Headline Articles

Reactions of Si–Si σ-Bonds with Bis(t-alkyl isocyanide)palladium(0) Complexes. Synthesis and Reactions of Cyclic Bis(organosilyl)palladium Complexes

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Four- to seven-membered cyclic bis(organosilyl)palladium(II) complexes were synthesized by oxidative addition of cyclic disilanes onto bis(t-butyl isocyanide)palladium(0) as well as by intramolecular metathesis of the two Si–Si bonds of bis(disilane)s with the palladium(0) complex. The 4-membered bis(organosilyl)bis(t-butyl isocyanide)palladium complex prepared from 2,2-bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane was characterized by a single-crystal X-ray method, which showed an unusually short cross-ring Si–Si distance in the 4-membered ring. The reactivities of the cyclic bis(organosilyl)bis(t-butyl isocyanide)palladium complexes toward phosphines, cyclic disilanes, and alkynes were also examined. Cyclic organosilicon compounds were synthesized by bis-silylation of alkynes with cyclic bis(organosilyl)-palladium intermediates generated by the intramolecular metathesis. The bis-silylation was also applicable for electron-deficient alkenes: α,β-unsaturated ketones gave 7-membered 1,4-bis-silylation adducts, whereas the corresponding ester and nitrile gave 5-membered 1,2-adducts in high yields.

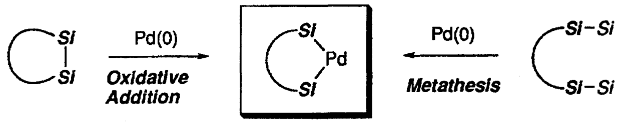
The intriguing chemical and physical properties of the Si–Si σ-bond are due to its high-lying HOMO and low-lying LUMO, which should be compared with those of a carbon–carbon double bond. The MO interaction with low valent transition metal complexes has made possible some synthetic uses of disilanes. Especially, palladium-catalyzed bis-silylation of unsaturated organic compounds,[1] e.g., alkynes,[2,3] alkenes,[2l,4,5] dienes,[2g,h,j,k,6] isocyanides,[7] and α,β-unsaturated ketones[8] provided a convenient method for formation of carbon–silicon bonds. The reactions commonly involve an oxidative addition of the Si–Si bond onto palladium, which is crucially important in the catalytic cycles. The relevant interaction of the Si–Si σ-bond with palladium complexes could lead to metathesis, i.e., disproportionation reaction of the Si–Si σ-bond.[2c,9—11] Cyclooligomerization of cyclic disilanes through Si–Si σ-bond metathesis has been reported, though the mechanistic details still remain to be understood.[2c,10,11]

Recently, generation and isolation, as well as synthetic application of bis(organosilyl)palladium complexes, have been reported by some research groups.[2l,12—14] We have also found a new catalytic system, t-alkyl isocyanide–Pd(OAc)$_2$, for use as a highly active catalyst for bis-silylations of alkynes and alkenes.[3,4,15] The synthetic usefulness of intramolecular bis-silylation of alkenes has been demonstrated by stereoselective synthesis of polyols.

In such catalysis, we presumed that bis(t-alkyl isocyanide)palladium(0) complexes might be responsible for the primary active species, onto which Si–Si bond would undergo oxidative addition to form bis(organosilyl)bis(t-alkyl isocyanide)palladium(II) complexes. Herein, we describe the palladium-catalyzed bis-silylation, focusing on preparation and reactions of cyclic bis(organosilyl)bis(t-alkyl isocyanide)palladium(II) complexes (Scheme 1).[16]

Results and Discussion

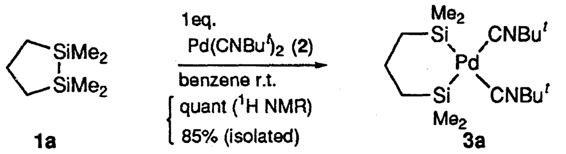
Generation of Cyclic Bis(organosilyl)bis(t-alkyl isocyanide)palladium(II) Complexes: Oxidative Addition of Si–Si Bonds onto Bis(t-alkyl isocyanide)palladium(0). It has been well documented that disilanes bearing electronegative substituents on silicon atoms as well as strained cyclic disilanes may readily undergo oxidative addition onto palladium(0). Though synthesis of bis(organosilyl)palladium complexes has been achieved by use of hydrodisilanes[13] as well as fluorodisilanes[2l] with low valent



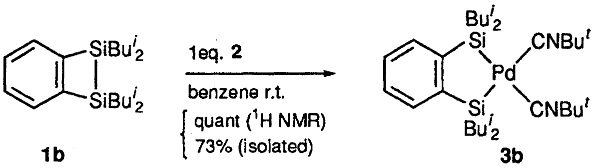
Scheme 1.

phosphine-palladium complexes,[17] isolation and characterization of the cyclic transition metal complexes from cyclic disilanes have never been reported.[18,19]

1,1,2,2-Tetramethyl-1,2-disilacyclopentane (**1a**), which has been known as a strained, reactive cyclic disilane, was reacted with bis(*t*-butyl isocyanide)palladium(0) (**2**) at room temperature in benzene. Monitoring of the reaction by ^{1}H NMR spectroscopy revealed a rapid conversion (5 min) to 6-membered bis(organosilyl)palladium complex **3a** (Eq. 1). The complex was isolated in 85% yield as colorless crystals. In this reaction, *t*-butyl isocyanide was a ligand of choice on palladium(0). Use of tetrakis(triphenylphosphine)palladium(0) did not give any complexes corresponding to **3a** in the reaction with **1a**, even at high temperature. The much-strained 4-membered cyclic disilane **1b** also gave the corresponding 5-membered bis(organosilyl)palladium complex **3b** in high yield (Eq. 2). But, 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**1c**) did not react at all under the same reaction conditions, presumably because of the lack of ring strain. However, substitution of the two methyl groups on the silicon atom (in **1c**) by two methoxy groups (in **1d**) resulted in clean formation of 7-membered bis(organosilyl)palladium complex **3d** (Eq. 3).



(1)



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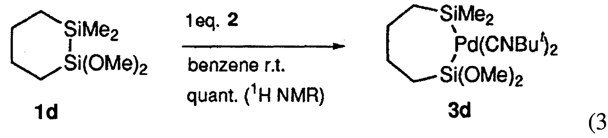
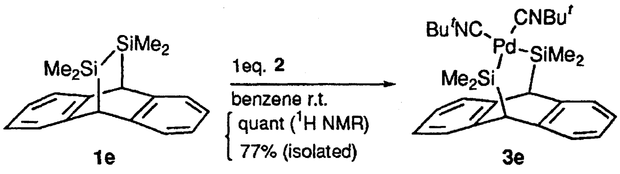


(3)

Bicyclic disilane **1e** was also reactive toward **2**, producing the corresponding bis(organosilyl)palladium complex **3e** in nearly quantitative yield (Eq. 4).



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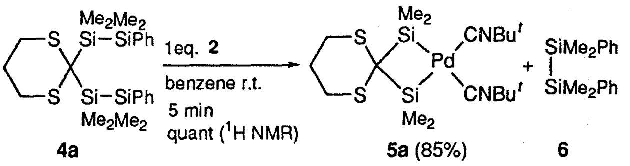
Generation of Cyclic Bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) Complexes: Intramolecular Metathesis of Si–Si Bonds onto Bis(*t*-alkyl isocyanide)palladium(0). Bis(*t*-butyl isocyanide)palladium(0) (**2**) also mediated simultaneous activation of two Si–Si bonds oriented appropriately in a molecule. Thus, the reaction of bis(disilanyl)dithiane **4a** with **2** was monitored by ^{1}H NMR, resulting in quantitative formation of 4-membered cyclic bis(organosilyl)palladium complex **5a** and *sym*-tetramethyldiphenyldisilane (**6**) (Eq. 5). The metathesis reaction completed within 5 min to afford **5a**, which was isolated as a crystalline solid in high yield on addition of pentane to the reaction mixture. It is noted that tetrakis(triphenylphosphine)palladium(0) failed to afford the complex corresponding to **5a**. The structure of **5a** was established by a single-crystal X-ray diffraction study. The crystal structure is shown in Fig. 1, together with selected bond distances and angles. The two silicon, two isocyano carbon, and palladium atoms are nearly on the same plane. The two isocyanide ligands coordinate to palladium with a relatively large angle (C–Pd–C=105.9(2)°). The unusual short cross-ring Si–Si distance (2.613(2) Å) may suggest a possibility of covalently bonded Si–Si in the 4-membered ring.[20,21]



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Reactions of some other bis(disilanyl)alkanes with **2** were examined. The success of the intramolecular metathesis depended on the tethers connecting the two disilanyl groups

