, 1H), 3.67 (s, 3 H), 3.66 (s, 3 H), 2.55 (dd, J = 6.4, 13.2 Hz, 1 H), 2.42 (dd, J = 6.4, 13.2 Hz, 1 H), 1.03 (m, 1 H), 1.00 (s, 9 H), 0.92 (t, J = 7.2 Hz, 3 H), 1.88−1.20 (m, 3 H), 1.81 (dd, J = 1.6, 13.2 Hz, 1 H), 1.67 (dd, J = 1.6, 13.2 Hz, 1 H), 1.55−1.62 (m, 1 H), 0.31 (dd, J = 3.6, 14.8 Hz, 1 H), 0.07 (d, J = 2.8 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 173.3, 136.1, 135.2, 134.0, 130.4, 129.4, 127.6, 63.9, 58.8, 52.9, 52.8, 42.3, 41.3, 40.6, 26.9, 25.7, 22.0, 19.3, 14.1, 1.7, 1.3. Anal. Calcd (found) for $C_{32}H_{46}O_5Si_2$: C, 67.80 (67.80); H, 8.18 (8.13).

(23) Li, T.-S.; Li, J.-T.; Li, H.-Z. *J. Chromatogr. A* **1995**, 372.
(24) Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A.; Pleuss, N. *Tetrahedron* **1998**, *54*, 7203.

Carbocycles **5**, **5**-d_1, **6**, and **9**−**11** were synthesized employing a procedure similar to that used to synthesize **4**. Yields and isomer ratios are given in Table 1.

(*E*)-*trans*-3-(1-Butenyl)-1,1-dicarbomethoxy-4-(triethylsilylmethyl)cyclopentane (5). ^{1}H NMR: δ 5.48 (dtd, J = 0.8, 6.0, 15.2 Hz, 1 H), 5.13 (tdd, J = 1.2, 8.4, 15.2 Hz, 1 H), 3.70 (s, 6 H), 2.57 (dd, J = 6.8, 13.2 Hz, 1 H), 2.48 (dd, J = 6.8, 13.2 Hz, 1 H), 1.96−2.02 (m, 3 H), 1.86 (dd, J = 11.2, 13.2 Hz, 1 H), 1.66 (dd, J = 11.2, 12.8 Hz, 1 H), 1.52−1.59 (m, 1 H), 0.95 (t, J = 7.6 Hz, 3 H), 0.90 (t, J = 8.0 Hz, 9 H), 0.87 (m, 1 H), 0.59 (q, J = 8.0 Hz, 6 H), 0.22 (dd, J = 11.2, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.5, 133.9, 130.9, 58.4, 53.2, 52.8, 42.6, 42.0, 40.6, 25.7, 14.4, 14.1, 7.5, 3.9. Anal. Calcd (found) for $C_{20}H_{36}SiO_4$: C, 65.17 (65.13); H, 9.84 (9.91).

(*E*)-*trans*-1,1-Dicarbomethoxy-3-(4-deuterio-1-butenyl)-4-(triethylsilylmethyl)cyclopentane (5-d_1). ^{1}H NMR: δ 5.44 (td, J = 6.0, 15.2 Hz, 1 H), 5.09 (dd, J = 8.0, 15.2 Hz, 1 H), 3.66 (s, 3 H). 3.65 (s, 3 H), 2.53 (dd, J = 6.8, 12.8 Hz, 1 H), 2.44 (dd, J = 6.8, 12.8 Hz, 1 H), 1.95 (q, J = 6.8 Hz, 2 H), 1.92 (m, 1 H), 1.82 (dd, J = 10.8, 12.8 Hz, 1 H), 1.62 (m, 1 H), 1.52 (m, 1 H), 0.86 (t, J = 8.0 Hz, 9 H), 0.88 (m, 2 H), 0.83 (m, 1 H), 0.46 (q, J = 8.0 Hz, 6 H), 0.19 (dd, J = 11.6, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.5, 134.0, 130.6, 58.5, 53.2, 52.8, 42.7, 42.1, 20.6, 25.8, 25.7, 14.5, 13.8 (t, J_{CD} = 19 Hz), 7.6, 3.9.

