

Syntheses of Substituted 1,4-Disila-2,5-cyclohexadienes from Cyclic Hexasilane Si₆Me₁₂ and Alkynes via Successive Si-Si Bond Activation by Pd/Isocyanide Catalysts

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Supporting Information

ABSTRACT: Palladium-catalyzed reactions of dodecamethylcyclohexasilane $[(SiMe_2)_6]$ (1) with alkynes led to efficient preparation of 1,1,4,4-tetramethyl-1,4-disilacyclohexadienes (3). The reactions were best catalyzed by Pd(0)species generated from Pd₂(dba)₃·CHCl₃ and 1-isocyanoadamantane (AdNC). Terminal and internal alkynes bearing aryl and alkyl substituents could be used as substrates, and the reaction allowed gram-scale preparation of 3. A dimethylsilylene (Me₂Si:) species, generated by activation of Si-Si



bonds in 1 by Pd(0) species, was involved in the reaction mechanism. The DFT calculations suggest that oxidative addition of Si-Si bonds in 1 to $Pd(CNAd)_2$ species is followed by extrusion of a $Me_2Si=Pd(CNAd)$ intermediate. Reaction of the resulting palladium-coordinated silylene with an alkyne forms a silacyclopropene, which dimerizes to give 3. The extrusion is accompanied by ring contraction of 1 to generate $(SiMe_2)_5$, which also contributes to formation of 3 and $(SiMe_2)_4$ by the Pd(0)-catalyzed reaction with an alkyne. Extrusion of Me₂Si=Pd(CNAd) and ring contraction generated more than five Me₂Si: species from $(SiMe_2)_6$ (1).

INTRODUCTION

Oxidative addition of a disilane Si-Si bond to coordinatively unsaturated organometallic species has been of interest to organometallic chemists since the 1970s.^{1,2} During a catalytic cycle, the reaction is followed by insertion of an unsaturated molecule, containing a $C \equiv C_1^3 C \equiv C_1^4$ or $C \equiv O^5$ bond, or an isocyanide,⁶ providing a method for synthesis of unique organosilicon compounds [Scheme 1(a)].¹ Palladium and nickel compounds often have been used as the catalyst for these disilane transformations. Work by Ito and co-workers in the 1990s expanded the conventional reactions of disilanes to include chemical modifications of oligosilanes. Typical examples included palladium-catalyzed reactions of linear tri-, tetra-, penta-, and hexasilanes, $Me_3Si(SiMe_2)_nSiMe_3$ (n = 1-4) with alkynes or isocyanides, which formed the corresponding insertion products.^{3h,6b,d} Insertion of alkynes into Si–Si bonds in polysilanes also was reported by Tanaka and co-workers.³ⁱ

The high reactivity of strained cyclic oligosilanes toward insertion of alkynes and isocyanides has been of special interest. Hexa(tert-butyl)cyclotrisilane (Si3),6e octaphenylcyclotetrasilane (Si₄),^{6f} and decamethylcyclopentasilane (Si₅)^{6d} underwent insertion of one molecule of isocyanide to form the corresponding cyclic imines by heating (Si₃) or the use of a palladium catalyst (Si₄, Si₅). Insertion of an alkyne into a Si-Si bond of octaethylcyclotetrasilane also was achieved using a palladium catalyst.^{3g} However, neither alkynes nor isocyanides Scheme 1. Pd-Catalyzed Formation of Carbon-Silicon Bonds, Including Activation of Silicon-Silicon Bonds of (a) Hexamethyldisilane and (b) Dodecamethylcyclohexasilane





reacted with dodecamethylcyclohexasilane (Si_6Me_{12}; 1), due to the lack of sufficient ring strain. $^{\rm 6d,7,8}$

In parallel with research into activation of Si-Si bonds, the chemistry of silylene has been compared with that of carbene. Free silvlenes are generated by reduction of R₂SiCl₂ by Na,

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thermolysis of dialkoxydisilanes, or photoirradiation of oligosilanes.¹⁰ In the 1980s, two practical methods for *in situ* generation of dimethylsilylene (Me₂Si:) were reported. Thermal decomposition of hexamethylsilirane gave Me₂Si: and an alkene,^{11a} photolysis of Si₆Me₁₂ produced extrusion of Me₂Si: and formation of Si₅Me₁₀.^{11b} Cyclotrisilanes also were investigated as precursors of silylene species.¹² The resulting silylenes were highly reactive toward alkynes or ketones to form silacyclopropenes or enol silyl ethers, respectively. Silylenes coordinated to transition metal species also were studied; most were isolated as adducts of bases,^{2,13–15} while a base-free silylene complex was reported by Tilley.^{14j}

An organosilicon compound, 1,4-disila-2,5-cyclohexadiene (3), consisting of two R₂Si units and two C==C units, recently received attention as a cross-hyperconjugated molecule.¹⁶ Synthetic methods for 3 on a preparative scale were investigated by several groups.^{3k,17,18} Tanaka and co-workers reported syntheses of 3 via treatment of $Cl(Me_2Si)_3Cl$ with an alkyne using $PdCl_2(PPh_3)_2$.^{3k} A total of 2 mol of Me_2Si : species and Me_2SiCl_2 were formed from $Cl(Me_2Si)_3Cl$. The yield of 3 was moderate due to side reactions such as formation of silacyclopentadiene and copolymers of Me_2Si_2 : species and alkynes. A recent report from the laboratory of Stratakis indicated that 3 was generated from $(Me_2SiH)_2$ catalyzed by supported Au-NPs.^{17c} This process has the advantage of easy separation of catalyst from product; however, reaction with internal alkenes did not occur.

In the course of our studies on isocyanide complexes of transition metals,¹⁹ we were interested in palladium-catalyzed reaction of $(Me_2Si)_6$ (1) with alkynes. Although a series of reactions of oligosilanes with either isocyanides or alkynes were examined by Ito and co-workers, no reaction occurred for 1.^{6d} Thus, reaction of 1 with phenylacetylene was reinvestigated in the presence of $Pd(OAc)_2$. While no products derived from insertion of alkynes into Si-Si bonds in 1 were observed, both 1 and phenylacetylene were consumed under the reaction conditions, and 1,4-disila-2,5-cyclohexadiene 3 was isolated from the crude product mixture in low yield. Further studies to develop better palladium catalysts and to optimize reaction conditions led to the discovery that Pd(0) species stabilized by isocyanide ligands catalyzed reaction of 1 with terminal and internal alkynes, leading to atom-economically efficient synthesis of 3 [Scheme 1b]. Mechanistic studies using DFT calculations suggested reasonable catalytic cycles involving Me₂Si species coordinated to palladium as the intermediate.