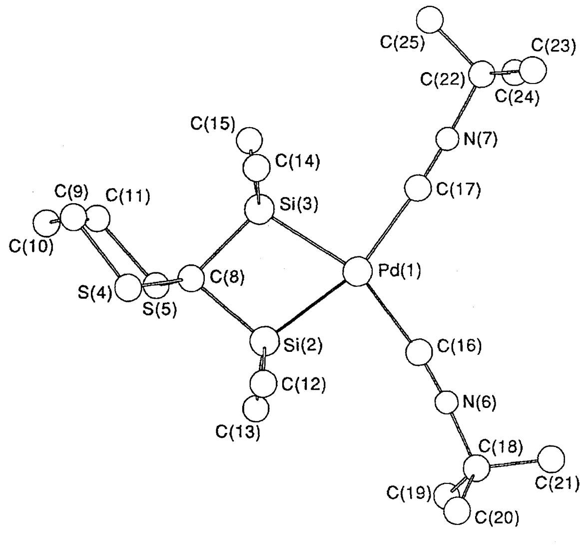
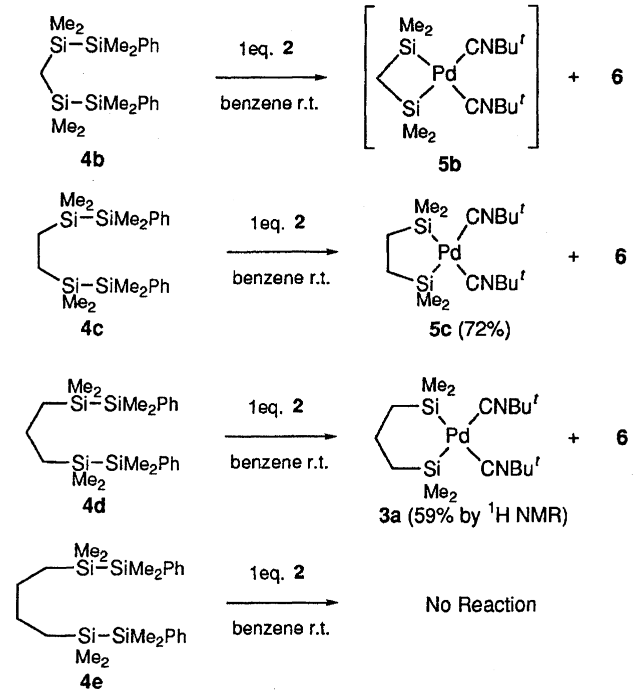


Fig. 1. Crystal structure of **5a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)–Si(2) = 2.336(1), Pd(1)–Si(3) = 2.356(1), Pd(1)–C(16) = 2.053(5), Pd(1)–C(17) = 2.053(4), Si(2)–Si(3) = 2.613(2), N(6)–C(16) = 1.151(6), N(7)–C(17) = 1.146(6); Si(2)–Pd(1)–Si(3) = 67.68(4), Si(2)–Pd(1)–C(16) = 92.0(1), C(16)–Pd(1)–C(17) = 105.9(2), Si(3)–Pd(1)–C(17) = 94.4(1), Pd(1)–Si(2)–C(8) = 103.0(1), Pd(1)–Si(3)–C(8) = 102.3(1), Si(2)–C(8)–Si(3) = 85.1(1), Pd(1)–C(16)–N(6) = 171.3(4), Pd(1)–C(17)–N(7) = 173.8(4), C(16)–N(6)–C(18) = 175.8(4), C(17)–N(7)–C(22) = 177.5(4).

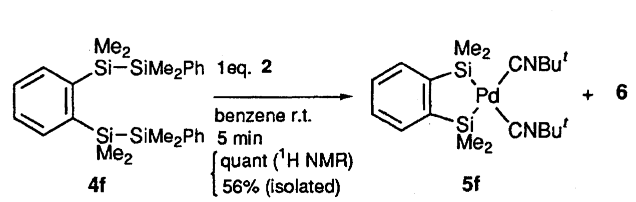


Scheme 2.

(Scheme 2). Bis(disilanyl)methane **4b** conceivably underwent the intramolecular metathesis to produce *sym*-tetramethyldiphenyldisilane, although the expected 4-membered bis(organosilyl)palladium complex **5b** could not be detected by ^{1}H NMR spectroscopy. 1,2-Bis(disilanyl)ethane **4c** and 1,3-bis(disilanyl)propane **4d** gave the corresponding cyclic bis(organosilyl)palladium complex **5c** and **3a**, respectively, the reaction of the latter being much slower. No reaction took place with 1,4-bis(disilanyl)butane **4e**, which had a longer tether.

o-Bis(disilanyl)benzene **4f** also underwent the intramolecular metathesis very rapidly to give **5f** in high yield (Eq. 6).

Ethylene glycol derived bis(disilanyl ether) **7a** underwent intramolecular metathesis to give 7-membered bis(organosilyl)palladium complex **8a** in good yield (Eq. 7). This may suggest, by comparison with results for **4e**, that the oxygen substituent and phenyl groups on the silicon atom favor the intramolecular metathesis. Accordingly, reaction of tartrate-derived **7b** proceeded smoothly to give **8b** in high yield (Eq. 8). Similarly, bis(disilanyl ether)s with longer tethers (**7c**, **d**) gave the corresponding cyclic complexes and *sym*-tetramethyldiphenyldisilane **6**, although the reactions were too sluggish to obtain the complexes in reasonable yields (Chart 1).



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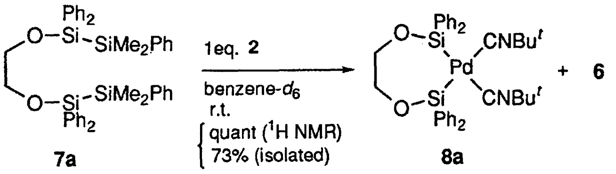

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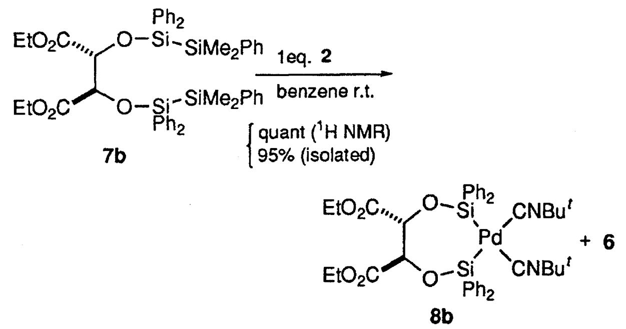

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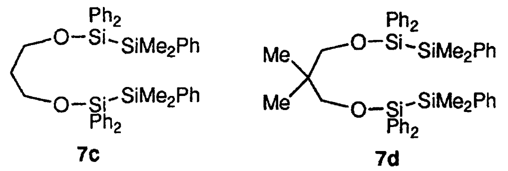
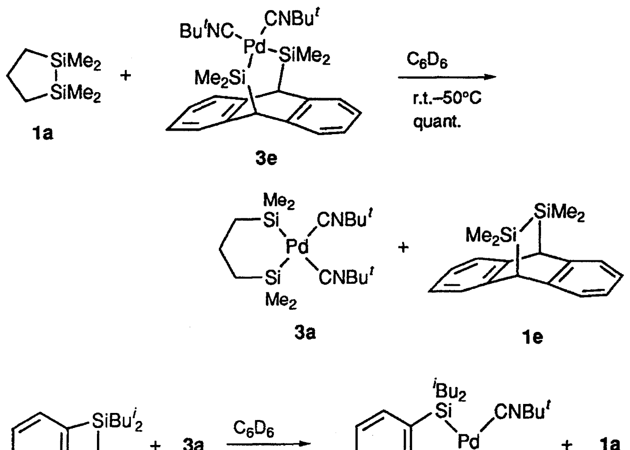


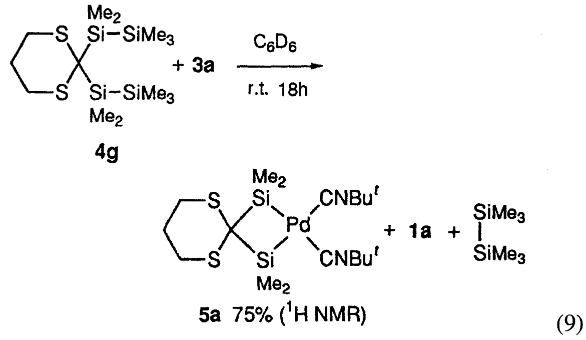
Chart 1.

