Cyclization/Hydrosilylation of Functionalized Dienes Catalyzed by a Cationic Palladium Phenanthroline Complex

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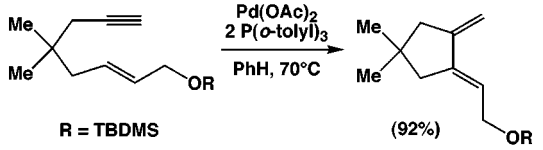
Mixtures of (phen)$PdMe_2$ (**2a**) and $HBAr'_4$ (**3a**) or (phen)PdMe(Cl) (**2b**) and $NaBAr'_4$ (**3b**) [phen = 1,10-phenanthroline; $Ar' = 3,5\text{-}C_6H_3(CF_3)_2$] catalyzed the cyclization/hydrosilylation of functionalized 1,6-dienes to form silylated cyclopentanes in good yield and with excellent trans selectivity about the newly formed C−C bond (typically >50:1). A range of tertiary hydrosilanes were employed in the procedure although unhindered trialkylsilanes provided the most consistent results. The protocol tolerated a range of polar functionality including esters, ethers, amides, sulfones, and cyano groups. 4,4-Disubstitution on the diene backbone promoted cyclization, and a homoallylic ester, ketone, or ether directing group was required for efficient cyclization. The procedure tolerated dienes which possessed a single trans-substituted olefin and also tolerated allylic substitution. These substituted dienes underwent cyclization/hydrosilylation to form carbocycles resulting from transfer of the silyl group to the less hindered olefin. Mixtures of **2a** and **3a** also catalyzed the cyclization/hydrosilylation of functionalized 1,7-dienes to form silylated cyclohexane derivatives. Cyclization/hydrosilylation of 1,7-dienes was typically slower, less stereoselective, and more sensitive to substitution than was cyclization of 1,6-dienes.

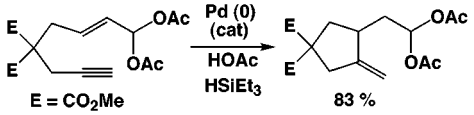
Introduction

Substituted carbocycles represent one of the most common structural subunits found in naturally occurring and biologically active molecules.[1] Due to the significance of carbocycles in natural products and medicinal chemistry, considerable effort has been directed toward the development of efficient annulation protocols. In this area, transition metal-based approaches have been particularly fruitful.[2] For example, Mo,[3] Ru,[4] and Ti[5] complexes catalyze the cycloisomerization of enynes to generate substituted cyclopentane derivatives.[6] Of particular significance is the palladium-catalyzed cycloisomerization of enynes (eq 1)[6,7] and the reductive cyclization of enynes[8]



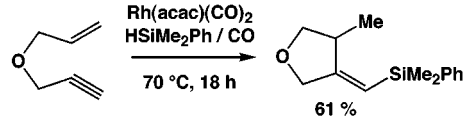
(1)

and diynes[9] (eq 2). The synthetic utility of these palladium-catalyzed protocols stems from their ability to construct complex cyclic structures from simple acyclic precursors coupled with the ready availability, low air- and moisture-sensitivity, and good functional group compatibility of the catalysts. As a result, a number of natural product syntheses have employed these procedures.[10]



(2)

A recent and potentially significant development in transition metal-catalyzed carbocyclization is the cyclization/hydrosilylation of diynes[11,12] and enynes[13−15] catalyzed by low-valent Ni(0) and Rh(I) complexes. These are synthetically useful reactions which form a C−C bond and also a C−Si bond which can often be manipulated in a separate step. For example, Rh(I) carbonyl complexes catalyze the cyclization/hydrosilylation of 1,6-enynes to form silylated alkylidene cyclopentane derivatives in good yield (eq 3).[11] Similarly, a Ni(0) complex generated from



(3)

$Ni(acac)_2$ (acac = acetylacetonate) and DIBAL (DIBAL = diisobutylaluminum hydride) catalyzes the cyclization/hydrosilylation of 1,6- and 1,7-diynes to form bicyclic

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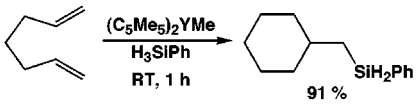
silacyclopentadienes[14] and silylated 1,2-dialkylidene cyclohexane derivatives, respectively.[13] Low-valent Pd, Ni, and Rh complexes also catalyze analogous cyclization/addition reactions of enynes, diynes, and tetraenes employing hydrostannanes,[16] borylstannanes,[17] borylsilanes,[18] trimethylsilyl cyanide,[19] trimethylgermyl cyanide,[20] distannanes,[21] disilanes,[21] and silastannanes[21] as stoichiometric reductants.

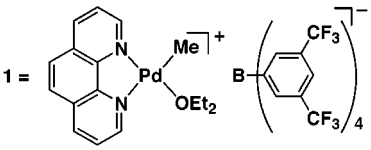
A major limitation of Rh(I)- and Ni(0)-catalyzed cyclization/hydrosilylation is the failure of dienes to cyclize under these conditions. In contrast, highly reactive d^0-metallocene complexes serve as active diene cyclization catalysts. For example, scandocene[22] and yttrocene[23] complexes catalyze diene cycloisomerization and reductive cyclization, respectively. Likewise, cationic zirconocene complexes catalyze the cyloisomerization,[24] cyclization/magnesiation,[25,26] and cyclization/carboalumination[27] of dienes. More importantly, neodymium[28] and, to a greater extent, yttrium[29,30] metallocene complexes serve as efficient diene cyclization/hydrosilylation catalysts (eq 4). Synthesis of the alkaloid (±)-epilupinine via yttrium-catalyzed cyclization/hydrosilylation points to the synthetic potential of these protocols.[31]



(4)

The high activity of the d^0-metallocene complexes relative to the Ni(0) and Rh(I) complexes toward diene cyclization/hydrosilylation stems from the electropositivity of the metal and the presence of an open coordination site. These features facilitate both olefin β-migratory insertion and σ-bond metathesis, the latter in preference to oxidative addition/reductive elimination processes. Unfortunately, the synthetic utility of these metallocene-catalyzed protocols is restricted by both limited functional group compatibility, particularly toward polar unsaturated functionality, and the excessive air- and moisture-sensitivity of the catalyst. Therefore, identification of a diene cyclization/hydrosilylation catalyst which possesses the activity of the d^0-metallocene catalyst and the functional group compatibility of a late transition metal complex would be of potential interest.[32]

Cationic Pd(II) complexes employed in conjunction with a weakly coordinating counterion such as the palladium phenanthroline complex (phen)Pd(Me)$(OEt_2)^+$ $BAr'_4{}^-$ [phen = 1,10-phenanthroline, Ar′ = 3,5-$C_6H_3(CF_3)_2$] (**1**) possess



an available coordination site and are highly electrophilic. As a result, these complexes display high activity with respect to olefin β-migratory insertion and catalyze the polymerization of α-olefins[33,34] and the copolymerization of ethylene[35] and propene[36] with CO. Complex **1** also cleaves Si−H bonds via low-energy σ-bond metathesis pathways and catalyzes olefin hydrosilylation.[37] The combination of high reactivity and excellent functional group compatibility displayed by **1** suggested that this complex might also serve as an effective catalyst for the cyclization/hydrosilylation of functionalized dienes. Here we describe the development and scope of a procedure for the cyclization/hydrosilylation of functionalized 1,6- and 1,7-dienes catalyzed by **1**.[38]

Results and Discussion

Cyclization of 1,6-Dienes. The isolable cationic complex **1** decomposes readily in solution at room temperature.[39] As a result, **1** was generated *in situ* from a 1:1 mixture of (phen)$PdMe_2$ (**2a**) and $HBAr'_4$ (**3a**) at 0 °C.[39] When trimethylsilane was bubbled through a colorless solution of dimethyl diallylmalonate (**4**) (0.05 M) and **1** (5 mol %) at 0 °C, the solution immediately turned pale yellow and within 5 min turned dark brown with complete consumption of **4** as determined by GC analysis. Evaporation of the solvent and flash chromatography of the residue gave the trans-silylated cyclopentane **5** in 80% yield (Table 1, entry 1). Both the identity and

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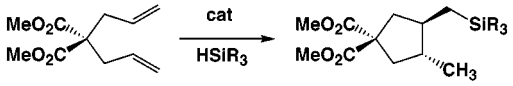
Table 1. Palladium-Catalyzed Cyclization/Hydrosilylation of 4 (0.5 mmol) at 25 °C