(*E*)-*trans*-4-Benzyldimethylsilylmethyl-3-(1-butenyl)-1,1-dicarbomethoxycyclopentane (6). ^{1}H NMR: δ 7.20 (t, J = 7.6 Hz, 2 H), 7.06 (t, J = 7.6 Hz, 1 H), 6.98 (dd, J = 1.2, 8.4 Hz, 2 H), 5.48 (td, J = 6.4, 15.2 Hz, 1 H), 5.13 (tdd, J = 1.2, 8.4, 15.2 Hz, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 2.59 (dd, J = 6.4, 12.4 Hz, 1 H), 2.51 (dd, J = 6.8, 13.2 Hz, 1 H), 2.08 (s, 2 H), 2.00 (m, 3 H), 1.88 (dd, J = 11.6, 13.2 Hz, 1 H), 1.58−1.71 (m, 2 H), 0.98 (t, J = 7.6 Hz, 3 H), 0.92 (dd, J = 2.4, 14.4 Hz, 1 H), 0.27 (dd, J = 10.8, 14.8 Hz, 1 H), 0.00 (s, 3 H), −0.01 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.4, 140.3, 134.1, 130.5, 128.3, 124.1, 58.5, 53.1, 52.9, 42.5, 42.2, 40.6, 26.2, 25.8, 18.3, 14.2, 6.8, −2.4, −2.7. IR (neat, cm^{-1}): 2955, 1736, 1732, 1253, 837. Anal. Calcd (found) for $C_{23}H_{34}O_4Si$: H, 8.51 (8.63); C, 68.62 (68.44).

(*E*)-*trans*-3-(1-Butenyl)-4-(triethylsilylmethyl)-1,1-bis-(trimethylacetoxymethyl)cyclopentane (9). ^{1}H NMR (300 MHz): δ 5.46 (td, J = 2.4, 15.2 Hz, 1 H), 5.12 (tdd, J = 1.2, 8.4, 15.2 Hz, 1 H), 3.94 (d, J = 10.4 Hz, 1 H), 3.93 (d, J = 10.8 Hz, 1 H), 3.89 (d, J = 10.8 Hz, 1 H), 3.88 (d, J = 10.8 Hz, 1 H), 1.99 (dq, J = 1.2, 7.2 Hz, 2 H), 1.97 (m, 1 H), 1.84 (dd, J = 7.2, 13.2 Hz, 1 H), 1.72 (dd, J = 7.2, 13.2 Hz, 1 H), 1.51 (m, 1 H), 1.19 (s, 9 H), 1.18 (m, 2 H), 1.03 (dd, J = 12.0, 13.2 Hz, 1 H), 0.96 (t, J = 7.2 Hz, 3 H), 0.89 (t, J = 8.0 Hz, 9 H), 0.48 (m, 6 H), 0.17 (dd, J = 11.6, 14.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 178.6, 133.5, 131.4, 68.4, 68.3, 53.1, 44.2, 41.6, 41.4, 39.2, 39.1, 27.4, 25.8, 14.8, 14.2, 7.6, 4.0. Anal. Calcd (found) for $C_{28}H_{52}O_4Si$: H, 10.90 (10.96); C, 69.95 (69.87).

(*E*)-*trans*-3-(1-Butenyl)-4-(3-*tert*-butyl-1,1-dimethyl-3,3-diphenyldisiloxymethyl)-1,1-bis(trimethylacetoxymethyl)cyclopentane (10). ^{1}H NMR: δ 7.64 (td, J = 1.2, 7.6 Hz, 4 H), 7.38 (m, 6 H), 5.44 (td, J = 9.6, 15.2 Hz, 1 H), 5.06 (dd, J = 8.4, 15.2 Hz, 1 H), 3.88, 3.84 (ABq, J = 10.2 Hz, 4 H), 2.01 (pent, J = 7.6 Hz, 2 H), 1.89−1.96 (m, 1 H), 1.83 (dd, J = 7.2, 13.2 Hz, 1 H), 1.72 (dd, J = 7.2, 13.2 Hz, 1 H), 1.56 (m, 1 H), 1.20 (s, 9 H), 1.19 (s, 9 H), 1.18 (m, 1 H), 1.05 (s, 1 H), 1.04 (m, 1 H), 0.98 (m, 1 H), 0.97 (t, J = 7.6 Hz, 3 H), 0.29 (dd, J = 11.2, 14.4 Hz, 1 H), 0.11 (s, 6 H). ^{13}C{^{1}H} NMR: δ 178.5, 178.4, 136.1, 135.2, 133.6, 131.3, 129.6, 127.7, 68.2, 52.8, 44.1, 40.9, 39.3, 39.1. Anal. Calcd (found) for $C_{40}H_{62}O_5Si_2$: H, 9.20 (9.27); C, 70.75 (70.69).