Reactions of Cyclic Bis(organosilyl)palladium Complexes *with Disilanes*. Reversibility of the oxidative addition of the Si–Si bonds onto palladium(0) was confirmed by exchange reaction with disilane in benzene-d_6. Addition of 1 equivalent of 5-membered disilane **1a** to bis(organosilyl)palladium complex **3e** afforded 6-membered **3a** and disilane **1e** in quantitative yield, as indicated by ^{1}H NMR (Scheme 3). Moreover, when 4-membered disilane **1b** was added to **3a** in benzene-d_6, disilane exchange reaction occurred rapidly to give 5-membered complex **3b** along with dissociated **1a**.



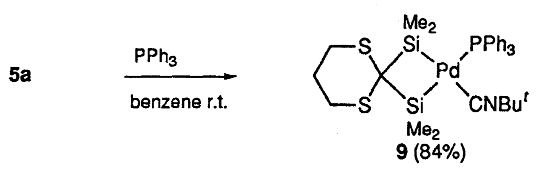
Scheme 3.

These results indicate that the disilane exchange proceeded via reversible oxidative addition/reductive elimination process with predominant dissociation of less-strained cyclic disilanes. The reversibility was also evidenced by reaction of **3a** with bis(disilanyl)dithiane **4g**, giving **5a** via intramolecular metathesis reaction (Eq. 9).

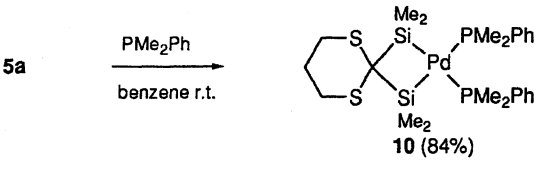


(9)

With Phosphines. One of the two *t*-butyl isocyanide ligands of the complex **5a** was selectively replaced by PPh_3 to give bis(organosilyl)complex **9**, having both isocyanide and phosphine as ligands (Eq. 10). Presumably, steric congestion on the palladium disfavored further ligand exchange. In contrast, Me_2PhP replaced the two isocyanides to give bis(organosilyl)bis(phosphine)palladium complex **10** in good yield, this complex has not been otherwise accessible (Eq. 11).

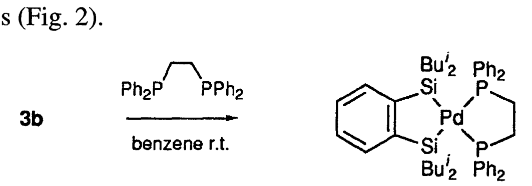


(10)



(11)

Similarly, bis(organosilyl)(dppe)palladium complexes **11** was synthesized by replacement of the two isocyanides of **3b** with bis(diphenylphosphino)ethane (dppe) (Eq. 12). The structure of **11** was confirmed by a single-crystal X-ray analysis (Fig. 2).



(12)

Unlike 4- and 5-membered bis(organosilyl)bis(*t*-butyl isocyanide)palladium complexes, addition of bis(diphenylphosphino)ethane to a benzene-d_6 solution of 6-membered complex **3a** resulted in reductive elimination of disilane **1a** (45% by ^{1}H NMR) with an unidentified palladium complex having a dppe ligand.

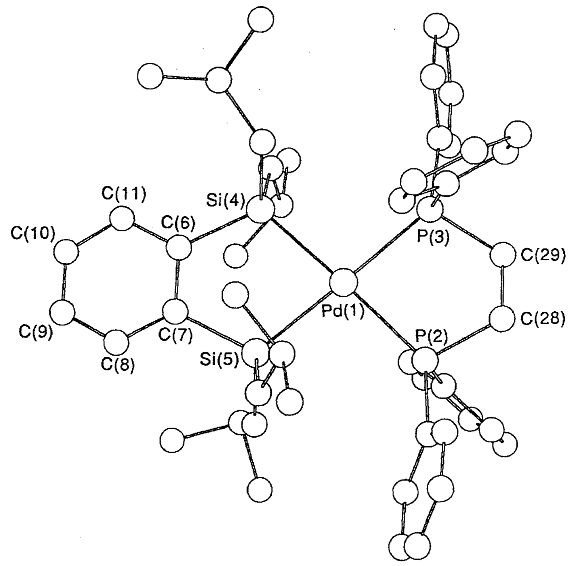
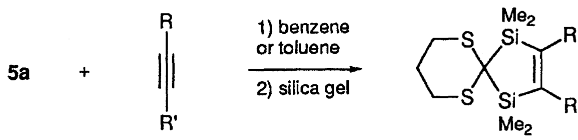


Fig. 2. Crystal structure of **11**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)–Si(4)=2.375(4), Pd(1)–Si(5)=2.368(4), Pd(1)–P(2)=2.365(4), Pd(1)–P(3)=2.364(4); Si(4)–Pd(1)–Si(5)=80.9(2), P(2)–Pd(1)–Si(5)=98.0(2), P(3)–Pd(1)–Si(4)=98.6(2), P(2)–Pd(1)–P(3)=83.9(2), Pd(1)–Si(4)–C(6)=113.1(5), Pd(1)–Si(5)–C(7)=113.6(5), Si(4)–C(6)–C(7)=116.8(10), Si(5)–C(7)–C(6)=115.0(10).

Catalytic Bis-Silylation of Alkynes and Alkenes via Intramolecular Metathesis of Si–Si Bonds. A stoichiometric reaction of 4-membered bis(organosilyl)palladium(II) complex **5a** with terminal and internal alkynes took place smoothly at room temperature, giving the corresponding spiro-disilacyclopentene derivatives in high yields, except for the reaction with diphenylacetylene, which was carried out in refluxing toluene (Table 1). However, the bis-silylation reactions with dialkylacetylenes have all failed.

Bis(disilanyl)alkanes were subjected to the reaction with phenylacetylene in the presence of a catalytic amount of palladium-isocyanide catalyst, which was generated in-situ from $Pd(OAc)_2$ and 1,1,3,3-tetramethylbutyl isocyanide (Eq. 13: Table 2). The reaction with bis(disilanyl)methane **4b** afforded 5-membered cyclic product **12b** only in low yield together with acyclic products **16b** and **17b** (76% in total, Entry 1).

Table 1. Stoichiometric Reaction of **5a** with Alkynes

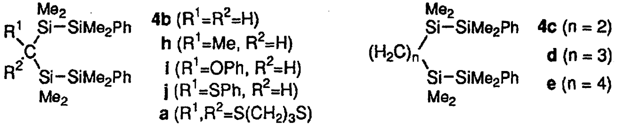


Entry	Alkyne	Conditions	Products (yield/%)
1	Ph—≡—H	Benzene, r.t., 5 min	**12a** (98)
2	Me_3Si—≡—H	Toluene, r.t., 3.5 h	**13** (90)
3	MeO_2C—≡—CO_2Me	Benzene, r.t., 5 min	**14** (99)
4	Ph—≡—Ph	Toluene, 90 °C, 12 h	**15** (96)

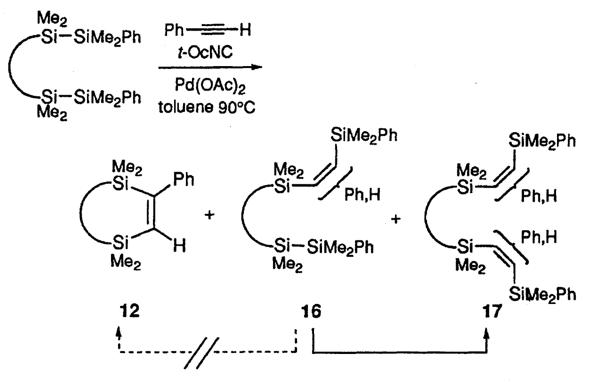
Table 2. Palladium-Catalyzed Reaction of Bis(disilanyl)-alkanes[a] with Phenylacetylene at 90 °C[b]

Entry	Substrate (**4**)	**12** (%yield)[c]	**16**	**17** (%yield)[c]
1	**b**	4	48	28
2[d]	**h**	67	18	<3
3	**i**	91	0	0
4	**j**	97	0	0
5	**a**	91	0	0
6	**c**	39	15	30
7	**d**	0	50	33
8	**e**	0	38	49

a) List of bis(disilanyl)alkanes used in the reaction:



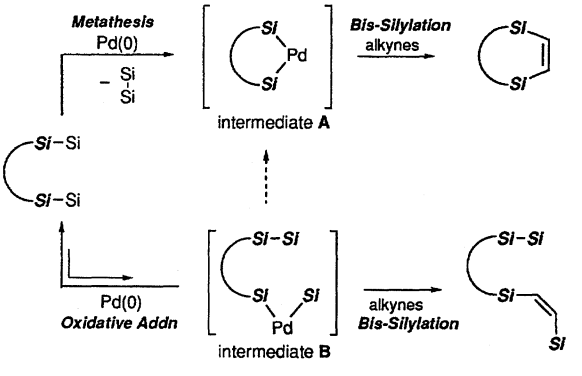
b) All reactions used $Pd(OAc)_2$ (0.02 equiv), 1,1,3,3-tetrametylbutyl isocyanide (0.3 equiv), and phenylacetylene (3 equiv) unless otherwise noted. c) Isolated yield. d) $Pd(OAc)_2$ (0.1 equiv), 1,1,3,3-tetrametylbutyl isocyanide (1.5 equiv) were used.