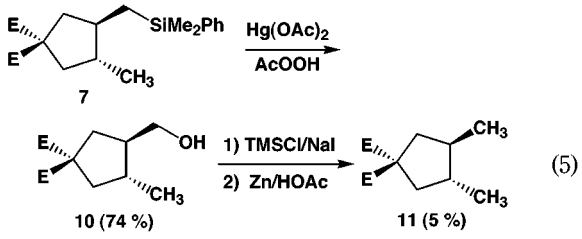


entry	catalyst	loading (mol %)	solvent	time (min)	temp (°C)	silane	cyclopentane	yield[a]	isomer ratio[b]
1	2a/3a	5	CH_2Cl_2	5	0	$HSiMe_3$	5	80	54:1
2		5		5	0	$HSiEt_3$	6	92	55:1
3		2		15	25	$HSiEt_3$	6	80	74:1
4		5		1	25	$HSiMe_2Ph$	7	93	53:1
5		5		10	25	$HSiMe_2t$-Bu	8	67	44:1
6		2		15	25	$HSiPh_3$	9	84	>25:1[c]
7	2b/3b	0.5	DCE	90	25	$HSiEt_3$	6	85	99:1
8		2[d]		90	25	$HSiMe_2Ph$	7	82	55:1
9		1[d]		25	0	$HSiEt_3$	6	93	55:1
10[e]		5		30	0	$HSiEt_3$	6	86	54:1
11[f]		5		10	25	$HSiEt_3$	6	85	97:1
12	2a/3c	5	CH_2Cl_2	10	0	$HSiEt_3$	6	85	99:1
13	2b/3c	5	CH_2Cl_2	30	0	$HSiEt_3$	6	40	35:1

[a] Yields refer to isolated material which was >95% pure as determined by ^{1}H NMR, GC, and/or elemental analysis. [b] Determined by capillary GC or HPLC analysis of the crude reaction mixture. [c] GC not obtained; a single isomer detected by ^{1}H NMR spectroscopy. [d] Reaction performed on 6 mmol scale. [e] Air (15 mL) added to reaction flask. [f] Water (3 mmol) added to reaction mixture.

stereochemistry of **5** were determined by comparison of the ^{1}H and ^{13}C NMR spectra of **5** to published data.[40] In addition to **5**, GC-MS analysis of the crude reaction mixture revealed the presence of a small quantity of an isomeric silylated product **5a** (**5**:**5a** = 54:1)[41] and traces (~5%) of hexamethyldisiloxane. Precatalysts **2a** or **3a** employed separately displayed no catalytic activity toward mixtures of **4** and silane.

Silane. A range of tertiary silanes possessing both alkyl and aryl groups such as triethylsilane, dimethylphenylsilane, dimethyl-*tert*-butylsilane, and triphenylsilane reacted with **3** to give the corresponding carbocycles (**6**−**9**) in good yield and with excellent diastereoselectivity (>25:1) (Table 1, entries 2−6). In contrast, attempted cyclization of **4** in the presence of 1° or 2° silanes, alkoxysilanes, or chlorosilanes resulted in immediate darkening of the solution and no formation of carbocycle. The successful employment of silanes substituted with one or more phenyl group is significant as the resulting hydrosilylation products can be oxidized to form the corresponding alcohol.[42] For example, the dimethylphenylsilyl derivative **7** was converted to alcohol **10** in 74% yield by treatment with mercuric acetate and peracetic acid (eq 5).[43] As further confirmation of carbocycle stereochemistry, **10** was deoxygenated employing the method of Morita[44] to form *trans*-1,1-dicarbomethoxy-3,4-dimethylcyclopentane (**11**) in low yield, which was identified by comparison to authentic sample[45,46] and by chiral GC analysis (eq 5).[47]



(5)

Catalyst Source and Conditions. Despite the high activity and good selectivity displayed by the **2a**/**3a** catalyst system, the procedure suffered from the rather involved syntheses and thermal instability of the catalyst precursors. However, mixtures of the thermally stable precursors (phen)PdMe(Cl) (**2b**) and $NaBAr'_4$ (**3b**) also generated an active cyclization/hydrosilylation catalyst.[35,36] In addition, when employed in conjunction with 1,1-dichloroethane (DCE) solvent, this catalyst system produced cleaner reaction mixtures and was more robust than was the catalyst generated from **2a** and **3a**. For example, complete conversion of **4** to carbocycles **6** or **7** was achieved in the presence of 0.5 and 2 mol % **2b**/**3b**, respectively (Table 1, entries 7 and 8). Similarly, gram quantities of **4** were converted within minutes to either **6** or **7** in high yield employing ≤2 mol % of the **2b**/**3b** precatalyst (Table 1, entries 8 and 9). Furthermore, addition of air (15 mL) or water (50 μL) to the reaction mixture led to no deterioration in rate, yield or selectivity for reactions catalyzed by **2b**/**3b** in DCE (Table 1, entries 10 and 11).

Methyl abstraction from **2a** with the Lewis acid $B(C_6F_5)_3$ (**3c**) also generated an active diene cyclization/hydrosilylation catalyst (Table 1, entry 12).[48] The active catalyst in this case is presumably either a cationic species analogous to **1** or a zwitterionic complex in which one methyl group bridges the palladium and boron centers.[48] For example, addition of **3c** to d^0-dimethylmetallocene complexes led to formation of zwitterionic complexes which displayed high activity toward olefin polymerization.[49] Likewise, reaction of **3c** with the dimethylplatinum complex (phen)$PtMe_2$ in the presence of an external ligand such as ethylene or CO formed the corresponding cationic platinum complex $[(phen)Pt(Me)L]^+$-

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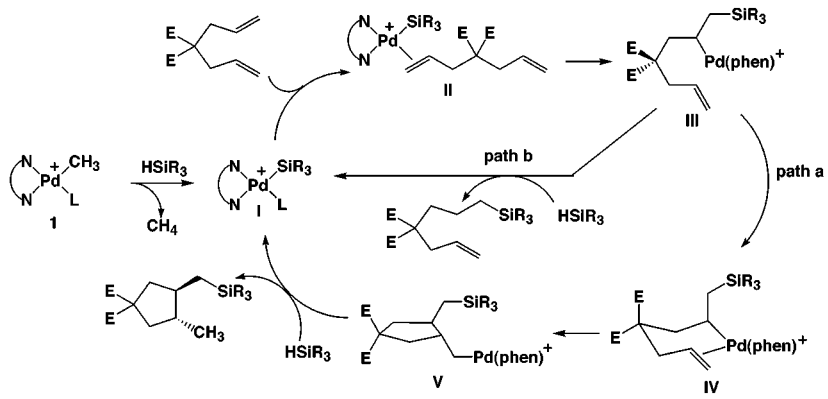
Scheme 1



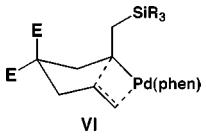
$[MeB(C_6F_5)_3]^-$.[50] Reaction of **4** and $HSiEt_3$ catalyzed by a mixture of **2a**/**3c** gave **6** with yields and diastereoselectivity comparable to that obtained with the **2a**/**3a** or **2b**/**3b** precatalysts and also benefited from the commercial availability of **3c** (Table 1, entry 12). Unfortunately, employment of this precatalyst mixture led to the formation of excessive amounts of disiloxane and required use of dimethyl precursor **2a**. Attempts to ameliorate this latter problem by employing **3c** with palladium methyl chloride complex **2b** were less successful (Table 1, entry 13).

It is noteworthy that the efficiency of palladium-catalyzed cyclization/hydrosilylation depended sharply on both the ligand and counterion. In contrast to palladium phenanthroline complexes, palladium complexes ligated by *N*,*N*,*N*′*N*′-tetramethylethylenediamine or (bisdimethylphosphino)ethane were ineffective. Similarly, attempts to employ counterions such as PF_6^- or BF_4^- in place of the tetraarylborate counterion were also unsuccessful. Also noteworthy is that the reactivity of these cationic palladium methyl complexes toward dienes differs markedly from simple Pd(II) complexes. For example, catalysts of the type $L_2Pd(H)OAc$ (L = phosphine or imine) catalyzed the cycloisomerization of enynes but were inactive toward dienes.[7] Furthermore, reaction of an enyne or diyne with a hydrosilane in the presence of L_2-Pd(H)OAc led to reductive cyclization rather than cyclization/hydrosilylation.[8,9]

Mechanism. The mechanism of the intermolecular hydrosilylation of unfunctionalized α-olefins catalyzed by **1** has been studied by Brookhart.[37,51] This work has shown that the cationic palladium methyl complex **1** reacts with hydrosilanes (presumably via σ-bond metathesis) to form the cationic palladium silyl complex **I** with release of methane (Scheme 1).[37] The Pd−Si complex **I** reacts readily with olefins to initially form a silylpalladium olefin complex which undergoes rapid and reversible 2,1-β-migratory insertion of the coordinated olefin into the Pd−Si bond. Reaction of silane with the resulting palladium alkyl complex releases the alkylsilane and regenerates palladium−silyl intermediate **I**.[37]

A plausible mechanism for palladium-catalyzed cyclization/hydrosilylation can be constructed on the basis of the mechanistic work of Brookhart. For example, coordination of one olefin of a functionalized diene to **I** would form the Pd−olefin complex **II** (Scheme 1). β-Migratory insertion of the olefin into the Pd−Si bond of **II** would form the palladium−alkyl intermediate **III**. Coordination of the pendant olefin would form palladium alkyl olefin intermediate **IV** which could undergo β-migratory insertion to form palladium cyclopentylmethyl intermediate **V** (Scheme 1, path a). Reaction of **V** with silane would then release the carbocycle and regenerate the palladium silyl complex **I**. Reaction of silane with the initially formed palladium alkyl intermediate **III** prior to intramolecular olefin insertion would lead to silylation without cyclization (Scheme 1, path b).