RESULTS

Optimization Reaction of 1 to 3. Determining optimum reaction conditions was accomplished by conducting reaction of 1 with phenylacetylene (2a). Two products, 2,6-diphenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (3a-1) and its 2,5-diphenyl isomer (3a-2), were identified. Table 1 shows the effect of palladium precursors when using $P(OCH_2)_3CEt$ as the ligand. Tanaka et al. reported that $P(OCH_2)_3CEt$ was a good ligand for palladium-catalyzed conversion of Cl-(Me₂Si)₃Cl and 2a to 3a.^{3k} The amount of charged Pd was adjusted to 30:1 [(mol of SiMe₂ units in 1)/(mol of Pd atom in catalyst precursor)], which was defined as 3.3 mol % Pd per SiMe₂ unit. As shown in entries 1-3, treatment of 1 with a mixture of Pd₂(dba)₃·CHCl₃ and P(OCH₂)₃CEt (4 equiv to one Pd atom charged) at 100 °C for 12 h resulted in complete consumption of 1 to form a mixture of 3a-1 and 3a-2 in 40-74% yield. The yield of 3a increased when 4 equiv of 2a were

Table 1. Optimization of Reaction of 1 with 2a $(1)^a$

-si ^{Si} si -si si si	$\frac{3.3 \text{ m}}{3.2 \text{ m}} + \text{Ph} = \frac{3.3 \text{ m}}{13.2 \text{ m}}$	tol Pd% Cat. precursor tol Pd% P(OCH ₂) ₃ CEt toluene, 100°C time	Ph Si Ph Si +	Ph S 3a	Ph Si Ba-2	
				yield	(%) ^c	
		2a (mol)/1	conv. of 1	-		
entry	cat. precursor	$(mol)^{b}$	(%) ^c	3a-1	3a-2	
1	Pd ₂ (dba) ₃ ·CHCl ₃	12 (2)	>99	28	12	
2	Pd ₂ (dba) ₃ ·CHCl ₃	24 (4)	>99	51	23	
3	Pd ₂ (dba) ₃ ·CHCl ₃	48 (8)	>99	30	17	
4	PdCl ₂	24 (4)	0			
5	$(cod)PdCl_2$	24 (4)	>99	29	12	
6	$Pd(OAc)_2$	24 (4)	60	18	10	

^{*a*}All reactions were carried out with 1 (0.042 mmol, i.e. 0.25 mmol of $SiMe_2$ moieties) in toluene (3 mL). ^{*b*}Data in parentheses are the ratio of mols of **2a** to Si atoms in 1. ^{*c*}Yield and conversion were determined by ¹H NMR with anisole as an internal standard.

added (entry 2). While most of **2a** was recovered, a mixture of isomers of **2a** trimer was obtained as a byproduct. As the catalyst precursor, $(COD)PdCl_2$ and $Pd(OAc)_2$ also were useful, but $PdCl_2$ was not effective (entries 4–6). No reaction occurred with either $Ni(COD)_2$ or $Pt(dba)_2$ as the catalyst precursor.

Thus, $Pd_2(dba)_3$ ·CHCl₃ was a good palladium precursor for catalysis. Table 2 shows results of ligand screening. No reaction occurred in the absence of a ligand (entry 1). Sterically small phosphites, $P(OMe)_3$ and $P(OEt)_3$, were useful but less effective than $P(OCH_2)_3CEt$ as the ligand. Conversion of 1 and yields of 3a-1 and 3a-2 after heating at 100 °C for 12 h were lower than those obtained with the $Pd/P(OCH_2)_3CEt$ catalyst system (entries 2-4). Three other sterically bulkier phosphites, $P(OPh)_3$, $P(OC_6F_5)_3$, and $P(Ot-Bu)_3$, were not useful ligands. Four phosphines, P(Oct)₃, PCy₃, PPh₂Cl, and dppe, three nitrogen ligands, Et₃N, TMEDA, and pyridine, and MeCN, Ph₂S, and NHC (IPr) were also examined, but none improved catalyst efficiency. However, the use of an isocyanide as the ligand was effective. When *t*-BuNC was used as a ligand, conversion of 1 reached >99%, and the yield of 3a (total yield of 3a-1 and 3a-2) was greater than 70% (entry 8). As shown by entries 8-18, 11 other isocyanides were used in the catalytic reaction, with nine of them acting as good ligands. The best yield of **3a** was obtained when 1-isocyanoadamantane (AdNC) was used (entry 12). Note that reaction occurred with a relatively low catalyst loading such as 1.0 mol Pd%. Thus, Pd₂(dba)₃·CHCl₃ and AdNC were used as the optimal palladium precursor and ligand, respectively, for further experiments.

Scope and Limitation of the Reaction. Table 3 summarizes results of applying the $Pd_2(dba)_3 \cdot CHCl_3/CNAd$ catalyst to reaction of 1 with several alkynes. After heating the reaction mixture at 100 °C in toluene for 12 h, six of seven arylacetylenes reacted with 1 to give the corresponding 1,4disila-2,5-cyclohexadienes. In addition to phenylacetylene (2a), an arylacetylene with an electron-donating group (2b) and those with electron-withdrawing substituents (2c, 2e, 2f, and 2g) were used as alkynes. Conversion of 1 was greater than 93% for all reactions, and corresponding product 3 was obtained in 58–78% yield. An alkyne containing an aliphatic alkyl substituent, 1-octyne (2i), also was converted to the corresponding 1,4-disila-2,5-cyclohexadiene in good yield

	_si_Si_si_	+ Ph	3.3 mo 13	l Pd% Pd ₂ 5.2 mol Pd ⁶	(db % L	a) ₃ ·CHCl ₃ igand	Ph Si Ph Si Ph Ph			
	−Śi ∕ŚíSí~∖		_	toluene, 1 12h	100°	°C	Si Ph Si			
	1	2a					3a-1 3a-2			
Entry	Ligand	Conv. of	Yield $(\%)^b$			Entry	Ligand	Conv. of	Yield $(\%)^b$	
		1 (%) ^b	3a-1	3a-2			Ligand	1 (%) ^b	3a-1	3a-2
1	None	0	_	-	1	2	P(OCH ₂) ₃ CEt	>99	51	23
3	P(OMe) ₃	60	20	11	1	4	P(OEt) ₃	65	15	8
5	P(OPh) ₃	0	-	-		6	P(O'Bu) ₃	0	-	-
7	$P(OC_6F_5)_3$	0	_	_		8		>99	50	16
9	-NC	>99	49	20		10		95	48	15
11	XX NC	85	34	12		12		>99	60	18
13		79	31	17		14	/Pr NC /Pr	70	20	11
15	NC	19	3	2		16		29	10	5
17	EtO ₂ C NC	0	_	_			Ts ^{NC}	0	_	_

^aAll reactions were carried out with 1 (0.042 mmol, i.e. 0.25 mmol of SiMe₂ moieties) in toluene (3 mL). ^bYield and conversion were determined by ¹H NMR with anisole as an internal standard.

(entry 9). In these reactions with terminal alkynes, the ratios of 3a-1 to 3a-2 were between 79:21 and 67:33. Two internal alkynes also reacted with 1 (entries 10 and 11). In contrast, pbromophenylacetylene, propargyl phenyl ether, 4-octyne, and bis(trimethylsilyl)acetylene did not react with 1 under the reaction conditions. Thus, the substrate scope is somewhat broader than that reported in the literature.^{3k,17c,18} To confirm the synthetic utility of this reaction, 3a was prepared on a gram scale. Treatment of 523.4 mg of Si₆Me₁₂ with PhC≡CH resulted in formation of 1.24 g of 3a (3a-1/3a-2 = 72:28) in 95% ¹H NMR yield and 86% isolated yield.

Mechanistic Studies. The compound Pd₂(dba)₃·CHCl₃ is a good Pd(0) source, which easily allows replacement of dba with an isocyanide to form Pd(CNR)₂ species.²⁰ The same species also could be generated by fragmentation of a palladium trinuclear cluster Pd₃(CNR)₆. Oxidative addition of a Si-Si bond to Pd(CNR)₂ species was investigated by Ito and co-workers.^{20b} Their results indicated that oxidative addition of Si-Si bonds in 1 to Pd(CNR), was highly probable and was involved in an elementary reaction during the catalytic cycle for reaction of 1 with alkynes. This conclusion was supported by the use of $Pd_3(CNAd)_6$ as the catalyst instead of Pd2(dba)3.CHCl3/CNAd under the conditions described in Table 1, entry 2. A mixture of 3a-1 and 3a-2 was formed, with yields nearly the same as those from reaction using the Pd₂(dba)₃·CHCl₃/CNAd catalyst.