(13)

The formation of **12b** may suggest that a cyclic bis(organosilyl)palladium(II) intermediate **A** is generated by concerted metathesis or stepwise metathesis via intermediate **B**, which undergoes a bis-silylation reaction with phenylacetylene. On the other hand, bis-silylation with intermediate **B** may lead to the formation of acyclic **16b** and **17b** (Scheme 4).

As shown in Table 2, introduction of substituents at the methylene tether of **4b** favored the formation of the cyclic intermediate **A** through the Si–Si metathesis, i.e., methyl substituted **4h** gave **12h** in 67% yield (Entry 2). Selective bis-silylation of phenyacetylene with intermediate **A** was carried out in the reactions of phenoxy-substituted **4i**, phenylthio-substituted **4j** and trimethylenedithio-substituted **4a** to provide exclusively the corresponding 5-membered cyclic products **12i**, **12j**, and **12a**, respectively, in high yields (Entries 3—5).



Scheme 4.

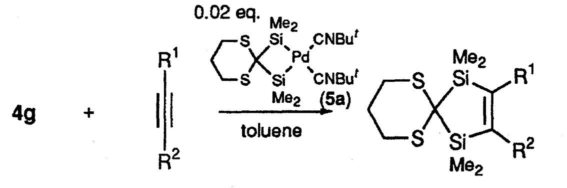
On the other hand, bis(disilanyl)alkanes **4c**, **4d**, and **4e** tethered by C_2, C_3, and C_4 chains preferred the bis-silylation with phenylacetylene via intermediate **B** (Entries 6—8), although 1,2-bis(disilanyl)ethane **4c** competitively underwent the reaction via intermediate **A**, leading to the 6-membered 1-phenyl-3,6-disila-1-cyclohexene **12c** (39%). As expected, the bis-silylation product **16c** once formed was reacted with phenylacetylene under the same reaction conditions to afford selectively acyclic diene **17c**.

The catalytic bis-silylation with **4g** also proceeded in the presence of a catalytic amount of isolated **5a** without an excess of *t*-butyl isocyanide (Table 3).[3,4] Not only terminal alkynes, but also conjugated ynone furnished the respective bis-silylation products in moderate to high yields. Internal alkyne, however, provided the corresponding products **15** only in low yield.

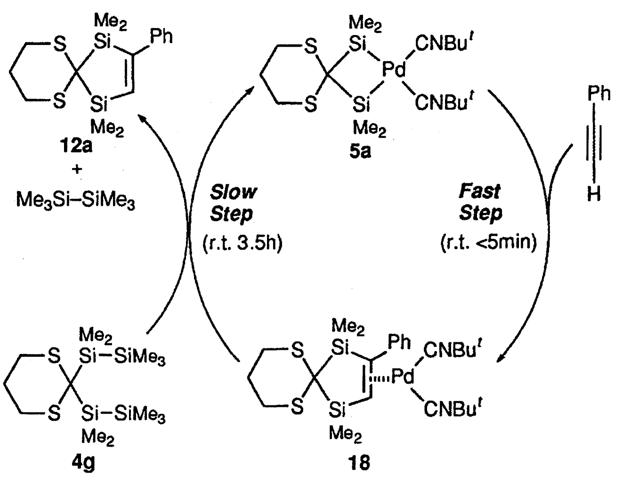
^{1}H NMR study of the stoichiometric bis-silylation of phenylacetylene with **5a** revealed a rapid formation of bis(*t*-butyl isocyanide)(spiro-disilacyclopentene)palladium(0) **18**, which is spectroscopically identified by comparison with the palladium complex formed in the reaction of **12a** with bis(*t*-butyl isocyanide)palladium(0) (**2**). It is notable that the oxidative metathesis of **4g** onto **18** is involved as a rate determining step, regenerating **5a** with **12a** (Scheme 5).

Furthermore, the catalytic bis-silylation with bis(disilanyl)dithiane **4g** was successfully applied to some electron-deficient olefins. α,β-Unsaturated ester and nitrile provided 1,2-bis-silylation adducts **21** (Eq. 14), whereas the corresponding ketones gave 1,4-adducts **22** (Eq. 15).[22] It may be remarked that no products derived from insertion of the alkenes into the Si–Si bonds of the starting **4g** and hexamethyldisilane produced in the reaction were detectable. This indicates the intramolecular metathesis of the Si–Si σ-bonds of **4g** by bis(*t*-butyl isocyanide)palladium(0) was a highly favorable process for giving reactive, cyclic bis(organosilyl)palladium complexes.

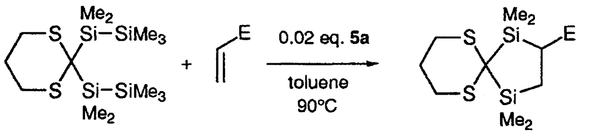
Table 3. Catalytic Bis-Silylation of Alkynes in the Presence of **5a**



Entry	Alkyne	Conditions	Products (yield/%)
1	Ph—≡—H	80 °C, 2 h	**12a** (93)
2	Me_3Si—≡—H	110 °C, 12 h	**13** (96)
3	*n*-Hex—≡—H	110 °C, 1 h	**19** (97)
4	*n*-Bu—≡—COMe	90 °C, 11 h	**20** (78)
5	Ph—≡—Ph	110 °C, 67 h	**15** (13)

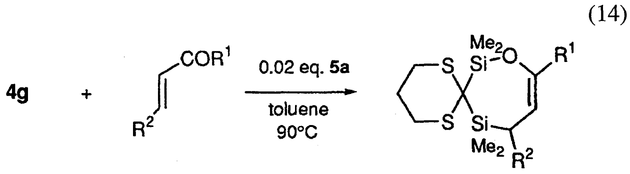


Scheme 5.



21a; E = CO_2Me (88%)
b; E = CN (86%)

(14)



22a; R^1=Me, R^2=H (96%)
b; R^1=R^2=Me (99%)
c; R^1=Ph, R^2=H (82%)

(15)

Conclusion

We found that 4- to 7-membered cyclic bis(organosilyl)bis(*t*-butyl isocyanide)palladium(II) complexes were formed by the reaction of bis(*t*-butyl isocyanide)palladium(0) with cyclic disilanes or acyclic bis(disilane)s. Especially, intramolecular metathesis of bis(disilanyl)methane derivatives made possible the synthesis of 4-membered bis(organosilyl)palladium complexes, which were otherwise difficult to synthesize. New synthetic access to cyclic organosilicon compounds was demonstrated by bis-silylation of alkynes and alkenes with the cyclic bis(organosilyl)palladium complex.

Experimental

General. All reactions were carried out under a dry nitrogen or an argon atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Varian VXR-200. Proton chemical shifts (ppm) are referenced to internal residual solvent protons: $CDCl_3$, 7.25; C_6D_6, 7.20; CD_2Cl_2, 5.35. Carbon chemical shifts (ppm) are referenced to the carbon signal of the deuterated solvents: $CDCl_3$, 77.0; C_6D_6, 128.0; CD_2Cl_2, 53.8. Silicon and phosphorous chemical shifts are referenced to the signals of tetramethylsilane and phosphoric acid (85%), respectively.

Starting Materials. Compounds **1a**,[23] **b**,[24] **c**,[23] **e**,[25] and **4c**[26] were prepared by the methods reported in the literature. Compound **1d** was prepared from 2,2-dimethyl-1,1-diphenyl-1,2-disilacyclohexane by the reaction with HCl gas in the presence of a catalytic amount of $AlCl_3$ followed by treatment with methanol in the presence of triethylamine. Compound **4b** was prepared from **4a** by reduction with Ca in liquid ammonia.[27] Compound **4d** was prepared by the reaction of dimethylphenylsilyllithium with 3-(chlorodimethylsilyl)-1-(1,1,2,2-tetramethyl-2-phenyldisilanyl)propane, which was synthesized by platinum-catalyzed hydrosilylation of 3-(1,1,2,2-tetramethyl-2-phenyldisilanyl)propene with chlorodimethylsilane. Compound **4e** was prepared by the reaction of 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane with 1,4-butanediylbis(magnesium bromide). Compound **4f** was prepared by the reaction of dimethylphenylsilyllithium with 1,2-bis(chlorodimethylsilyl)benzene.[28] Compounds **7a** and **7b** were prepared from the corresponding alcohols and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane in the presence of triethylamine. Compound **4h** was prepared from **4j** by the reaction with lithium naphthalenide followed by treatment with iodomethane.[29] Procedures for preparation of **2**, **4a**, **4g**, **4i**, and **4j** are described below.