The diastereoselectivity of carbocyclization employing 1,6- and 1,7-dienes and related substrates has often been rationalized by maximizing the number of pseudoequatorial substituents in a chairlike transition state for ring closure.[23,29,52−55] In contrast, the chairlike transition state (**VI**) which would convert palladium alkyl olefin intermediate **IV** to palladium cyclopentylmethyl intermediate **V** requires a pseudoaxial α-(trialkylsilyl)methyl substituent. The α-(trialkylsilyl)methyl group may adopt this orientation in an effort to avoid unfavorable steric interaction with the phenanthroline group which projects steric bulk in the coordination plane but neither above nor below this plane. However, the validity of this simple model may be affected by chelation of a homoallylic ester group to the palladium center (see below).



VI

Olefinic Substitution. Transition metal-based carbocyclization is often sensitive to olefinic substitution. For example, the zirconocene-mediated reductive cyclization of 1,6-enynes[56] and 1,6-dienes[25,57] tolerates a single sub-

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(51) For related mechanistic work see: (a) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151. (b) Marciniec, B.; Pietraszuk, C. *Organometallics* **1997**, *16*, 4320. (c) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (d) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (e) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128.

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(55) Negishi, E.-i.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* **1994**, *116*, 8404.

(56) Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

(57) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435.

stituent at a terminal or internal olefinic carbon atom, although the latter are sometimes problematic.[56] Similarly, the efficiency of the $Co_2(CO)_8$-mediated cyclocarbonylation of 1,6-enynes (Pauson−Khand) decreases with increasing olefinic substitution[58] but tolerates di- and even trisubstituted olefins.[59] Palladium-catalyzed protocols such as enyne cycloisomerization[6] or the intramolecular Heck reaction[60] also tolerate di- and trisubstituted olefins. In contrast, several related titanium-catalyzed enyne cyclization/insertion procedures have proven quite sensitive to olefinic substitution and tolerate a single internal substituent only with high (20%) catalyst loading.[52,61] Similarly, neither the Rh(I)-catalyzed cyclization/hydrosilylation of enynes[11] nor the neodymium-[28] or yttrium-catalyzed[29] cyclization/hydrosilylation of dienes tolerates olefinic substitution. However, a modified silane-bridged yttrocene catalyst catalyzes the cyclization/hydrosilylation of dienes which possess an internal olefinic substituent.[62]

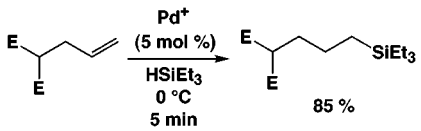
Palladium-catalyzed cyclization/hydrosilylation tolerated a terminal olefinic substituent on the diene. For example, reaction of *trans*-4,4-dicarbomethoxy-1,7-octadiene (*trans*-**12**), which possessed a single trans methyl group, with $HSiEt_3$ in the presence of **2b**/**3b** (5 mol %) at 0 °C for 5 min formed carbocycle **13** in 88% yield as a 10:1 mixture of isomers (Table 2, entry 1). Diene *trans*-**12** also reacted slowly with $HSiMe_2Ph$ to form carbocycle **14** in 78% yield as an 8:1 mixture of isomers (Table 2, entry 2). The presence of a three proton triplet (δ 0.83, J = 7.6 Hz) in the ^{1}H NMR spectrum of **14** assigned to the methyl group of the exocyclic ethyl substituent established transfer of silane to the less substituted olefin. Note that the regiochemistry of cyclization is in accord with a mechanism initiated by silylpalladation (Scheme 1).

The efficiency of cyclization/hydrosilylation depended strongly on the stereochemistry of the substituted olefin. For example, palladium-catalyzed reaction of *cis*-**12** and $HSiEt_3$ at 0 °C was an order of magnitude slower than was reaction of *trans*-**12** and $HSiEt_3$. Furthermore, reaction of *cis*-**12** and $HSiEt_3$ led to the isolation of a 1:1 mixture of **13** (>98% trans) and the silylated uncyclized isomer 4,4-dicarbomethoxy-7-(triethylsilyl)-1-heptene (**15**) in 60% combined yield (Table 2, entry 3). Alkenylsilane **15** was identified on the basis of the diagnostic olefinic resonances at δ 132 and 142 in the ^{13}C NMR spectrum. Other limitations of the palladium-catalyzed protocol with respect to olefinic substitution included dienes which possessed more than one terminal olefinic substituent or an internal olefinic substituent.[63]

In addition to a methyl group, a range of terminal olefinic substitution was tolerated by the cyclization/hydrosilylation procedure. For example, relatively unhindered dienes such as those substituted with a butyl (**16**) or phenoxymethyl (**18**) group underwent cyclization/hydrosilylation within 30 min at room temperature to form carbocycles **17** and **19**, respectively, in >70% yield with excellent regio- and stereoselectivity (Table 2, entries 4 and 5). In contrast, cyclization/hydrosilylation of the more hindered phenyl substituted diene **20** required 12 h at room temperature to form carbocycle **21** (Table 2, entry 6). Heavily oxygenated derivatives such as the phthalamidomethyl (**22**), carbomethoxy (**24**), or (dicarbomethoxy)ethyl (**26**) substituted dienes also underwent palladium-catalyzed cyclization/hydrosilylation within 12 h at room temperature to form the corresponding carbocycles in 51−72% isolated yield with excellent selectivity (Table 2, entries 7−9).

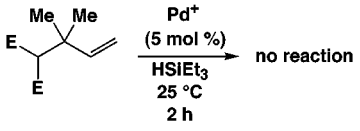
Palladium-catalyzed cyclization/hydrosilylation of dienes which possessed a terminal allylic halide atom was accompanied by dehalogenation. For example, palladium-catalyzed reaction of *cis*-allylic chloride **28** and $HSiEt_3$ led to formation of a 1:1 mixture of ethyl-substituted cyclopentane **13** and the vinyl-substituted carbocycle **29** in 55% combined yield (Table 2, entry 10). Cyclopentane **29** was identified on the basis of diagnostic vinyl resonances in the ^{1}H (δ 5.52, 5.00, and 4.98) and ^{13}C (δ 140 and 116) NMR spectra and from the mass spectrum (m/z = 340). Similarly, *trans*-allyl bromide **30** reacted with $HSiEt_3$ to form a 4.7:1 mixture of **13** and the doubly silylated cyclopentane **31** in 54% combined yield (Table 2, entry 11). Disilylated carbocycle **31** is presumably formed via hydrosilylation of the initially formed vinyl cyclopentane **29**.[37]

Allylic Substitution. Palladium-catalyzed cyclization/hydrosilylation also tolerated allylic substitution. For example, reaction of diene **32**, which possessed a single disubstituted allylic carbon atom, and $HSiEt_3$ in the presence of **2b**/**3b** at room temperature for 1 h led to the isolation of carbocycle **33** in 69% yield as a single isomer (Table 2, entry 12). Although it proved difficult to unambiguously assign regiochemistry on the basis of spectroscopy, **33** is assigned the structure resulting from delivery of the silyl group to the less hindered olefin. This regiochemical assignment is supported by related experiments which indicate that silylpalladation is slowed dramatically by proximal diallylic substitution. For example, palladium-catalyzed reaction of dimethyl allylmalonate and $HSiEt_3$ at 0 °C for 5 min formed 3-(triethylsilyl)propyl malonate in 85% yield (eq 6). In contrast,



(6)

dimethyl 1,1-dimethyl-2-propenylmalonate failed to react with $HSiEt_3$ in the presence of palladium catalyst within 2 h at room temperature (eq 7).