(*E*)-*trans*-1,1-Bis(acetoxymethyl)-3-(1-butenyl)-4-(3-*tert*-butyl-1,1-dimethyl-3,3-diphenyl-disiloxymethyl)cyclopentane (11). ^{1}H NMR: δ 7.61−7.63 (m, 4 H), 7.38 (m, 6 H), 5.42 (td, J = 6.4, 15.2 Hz, 1 H), 5.04 (dd, J = 8.4, 15.2 Hz, 1 H), 3.86 (s, 2 H), 3.84 (d, J = 10.8 Hz, 1 H), 3.82 (d, J = 10.8 Hz, 1 H), 2.00 (s, 3 H), 2.00 (s, 3 H), 2.00 (m, 2 H), 1.88 (m, 1 H), 1.14 (dd, J = 7.2, 13.6 Hz, 1 H), 1.03 (s, 9 H), 0.95 (t, J =

7.2 Hz, 3 H), 0.96 (m, 1 H), 0.27 (dd, J = 11.6, 14.8 Hz, 1 H), 0.09 (s, 3 H), 0.08 (s, 3 H). $^{13}C\{^1H\}$ NMR: δ 171.4, 171.3, 136.1, 135.2, 133.6, 131.2, 129.6, 127.7, 68.5, 68.3, 52.6, 43.6, 41.2, 40.9, 39.3, 27.0, 25.8, 22.5, 21.1, 19.4, 14.2, 1.6, 1.5. Anal. Calcd (found) for $C_{34}H_{50}O_5Si_2$: H, 8.47 (8.53); C, 68.64 (68.61).

(*E*)-*trans*-4-(3-*tert*-Butyl-1,1-dimethyl-3,3-diphenyldisiloxymethyl)-1,1-dicarbomethoxy-3-(1-pentenyl)cyclopentane (13a). $HSiMe_2OTBDPS$ (400 mg, 1.27 mmol) was added to a solution of **12a** (130 mg, 0.49 mmol), **2** (8.0 mg, 0.024 mmol), and $NaBAr_4$ (22 mg, 0.025 mmol) in CH_2Cl_2 (10 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 2 days. Solvent was evaporated and the residue was chromatographed (SiO_2; hexanes−EtOAc = 30:1) to give a 1.9:1 ratio of **13a**:**14a** (210 mg, 73%) as a colorless oil. Additional chromatography ($AgNO_3/SiO_2$; hexanes−ether = 100:1 → 20:1) gave **13a** (60 mg, 21%) as a colorless oil in >96% isomeric purity. ^1H NMR: δ 7.62 (m, 4 H), 7.38 (m, 6 H), 5.40 (td, J = 6.8 15.2 Hz, 1 H), 5.06 (dd, J = 8.0, 15.2 Hz, 1 H). 3.70 (s, 3 H), 3.69 (s, 3 H), 2.58 (dd, J = 6.8, 12.8 Hz, 1 H), 2.46 (dd, J = 6.8, 13.2 Hz, 1 H), 1.95 (q, J = 6.8 Hz, 2 H), 1.97 (m, 1 H), 1.85 (dd, J = 11.2, 13.2 Hz, 1 H), 1.70 (dd, J = 11.2, 12.8 Hz, 1 H), 1.60 (m, 1 H), 1.34 (hextet, J = 7.2 Hz, 2 H), 1.03 (s, 18 H), 1.00−1.04 (m, 1 H), 0.87 (t, J = 7.2 Hz, 3 H), 0.34 (dd, J = 11.6, 14.4 Hz, 1 H), 0.11 (s, 3 H), 0.10 (s, 3 H). $^{13}C\{^1H\}$ NMR: δ 173.5, 173.3, 136.1, 135.3, 132.3, 131.7, 129.5, 127.7, 58.5, 53.1, 52.8, 52.7, 42.3, 41.4, 40.6, 34.8, 27.0, 22.8, 22.1, 19.4, 13.8, 1.8, 1.3. IR (neat, cm^{-1}): 2954, 2930, 1735, 1254, 1109, 1077, 839, 701. Anal. Calcd (found) for $C_{33}H_{48}O_5Si_2$: H, 8.33 (8.41); C, 68.23 (68.39).