Preparation of Bis(*t*-butyl isocyanide)palladium(0) (2). The procedure reported by Otsuka et al.[30] was followed with slight modification. To a pentane solution of $Pd(C_3H_5)(C_5H_5)$ (117 mg, 0.55 mmol) was added *t*-butyl isocyanide (183 mg, 2.2 mmol) at −10 °C under argon. After 30 min, removal of supernatant liquid gave **2** as orange solid, which was washed twice with pentane, dried in vacuo, and used for further reaction in the same flask. Complex **2** was obtained nearly quantitatively, though the yield was not determined for the each reaction.

Synthesis of Complex 3a. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (106 mg, 0.5 mmol) and *t*-butyl isocyanide (166 mg, 2.0 mmol), was added **1a** (79 mg, 0.5 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by washing with cold 2-propanol afforded spectroscopically pure **3a** (184 mg, 85%) as a crystalline solid.

3a: Mp 79—81 °C (decomp); ^1H NMR (C_6D_6) δ=0.83 (s, 12 H), 1.00 (s, 18 H), 1.24—1.33 (m, 4 H), 2.47—2.51 (m, 2 H); ^{13}C NMR (C_6D_6) δ=7.1, 22.3, 22.8, 29.7, 55.8, 147.5 (br); ^{29}Si NMR (C_6D_6) δ=−0.4; IR (C_6H_6) 2168, 2148 cm^{-1}. Anal. Calcd for $C_{17}H_{36}N_2PdSi_2$: C, 47.37; H, 8.42; N, 6.50%. Found: C, 47.14; H, 8.59; N, 6.38%.

Synthesis of Complex 3b. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **1b** (36 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 30 min, evaporation of the solvent followed by recrystalization from 2-propanol afforded **3b** (46 mg, 73%) as colorless crystals.

3b: Mp 142.0—143.5 (decomp); ^1H NMR (C_6D_6) δ=1.00 (s, 18 H), 1.11 (d, *J*=6.5 Hz, 12 H), 1.18 (dd, *J*=13.7, 7.0 Hz, 4 H), 1.27 (d, *J*=6.5 Hz, 12 H), 1.44 (dd, *J*=13.7, 6.4 Hz, 4 H), 2.04—2.26 (m, 4 H), 7.36—7.42 (m, 2 H), 7.80—7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ=26.5, 27.0, 27.4, 30.4, 33.2, 56.2, 126.4, 131.2, 145.9 (br), 157.5; ^{29}Si NMR ($CDCl_3$) δ=37.3; IR (C_6H_6) 2152 cm^{-1}. Anal. Calcd for $C_{32}H_{42}N_2PdSi_2$: C, 60.68; H, 9.23; N, 4.42%. Found: C, 60.70; H, 9.44; N, 4.32%.

Synthesis of Complex 3d. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **1d** (20 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 30 min, evaporation of the solvent gave spectroscopically pure **3d** (46 mg, 96%).

3d: ^{1}H NMR (C_6D_6) $\delta=0.72$ (s, 6 H), 1.01 (s, 18 H), 1.30—1.38 (m, 2 H), 1.58—1.66 (m, 2 H), 2.04—2.20 (m, 2 H), 2.22—2.36 (m, 2 H), 3.76 (s, 6 H); ^{13}C NMR (C_6D_6) $\delta=6.3$, 19.9, 21.0, 25.6, 26.8, 30.0, 50.3, 55.8, 147.0 (br); ^{29}Si NMR (C_6D_6) $\delta=3.4$, 43.3; IR (C_6H_6) 2176, 2160 cm^{-1}.

Synthesis of Complex 3e. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from Pd(C_5H_5)(C_3H_5) (42 mg, 0.2 mmol) and *t*-butyl isocyanide (67 mg, 0.8 mmol), was added **1e** (59 mg, 0.2 mmol) at room temperature under an argon atmosphere. The reaction mixture was stood for 1 h to precipitate crystalline **3e** containing 1 equiv of benzene (100 mg, 77%).

3e: Mp 160—165 °C (decomp); ^{1}H NMR (CD_2Cl_2) $\delta=0.25$ (s, 12 H), 1.51 (s, 18 H), 3.45 (br s, 2 H), 7.04—7.08 (m, 8 H); ^{13}C NMR (CD_2Cl_2) $\delta=5.9$ (br), 30.3, 48.5 (br), 57.0, 123.9, 125.9, 139.8, 143.7 (br); ^{29}Si NMR (CD_2Cl_2) $\delta=-13.5$; IR (KBr) 2176, 2156 cm^{-1}. Anal. Calcd for $C_{28}H_{40}N_2PdSi_2\cdot C_6H_6$: C, 63.28; H, 7.18; N, 4.34%. Found: C, 63.47; H, 7.26; N, 4.25%.

2,2-Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane (4a). To a THF (20 mL) solution of 2-(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane, prepared quantitatively from 1,3-dithiane (1 g, 8.3 mmol), *n*-butyllithium (8.3 mmol), and 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (1.9 g, 8.3 mmol) in ether, was added *n*-butyl lithium (8.3 mmol) at −15 °C. The mixture was stirred at −15 °C for 15 min and at 0 °C for 45 min, and then treated with 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (1.9 g, 8.3 mmol) in THF (10 mL). After stirring at room temperature for 2 h, saturated aqueous NH_4Cl (20 mL) was added to the solution. Extractive work-up followed by column chromatography on silica gel (hexane) afforded **4a** (3.4 g, 81% from 1,3-dithiane).

4a: Mp 50.5—51.5 °C. ^{1}H NMR (C_6D_6) $\delta=0.30$ (s, 12 H), 0.65 (s, 12H), 1.34—1.46 (m, 2 H), 2.10—2.16 (m, 4 H), 7.16—7.28 (m, 6 H), 7.56—7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) $\delta=-1.5$, −0.7, 23.2, 23.7, 27.0, 127.5, 128.1, 134.3, 140.5; IR (KBr) 2904, 1430, 1250 cm^{-1}. Anal. Calcd for $C_{24}H_{40}S_2Si_4$: C, 57.08; H, 7.98%. Found: C, 56.95; H, 8.04%.

2,2-Bis(pentamethyldisilanyl)-1,3-dithiane (4g). By the procedure similar to that used for **4a**, the title compound was prepared in 80% yield from 1,3-dithiane.

4g: ^{1}H NMR (C_6D_6) $\delta=0.35$ (s, 18 H), 0.39 (s, 12H), 1.44—1.56 (m, 2 H), 2.25—2.32 (m, 4 H); ^{13}C NMR (C_6D_6) $\delta=-0.6$, 0.3, 23.3, 24.2, 27.1. Anal. Calcd for $C_{14}H_{36}S_2Si_4$: C, 44.14; H, 9.53%. Found: C, 44.01; H, 9.61%.

Synthesis of Complex 5a. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**) (0.5 mmol) was added **4a** (253 mg, 0.50 mmol) at room temperature under argon. After 10 min, pentane (4 mL) was added to the solution to precipitate colorless crystals of **5a**, which was washed with MeOH (2 mL×3) and dried in vacuo. The complex **5a** (214 mg, 0.43 mmol, 85%) was thermally stable under nitrogen but gradually decomposed by exposure to the air.

5a: Mp 168—170 °C (decomp); ^{1}H NMR (C_6D_6) $\delta=0.84$ (s, 18 H), 1.00 (s, 12 H), 1.96—2.09 (m, 2 H), 2.68—2.76 (m, 4 H); ^{13}C NMR (C_6D_6) $\delta=3.1$, 27.5, 27.8, 30.0, 30.7, 55.9, 147.5 (br); ^{29}Si NMR (C_6D_6) $\delta=-21.8$; IR (C_6H_6) 2164, 2144 cm^{-1}. Anal. Calcd for $C_{18}H_{36}N_2PdS_2Si_2$: C, 42.62; H, 7.15%. Found: C, 42.34; H, 7.35%.