The DFT calculations provided insights into the mechanism of generation of 1,4-disilacyclohexadienes 3 from 1 and alkyne 2. As described above, 1,4-disilacyclohexadiene was formed by dimerization of silacyclopropene. Therefore, the calculations were focused on elucidation of reaction pathways from 1 and 2a to silacyclopropene by catalysis of Pd(CNAd)₂. Six "Me₂Si" units are formed from 1, and each "Me2Si" unit reacts with an equimolar amount of an alkyne to form the corresponding silacyclopropene. Consequently, six catalytic cycles are carried out for reaction of 1 mol of 1 (containing six Me₂Si units) with 6 mol of PhC≡CH to give 3 mol of 3. Among the six catalytic cycles, the first four cycles (the Si₆-Si₃ cycles depicted in Scheme 2) can be explained by the same principle.

Oxidative addition of a Si-Si bond of 1 to Pd(CNAd)₂ initiates the Si₆ cycle to form the square planar intermediate A2^{Si6}. This species has 12.8 kcal/mol higher energy than that of 1. The reaction proceeds through a transition state, $TS_{A1/A2}^{Si6}$, with an energy barrier of $\Delta G^{\ddagger} = 26.2$ kcal/mol. Dissociation of one AdNC ligand from A2^{Si6} affords intermediate $A3^{Si6}$ during an exergonic process. An important structural feature of $A3^{Si6}$ is the weak interaction of the β silicon atom (Si²) to the palladium center, as shown in Figure 1 $[Pd-Si^2 bond order = 0.05$, which is higher than the Pd-Si^3 and $Pd-Si^4$ interaction (bond order = 0)]. The calculations suggest that the hexasilapalladacyclic structure in A3^{Si6} is easily deformed to produce intermediates $A3'^{Si6}$ through $TS_{A3/A3'}^{Si6}$

	si^Sisi- si_si_si- /∫∫∫ + R-= 1	1 n ━R' — 2	nol Pd% Pd ₂ 4 mol Pd% toluene, 12	(dba)₃·CHCl∢ <u>⁄6 AdNC</u> 100°C h	3	R Si R' Si 3-1	R R' Si R Ad R' R Si R' Ad 3-2	NC =	-NC	
Entry	Alkyne 2	Conv. of 1 (%) ^b	Yield of 3 (%) ^c	Ratio of 3- 1 : 3-2		Entry	Alkyne 2	Conv. of 1 (%) ^b	Yield of 3 (%) ^c	Ratio of 3-1 : 3-2
1	H-(2a)	>99	78	77:23		2	MeO-(2b)	>99	77	79:21
3	F	>99	67	75:25		4	Br-(2d)	0	-	-
5	F (2e)	>99	57	67:33		6		>99	73	68:32
7	(2g)	93	58	76:24		8	—————————————————————————————————————	0	_	_
9	H (2i)	93	44	73:27		10 ^d	(2j)	65	34	_
11	O O (2k)	>99	86	_		12	(21)	0	_	_
13		0	_	_						

Table 3. Formation of 1,4-Disila-2,5-cyclohexadienes^a

^{*a*}All reactions were carried out with 1 (0.2 mmol, i.e. 1.2 mmol of SiMe₂ moieties) in toluene (4 mL). ^{*b*}Conversion was determined by ¹H NMR with anisole as an internal standard. ^{*c*}Isolated yield. ^{*d*}Conditions: 3.3 mol Pd% Pd₂(dba)₃·CHCl₃, 13.2 mol Pd% AdNC, 26 h.





 $(\Delta G^{\ddagger} = 21.9 \text{ kcal/mol})$. The structure of A3'^{Si6} is particularly interesting because it appears to be a silylimidoyl palladium species formed upon insertion of CNAd between a Si–Pd

bond of $A3^{si6}$ (Figure 1). The palladium atom is bonded with the imidoylcarbon with a C¹–Pd distance of 1.946 Å, and with a Si⁶–Pd bond of 2.360 Å. Besides these strong bonds (bond



Figure 1. Optimized structures of A3^{Si6} to A4^{Si6} and interatomic distances (Å) and angles (deg) with Mayer bond orders in parentheses.



Figure 2. Relative energy diagrams for conversion of A1 and Si_nMe_{2n} to $A4^{Sin}$ [ΔG (kcal/mol)].

orders; Pd–CNAd = 0.81, Pd–Si⁶ = 0.93), two secondary interactions are observed between Pd and Si¹ (2.757 Å; bond order = 0.21) and between Pd and Si² (3.169 Å, bond order = 0.09). Bond formation between Pd and Si² induces generation of Pd=Si¹ Me₂ species and a terminal isocyanide ligand to afford A4^{Si6} through TS_{A3'/A4}^{Si6} (ΔG^{\ddagger} of 8.5 kcal/mol). The geometry of Me₂Si¹ species in A4^{Si6} is trigonal and has relatively strong secondary interactions with Si² and weak interactions with C¹. Geometry around the Pd center in A4^{Si6} is distorted square planar, in which Pd, Si¹, Si², Si⁶, and C¹ exist in the same plane. The angle of both Si²–Pd–Si⁶ and Si⁶–Pd–C¹ is approximately 90°, forming a T-shape, with the Si¹ atom located closer to Si².

Two possible reaction pathways existed for $A4^{Si6}$. One was reaction leading to extrusion of $(Me_2Si)_5$ and production of Me_2Si : species bound to palladium (path a). The other was liberation of free Me_2Si : and the 14-electron pentasilapalladacyclic species $A3^{Si5}$ (path b). The coordinated and uncoordinated Me_2Si : species both produce silacyclopentene. The fate of the product other than Me_2Si also is important. Path a forms $(Me_2Si)_5$, which reacts with $Pd(CNAd)_2$ to initiate the Si₅ cycle. In contrast, path b produces $A3^{Si5}$ species, an intermediate of the Si₅ cycle. Consequently, the Si₆ cycle supplies Me_2Si : species to form final product 3 and at the same time delivers the species by way of path a or b to promote the Si₅ cycle. The Si₅ cycle proceeds in a manner similar to that of the Si₆ cycle, participating in production of 3 and initiation of the Si₄ cycle. This sequence also could be adapted to the Si₃ cycle. Scheme 2 outlines the Si₆ cycle and Si₅ cycle; total catalytic cycles, including the Si₄ cycle and the Si₃ cycle, are described in the Supporting Information.

Figure 2 shows energy diagrams of the Si₆–Si₃ cycles, i.e., reactions of Pd(CNAd)₂ with $(Me_2Si)_n$ (n = 3-6) to form silylene-palladacyclic intermediates $A4^{Sin}$ (n = 3-6). Two energy barriers exist in each process: at the oxidative addition step $[A1 + (Me_2Si)_n$ to $A2^{Sin}]$ (step 1) and during conversion of disilametallacycle $A3^{Sin}$ to silylene species $A4^{Sin}$ (step 2). In step 1, the energy barrier is decreased by reducing the ring size of $(Me_2Si)_n$; the order of ΔG^{\ddagger} from $A1^{Sin}$ to $TS_{A1/A2}^{Sin}$ is 26.2 (n = 6) > 19.6 (n = 5) > 14.3 (n = 4) > 5.1 (n = 3). In step 2

where n = 4-6, the reactions proceed through intermediate A3'^{Sin}, which is not observed for reaction of A3^{Si3} to A4^{Si3}. The energy barriers of step 2 are similar; ΔG^{\ddagger} is 21.9 (n = 6), 22.5 (n = 5), 24.1 (n = 4), and 18.4 (n = 3).

Figure 3 depicts the energy diagram for the two possible reaction pathways, path a and path b, included in the Si_6-Si_3



Figure 3. Relative energy diagrams of conversion of $A4^{Sin}$ via path a or path b [ΔG (kcal/mol)].

cycles. Except for the Si₃ cycle, the energy barriers of path a for the Si₆-Si₄ cycles are less than those of path b. For the Si₃ cycle, the ΔG^{\ddagger} of path b is less than that of path a, but the difference is only 5 kcal/mol. These results indicate that at least from the Si₆ to Si₄ cycle the reaction proceeds through path a and that both paths a and b are possible for the Si₃ cycle.