(7)

Transition metal-based carbocyclization protocols employing allylically substituted dienes,[57,64] enynes,[54,65] or enones[52,61,66] are often highly diastereoselective and form

(58) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1037.
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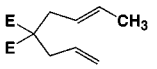
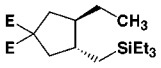
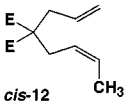
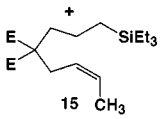
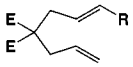
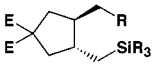
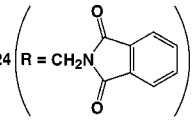
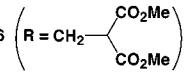
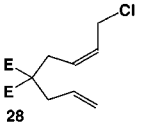
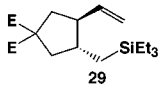
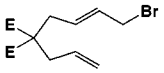
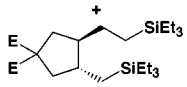
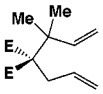
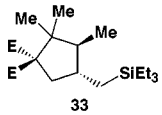
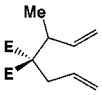
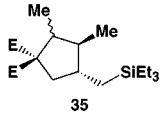
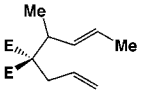
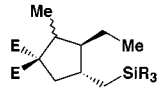
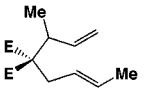
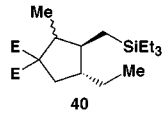
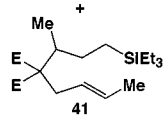
(60) (a) Laschat, S.; Narjes, F.; Overman, L. E. *Tetrahedron* **1994**, *50*, 347. (b) Carbri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (c) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379.
(61) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688.
(62) Molander, G. A.; Dowdy, E. D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386.
(63) For example, treatment of dimethyl-7-methyl-1,6-octadiene-4,4-dicarboxylate with $HSiEt_3$ led to the isolation of a 1:1:1:1 mixture of silylated products in 28% combined yield. Likewise, reaction of triethylsilane with 5,5-dicarbomethoxy-2,8-nonadiene led to <50% conversion with formation of four isomeric silylated products. 4,4-Dicarbomethoxy-2-methyl-1,6-heptadiene failed to react with $HSiEt_3$ in the presence of palladium catalyst after 2 h at room temperature.

Table 2. Palladium-Catalyzed Cyclization/Hydrosilylation of Dienes Which Possessed Allylic and/or Olefinic Substitution Employing 5 mol % Catalyst

entry	diene	silane	cat[a]	temp (°C)	time	product(s)	yield[b]	isomer ratio[c]
								
1	*trans*-12	$HSiEt_3$	B	0	5 min	13	88	10:1
2		$HSiMe_2Ph$		25	3 h	14	78	8:1
3	 *cis*-12	$HSiEt_3$		0	1 h	13	30[e]	95:1
						+  15	30[e]	—
								
4	16 (R = Bu)	$HSiEt_3$		25	10 min	17	88	50:1
5	18 ($R = CH_2OPh$)		A		30 min	19	71	>25:1[d]
6	20 (R = Ph)		A		12 h	21	76	12:1
7	22 ($R = CO_2Me$)		B		12 h	23	51	>50:1
8	24 				12 h	25	72	20:1[d]
9	26 				4 h	27	55	20:1
10	 28		A	0	20 min	13 +  29	23[e]	>50:1
							23[e]	>50:1
11	 30		B	25	20 min	13 +  31	45[e]	14:1
							9[e]	10:1
12	 32 ($E = CO_2Et$)	$HSiEt_3$		25	60 min	 33	69	44:1
13	 34 ($E = CO_2Et$)	$HSiEt_3$		0	15 min	 35	81	1:1
								
14	36 ($E = CO_2Me$)	$HSiMe_2Et$		25	5 min	37	79	1:1
15		$HSiMe_2Ph$	A		30 min	38	75	1:1
16[f]	 39 ($E = CO_2Et$)	$HSiEt_3$	B		15 min	 40	79[e]	3.3:1
						+  41	10[e]	—

[a] A = **2a**/**3a** in CH_2Cl_2; B = **2b**/**3b** in DCE. [b] Yields refer to isolated material which was >95% pure as determined by ^1H NMR and GC analysis. [c] Determined by capillary GC analysis of the crude reaction mixture. [d] Determined by ^1H and ^{13}C NMR. [e] Product isolated as a mixture of isomers. [f] 10 mol % catalyst employed.

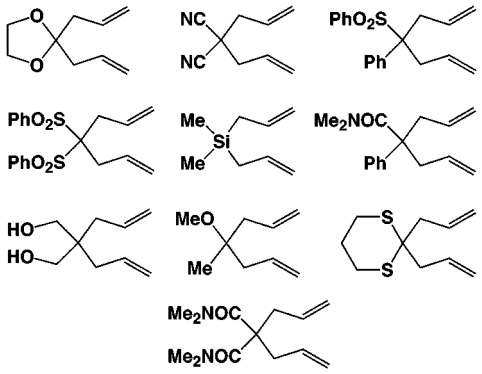
products consistent with cyclization via a chairlike transition state. In contrast, palladium-catalyzed cyclization/hydrosilylation of 4,4-dicarboethoxy-3-methyl-1,6-heptadiene (**34**), which possessed a single allylic methyl group, led to the formation of carbocycle **35** as a 1:1 mixture of C-2 diastereomers (Table 2, entry 13). In addition, ^{13}C NMR analysis of **35** revealed the presence of traces (5%) of a third isomer, pointing to competitive silylpalladation of the allylically substituted olefin. In an effort to preclude silylpalladation of the allylically substituted olefin, diene **36**, which possessed proximal allylic and olefinic substitution, was employed in the cyclization protocol. Reaction of **36** with $HSiMe_2Et$ or $HSiMe_2Ph$ gave carbocycles **37** and **38**, respectively, as 1:1 mixtures of C-2 diastereomers without formation of additional isomers (Table 2, entries 14, 15).

Dienes **34** and **36** failed to undergo diastereoselective cyclization/hydrosilylation presumably because the allylic chiral center was too far removed from the unhindered (distal) olefin to affect the facial selectivity of silylpalladation. We reasoned that if silylpalladation was directed toward the olefin proximal to the allylic substituent, the potential for diastereoselective cyclization would improve. To this end, 4,4-dicarboethoxy-3-methyl-1,6-octadiene (**39**), which possessed distal allylic and olefinic substitution, was employed in the cyclization/hydrosilylation protocol. In accord with the above analysis, reaction of **39** and $HSiEt_3$ in the presence of 10 mol % palladium catalyst formed carbocycle **40** as a 3.3:1 mixture of diastereomers along with ~10% of the open chain isomer **41** in 89% combined yield (Table 2, entry 16). A three proton doublet in the ^1H NMR spectrum of **40** (0.86, J = 7.6 Hz) assigned to the methyl group of the exocyclic ethyl substituent confirmed delivery of the silane to the allylically substituted olefin.

Homoallylic Substitution. The compatibility of palladium-catalyzed cyclization/hydrosilylation with the homoallylic diester groups of dienes such as **4** was significant as cyclization protocols employing d^0-metallocene complexes are often incompatible with unsaturated polar functionality.[25−30] For example, the yttrium-catalyzed reductive cyclization of 1,6-dienes did not tolerate the presence of homoallylic carbomethoxy, phenylsulfonyl, or cyano groups.[23] As a result, the tolerance of palladium-catalyzed cyclization with respect to homoallylic substitution was investigated further. In addition to carbomethoxy groups, the protocol tolerated a range of homoallylic substituents including *tert*-butyl esters (**44**, **80**), acetyl (**42**, **58**) and benzoyl (**70**, **77**) groups, methyl (**53**, **74**) and benzyl (**56**) ethers, acetoxy (**48**, **72**, **82**) and trimethylacetoxy (**51**) groups, amides (**61**), sulfones (**63**), and cyano (**65**) groups (Table 3, entries 1−24).

Cyclization/hydrosilylation of dienes which possessed two dissimilar homoallyllic substituents (Table 3, entries 10−24) led to the formation of the corresponding carbocycles as mixtures of C-1 diastereomers. The low to modest diastereoselectivity observed in these cases, which ranged from 1:1 for cyclization of dienes **70** and **72** to 5:1 for cyclization of malonamide derivative **61**, was not surprising as homoallylic stereochemistry has proven difficult to control in related carbocyclization procedures. For example, cobalt-mediated cyclocarbonylation of a 4-carbomethoxy-4-methyl-1,6-enyne led to formation of the corresponding bicyclic enone as a 45/55 mixture of diastereomers.[67] Similarly, palladium-catalyzed cycloisomerization of a substituted 4-carbomethoxy-1,6-enyne formed a 5:1 mixture of diastereomeric cyclopentanes.[68] The titanium-catalyzed cyclization of a 4-phenyl-1,6-enone displayed unusually good selectivity with formation of the corresponding cyclopentanol as a 12:1 mixture of diastereomers.[69]

Chart 1. 4,4-Disubstituted-1,6-dienes Which Failed To Undergo Palladium-Catalyzed Cyclization/Hydrosilylation



In contrast to the facile cyclization observed with the oxygenated dienes found in Table 3, a range of 4,4-disubstituted dienes substituted with homoallylic carbamoyl, sulfonyl, cyano, methyl, phenyl, hydroxymethyl, and ether groups failed to undergo palladium-catalyzed cyclization/hydrosilylation (Chart 1). In each case the diene was recovered unchanged from the reaction mixture. The failure of these dienes (Chart 1) to undergo palladium-catalyzed cyclization/hydrosilylation was somewhat surprising in light of the facile cyclization/hydrosilylation of the functionalized dienes found in Table 3. However, comparison of the dienes shown in Table 3 with those depicted in Chart 1 pointed to the key role oxygen functionality played in palladium-catalyzed cyclization/hydrosilylation. Specifically, only dienes which possessed one or more homoallylic ester, ketone, or ether group underwent efficient cyclization/hydrosilylation.