Single Crystal X-Ray Analysis of 5a.[31] Crystal data for **5a**: crystal size 0.35×0.15×0.30 mm (recrystallized from benzene–pentane (1/4)); triclinic, space group $P\bar{1}$ (no. 2), $Z=2$; $a=8.257(1)$, $b=10.829(3)$, $c=15.360(3)$ Å; $\alpha=94.14(2)$, $\beta=99.72(2)$, $\gamma=101.92(2)°$; $V=1316.2(4)$ Å^3, $\rho_{\text{calcd}}=1.28$ g cm^{-3}; max $2\theta=50°$ (Mo $K\alpha$, $\lambda=0.70930$ Å, graphite monochrometor, $\omega/2\theta$-Scan, $T=293$ K); 4792 reflections measured, 4389 independent, 4135 included in the refinement, Lorentzian polarization and absorption corrections by analytical function ($\mu=8.70$ cm^{-1}); direct method (MULTAN 78), anisotropical refinement for non-hydrogen atoms by full-matrix least-squares against $|F^2|$ with program package CrystanG (Mac Science), 337 parameters; $R=0.048$, $R_w=0.048$; residual electron density $+0.58/-0.64$ eÅ^{-3}. All hydrogen atoms except for that on C(19) were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms.

Synthesis of Complex 5c. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from Pd(C_5H_5)(C_3H_5) (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **4c** (42 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 6 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **5c** (30 mg, 72%), which was washed with cold 2-propanol.

5c: Mp 115—120 °C (decomp); ^{1}H NMR (C_6D_6) $\delta=0.76$ (s, 12 H), 0.89 (s, 18 H), 1.42 (s, 4 H); ^{13}C NMR (C_6D_6) $\delta=5.4$, 18.7, 29.8, 55.8, 148.2 (br); ^{29}Si NMR (C_6D_6) $\delta=36.4$; IR (C_6H_6) 2164, 2144 cm^{-1}. Anal. Calcd for $C_{16}H_{34}N_2PdSi_2$: C, 46.08; H, 8.22; N, 6.72%. Found: C, 45.81; H, 8.16; N, 6.68%.

Synthesis of Complex 5f. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from Pd(C_5H_5)(C_3H_5) (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **4f** (46 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 3.5 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **5f** (26 mg, 56%), which was washed with cold 2-propanol.

5f: Mp 145 °C (decomp); ^{1}H NMR (C_6D_6) $\delta=0.86$ (s, 12H), 0.93 (s, 18 H), 7.39—7.45 (m, 2 H), 7.84—7.90 (m, 2 H); ^{13}C NMR (CD_2Cl_2) $\delta=5.5$, 30.6, 57.0, 127.6, 131.0, 145.5 (br), 158.2; ^{29}Si NMR (C_6D_6) $\delta=30.5$; IR (C_6H_6) 2168, 2148 cm^{-1}. Anal. Calcd for $C_{20}H_{34}N_2PdSi_2$: C, 51.65; H, 7.37; N, 6.02%. Found: C, 51.62; H, 7.66; N, 5.74%.

Synthesis of Complex 8a. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from Pd(C_5H_5)(C_3H_5) (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **7a** (70 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 6 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **8a** (51 mg, 73%), which was washed with cold 2-propanol.

8a: Mp 162.5—164.5 °C (decomp); ^{1}H NMR (C_6D_6) $\delta=0.67$ (s, 18 H), 4.14 (s, 4 H), 7.16—7.32 (m, 12 H), 7.98—8.06 (m, 8 H); ^{13}C NMR (CD_2Cl_2) $\delta=29.8$, 56.9, 66.7, 127.3, 127.8, 135.3, 143.1 (br), 146.6; IR (C_6H_6) 2180, 2170 cm^{-1}. Anal. Calcd for $C_{36}H_{42}N_2O_2PdSi_2$: C, 62.01; H, 6.07; N, 4.02%. Found: C, 61.76; H, 6.08; N, 3.90%.

Synthesis of Complex 8b. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from Pd(C_5H_5)(C_3H_5) (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **7b** (84 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 4 h, evaporation of the solvent was followed by addition of 2-propanol (0.3 mL) to precipitate crystalline **8b** (80 mg, 95%), which was washed with cold 2-propanol.

8b: Mp 148—151 °C (decomp); ^{1}H NMR (C_6D_6) $\delta=0.63$ (s, 18 H), 0.86 (t, $J=7.2$ Hz, 6 H), 3.68—3.94 (m, 4 H), 5.34 (s, 2 H), 7.16—7.28 (m, 12 H), 8.10—8.16 (m, 8 H); ^{13}C NMR (CD_2Cl_2) $\delta=14.1$, 29.8, 57.0, 60.9, 76.6, 127.3, 127.4, 127.8, 128.5, 135.1, 136.3, 142.7 (br), 143.8, 147.0, 170.6; IR (C_6H_6) 2176, 1740 cm^{-1}. Anal. Calcd for $C_{42}H_{50}N_2O_6PdSi_2$: C, 59.95; H, 5.99; N, 3.33%. Found: C, 60.20; H, 6.06; N, 3.26%.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3e with Cyclic Disilane 1a (Illustrated in Scheme 3). To a benzene-d_6 (0.5 mL) suspension of **3e** (0.05 mmol) in an NMR tube was added **1a** (8 mg, 0.05 mmol) at room temperature under an argon atmosphere. The mixture was heated at 50 °C to dissolve **3e**. After 6 h, ^{1}H NMR showed that clean disilane exchange reaction occurred to give bis(organosilyl)palladium complex **3a** and disilane **1e**.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3a with Cyclic Disilane 1b (Illustrated in Scheme 3). To a benzene-d_6 (0.5 mL) solution of **3a** (43 mg, 0.1 mmol) in an NMR tube was added **1b** (36 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 5 min, ^{1}H NMR showed that clean disilane exchange reaction occurred to give bis(organosilyl)-palladium complex **3b** and disilane **1a**.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3a with 4g (Illustrated in Eq. 9). To a benzene-d_6 (0.5 mL) solution of **3a** (0.05 mmol) in an NMR tube was added **4g** (19 mg, 0.05 mmol) at room temperature under an argon atmosphere. After 18 h, ^{1}H NMR showed the formation of **5a**, **1a**, and hexamethyldisilane together with unchanged **3a** and **4g**. The ratio of **5a**, **1a**, hexamethyldisilane, **3a**, **4g** was determined to be 3/3/3/1/1.

Synthesis of Complex 9. To a benzene (1 mL) solution of **5a** (101 mg, 0.2 mmol) was added triphenylphosphine (52 mg, 0.2 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystalization from benzene–pentane (1/4) gave **9** containing 1/3 equiv of pentane (119 mg, 84%) as colorless crystals.

9: Mp 80.5—82.0 °C ^{1}H NMR (C_6D_6) δ=0.82 (s, 9 H), 0.83 (s, 12 H), 1.92—2.04 (m, 2 H), 2.65—2.73 (m, 4 H), 7.00—7.08 (m, 9 H), 7.56—7.68 (m, 6 H); ^{13}C NMR (CD_2Cl_2) δ=2.3, 27.6, 28.4, 30.2, 30.5, 56.7, 128.5 (d, J=10.8 Hz), 129.5, 134.1 (d, J=15.4 Hz), 137.0 (m), 147.0 (br); ^{29}Si NMR (C_6D_6) δ=−19.3 (m); ^{31}P NMR (C_6D_6) δ=16.7 (s); IR (C_6H_6) 2956, 2152, 1437, 1095 cm^{-1}. Anal. Calcd for $C_{31}H_{42}NPPdS_2Si_2\cdot 1/3C_5H_{12}$: C, 55.23; H, 6.52; N, 1.97%. Found: C, 55.84; H, 6.65; N, 1.85%.

Synthesis of Complex 10. To a benzene (1 mL) solution of **5a** (101 mg, 0.2 mmol) was added dimethylphenylphosphine (68 mg, 0.48 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystalization from benzene–pentane (1/10) gave **10** (104 mg, 84%) as colorless needles.

10: Mp 132.0—134.0 °C (decomp); ^{1}H NMR (C_6D_6) δ=0.84 (s, 12 H), 1.09 (d, J=4.7 Hz, 12 H), 1.92—2.04 (m, 2 H), 2.62—2.68 (m, 4 H), 6.98—7.06 (m, 6 H), 7.26—7.36 (m, 4 H); ^{13}C NMR (CD_2Cl_2) δ=2.7, 17.7 (d, J=14.3 Hz), 27.5, 28.2, 30.2, 128.7 (d, J=8.0 Hz), 129.5, 131.1 (d, J=13.8 Hz), 140.3 (m); ^{29}Si NMR (C_6D_6) δ=−18.8 (m); ^{31}P NMR (C_6D_6) δ=−18.9 (s); IR (C_6H_6) 2916, 1438, 1236, 834 cm^{-1}. Anal. Calcd for $C_{24}H_{40}P_2PdS_2Si_2$: C, 46.70; H, 6.53%. Found: C, 47.20; H, 6.57%.

Synthesis of Complex 11. To a benzene (1 mL) solution of **3b** (63 mg, 0.1 mmol) was added 1,2-bis(diphenylphosphino)-ethane (40 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystalization from CH_2Cl_2–2-propanol (1/3) gave **11** (79 mg, 91%) as colorless crystals.