Two other catalytic cycles occur after the Si₃ cycle. Since path a of the Si₃ cycle generates (AdNC)Pd=SiMe₂ [A5] and Me₂Si=SiMe₂, the Si₂ cycle involves reaction of Me₂Si= SiMe₂ with Pd(CNAd)₂ to form A2^{Si2}, as shown in Scheme 3. Replacement of one of the AdNC ligands with PhC=CH provides A6 as a mixture of two isomers. An alternative route to A6 involves coordination of PhC=CH to A3^{Si2}, formed from A4^{Si3} through path b in the Si₃ cycle. Cleavage of the Si– Si bond in A6 generates silapalladacyclobutene A7 containing a silylene ligand on the palladium atom. Reductive elimination of silacyclopropene is accompanied by formation of A5, which reacts with PhC=CH to give another molecule of silacyclopropene.

The Si_1 cycle is the reaction of coordinated silylene with PhC=CH to form a silacyclopropene, which also is output by the Si_6 - Si_2 cycles. As shown in Scheme 4, Pd=Si species AS, formed by path a of the Si_6 - Si_3 cycles and the Si_2 cycle, reacts with PhC=CH to form A8 as a mixture of two isomers. The silylene and alkyne are coupled on the palladium of A8 to give silapalladacyclobutenes A9 ($\Delta G^{\ddagger} = 12-13$ kcal/mol). Coordination of CNAd and subsequent reductive elimination regenerates A1 to produce a silacyclopropene ($\Delta G^{\ddagger} = ca. 17$ kcal/mol).

Both free Me₂Si: and "Pd=SiMe₂" form **3** through a silacyclopropene. Calculations suggest that a pathway through

Scheme 3. Relative Energy Diagrams for Formation of Silacyclopropene from Pd-Si₂ Species [ΔG (kcal/mol)]



Scheme 4. Relative Energy Diagrams for Formation of Silacyclopropene from Pd=Si Species [ΔG (kcal/mol)]



"Pd=SiMe₂" is reasonable for the Si₆-Si₄ and Si₂ and Si₁ cycles. To obtain supporting evidence to exclude the free silylene mechanism, reaction of **1** with **2a** was conducted in the presence of 4-*tert*-butylcyclohexanone. As described previously, Ikeno and co-workers reported photolysis of Si₆Me₁₂ in the presence of ketones, in which free Me₂Si: was generated from

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 Si_6Me_{12} and trapped by a C=O double bond.^{7a} Subsequent rearrangement of oxasilacyclopropane afforded silyl enol ethers. If free silylene is involved in the palladium-catalyzed reaction of 1 with 2a, then it could be trapped by 4-tertbutylcyclohexanone. As shown in Scheme 5, 1 was treated

Scheme 5. Attempted Trapping of Free Silylene



with a 1:1 mixture of 4-*tert*-butylcyclohexanone under standard conditions of palladium-catalyzed reactions of 1 to 3. The yield and selectivity of products **3a-1** and **3a-2** were similar to those shown in Table 3. No silyl enol ether was detected.

DISCUSSION

Palladium-catalyzed reactions involving cleavage of a Si-Si bond of oligosilanes and subsequent reaction with an alkyne have been studied extensively, especially by Sakurai.^{3a} In the 1990s, Ito and co-workers reported a series of reactions using isocyanide as a palladium ligand.^{2b,3h,20b} Insertion of alkynes into Si-Si bonds of oligosilanes were catalyzed efficiently by Pd/alkylisocyanide catalysts.^{3h} Using an arylisocyanide as both the ligand and reagent results in insertion of an isocyanide instead of an alkyne.^{6a-d6g} Interestingly, few studies of reactions of cyclohexasilanes, such as 1, with alkynes or isocyanides existed.^{6d} The present report describes the first successful cleavage of Si-Si bonds in cyclohexasilanes by Pd/ isocyanide catalysts leading to generation of Me₂Si:, which was then efficiently trapped by an alkyne. Tanaka and co-workers reported an alternative palladium-catalyzed method for generation of Me₂Si: involving activation of (ClMe₂Si)₂SiMe₂ by $PdCl_2(PPh_3)_2$.^{3k} The reaction was accompanied by formation of Me₂SiCl₂ as a byproduct and was less efficient from an atom-economy view compared with the present method.

The DFT calculations helped clarify possible reaction mechanisms. The present reaction produced six Me₂Si: species from 1, which were efficiently trapped by alkynes. Calculations of four catalytic cycles, the Si₆–Si₃ cycles, indicates that they proceed through similar reaction pathways involving oxidative addition of a Si–Si bond to Pd(CNAd)₂ and ring contraction of palladaoligosilacycles. The Si₃ cycle is followed by two catalytic cycles, the Si₂ cycle and Si₁ cycle. The Si₂ cycle proceeds through silapalladacyclobutene intermediates. All five catalytic cycles produce a Me₂Si=Pd(CNAd) intermediate, which reacts with alkynes the same as the sixth catalytic cycle, the Si₁ cycle. In total, six Me₂Si=Pd(CNAd) participate in the reaction with alkynes to form silacyclopropene, which then dimerizes to give 3.

Uncoordinated free silylene species react with alkynes to give silacyclopropenes. The present calculations suggest generation of free Me₂Si: species from the Si₆–Si₃ cycles. However, comparison of energy profiles from the pathway through Me₂Si=Pd(CNAd) and that involving free Me₂Si: species revealed that the former is preferable, except for the Si₃

cycle. In the Si₃ cycle, the energy barrier of the reaction involving free silylene is less than that through coordinated silylene, but that energy difference is small. Considering the unsuccessful trapping of free silylene by a ketone (Scheme 5), Me₂Si=Pd(CNAd) likely is involved as a net catalytic species to form silacyclopropene in all of the Si₆-Si₁ cycles.

Oxidative addition of a Si–Si bond of 1 to $Pd(CN'Bu)_2$ is a reasonable process as indicated by experiments by Suginome and Ito, who isolated a series of bis(isocyanide)disilyl palladium(II) complexes from corresponding disilanes and $Pd(CN'Bu)_2$.^{20b} The calculated activation energy of oxidative addition from A1 to A2^{Si6} was higher than 26 kcal/mol, and this step involved the highest energy of the Si₆ cycle, which is reasonable because the reaction required a temperature higher than 100 °C.

A highlight of the mechanisms of the present reaction is "silyl–silylene rearrangement", from $A2^{Sin}$ to $A4^{Sin}$ (n = 3-6). As shown in Scheme 6, a "silyl–silylene rearrangement" was

Scheme 6. Silyl-Silylene Rearrangement



proposed from reaction of CpFe(CO)₂SiMe₂SiMe₃ (X1) to $CpFe(CO)_2SiMe_3$ (X4), in which photoassisted dissociation of CO resulted in the formation of $CpFe(CO)(=SiMe_2)SiMe_3$ (X3) and subsequent elimination of free silvlene and coordination of CO afforded X4 (Scheme 6, eq 1).^{2,13,21} Tobita successfully isolated a key intermediate, iron silyl-(silylene)complex (X7), as the OMe group adduct (Scheme 6, eq 2).^{13c} In these reactions, photolysis promoted dissociation of CO. Transformation of $A2^{Sin}$ to $A4^{Sin^{1}}(n = 3-6)$ also occurs through "silyl-silvlene rearrangement" triggered by dissociation of CNR. An interesting and unexpected outcome of the calculations was found for the pathway from A2^{Sin} to A4^{Sin} in the Si_6-Si_4 cycles, which proceeds through A3^{Sin} and A3'^{Sin}. No interaction was observed between Pd and the Si² atom in A2^{Sin}. In contrast, dissociation of CNAd from A2^{Sin} provides weak Pd–Si² interactions in $A2^{Sin}$, which strengthens during conversion from $A3^{Sin}$ to $A3'^{Sin}$ and from $A3'^{Sin}$ to $A4'^{Sin}$, and finally leads to formation of the Pd-Si² bond in the silapalladacycle. Meanwhile, the terminal isocyanide ligand in $A3^{Sin}$ is inserted within the Pd-Si¹ bond to form $A3'^{Sin}$, which weakens the Pd-Si1 bond and increases the Pd-Si2 interactions. In the transformation from $A3'^{Sin}$ to $A4^{Sin}$, the bridging isocyanide moves back to the terminal position, accompanied by creation of Pd=Si1 and Pd-Si2 bonds to complete the "silyl-silylene rearrangement".