The efficiency of cyclization also depended strongly on the spatial relationship between the homoallylic oxygen atom and the olefinic groups. Specifically, only when the homoallylic oxygen atom and the olefinic groups were separated by three or four atoms was efficient cyclization observed. For example, dienes such as 2,2-diallyl-1,3-dioxolane or 4-methoxy-4-methyl-1,6-heptadiene (Chart 1), in which two atoms separated the oxygen atom and the olefins, failed to undergo cyclization/hydrosilylation.

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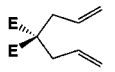
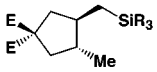
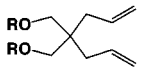
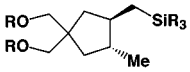
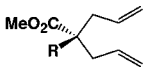
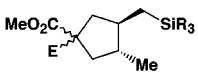
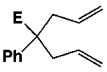
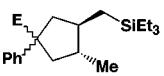
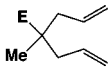
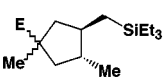
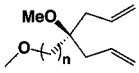
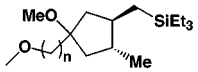
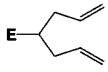
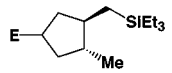
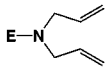
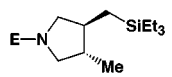
Table 3. Effect of Homoallylic Substitution on the Palladium-Catalyzed Cyclization/Hydrosilylation of 1,6-Dienes Employing 5 mol % Pd

entry	diene	silane	cat[a]	temp (°C)	time	cyclopentane	yield[b]	isomer ratio[c]
								
1	42 (E = COMe)	$HSiEt_3$	A	25	5 min	43	64	> 50:1
2	44 (E = CO_2*t*-Bu)		B	0	5 min	45	94	> 50:1
3	46 (E = CO_2Bn)		B	25	2 min	47	97	> 50:1
								
4	48 (R = COMe)	$HSiEt_3$	A	25	2 min	49	99	30:1
5		$HSiMe_2Ph$	B	25	2 h	50	41	> 50:1
6	51 (R = $COCMe_3$)	$HSiEt_3$		0	2 min	52	85	> 50:1
7	53 (R = Me)	$HSiEt_3$		0	2 min	54	92	> 50:1
8		$HSiMe_2Ph$		25	24 h	55	72	> 50:1
9	56 (R = Bn)	$HSiEt_3$		0	5 min	57	99	> 50:1
								
10	58 (R = COMe)	$HSiMe_2$*t*-Bu	A	25	30 min	59	78	1.5:1
11		$HSiMe_2Ph$	B	25	24 h	60	40	2.4:1
12	61 (R = $CONMe_2$)	$HSiEt_3$	A	0	1 min	62	99	5:1
13	63 (R = SO_2Me)			0	5 min	64	88	2:1
14	65 (R = CN)			25	12 h	66	60	2:1
								
15	67 (E = CO_2Me)	$HSiEt_3$	C	25	10 min	68	98	2.4:1
16		$HSiMe_2Ph$	B	0	12 h	69	32	2:1
17	70 (E = COPh)	$HSiEt_3$	B	25	5 min	71	96	1:1
18	72 (E = CH_2OAc)		C		1 mln	73	78	1:1
19	74 (E = CH_2OMe)		C		5 min	75	76	1.7:1
20		$HSiMe_2Ph$	B		1 h	76	77	1:1
								
21	77 (E = COPh)	$HSiEt_3$		25	5 min	78	93	2.1:1
22		$HSiMe_2Ph$			20 min	79	42	2:1
23	80 (E = CO_2CMe_3)	$HSiEt_3$	C		10 min	81	93	1.7:1
24	82 (E = OAc)				15 min	83	71	1.2:1
								
25	84 (n = 1)				5 min	85	80	1.7:1
26	86 (n = 2)		B		5 min	87	96	1.7:1
27	88 (n = 3)				90 min	89	74	7:5:1:1
								
28	90 (E = CO_2Me)				2 h	91	86	16:5:4:1
29	92 (E = COPh)		C		2 h	93	89	20:6:4:1
								
30	94 (E = $COCF_3$)		B		5 h	95	87	33:1

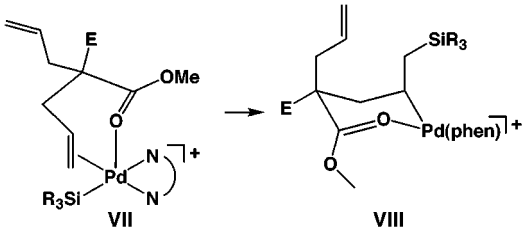
[a] Catalyst A = **2a**/**3a** in CH_2Cl_2; B = **2b**/**3b** in DCE; C = **2a**/**3a** in DCE. [b] Yields refer to isolated material which was >95% pure as determined by ^{1}H NMR and GC analysis. [c] Determined by capillary GC analysis of the crude reaction mixture.

However, dienes such as **53**, **74**, and **84** (three atom separation) and the methoxyethyl derivative **86** (four atom separation) underwent cyclization/hydrosilylation within minutes at room temperature to form the corresponding carbocycles in good yield (Table 3, entries 7, 19, 25, and 26). In contrast, the methoxypropyl derivative **88** (five atom separation) reacted approximately 20 times slower than did dienes **84** or **86** to form an intractable 7:5:1:1 mixture of silylated products (Table 3, entry 27), while 4-methoxy-4-(4-methoxybutyl)-1,6-heptadiene (six atom separation) failed to react with $HSiEt_3$ after 2 h at room temperature.

The above observations are consistent with the homoallylic oxygen atoms of the diene serving as directing groups which promote cyclization/hydrosilylation. For example, because both electron-withdrawing ester groups and electron-donating ether groups facilitated cyclization, the oxygen effect is not likely electronic in nature. Likewise, it is unlikely that steric effects play a major role since bulky groups such as carbo-*tert*-butoxy and trimethylacetoxy and smaller groups such as methoxymethyl promoted cyclization with equal efficiency. The directing group hypothesis is also supported by the correlation between the efficiency of cyclization and the separation between the oxygen directing atom and the olefinic groups.

There are myriad examples of reactions catalyzed by late transition metal complexes in which oxygen functionality has either facilitated or affected the regio- or stereochemistry of the transformation.[70] For example, free hydroxyl groups have been found to direct catalytic hydrogenation employing cationic rhodium(I)[71] or iridium(I)[72] or neutral ruthenium(II) complexes.[73] Similarly, amide groups controlled the stereochemistry of the Ir^+-catalyzed hydroboration of alkenes[74] while ester groups affected the regioselectivity of the Pt(II)-catalyzed hydrosilylation of alkynes.[75] Likewise, unsaturated benzylamides underwent highly regioselectivity hydrocarbonylation in the presence of Wilkinson's catalyst.[76] In a reaction which may be related to Pd-catalyzed cyclization/hydrosilylation, mixtures of $Pd(OAc)_2$ and HCl in refluxing chloroform catalyzed the cycloisomerization of dimethyl diallylmalonate but failed to catalyze the cycloisomerization of unfunctionalized dienes.[77]

We propose two plausible mechanisms by which oxygen functionality could facilitate palladium-catalyzed cyclization/hydrosilylation. For example, the appropriately positioned oxygen atom could facilitate the initial silylpalladation step by coordination and delivery of the olefin to the metal center via a pentacoordinate chelate complex such as **VII**. However, the facile hydrosilylation of unfunctionalized olefins catalyzed by **1** suggests that chelation is not required for olefin insertion into the Pd−Si bond of **I**.[37] Alternatively, oxygen coordination could serve to stabilize the resulting palladium−alkyl intermediate **VIII** with respect to undesired processes such as β-hydride and β-silyl elimination. This latter mechanism requires that oxygen chelation does not impede olefin insertion and points to the possibility of either associative ligand exchange or olefin insertion from a five-coordinate complex. Significantly, cationic palladium[33−36,78] and rhodium[79] metallacyclic complexes analogous to **VIII** have been observed as intermediates in catalytic processes involving CO or functionalized olefins.