11: Mp 196 °C (decomp); ^{1}H NMR (C_6D_6) δ=0.83 (dd, J=13.9, 4.8 Hz, 4 H), 0.95 (d, J=6.3 Hz, 24 H), 1.06—1.22 (m, 4 H), 1.64—1.72 (m, 2 H), 1.78—1.86 (m, 2 H), 1.96—2.18 (m, 4 H), 7.10—7.20 (m, 12 H), 7.32—7.36 (m, 2 H), 7.54—7.66 (m, 8 H), 7.78—7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ=26.1, 26.8, 27.6, 27.8 (t, J=18.0 Hz), 32.6 (t, J=5.7 Hz), 126.1, 128.5 (m), 130.0, 132.1, 133.5 (m), 134.4 (m), 157.4 (t, J=3.9 Hz); ^{29}Si NMR ($CDCl_3$) δ=39.2 (dd, J=128, 13 Hz); ^{31}P NMR (C_6D_6) δ=30.8; IR (KBr) 3040, 2952, 1438, 1100, 742 cm^{-1}. Anal. Calcd for $C_{48}H_{64}P_2PdSi_2$: C, 66.61; H, 7.45%. Found: C, 66.38; H, 7.64%.

Single Crystal X-Ray Analysis of 11.[31] Crystal data for **11**: Crystal size 0.55×0.40×0.30 mm (recrystallized from benzene–ethanol (2/1)); monoclinic, space group $P2_1/n$ (no. 14), Z=4; a=23.312(6), b=18.541(4), c=11.094(4) Å; β=97.62(2)°; V= 4753(2) Å^3, ρ_{calcd}=1.21 g/cm^3; μ=45.73 cm^{-1}; max 2θ=125° (Cu $K\alpha$, λ=1.54178 Å, graphite monochrometor, $\omega/2\theta$-scan, T= 293 K); 8826 reflections measured, 7945 independent, 5348 included in the refinement, Lorentzian polarization and empirical absorption correction based on azimuthal scans of several reflections; direct method, anisotropical refinement for non-hydrogen atoms by full-matrix least-squares against $|F|$ with program package CrystanG (Mac Science), 500 parameters; R=0.062, R_w=0.086. Hydrogen atoms were partially included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters.

Stoichiometric Reaction of the Complex 5a with Phenylacetylene. To a solution of **5a** (13.2 mg, 0.026 mmol) in benzene-d_6 (0.5 mL) was added phenylacetylene (3.1 mg, 0.030 mmol) at room temperature. After 5 min, the reaction mixture was subjected to preparative TLC (hexane/ether=10/1) to furnish **12a** (8.6 mg, 98%).

12a: Mp 53.5—54.5 °C; ^{1}H NMR ($CDCl_3$) δ=0.46 (s, 6 H), 0.50 (s, 6H), 1.96—2.12 (m, 2 H), 2.68—2.76 (m, 4 H), 6.90 (s, 1 H), 7.20—7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ=−0.8, −0.6, 22.9, 25.6, 28.8, 126.2, 127.2, 128.3, 142.6, 145.4, 163.3; IR (KBr) 2960, 1490, 1252 cm^{-1}. Anal. Calcd for $C_{16}H_{24}S_2Si_2$: C, 57.08; H, 7.19%. Found: C, 56.93; H, 7.28%.

Stoichiometric Reaction of the Complex 5a with Trimethylsilylacetylene. To a solution of **5a** (58 mg, 0.11 mmol) in toluene (1 mL) was added trimethylsilylacetylene (17 mg, 0.17 mmol) at room temperature. After 8 h, the reaction mixture was subjected to column chromatography on silica gel (hexane/ether=10/1) to furnish **13** (33 mg, 90%). ^{1}H NMR-monitoring showed the reaction completed within 3.5 h.

13: Mp 53.0—53.5 °C; ^{1}H NMR (C_6D_6) δ=0.14 (s, 9 H), 0.46 (s, 6 H), 0.54 (s, 6 H), 1.56—1.76 (m, 2 H), 2.24—2.46 (m, 4 H), 7.59 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ=−0.8, −0.6, −0.4, 22.7, 25.7, 28.9, 163.5, 171.7; IR (neat) 2964, 1250, 832 cm^{-1}. Anal. Calcd for $C_{13}H_{28}S_2Si_3$: C, 46.94; H, 8.48%. Found: C, 46.99; H, 8.70%.

Stoichiometric Reaction of the Complex 5a with Dimethyl Acetylenedicarboxylate. To a solution of **5a** (16 mg, 0.032 mmol) in benzene-d_6 (0.5 mL) was added dimethyl acetylenedicarboxylate (4.5 mg, 0.032 mmol) at room temperature. Within 10 min, bis-silylation completed to form bis(t-butyl isocyanide)-(bis-silylated alkene)palladium(0) (**14**) complexes, from which **14** was liberated by addition of dimethyl acetylenedicarboxylate (9 mg, 0.064 mmol). The reaction mixture was stirred for 2 h, and then subjected to column chromatography on silica gel (CH_2Cl_2) to furnish **14** (12 mg, 99%).

14: ^{1}H NMR (C_6D_6) δ=0.57 (s, 12 H), 1.50—1.60 (m, 2 H), 2.16—2.24 (m, 4 H), 3.42 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ=−1.7, 21.8, 25.2, 28.9, 52.0, 156.2, 168.5; IR (neat) 2960, 1726, 1240 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4S_2Si_2$: C, 44.65; H, 6.42%. Found: C, 44.48; H, 6.32%.

Stoichiometric Reaction of the Complex 5a with Diphenylacetylene. To a solution of **5a** (46 mg, 0.091 mmol) in toluene

(1 mL) was added diphenylacetylene (24 mg, 0.14 mmol) at room temperature. After 12 h at 90 °C, the reaction mixture was subjected to preparative TLC (hexane/ether=10/1) to furnish **15** (36 mg, 96%).

15: Mp 162—163 °C; ^{1}H NMR (C_6D_6) δ=0.53 (s, 12 H), 1.64—1.74 (m, 2 H), 2.34—2.40 (m, 4 H), 6.84—7.02 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ=−1.2, 22.1, 25.6, 28.8, 125.5, 127.7, 141.4, 158.1; IR (KBr) 2920, 1482, 1248 cm^{-1}. Anal. Calcd for $C_{22}H_{28}S_2Si_2$: C, 64.03; H, 6.84%. Found: C, 63.92; H, 6.87%.

Reaction of 4b and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (0.9 mg, 4 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (8.4 mg, 0.06 mmol) in toluene (0.3 mL) were added **4b** (80 mg, 0.20 mmol) and phenylacetylene (61 mg, 0.60 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 7 h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12b** (2 mg, 4%), **16b** (48 mg, 48%), and **17b** (34 mg, 28%). **16b** and **17b** consisted of two and three regio isomers, respectively, and the isomers could not be separated by preparative GLC nor by preparative gel permeation chromatography (GPC) from each other.

12b: ^{1}H NMR ($CDCl_3$) δ=−0.15 (s, 2 H), 0.20 (s, 6H), 0.30 (s, 6 H), 7.02 (s, 1 H), 7.20—7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ=−2.1, 0.4, 1.1, 126.3, 126.9, 128.3, 143.0, 148.5, 165.8. Anal. Calcd for $C_{13}H_{20}Si_2$: C, 67.17; H, 8.67%. Found: C, 67.03; H, 8.77%.

16b: ^{1}H NMR for the major isomer ($CDCl_3$) δ=−0.22 (s, 2 H), 0.00 (s, 12 H), 0.32 (s, 6H), 0.33 (s, 6H), 6.63 (s, 1H), 7.04—7.10 (m, 2 H), 7.16—7.46 (m, 11 H), 7.54—7.60 (m, 2 H); MS (20 eV) *m/z* 502 (M^+). Anal. Calcd for $C_{29}H_{42}Si_4$: C, 69.25; H, 8.42%. Found: C, 68.95; H, 8.37%.

17b: ^{1}H NMR for the major isomer ($CDCl_3$) δ=−0.30 (s, 2 H), −0.03 (s, 12 H), 0.30 (s, 12 H), 6.57 (s, 2 H), 6.98—7.06 (m, 4 H), 7.16—7.36 (m, 12 H), 7.50—7.60 (m, 4 H); MS (20 eV) *m/z* 604 (M^+). Anal. Calcd for $C_{37}H_{48}Si_4$: C, 73.44; H, 7.99%. Found: C, 73.29; H, 8.16%.

Reaction of 4h and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (4.5 mg, 0.02 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (42 mg, 0.30 mmol) in toluene (1 mL) were added **4h** (83 mg, 0.20 mmol) and phenylacetylene (61 mg, 0.60 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 7 h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12h** (33 mg, 67%) and **16h** (19 mg, 18%).