The "silyl–silylene rearrangement" is also involved in the Si₃ cycle. However, the pathway from A2^{Si3} to A4^{Si3} is significantly different from that observed for the Si₆–Si₄ cycles. As shown in Figure 2, A2^{Si3} forms by oxidative addition of a Si–Si bond of (Me₂Si)₃ to A1, followed by dissociation of CNAd to form A3^{Si3} (structures in Figure 4). The Si¹–Si² bond elongates and a Pd–Si² bond forms, allowing conversion of A3^{Si3} to A4^{Si3} through a TS_{A3/A4}^{Si3} transition state ($\Delta G^{\ddagger} = 18.4 \text{ kcal/mol}$).

Organometallics

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Figure 4. Optimized structures of A3^{Si3}, TS_{A3/A4}^{Si3}, and A4^{Si}.

Unlike the reaction pathways from $A3^{Sin}$ to $A4^{Sin}$, where n = 4-6, intermediates and transition states having a bridging isocyanide were not observed.

The Si₂ cycle does not involve "silyl-silylene rearrangement". After completion of the Si₃ cycle, Me₂Si=SiMe₂ forms, which reacts with A1 to form A2^{Si2}. Dissociation of CNAd from A2^{Si2} is followed by coordination of PhC=CH to form A6. The structure of A6, in which a Si=Si moiety and a C=C bond are coordinated to Pd, resembles the intermediary species of ene-yne cyclization, in which a Si=Si moiety and a C=C bond are bound to Pd. While oxidative cyclization of an alkene and alkyne generates a metallacyclopentene intermediate during ene-yne cyclization,^{22a} coordination of the Si=Si moiety to Pd in A6 is considered to produce a disilapalladacyclopropane, and cleavage of the Si-Si bond and formation of the Si-C bond affords silylene-silapalladacyclobutene intermediate A7. Reductive elimination of silacyclopropene from A7 affords A5.

The Si_1 cycle is similar to the initial reaction mechanism of alkyne metathesis, in which metal silylene species reacts with an alkyne to form silapalladacyclobutene.^{22b} Reaction of A9 with AdNC results in reductive elimination of silacyclopropene and regeneration of A1. The resulting silacyclopropene is dimerized to 3 thermally or by catalysis of palladium; the latter was proposed in the literature.^{3k,18c,23}

An overall energy diagram of the Si₆–Si₁ cycles suggests the following: (1) The initial step of the catalytic cycle for the Si₆–Si₃ cycles is oxidative addition of a Si–Si bond in cyclic oligosilanes to Pd(CNR)₂. The ΔG^{\ddagger} of this process is the highest for the Si₆ cycle (26.2 kcal/mol) and decreased in the order Si₆ > Si₅ > Si₄ > Si₃ cycle. This order corresponds to the increasing ring strain of cyclic oligosilanes, which is favorable for formation of the oxidative adduct. (2) The reaction barrier of the first three cycles (Si₆–Si₄) is in the range of 3.8–27.8 kcal/mol, whereas that of the Si₃ cycle is 38 kcal/mol. These values are reasonable for the reaction which proceeded at temperatures higher than 100 °C. (3) The Si₂ and Si₁ cycles proceed with a lower activation energy than that of the previous four cycles. (4) As a consequence, once the Si₆ cycle starts, the Si₆–Si₁ cycles occur spontaneously.²⁴

CONCLUSION

Successive palladium-catalyzed Si–Si bond activation of Si_6Me_{12} (1) resulted in its reaction with various alkynes to form a 1,4-disilacyclohexadiene. The present reaction has advantages over the previously reported reaction by Tanaka's group using $ClSiMe_2SiMe_2Cl$ as a silylene source, because Si_6Me_{12} is easily handled and the reaction is highly

atom-economical. The mechanism was investigated using DFT calculations, which reveal that oxidative addition of a Si–Si bond of 1 by $Pd(CNAd)_2$ is followed by generation of a $Me_2Si=Pd(CNAd)$ species. Reaction of $Me_2Si=Pd(CNAd)$ with an alkyne formed a 1,4-disilacyclohexadiene. Extrusion of Me_2Si : species from 1 is accompanied by ring contraction of cyclohexasilane to cyclopentasilane, which also is a source of $Me_2Si=Pd(CNAd)$ species. Thus, all Me_2Si : moieties in 1 can be used for preparation of 1,4-silacyclohexadienes.

EXPERIMENTAL SECTION

General. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or performed in a N2-filled glovebox. ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were measured on JEOL ECA400 (396 MHz) and ECA600 (600 MHz) spectrometers. Chemical shifts for ¹H and ¹³C were given in parts per million relative to the solvent signal. Chemical shifts for ¹⁹F and ²⁹Si were given in parts per million downfield from hexafluorobenzene ($\delta_{\rm F} = -163.6$) and tetramethylsilane ($\delta_{Si} = 0$) as an external standard, respectively. IR spectra were measured on a JASCO FT/IR 4200 spectrometer. UV spectra were measured on a JASCO V-650 spectrometer. Elemental analyses were measured on a PerkinElmer 2400II/CHN analyzer. HR-MS analyses, ICP-MS analyses, and X-ray diffraction analyses were performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. Deuterated solvents [CDCl₃, C₆D₆] were used after dehydration. Dehydrated solvents [toluene, heptane] were purchased from Kanto Chemical Co. Ltd. and used as received. PdCl₂, Pd(OAc)₂, Ni(cod)₂, Pt(dba)₂, 4-tertbutylcyclo-hexanone, Si_6Me_{12} (1), alkynes 2, isocyanides, and the other ligands described in Table 2 were purchased from Wako Pure Chemical Industries, AZmax Co., Ltd., Tokyo Chemical Industry Co., Ltd., and Merck. Pd₂(dba)₃·CHCl₃,^{25a} (cod)PdCl₂,^{25b} and $Pd_3(CNAd)_6^{20}$ were prepared according to the literature.

General Procedure for the Reaction of 1 with Various Types of Alkynes 2 in the Presence of $Pd_2(dba)_3$ ·CHCl₃ and 1-Isocyano-adamantane (Table 3). In a 50 mL Schlenk tube, 1 (70 mg, 0.20 mmol), $Pd_2(dba)_3$ ·CHCl₃ (1 mol Pd%), 1-isocyanoadamantane (4 mol Pd%), and alkyne (4.8 mmol) were dissolved in toluene (4 mL). The resulting mixture was stirred at 100 °C for 12 h. Then, anisole (65 μ L, 0.6 mmol) was added as an internal standard, and the conversion of 1 and the yield of 3-1 and 3-2 were determined by ¹H NMR analysis. After removal of the solvent, purification of the residue by silica column chromatography (hexane) gave the mixture of 3-1 and 3-2 as a white solid.