The rates of many cyclization reactions,[80] including the cobalt-mediated cyclocarbonylation of enynes,[58] are accelerated by the presence of *gem*-dialkyl groups on the substrate backbone (Thorpe−Ingold effect). Although the failure of dienes such as 1,6-heptadiene and diallyl ketone to undergo palladium-catalyzed cyclization/hydrosilylation can be traced to the absence of a suitable directing group, cyclization was clearly facilitated by the presence of 4,4-disubstitution. For example, in contrast to the efficient cyclization/hydrosilylation of 4,4-disubstituted dienes **67** and **70** (Table 3, entries 15 and 17), reaction of 4-carbomethoxy-1,6-heptadiene (**90**) or 4-benzoyl-1,6-heptadiene (**92**) with $HSiEt_3$ required 2 h at room temperature to reach completion and led to the formation of intractable mixtures of silylated carbocycles (Table 3, entries 28 and 29). Similarly, reaction of diallyl trifluoroacetamide (**94**) with $HSiEt_3$ required 5 h at room temperature to form the corresponding pyrrolidine derivative (**95**) in 87% yield as a 33:1 mixture of isomers (Table 3, entry 30).[81]

1,7-Dienes. Six-membered carbocycles represent the most stable and most common ring size found in naturally occurring compounds. However, intramolecular cyclization is typically more effective for the formation of five-membered rings than six-membered rings. For example, five-membered rings are typically formed 2−3 orders of magnitude faster than six-membered rings via an intramolecular S_N2 reaction.[82] More importantly, palladium-catalyzed carbocyclization protocols are consistently more effective for the formation of five-membered rings than for six-membered rings.[6] Regardless, we hoped to apply palladium-catalyzed cyclization/hydrosilylation to the synthesis of silylated cyclohexane derivatives. To this end, treatment of dimethyl-4,4-dicarboxy-

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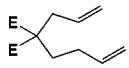
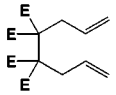
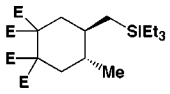
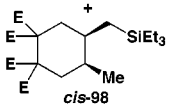
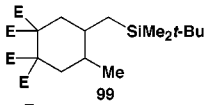
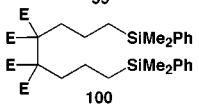
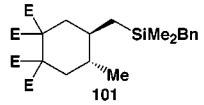
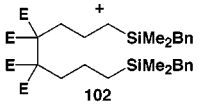
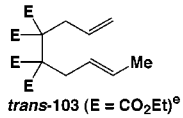
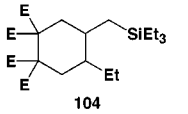
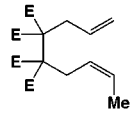
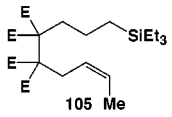
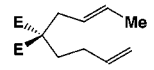
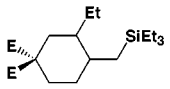
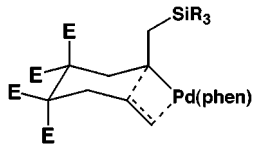
Table 4. Cyclization/Hydrosilylation of 1,7-Dienes Catalyzed by a Mixture of 2a and 3a (5 mol %) in DCE at 25 °C

entry	diene	silane	time (h)	silylated product(s)	yield[a]	trans:cis ratio
1	 96 (E = CO_2Me)	$HSiEt_3$	0.5	mono-silylated products	71	—
2	 97 (E = CO_2Et)	$HSiEt_3$	0.25	 *trans*-98 +  *cis*-98	93 3	— —
3		$HSiMe_2t$-Bu	3.0	 99	94	>25:1[b]
4		$HSiMe_2Ph$	2.0	 100	62	—
5		$HSiMe_2Bn$	0.75	 101 +  102	35 8	>25:1[b] —
6[d]	 *trans*-103 (E = CO_2Et)[e]	$HSiEt_3$	1.5	 104	79	8:1[c]
7[d]	 *cis*-103 (E = CO_2Et)		4.0	 105 Me	78	—
8	 106 (E = CO_2Me)[f]		2.0	 107	69	1.6:1[c]

[a] Yields refer to isolated material of >95% purity as determined by ^1H NMR and GC analysis. [b] Determined by ^1H and ^{13}C NMR analysis. [c] Determined by capillary GC or HPLC analysis of the crude reaction mixture. [d] 10 mol % catalyst employed. [e] 9:1 mixture of trans:cis isomers. [f] 4:1 mixture of trans:cis isomers.

1,7-octadiene (**96**) with triethylsilane and a 1:1 mixture of **2a**/**3a** (5 mol %) led to rapid and complete conversion to an intractable mixture of monosilylated products in 71% combined yield (Table 4, entry 1). We reasoned that the lack of selectivity arose, at least in part, from indiscriminate silylpalladation of either olefin of the diene.

In an effort to circumvent the selectivity problems observed with diene **96**, the symmetric tetracarboxylate derivative **97** was employed in the cyclization/hydrosilylation procedure. Palladium-catalyzed reaction of **97** with triethylsilane was complete within 15 min at room temperature with formation of a 22:1 mixture of isomeric cyclohexanes **98** as determined by GC analysis (Table 4, entry 2). Evaporation of solvent and flash chromatography of the residue gave *trans*-**98** in 93% yield and *cis*-**98** in 3% yield. The presence of three proton doublets in the ^1H NMR spectra of both *trans*-**98** (δ 0.90, J = 6.3 Hz) and *cis*-**98** (δ 0.90, J = 6.3 Hz) assigned to the exocyclic methyl groups established the formation of the six-membered carbocycles. In addition, *trans*-**98** and *cis*-**98** were readily distinguished by their ^1H NMR spectra. While the ring protons of *trans*-**98** appeared as sharp signals in the range δ 2.2−1.3, the ring protons of *cis*-**98** appeared as broad bands in the same region due to time averaging of the two stable chair conformers.[83] The high trans-selectivity observed for cyclization of **97**



IX

is rationalized by evoking chairlike transition state **IX** for ring closure.[55]

(83) While *trans*-**93** should exist predominately as a single equatorial−equatorial conformer, *cis*-**93** is expected to exist as a mixture of two contributing equatorial−axial chair conformations.

Palladium-catalyzed cyclization/hydrosilylation of 1,7-dienes was less general with respect to silane than was the cyclization of 1,6-dienes. For example, in addition to $HSiEt_3$, diene **97** also reacted with dimethyl-*tert*-butylsilane to give carbocycle **99** in good yield and diastereoselectivity (Table 4, entry 3). In contrast, reaction of **97** with dimethylphenylsilane formed the disilylated uncyclized product **100** without formation of the desired carbocycle (Table 4, entry 4). Similarly, **97** reacted with benzyldimethylsilane to form a separable mixture of carbocycle **101** and disilylated uncyclized product **102** (Table 4, entry 5).

As was observed for the cyclization/hydrosilylation of 1,6-dienes, cyclization of 1,7-dienes tolerated a *trans*-olefin but did not tolerate a *cis*-olefin. For example, reaction of triethylsilane with *trans*-tetraethyl-1,7-nonadiene-4,4,5,5-tetracarboxylate (*trans*-**103**) formed carbocycle **104** in 79% yield as an 8:1 mixture of isomers (Table 4, entry 6). In contrast, palladium-catalyzed reaction of *cis*-**103** and $HSiEt_3$ for 4 h at room temperature led to the exclusive formation of the uncyclized silylated product **105** in 78% isolated yield (Table 4, entry 7). Reaction of $HSiEt_3$ with the substituted dicarboxylate derivative **106** (4:1, trans:cis) formed carbocycle **107** in 68% yield as a 1.6:1 mixture of trans:cis isomers (Table 4, entry 8).

Conclusions

Cationic palladium phenanthroline complexes generated in situ from either (phen)$PdMe_2$ (**2a**) and $HBAr'_4$ (**3a**) or (phen)PdMe(Cl) (**2b**) and $NaBAr'_4$ (**3b**) serve as active catalysts for the cyclization/hydrosilylation of functionalized 1,6-dienes to form silylated cyclopentanes in good yield with excellent trans-selectivity. This catalyst system is stable to moderate amounts of both air and water and provides up to 200 turnovers. The protocol tolerates a range of functionality including esters, ethers, amides, sulfones, and cyano groups. The compatibility of the procedure with polar unsaturated functionality such as esters is significant as metallocene-catalyzed cyclization/hydrosilylation typically fails to tolerate these types of functionality. In addition, a range of tertiary hydrosilanes are tolerated by the protocol although sterically unhindered trialkyl silanes such as triethylsilane provide the most consistent results.