***trans*-4-(3-*tert*-Butyl-1,1-dimethyl-3,3-diphenyldisiloxymethyl)-3-cyclobutylmethyl-1,1-dicarbomethoxycyclopentane (14a).** Diene **12a** (130 mg, 0.49 mmol) and $HSiMe_2OTBDPS$ (1.6 g, 5.0 mmol) were added sequentially to a solution of **2** (8.0 mg, 0.024 mmol) and $NaBAr_4$ (22 mg, 0.025 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The resulting solution was stirred at 0 °C for 20 min, concentrated, and chromatographed (SiO_2; hexanes−ether = 100:1 → 20:1) to give a 1:2.7 mixture of **13a**:**14a** (246 mg, 0.424 mmol, 87%) as a colorless oil. Additional chromatography ($AgNO_3/SiO_2$; hexanes−ether = 100:1 → 20:1) gave **14a** (70 mg, 25%) as a colorless oil in >95% isomeric purity. ^1H NMR: δ 7.64 (dd, J = 1.6, 8.0 Hz, 1 H), 7.38 (m, 6 H), 3.68 (s, 3 H), 2.53 (dd, J = 7.2, 13.6 Hz, 1 H), 2.43 (dd, J = 7.2, 13.6 Hz, 1 H), 2.25 (heptet, J = 7.6 Hz, 1 H), 1.99 (m, 2 H), 1.72−1.88 (m, 2 H), 1.66 (dd, J = 8.4, 10.8 Hz, 1 H), 1.63 (dd, J = 8.8, 10.8 Hz, 1 H), 1.44−1.59 (m, 4 H), 1.23−1.34 (m, 1 H), 1.04 (s, 9 H), 1.01−1.04 (m, 1 H), 0.96 (dd, J = 2.4, 14.8 Hz, 1 H), 0.37 (dd, J = 11.2, 14.8 Hz, 1 H), 0.12 (s, 3 H), 0.12 (s, 3 H). $^{13}C\{^1H\}$ NMR: δ 173.6, 173.5, 136.1, 135.3, 129.5, 127.7, 58.6, 52.8, 47.3, 42.6, 41.2, 40.6, 40.1, 35.3, 29.6, 28.6, 27.0, 22.7, 19.4, 18.7, 1.9, 1.4. IR (neat, cm^{-1}): 2971, 2954, 2932, 2894, 2859, 1737, 1731, 1255. HRMS calcd (found) for $C_{33}H_{47}O_5Si_2$ ($M - H^+$): 579.2960 (579.2943). Anal. Calcd (found) for $C_{33}H_{48}O_5Si_2$: H, 8.33 (8.31); C, 68.23 (68.25).

Cyclization/Hydrosilylation of 12b. $HSiMe_2OTBDPS$ (0.46 g, 1.5 mmol) was added to a solution of diene **12b** (187 mg, 0.50 mmol), **2** (8 mg, 0.024 mmol), and $NaBAr_4$ (22 mg, 0.025 mmol) in CH_2Cl_2 (5 mL) at 0 °C, stirred for 10 h, concentrated, and chromatographed (SiO_2; hexanes−ether = 100:1 → 20:1) to give a 1.9:1 mixture of **13b**:**14b** (298 mg, 87%) as a colorless oil. The 1.9:1 mixture of **13b**:**14b** was analyzed by ^1H and ^{13}C NMR spectroscopy without further purification. HRMS calcd (found) for $C_{37}H_{55}O_5Si_2$ ($M^+ - CMe_3$): 635.3588 (635.3604).

For 13b: ^1H NMR: δ 7.65 (m, 4 H), 7.35 (m, 6 H), 5.40 (td, J = 8.4, 15.2 Hz, 1 H), 3.87 (m, 4 H), 1.97 (q, J = 7.2 Hz, 2 H), 1.98 (m, 1 H), 1.80 (m, 2 H), 1.71 (dt, J = 7.2, 14.0 Hz, 1 H), 1.58 (m, 2 H), 1.39 (q, J = 7.2 Hz, 2 H), 1.20 (s, 9 H), 1.20 (s, 9 H), 0.30 (dd, J = 11.2, 14.4 Hz, 1 H), 0.12 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 178.5, 178.4, 136.1, 135.2, 132.6, 131.8, 129.6, 127.7, 68.2, 52.9, 47.1, 44.2, 41.2, 40.9, 39.1, 34.9, 27.4, 27.4, 22.9, 22.6, 19.4, 13.9, 1.8, 1.5.

For 14b: ^1H NMR: δ 7.65 (m, 4 H), 7.35 (m, 6 H), 3.87 (m, 4 H), 2.24 (heptet, J = 3.6 Hz, 1 H), 1.98 (m, 3 H), 1.67 (m, 4 H), 1.58 (m, 1 H), 1.28−1.42 (m, 2 H), 1.20 (s, 18 H), 1.04 (s, 9 H), 1.00 (m, 1 H), 0.31 (dd, J = 11.6, 14.4 Hz, 1 H), 0.14 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 178.5, 178.4, 136.1, 135.2, 129.6, 127.7, 68.3, 47.1, 44.1, 41.8, 41.3, 39.3, 38.7, 35.4, 29.6, 28.6, 27.4, 23.1, 18.7, 1.9, 1.6.

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for new dienes. This material is available free of charge via the Internet at http://pubs.acs.org.

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