2,6-Diphenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3a-1**) and 2,5-Diphenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3a-2**).^{17C} From **1** (70 mg, 0.20 mmol) and phenyl-acetylene **2a** (492 mg, 4.8 mmol), **3a** was obtained as a 77:23 mixture of **3a-1** and **3a-2** (149.8 mg, 78%). ¹H NMR of **3a-1** (600 MHz, CDCl₃, r.t.): δ 0.24 (s, 6H, -SiCH₃), 0.25 (s, 6H, -SiCH₃), 6.74 (s, 2H, CH), 7.19 (d, J_{H-H} = 8.9 Hz, 4H, o-Ph), 7.23 (t, J_{H-H} = 8.9 Hz, 2H, p-Ph), 7.31 (dd, J_{H-H} = 8.9 Hz, 4H, m-Ph). ¹H NMR of **3a-2** (600 MHz, CDCl₃, rt): δ 0.28 (s, 12H, -SiCH₃), δ 6.79 (s, 2H, CH), 7.33 (dd, J_{H-H} = 8.9 Hz, 4H, m-Ph). ¹³C{¹H} NMR of **3a-1** (151 MHz, CDCl₃, rt.): δ -1.1, -0.6, 126.3, 126.5, 128.1, 145.4, 147.3, 162.1. ¹³C{¹H} NMR of **3a-2** (151 MHz, CDCl₃, rt.): δ -25.12. mp.: 91–93 °C. HRMS-EI(+) (m/z): [M]⁺ calcd for C₂₀H₂₄Si₂, 320.1417; found, 320.1417.

2,6-Bis(4-methoxy)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3b-1**) and 2,5-Bis(4-methoxy)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3b-2**). From 1 (70 mg, 0.20 mmol) and 4-methoxyphenylacetylene **2b** (634 mg, 4.8 mmol), **3b** was obtained as a 79:21 mixture of **3b-1** and **3b-2** (175.6 mg, 77%). ¹H NMR of **3b-1** (600 MHz, CDCl₃, r.t.): δ 0.25 (s, 6H, -SiCH₃), 0.28 (s, 6H, -SiCH₃), 3.82 (s, 6H, -OCH₃), 6.72 (s, 2H, CH), 6.87 (d, J_{H-H} = 8.9 Hz, 4H, Ar), 7.19 (d, J_{H-H} = 8.9 Hz, 4H, Ar). ¹H NMR of **3b-2** (600 MHz, CDCl₃, rt): δ 0.30 (s, 12H, $-\text{SiCH}_3$), 3.83 (s, 6H, $-\text{OCH}_3$), 6.77 (s, 2H, CH), 6.90 (d, $J_{\text{H-H}}$ = 8.9 Hz, 4H, Ar), 7.27 (d, $J_{\text{H-H}}$ = 8.9 Hz, 4H, Ar). ¹³C{¹H} NMR of **3b-1** (151 MHz, CDCl₃, r.t.): δ -0.9, -0.2, 55.3, 113.6, 127.7, 139.9, 144.4, 158.5, 161.4. ¹³C{¹H} NMR of **3b-2** (151 MHz, CDCl₃, r.t.): δ -0.1, 55.4, 113.8, 127.4, 138.6, 144.0, 158.8, 159.6. ²⁹Si NMR for **3b-1** (119 MHz, CDCl₃, r.t.): δ -25.16, -23.85. ²⁹Si NMR for **3b-2** (119 MHz, CDCl₃, r.t.): δ -22.81. m.p.: 92-94 °C. HRMS-EI(+) (m/z): [M]⁺ calcd for C₂₂H₂₈O₂Si₂: Solution 280.1628; found, 380.1628. Anal. Calcd for C₂₂H₂₈O₂Si₂: C, 69.42, H, 7.41; Found: C, 64.39, H, 7.34.

2,6-Bis(4-fluoro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3c-1**) and 2,5-Bis(4-fluoro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3c-2**).^{17c} From **1** (70 mg, 0.20 mmol) and 4-fluorophenylacetylene 2c (577 mg, 4.8 mmol), 3c was obtained as a 75:25 mixture of 3c-1 and 3c-2 (143.2 mg, 67%). ¹H NMR of 3c-1 (600 MHz, CDCl₃, r.t.): δ 0.23 (s, 6H, -SiCH₃), 0.26 (s, 6H, $-SiCH_3$, 6.71 (s, 2H, CH), 7.01 (dd, $J_{H-H} = 8.2$ Hz, $J_{H-F} = 8.2$ Hz, 4H, Ar), 7.16 (dd, J_{H-H} = 8.2 Hz, J_{H-F} = 6.2 Hz, 4H, Ar). ¹H NMR of 3c-2 (600 MHz, CDCl₃, rt): δ 0.28 (s, 12H, -SiCH₃), 6.75 (s, 2H, CH), 7.03 (dd, J_{H-H} = 8.2 Hz, J_{H-F} = 8.2 Hz, 4H, Ar, overlapped with Ar of 3c-1), 7.24 (dd, $J_{H-H} = 8.2$ Hz, $J_{H-F} = 6.2$ Hz, 4H, Ar). ¹³C{¹H} NMR of 3c-1 (151 MHz, CDCl₃, r.t.): δ –1.1, –0.5, 115.1 (d, J_{C-F} = 21.7 Hz), 128.1 (d, J_{C-F} = 8.7 Hz), 143.3 (d, J_{C-F} = 2.9 Hz), 145.9, 161.0, 161.9 (d, J_{C-F} = 244.5 Hz). ¹³C{¹H} NMR of 3c-2 (151 MHz, CDCl₃, r.t.): signals of 3c-2 were too small to be characterized. ¹⁹F NMR of 3c-1 (565 MHz, CDCl₃, r.t.): δ -65.73. ¹⁹F NMR of 3c-2 (565 MHz, CDCl₃, r.t.): δ -65.33. ²⁹Si NMR for 3c-1 (119 MHz, $CDCl_3$, r.t.): $\delta - 9.38$, -7.95. ²⁹Si NMR for 3c-2 (119 MHz, CDCl₃) r.t.): δ -6.96. m.p.: 126-129 °C. HRMS-EI(+) (m/z): [M]⁺ calcd for C₂₀H₂₂F₂Si₂, 356.1228. Found, 356.1227.

2,6-Bis(2-fluoro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (3e-1) and 2,5-Bis(2-fluoro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3e-2**). From 1 (70 mg, 0.20 mmol) and 2-fluorophenylacetylene 2e (577 mg, 4.8 mmol), 3e was obtained as a 67:33 mixture of 3e-1 and 3e-2 (121.8 mg, 57%). ¹H NMR of 3e-1 (600 MHz, CDCl₃, r.t.): δ 0.14 (t, 6H, J_{H-F} = 2.1 Hz, -SiCH₃), 0.27 (s, 6H, $-SiCH_3$), 6.74 (s, 2H, CH), 7.01 (dd, $J_{H-H} = 7.6$, $J_{H-F} =$ 8.9 Hz, 2H, Ar), 7.07-7.10 (a mixture of signals, 4H, Ar), 7.17-7.23 (m, 2H, Ar, overlapped with Ar of 3e-2). Ar-H were confirmed by $^{1}\text{H}-^{1}\text{H}$ COSY. ^{1}H NMR of 3e-2 (600 MHz, CDCl₃, rt): δ 0.24 (d, 12H, $J_{H-F} = 2.1$ Hz, $-SiCH_3$), 6.83 (s, 2H, CH), 7.03 (dd, $J_{H-H} = 7.6$, $J_{\rm H-F}$ = 8.9 Hz, 2H, Ar), 7.12-7.16 (a mixture of signals, 4H, Ar), 7.17–7.23 (m, 2H, Ar, overlapped with Ar of 3e-1). Ar–H were confirmed by ${}^{1}H{-}^{1}H$ COSY. ${}^{13}C{}^{1}H{}$ NMR of 3e-1 (151 MHz, CDCl₃, r.t.): δ -1.4 (t, J_{C-F} = 4.3 Hz), -0.8, 115.9, 124.6 (d, J_{C-F} = 4.3 Hz), 128.5 (d, J_{C-F} = 7.2 Hz), 130.2 (d, J_{C-F} = 4.3 Hz), 135.2 (d, $J_{C-F} = 17.3 \text{ Hz}$, 148.5, 158.3, 159.1 (d, $J_{C-F} = 244.1 \text{ Hz}$). ¹³C{¹H} NMR of 3e-2 (151 MHz, $CDCl_3$, r.t.): -0.9 (t, J_{C-F} = 4.3 Hz), 115.7, 124.7 (d, J_{C-F} = 4.3 Hz), 128.7 (d, J_{C-F} = 7.2 Hz), 129.9 (d, J_{C-F} = 4.3 Hz), 134.6 (d, J_{C-F} = 17.3 Hz), 149.7, 156.7, 159.3 (d, J_{C-F} = 244.1 Hz). ¹⁹F NMR of **3e-1** (565 MHz, CDCl₃, r.t.): δ –133.80. ¹⁹F NMR of 3e-2 (565 MHz, CDCl₃, r.t.): δ –133.80 (overlapped with **3e-1**). ²⁹Si NMR for **3e-1** (119 MHz, CDCl₃, r.t.): δ -8.68, -7.14. ²⁹Si NMR for **3e-2** (119 MHz, CDCl₃, r.t.): δ –7.99. m.p.: 67–71 °C. HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{20}H_{22}F_2Si_{22}$ 356.1228. Found, 356.1231. Anal. Calcd for C20H22F2Si2: C, 67.37, H, 6.22; Found: C, 66.99, H, 6.34.