Palladium-catalyzed cyclization/hydrosilylation is facilitated by 4,4-disubstitution on the diene and requires the presence of a single ether, ketone, or ester oxygen atom separated by three or four atoms from the olefinic groups for efficient cyclization. The protocol tolerates a single *trans*-olefin and also tolerates substitution at an internal allylic carbon atom. In both cases, products resulting from transfer of the silane to the less hindered carbon atom are formed, consistent with a mechanism initiated by silylpalladation. The regioselectivity of the palladium-catalyzed protocol is complementary to yttrium-catalyzed cyclization/hydrosilylation, which selectively transfers the silane to the more substituted olefin.[29]

Mixtures of **2a** and **3a** also catalyze the cyclization/hydrosilylation of functionalized 1,7-dienes to form silylated cyclohexane derivatives. However, cyclization/hydrosilylation of 1,7-dienes is slower, less stereoselective, and more sensitive to silane and substitution than is cyclization/hydrosilylation of 1,6-dienes.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR were obtained in $CDCl_3$ on a spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C unless otherwise noted. Gas chromatography was performed employing a 25 m poly(dimethylsiloxane) capillary column. Flash chromatography was performed on 200−400 mesh silica gel eluting with mixtures of hexane and ethyl acetate. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsipanny, NJ). THF was distilled from sodium/benzophenone ketyl under nitrogen; CH_2Cl_2 and 1,1-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Silanes, dimethyl diallylmalonate, peracetic acid (32% in acetic acid), (Aldrich), $B(C_6F_5)_3$ (Strem), dimethyl allylmalonate, and trimethylsilane (Lancaster) were used as received. (Phen)$PdMe_2$ (**2a**)[84] was synthesized from (TMEDA)$PdMe_2$ (TMEDA = *N*,*N*,*N*′*N*′-tetramethylethylenediamine) and phenanthroline.[85] (phen)PdMe(Cl) (**2b**),[86] was prepared from reaction of phenanthroline and (COD)Pd(Me)Cl[87] (COD = 1,5-cyclooctadiene) in benzene. $HB[3,5\text{-}C_6H_3(CF_3)_2]_4(OEt_2)_2$ (**3a**)[88] and $NaB[3,5\text{-}C_6H_3(CF_3)_2]_4$ (**3b**)[88] were prepared by known procedures, and **3a** was stored at −30 °C.

General Procedure for Carbocycle Synthesis. The procedure described for the synthesis of **6** was applied to the synthesis of all other carbocycles except where specified. Reaction times and temperatures, precatalysts, and solvents employed are recorded in Tables 1−4.

***trans*-1,1-Dicarbomethoxy-4-methyl-3-[(trimethylsilyl)methyl]cyclopentane (5).**[40] Triethylsilane was bubbled through a solution of **4** (100 mg, 0.47 mmol), **2a** (8 mg, 0.025 mmol), and **3a** (24 mg, 0.024 mmol) in CH_2Cl_2 at 0 °C for 1 min to form a dark solution. Evaporation of solvent and chromatography (24:1) gave **5** (106 mg, 80%) as a colorless oil. ^1H NMR: δ 3.69 (s, 6 H), 2.52 (m, 2 H), 1.64 (dd, J = 10.8, 13.0 Hz, 2 H), 1.42 (m, 2 H), 0.93 (d, J = 6.0 Hz, 3 H), 0.84 (dd, J = 14.7, 2.5 Hz, 1 H), 0.26 (dd, J = 14.5, 10.9 Hz, 1 H), −0.01 (s, 9 H). $^{13}C\{^1H\}$ NMR: δ −0.7, 17.2, 20.3, 42.2, 43.6, 52.7 (br), 58.2, 173.5. IR (neat, cm^{-1}): 1735 (C=O).

***trans*-1,1-Dicarbomethoxy-3-[(triethylsilyl)methyl]-4-methylcyclopentane (6).** Dichloromethane (10 mL) and triethylsilane (230 mg, 2.0 mmol) were added sequentially via syringe to a mixture of **4** (100 mg, 0.47 mmol), **2a** (7 mg, 0.022 mmol), and **3a** (24 mg, 0.024 mmol) at 0 °C and stirred for 5 min to form a dark brown solution. Evaporation of solvent and chromatography (12:1) gave **6** (142 mg, 92%) as a colorless oil. ^1H NMR (C_6D_6): δ 3.37 (s, 6 H), 2.97 (dd, J = 6.3, 13.2 Hz, 1 H), 2.83 (dd, J = 6.3, 13.4 Hz, 1 H), 1.92 (m, 2 H), 1.58 (m, 2 H), 0.98 (t, J = 7.9 Hz, 6 H), 0.93 (d, J = 5.9 Hz, 3 H), 0.56 (q, J = 8.0 Hz, 6 H), 0.31 (dd, J = 11.0, 14.6 Hz, 1 H), one Et_3SiCH_2 proton obscured. $^{13}C\{^1H\}$ NMR: δ 173.4, 58.1, 52.6, 52.4, 43.8, 43.4, 42.9, 42.0, 17.2, 14.7, 7.5, 3.9. IR (neat, cm^{-1}): 1736 (C=O). MS (CI) (*m*/*e*) calcd (found) for $C_{17}H_{31}SiO_4$: 328.2 (329, MH^+). Anal. Calcd (found) for $C_{17}H_{32}SiO_4$: H, 9.82 (10.09); C, 62.15 (62.18).

***trans*-1,1-Dicarbomethoxy-3-hydroxymethyl-4-methylcyclopentane (10).** Reaction of mercuric acetate (450 mg, 1.41 mmol) and **7** (300 mg, 0.86 mmol) in peracetic acid/acetic acid (10 mL, 32%/45%) following the procedure of Fleming[43] followed by chromatography (1:1) gave **10** (141 mg, 74%) as a colorless oil. ^1H NMR: δ 3.71 (s, 6 H), 3.52 (dd, J = 5.3, 10.4 Hz, 1 H), 2.47 (m, 2 H), 2.07 (dd, J = 8.7, 13.9 Hz, 1 H), 1.80 (m, 3 H), 1.62 (br s, 1 H), 1.55 (br s, 1 H), 1.01 (d, J = 5.2 Hz, 3 H). $^{13}C\{^1H\}$ NMR: δ 173.6, 173.3, 64.6, 58.8, 53.0, 52.9, 48.9, 43.0, 37.6, 36.0, 18.5. HRMS (EI) calcd (found) for $C_{11}H_{19}O_5$

(84) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.
(85) de Graff, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.
(86) De Delice, V.; Albano, B. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem*. **1991**, *403*, 269.
(87) Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem*. **1993**, *32*, 5769.
(88) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(MH^+): 231.1232 (231.1240). Anal. Calcd (found) for $C_{11}H_{19}O_5$: H, 7.88 (7.73); C, 57.36 (56.94).

1,1-Dicarbomethoxy-3,4-dimethylcyclopentane (11).[45,46] Chlorotrimethylsilane (0.48 g, 4.4 mmol) was added dropwise over a 20 min period to a mixture of **10** (500 mg, 2.18 mmol) and sodium iodide (825 mg, 5.5 mmol) in acetonitrile (5 mL), and the resulting suspension was heated at 55 °C for 2 h. The mixture was then cooled to room temperature and diluted with acetonitrile (1 mL) and acetic acid (1 mL). Zinc dust (720 mg, 11.0 mmol) was added portionwise, and the mixture was heated at 85 °C for 12 h. The resulting suspension was filtered through a small plug of silica gel, concentrated, and chromatographed (12:1) to give **11** (26 mg, 5%). ^{1}H NMR: δ 3.68 (s, 6 H), 2.50 (dd, J = 6.4, 13.2 Hz, 2 H), 1.70 (dd, J = 10.8, 13.2 Hz, 2 H), 1.50−1.40 (m, 2 H), 0.94 (d, J = 6.0 Hz, 6 H). HRMS (CI): calcd (found) for $C_{10}H_{15}O_3$ ($M^+ - CH_3O$): 183.1021 (183.1019).

Cyclization of *cis*-12 (Table 2, Entry 3). Reaction of *cis*-**12** (120 mg, 0.53 mmol), $HSiEt_3$ (195 mg, 1.6 mmol), **3a** (8 mg, 0.024 mmol), and **3b** (24 mg, 0.023 mmol) in DCE at 0 °C for 1 h followed by evaporation of solvent and chromatography (24:1) gave 127 mg (61%) of a colorless oil consisting of a 1:1 mixture of **13** and 5,5-bis(carbomethoxy)-8-(triethylsilyl)-2-octene (**15**). Spectroscopy was performed on this mixture.

15. ^{1}H NMR: δ 5.85−5.60 (m, 2 H), 3.69 (s, 6 H), 2.82 (d, J = 6.3 Hz, 2 H), 1.95 (m, 2 H), 1.30 (m, 2 H), 1.20 (t, J = 8.0 Hz, 9 H), 0.63 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 172.0, 141.8, 131.9, 57.8, 52.4, 40.5, 32.4, 26.3, 23.1, 14.1, 7.5, 3.6.

Cyclization 28 (Table 2, Entry 10). Reaction of **28** (115 mg, 0.44 mmol), $HSiEt_3$ (195 mg, 1.6 mmol), **2a** (7 mg, 0.022 mmol), and **2b** (24 mg, 0.024 mmol) in CH_2Cl_2 at 0 °C for 20 min followed by evaporation of solvent and chromatography (24:1) gave 72 mg (55%) of a colorless oil consisting of a 1:1 mixture of **13** and *trans*-1,1-dicarbomethoxy-3-[(triethylsilyl)-methyl]-4-vinylcyclopentane (**29**).

29. ^{1}H NMR: δ 5.52 (ddd, J = 8.1, 10.2, 16.9 Hz, 1 H), 5.00 (d, J = 16.9 Hz, 1 H), 4.98 (d, J = 11.1 Hz, 1 H), 3.67 (s, 3 H), 3.66 (s, 3 H), 2.60−2.40 (m, 2 H), 1.80 (m, 2 H), 0.88 (t, J = 7.9 Hz, 9 H), 0.47 (q, J = 7.9 Hz, 6 H), 0.24 (dd, J = 11.7, 15.0 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.6, 140.1, 116.0, 58.5, 54.5, 52.9, 42.6, 41.9, 40.1, 14.5, 3.98. GC/MS (EI) (*m/e*) calcd (found) for $C_{18}H_{32}SiO_4$ (M^+): 340.2 (340).

Cyclization of 30 (Table 2, Entry 11). Reaction of **30** (134 mg, 0.44 mmol), $HSiEt_3$ (195 mg, 1.6 mmol), **2b** (7 mg, 0.023 mmol), and **3b** (25 mg, 0.024 mmol) in DCE at room temperature for 25 min followed by evaporation of solvent and chromatography (24:1) gave 81 mg (54%) of a colorless oil consisting of a 4.7:1 mixture of **13** and *trans*-1,1-dicarbomethoxy-3-[2-(triethylsilyl)ethyl]-4-[(triethylsilyl)methyl] cyclopentane (**31**). Additional chromatography afforded approximately 12 mg of **31** (92% pure by GC analysis) which was used for spectroscopy.

31. ^{1}H NMR: δ 3.70 (s, 6 H), 2.56 (dd, J = 6.8, 12.8 Hz, 1 H), 2.54 (dd, J = 7.2, 13.2 Hz, 1 H), 1.7−1.4 (m, 6 H), 0.92 (t, J = 7.7 Hz, 9 H), 0.91 (t, J = 8.0 Hz, 9 H), 0.51 (q, J = 7.9 Hz, 6 H), 0.48 (q, J = 7.9 Hz, 6 H), 0.29 (dd, J = 10.2, 13.8 Hz, 1 H). MS calcd (found) for $C_{24}H_{48}Si_2O_4$: 456.6 (456).

Reaction of 97 with $HSiEt_3$ (Table 4, Entry 2). A solution of **97** (100 mg, 0.25 mmol), triethylsilane (350 mg, 3.01 mmol), **2a** (4 mg, 0.013 mmol), and **3a** (13 mg, 0.013 mmol) in DCE was stirred at room temperature for 15 min. The resulting brown solution (22:1 ratio of isomers by GC analysis) was concentrated and chromatographed (9:1) to give *trans*-tetraethyl-4-[(triethylsilyl)methyl]-5-methylcyclohexane-1,1,2,2-tetracarboxylate (*trans*-**98**) (115 mg, 96%) and *cis*-tetraethyl-4-[(triethylsilyl)methyl]-5-methylcyclohexane-1,1,2,2-tetracarboxylate (*cis*-**98**) (4 mg, 3%) as colorless oils.

***trans*-98.** ^{1}H NMR: δ 4.23−4.10 (m, 8 H), 2.26 (dd, J = 4.1, 14.2 Hz, 1 H), 2.15 (dd, J = 4.1, 14.3 Hz, 1 H), 2.07 (dd, J = 12.1, 14.0 Hz, 1 H), 1.97 (dd, J = 12.1, 14.2 Hz, 1 H), 1.50−1.35 (m, 2 H), 1.22 (t, J = 6.2 Hz, 12 H), 0.90 (t, J = 7.9 Hz, 9 H), 0.89 (d, J = 6.3 Hz, 3 H), 0.50 (q, J = 7.9 Hz, 6 H), 0.22 (dd, J = 10.5, 15.0 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 170.8, 169.5, 169.4, 65.8, 61.5, 61.4, 61.2, 61.1, 59.5, 58.7, 37.4, 37.2, 35.2, 34.9, 19.8, 15.7, 15.2, 13.8, 13.73, 13.72, 7.3, 3.9. IR (neat, cm^{-1}): 1729 (C=O). HRMS (CI) calcd (found) for $C_{26}H_{47}O_8Si$ (MH^+): 515.7399 (515.3074). Anal. Calcd (found) for $C_{26}H_{46}O_8Si$: H, 9.01 (8.76); C, 60.67 (60.46).

***cis*-98.** ^{1}H NMR: 4.22−4.09 (m, 8 H), 2.08−1.93 (m, 4 H), 1.50−1.35 (m, 2H), 1.24 (t, J = 7.2 Hz, 12 H), 0.90 (d, J = 6.3 Hz, 3 H), 0.89 (t, J = 8.0 Hz, 9 H), 0.46 (q, J = 8.0 Hz, 6 H), $SiCH_2CH_3$ protons obscured.

Reaction of 97 with Dimethybenzylsilane (Table 4, Entry 5). Reaction of **97** (100 mg, 0.25 mmol), dimethylbenzylsilane (350 μL, 2.33 mmol), **2a** (4 mg, 0.013 mmol), and **3a** (13 mg, 0.013 mmol) in DCE stirred at room temperature for 45 min followed by evaporation of solvent and chromatography (5:1) gave *trans*-tetraethyl-5-methyl-4-[(dimethylbenzylsilyl)-methyl]cyclohexane-1,1,2,2-tetracarboxylate (**101**) (48 mg, 35%) and tetraethyl-1,8-bis(dimethylbenzylsilyl)octane-4,4,5,5-tetracarboxylate (**102**) (11 mg, 8%).

101. ^{1}H NMR: δ 7.20−7.16 (m, 2 H), 7.04 (t, J = 7.6 Hz, 1 H), 6.96 (d, J = 7.2 Hz, 2 H), 4.28−4.10 (m, 8 H), 2.27 (dd, J = 4.0, 10.0 Hz, 1 H), 2.16 (dd, J = 4.0, 10.0 Hz, 1 H), 2.08 (dd, J = 1.6, 12.4 Hz, 1 H), 2.06 (s, 2 H), 1.94 (dd, J = 12.0, 14.0 Hz, 1 H), 1.29−1.20 (m, 14 H), 0.91 (dd, J = 2.4, 14.8 Hz, 1 H), 0.86 (d, J = 6.4 Hz, 3 H), 0.26 (dd, J = 10.4, 15.2 Hz, 1 H), −0.023 (s, 3 H), −0.03 (s, 3 H). ^{13}C{^{1}H} NMR: δ 171.2, 171.1, 169.9, 169.8, 140.4, 128.44, 128.42, 124.3, 62.0, 61.8, 61.7, 61.5, 60.0, 59.0, 37.7, 37.6, 35.8, 34.9, 26.6, 20.1, 19.7, 19.6, 14.3, 14.2, 14.1, −1.95, −2.41. IR (neat, cm^{-1}): 1730 (C=O). HRMS (CI) calcd for $C_{29}H_{45}SiO_8$ (MH^+): 549.2884; found 549.2870. Anal. Calcd (found) for $C_{29}H_{44}O_8Si$: H, 8.08 (7.99); C, 63.47 (63.82).

102. ^{1}H NMR: δ 7.19−7.15 (m, 4 H), 7.03 (t, J = 7.2 Hz, 2 H), 6.95 (d, J = 7.2 Hz, 4 H), 4.23−4.08 (m, 8 H), 2.04−1.99 (m, 4 H), 2.03 (s, 4 H), 1.43−1.34 (m, 4 H), 1.23 (t, J = 6.8 Hz, 12 H), 0.52−0.46 (m, 4 H), −0.09 (s, 12 H). HRMS (CI) calcd (found) for $C_{38}H_{59}O_8Si_2$ (MH^+): 699.3749 (699.3738).

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Supporting Information Available: General experimental methods, along with experimental procedures, spectroscopic and analytical data, for new substrates and carbocycles. This material is available free of charge via the Internet at http://pubs.acs.org.

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