2,6-Bis(2-chloro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3f-1**) and 2,5-Bis(2-chloro)phenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3f-2**). From 1 (70 mg, 0.20 mmol) and 2-chlorophenylacetylene 2f (656 mg, 4.8 mmol), 3f was obtained as a 68:32 mixture of **3f-1** and **3f-2** (170.0 mg, 73%). ¹H NMR of **3f-1** (600 MHz, CDCl₃, r.t.): δ 0.08 (s, 6H, -SiCH₃), 0.27 (s, 6H, -SiCH₃), 6.61 (s, 2H, CH), 7.03 (dd, J_{H-H} = 1.4, 7.6 Hz, 2H, Ar), 7.14 (ddd, J_{H-H} = 1.4, 7.6, 7.6 Hz, 2H, Ar), 7.19 (ddd, J_{H-H} = 1.4, 7.6, 7.6 Hz, 2H, Ar), 7.38 (dd, J_{H-H} = 1.4, 7.6 Hz, 2H, Ar). Ar–H were confirmed by ¹H–¹H COSY. ¹H NMR of **3f-2** (600 MHz, CDCl₃, rt): δ 0.19 (s, 12H, -SiCH₃), 6.60 (s, 2H, CH), 7.04 (dd, J_{H-H} = 1.4, 7.6 Hz, 2H, Ar), 7.15 (ddd, J_{H-H} = 1.4, 7.6, 7.6 Hz, 2H, Ar), 7.21 (ddd, J_{H-H} = 1.4, 7.6, 7.6 Hz, 2H, Ar), 7.39 (dd, J_{H-H} = 1.4, 7.6 Hz, 2H, Ar).

Ar–*H* were confirmed by ¹H–¹H COSY. ¹³C{¹H} NMR of **3f-1** (151 MHz, CDCl₃, r.t.): δ –1.2, –0.9, 126.7, 127.8, 129.3, 130.2, 131.8, 145.8, 147.9, 160.4. ¹³C{¹H} NMR of **3f-2** (151 MHz, CDCl₃, r.t.): –0.9, 126.8, 127.8, 129.3, 130.2, 131.7, 145.7, 148.0, 160.3. ²⁹Si NMR for **3f-1** (119 MHz, CDCl₃, r.t.): δ –8.38, –7.41. ²⁹Si NMR for **3f-2** (119 MHz, CDCl₃, r.t.): δ –8.64. m.p.: 122–123 °C. HRMS-EI(+) (*m*/*z*): [M]⁺ calcd for C₂₀H₂₂Cl₂Si₂, 388.0637. Found, 388.0637. Anal. Calcd for C₂₀H₂₂Cl₂Si₂: C, 61.68, H, 5.69. Found: C, 61.84, H, 6.00.

2,6-Bis(4-biphenyl)-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (3g-1) and 2,5-Bis(4-biphenyl)-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (3g-2). From 1 (70 mg, 0.20 mmol) and 4ethynyl-1,1'-biphenyl 2g (856 mg, 4.8 mmol), 3g was obtained as a 76:24 mixture of 3g-1 and 3g-2 (164.3 mg, 58%). ¹H NMR of 3g-1 (600 MHz, CDCl₃, r.t.): δ 0.31 (s, 6H, -SiCH₃), 0.37 (s, 6H, $-SiCH_3$, 6.84 (s, 2H, CH), 7.33 (d, J_{H-H} = 8.2 Hz, 4H, Ar), 7.36 (t, $J_{\rm H-H}$ = 7.6 Hz, 2H, p-Ph), 7.47 (dd, $J_{\rm H-H}$ = 7.6 Hz, 4H, m-Ph), 7.59 (d, $J_{H-H} = 8.2$ Hz, 4H, Ar), 7.65 (d, $J_{H-H} = 7.6$ Hz, 4H, o-Ph). ¹H NMR of 3g-2 (600 MHz, CDCl₃, rt): δ 0.38 (s, 12H, -SiCH₃), 6.91 (s, 2H, CH), 7.38 (t, J_{H-H} = 7.6 Hz, 2H, p-Ph), 7.41 (d, J_{H-H} = 8.2 Hz, 4H, Ar), 7.48 (dd, J_{H-H} = 7.6 Hz, 4H, *m*-Ph), 7.61 (d, J_{H-H} = 8.2 Hz, 4H, Ar), 7.66 (d, J_{H-H} = 7.6 Hz, 4H, *o*-Ph). ¹³C{¹H} NMR of 3g-1 (151 MHz, CDCl₃, r.t.): δ -1.0, -0.2, 127.0, 127.1, 127.1, 127.3, 128.9, 141.0, 145.7, 146.4, 161.7. ¹³C{¹H} NMR of 3g-2 (151 MHz, CDCl₃, r.t.): δ -0.3, 126.8, 127.1, 127.2, 127.3, 128.9, 139.7, 141.0, 145.2, 145.5, 160.1. ²⁹Si NMR for 3g-1 (119 MHz, CDCl₃, r.t.): δ -25.00, -23.69. ²⁹Si NMR for **3g-2** (119 MHz, CDCl₃, r.t.): δ -22.69. m.p.: 95–104 °C. HRMŠ-EI(+) (m/z): [M]⁺ calcd for $C_{32}H_{32}Si_2$, 472.2043. Found, 472.2042. Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.30, H, 6.82. Found: C, 80.99, H, 6.58.

2,6-Dihexyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (3i-1) and 2,5-Dihexyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohex-adiene (3i-2).^{17c} From 1 (70 mg, 0.20 mmol) and 1-octyne 2i (529 mg, 4.8 mmol), colorless liquid of 3i was obtained as a 73:27 mixture of 3i-1 and 3i-2 (80.7 mg, 44%). ¹H NMR of 3i-1 (600 MHz, CDCl₃, r.t.): δ 0.07 (s, 6H, -SiCH₃), 0.15 (s, 6H, -SiCH₃), 0.89 (t, J_{H-H} = 7.2 Hz, 6H, $-CH_3$), 1.20–1.32 (a mixture of signals, 12H, $-CH_2$ -), 1.43 (a mixture of signals, 4H, $-CH_2$ -), 2.18 (a mixture of signals, 4H, -CH₂-), 6.41 (s, 2H, CH). ¹H NMR of 3i-2 (600 MHz, CDCl₃, rt): δ 0.11 (s, 12H, -SiCH₃) 0.89 (t, J_{H-H} = 7.2 Hz, 6H, -CH₃), 1.20–1.32 (a mixture of signals, 12H, $-CH_2$ -), 1.43 (a mixture of signals, 4H, $-CH_2$ -), 2.18 (a mixture of signals, 4H, $-CH_2$ -), 6.36 (s, 2H, CH). ¹³C $\{^{1}H\}$ NMR of 3i-1 (151 MHz, CDCl₃, r.t.): δ -1.8, -0.7, 14.3, 22.8, 28.7, 29.4, 32.0, 39.5, 140.4, 162.1. ¹³C{¹H} NMR of 3i-2 (151 MHz, CDCl₃, r.t.): δ –1.1, 14.3, 22.8, 28.6, 29.4, 31.8, 39.7, 140.5, 162.4. ²⁹Si NMR for 3i-1 (119 MHz, CDCl₃, r.t.): δ –23.60, -22.91. ²⁹Si NMR for 3i-2 (119 MHz, CDCl₃, r.t.): δ -23.80. HRMS-EI(+) (m/z): $[M]^+$ calcd for C₂₀H₄₀Si₂, 336.2669. Found, 336.2669.

2,3,5,6-Tetraphenyl-1,1,4,4-tetramethyl-1,4-disila-2,5-cyclohexadiene (**3***j*).^{3k} From 1 (70 mg, 0.20 mmol) and diphenylacetylene 2j (856 mg, 4.8 mmol), **3***j* was obtained (96.3 mg, 34%). ¹H NMR of **3***j* (600 MHz, CDCl₃, r.t.): δ 0.10 (s, 12H, $-\text{SiCH}_3$), 6.86 (d, $J_{\text{H-H}} = 7.6$ Hz, 8H, *o*-Ph), 6.96 (t, $J_{\text{H-H}} = 7.6$ Hz, 4H, *p*-Ph), 7.08 (dd, $J_{\text{H-H}} = 7.6$ Hz, 8H, *m*-Ph). ¹³C{¹H} NMR of **3***j* (151 MHz, CDCl₃, r.t.): δ 2.0, 125.2, 127.5, 128.3, 143.1, 157.2. ²⁹Si NMR for **3***j* (119 MHz, CDCl₃, r.t.): δ -22.24. m.p.: 321-322 °C. HRMS-EI(+) (m/z): [M]⁺ calcd for C₃₂H₃₂Si₂, 472.2043. Found, 472.2040.

Tetramethyl 1,1,4,4-Tetramethyl-1,4-disila-2,5-cyclohexadiene 2,3,5,6-tetracarboxylate (**3**k). From 1 (70 mg, 0.20 mmol) and dimethyl acetylene dicarboxylate **2**k (682 mg, 4.8 mmol), **3**k was obtained (206.5 mg, 86%). ¹H NMR of **3**k (600 MHz, CDCl₃, r.t.): δ 0.40 (s, 12H, -SiCH₃), 3.79 (s, 12H, OCOCH₃). ¹³C{¹H} NMR of **3**k (151 MHz, CDCl₃, r.t.): δ 2.1, 52.4, 152.7, 169.1. ²⁹Si NMR for **3**j (119 MHz, CDCl₃, r.t.): δ -16.14. m.p.: 134–136 °C. IR(ATR, cm⁻¹): 1720.19, 1706.69 (ν_{co}). HRMS-EI(+) (m/z): [M]⁺ calcd for C₁₆H₂₄O₈Si₂, 400.1010. Found, 400.1011. Anal. Calcd for C₁₆H₂₄O₈Si₂: C, 47.98, H, 6.04. Found: C, 47.95, H, 6.44.

Large-Scale Experiments for the Reaction of 1 with Phenylacetylene 2a in the Presence of $Pd_2(dba)_3$ ·CHCl₃ and 1-lsocyano-adamantane. In a 100 mL Schlenk tube, 1 (523.4 mg,

1.50 mmol), $Pd_2(dba)_3$ ·CHCl₃ (1 mol Pd%), 1-isocyanoadamantane (4 mol Pd%), and alkyne (3.7 g, 36.0 mmol) were dissolved in toluene (30 mL). The resulting mixture was stirred at 100 °C for 24 h. Then anisole (486 μ L, 4.5 mmol) was added as an internal standard, and the conversion of 1 and the yield of **3a-1** and **3a-2** were determined by ¹H NMR analysis. After removal of the solvent, purification of the residue by silica column chromatography (hexane) gave a 72:28 mixture of **3a-1** and **3a-2** (1.24 g, 86%) as a white solid.

Reaction of 1 with Phenylacetylene 2a in the Presence of Pd₃(CNAd)₆. In a 50 mL Schlenk tube, 1 (70 mg, 0.20 mmol), Pd₃(CNAd)₆ (1 mol Pd%), and phenylacetylene 2a (492 mg, 4.8 mmol) were dissolved in toluene (4 mL). The resulting mixture was stirred at 100 °C for 12 h. Then, anisole (65 μ L, 0.6 mmol) was added as an internal standard, and the conversion of 1 (>99%) and the yield of 3a-1 (50%) and 3a-2 (20%) were determined by ¹H NMR analysis.

Reaction of 1 with Phenylacetylene 2a in the Presence of $Pd_2(dba)_3$ ·CHCl₃, 1-Isocyanoadamantane, and 4-*tert*-Butylcyclo-hexanone (Scheme 5). In a 50 mL Schlenk tube, 1 (70 mg, 0.20 mmol), $Pd_2(dba)_3$ ·CHCl₃ (1 mol Pd%), 1-isocyanoadamantane (4 mol Pd%), phenylacetylene 2a (492 mg, 4.8 mmol), and 4-*tert*butylcyclohexanone (740 mg, 4.8 mmol) were dissolved in toluene (4 mL). The resulting mixture was stirred at 100 °C for 12 h. Then, anisole (65 μ L, 0.6 mmol) was added as an internal standard, and the conversion of 1 (>99%) and the yield of 3a-1 (50%) and 3a-2 (15%) were determined by ¹H NMR analysis. No silylenolethers was observed.

DFT Calculations. All of the calculations were performed using the Gaussian 09 program to search for all intermediates and transition structures on potential energy surfaces.²⁶ For optimization, the B3LYP-D functional²⁷ was selected based on "the selection of functionals" (in the Supporting Information). We also employed the SDD $(Stuttgart/Dresden pseudopotentials)^{28}$ and $6-31G^{**}$ basis sets²⁹ for Pd atoms and the other atoms, respectively. All stationarypoint structures were found to have the appropriate number of imaginary frequencies. An appropriate connection between a reactant and a product was confirmed by intrinsic reaction coordinate (IRC)³ and quasi-IRC (qIRC) calculations. In the quasi-IRC calculation, the geometry of a transition state was first shifted by perturbing the geometries very slightly along the reaction coordinate, and then released for equilibrium optimization. Energy profiles of the calculated reaction pathways are presented as Gibbs free energy changes (ΔG) involving thermal corrections at 298.15 K. All of the optimized structures (ball-and-stick models) and optimized geometries (in XYZ file format) are summarized in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00302.

Molecular structures of 3a-1, 3a-2, and 3j, chart of compounds 3, and optimized structures of the calculation (PDF)

Cartesian coordinates of all molecules, intermediates, and transition states (XYZ)

Accession Codes

CCDC 1839109–1839111 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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(24) The energy barrier of 38 kcal/mon in the Si₃ cycle may be enough high to induce possible side reactions concomitantly occurring. For instance, it is known that $(Me_2Si)_3$ is thermally unstable and easily decomposed to intractable products. As shown in Tables 1–3, the reaction of 1 with 2a often afforded the products 3 in lower than 80% yields. The low yields of the products may be due to the side reactions occurring in the Si₃ cycle.

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