12h: ^{1}H NMR ($CDCl_3$) δ=0.11 (q, *J*=7.8 Hz, 1 H), 0.13 (s, 3H), 0.19 (s, 3 H), 0.25 (s, 3 H), 0.27 (s, 3 H), 1.11 (d, *J*=7.8 Hz, 3 H), 7.01 (s, 1 H), 7.16—7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ=−3.2, −2.5, −0.5, 0.0, 3.4, 8.3, 126.2, 126.9, 128.3, 143.1, 147.7, 165.3; IR (neat) 2960, 1490, 1250, 852, 778 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00%. Found: C, 68.40; 9.28%.

16h: ^{1}H NMR for major isomer (500 MHz, $CDCl_3$) δ=−0.10 (s, 6H), −0.02 (q, *J*=7.6 Hz, 1 H), 0.018 (s, 3H), 0.024 (s, 3 H), 0.25 (s, 3 H), 0.28 (s, 3 H), 0.31 (s, 3 H), 0.32 (s, 3 H), 0.92 (d, *J*=7.6 Hz, 3 H), 6.55 (s, 1 H), 6.99—7.02 (m, 2 H), 7.11—7.23 (m, 3 H), 7.27—7.32 (m, 6 H), 7.40—7.42 (m, 2 H), 7.49—7.52 (m, 2 H); MS (20 eV) *m/z* 516 (M^+). Anal. Calcd for $C_{30}H_{44}Si_4$: C, 69.69; H, 8.58%. Found: C, 69.55; H, 8.48%.

Reaction of 4i and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4i** (78 mg, 0.16 mmol) with phenylacetylene was carried out to give **12i** (47 mg, 91%).

12i: ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 3 H), 0.37 (s, 3H), 0.38 (s, 3 H), 0.41 (s, 3 H), 4.00 (s, 1 H), 6.86—7.00 (m, 3 H), 7.01 (s, 1 H), 7.24—7.40 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ=−3.5, −2.9, −0.2, −0.1, 62.2, 114.6, 119.8, 126.3, 127.3, 128.4, 129.2, 142.7, 146.2, 161.6, 164.3; IR (neat) 2968, 1600, 1490, 1238, 858 cm^{-1}. Anal. Calcd for $C_{19}H_{24}OSi_2$: C, 70.31; H, 7.45%. Found: C, 70.22; H, 7.51%.

Reaction of 4j and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4j** (102 mg, 0.2 mmol) with phenylacetylene was carried out to give **12j** (66 mg, 97%).

12j: ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 3 H), 0.30 (s, 3H), 0.35 (s, 6 H), 2.02 (s, 1 H), 7.00 (s, 1 H), 7.08—7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ=−2.5, −1.8, 0.5, 0.8, 13.5, 125.0, 126.2, 127.3, 127.6, 128.4, 128.5, 140.2, 142.5, 147.0, 164.9; IR (neat) 3064, 2968, 1586, 1482, 1252, 860 cm^{-1}. Anal. Calcd for $C_{19}H_{24}SSi_2$: C, 67.00; H, 7.10%. Found: C, 67.05; H, 7.13%.

Reaction of 4a and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4a** (202 mg, 0.40 mmol) with phenylacetylene was carried out to give **12a** (123 mg, 91%).

Reaction of 4c and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4c** (83 mg, 0.20 mmol) with phenylacetylene was carried out to give **12c** (19 mg, 39%), **16c** (16 mg, 15%), and **17c** (37 mg, 30%).

12c: ^{1}H NMR ($CDCl_3$) δ=0.13 (s, 6 H), 0.15 (s, 6H), 0.84—0.98 (m, 4 H), 6.60 (s, 1 H), 7.16—7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ=−2.1, −1.8, 7.0, 8.8, 126.2, 128.1, 145.9, 147.3, 161.8; IR (neat) 2908, 1490, 1250, 832, 776 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00%. Found: C, 68.29; H, 8.98%.

16c: ^{1}H NMR for major isomer ($CDCl_3$) δ=−0.08 (s, 6 H), −0.01 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.37—0.44 (m, 4 H), 6.59 (s, 1H), 7.02—7.08 (m, 2 H), 7.14—7.46 (m, 11 H), 7.56—7.61 (m, 2 H); MS (20 eV) *m/z* 516 (M^+). Anal. Calcd for $C_{30}H_{44}Si_4$: C, 69.69; H, 8.58%. Found: C, 69.52; H, 8.64%.

17c: ^{1}H NMR for major isomer ($CDCl_3$) δ=−0.09 (s, 12 H), 0.32 (s, 12 H), 0.28—0.36 (m, 4 H), 6.60 (s, 2 H), 7.02—7.08 (m, 4 H), 7.16—7.36 (m, 12 H), 7.54—7.60 (m, 4 H); MS (20 eV) *m/z* 618 (M^+). Anal. Calcd for $C_{38}H_{50}Si_4$: C, 73.72; H, 8.14%. Found: C, 73.42; H, 8.35%.

Reaction of 4d and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4d** (86 mg, 0.20 mmol) with phenylacetylene was carried out to give **16d** (53 mg, 50%) and **17d** (42 mg, 33%).

16d: ^{1}H NMR for major isomer ($CDCl_3$) δ=−0.09 (s, 6 H), 0.02 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.43—0.63 (m, 4 H), 1.16—1.34 (m, 2 H), 6.57 (s, 1 H), 7.00—7.06 (m, 2 H), 7.14—7.38 (m, 9 H), 7.39—7.45 (m, 2 H), 7.54—7.60 (m, 2 H); MS (20 eV) *m/z* 530 (M^+). Anal. Calcd for $C_{31}H_{46}Si_4$: C, 70.11; H, 8.73%. Found: C, 70.34; H, 8.88%.

17d: ^{1}H NMR for major isomer ($CDCl_3$) δ=−0.06 (s, 12 H), 0.32 (s, 12 H), 0.43—0.55 (m, 4 H), 1.16—1.36 (m, 2 H), 6.59 (s, 2 H), 7.01—7.07 (m, 4 H), 7.16—7.36 (m, 12 H), 7.54—7.60 (m, 4 H); MS (20 eV) *m/z* 632 (M^+). Anal. Calcd for $C_{39}H_{52}Si_4$: C, 73.98; H, 8.28%. Found: C, 74.04; H, 8.51%.

Reaction of 4e and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4e** (89 mg, 0.20 mmol) with phenylacetylene was carried out to give **16e** (41 mg, 38%) and **17e** (64 mg, 49%).

16e: ^{1}H NMR for major isomer ($CDCl_3$) δ=−0.06 (s, 6 H), 0.02 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.38—0.58 (m, 4 H), 1.16—

1.28 (m, 4 H), 6.60 (s, 1H), 7.04—7.10 (m, 2 H), 7.16—7.38 (m, 9 H), 7.40—7.46 (m, 2 H), 7.56—7.62 (m, 2 H); MS (20 eV) *m/z* 544 (M^+). Anal. Calcd for $C_{32}H_{48}Si_4$: C, 70.51; H, 8.88%. Found: C, 70.74; H, 9.16%.

17e: ^{1}H NMR for major isomer ($CDCl_3$) δ=0.06 (s, 12 H), 0.32 (s, 12 H), 0.38—0.46 (m, 4 H), 1.14—1.26 (m, 4 H), 6.60 (s, 2 H), 7.04—7.08 (m, 4 H), 7.16—7.28 (m, 6 H), 7.30—7.36 (m, 6 H), 7.54—7.60 (m, 4 H); MS (20 eV) *m/z* 646 (M^+). Anal. Calcd for $C_{40}H_{54}Si_4$: C, 74.23; H, 8.41%. Found: C, 73.94; H, 8.58%.

Reactions of 16c and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (0.4 mg, 1.8 µmol) and 1,1,3,3-tetramethylbutyl isocyanide (3.7 mg, 0.027 mmol) in toluene (0.1 mL) were added **16c** (46 mg, 0.09 mmol) and phenylacetylene (14 mg, 0.14 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 7 h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **17c** (20 mg, 36%) and recovered **16c** (27 mg, 59%).

Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)phenoxymethane (4i). To a THF (20 mL) solution of phenoxy(1,1,2,2-tetramethyl-2-phenyldisilanyl)methane (150 mg, 0.5 mmol), prepared from phenoxymethyllithium and 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane in 75% yield,[32] was added *s*-butyllithium (1.1 M in cyclohexane, 0.54 mmol, M=mol dm^{-3}) at −78 °C. The mixture was allowed to warm to −25 °C and held at the temperature for 0.5 h. To the mixture cooled to −40 °C was added 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (114 mg, 0.5 mmol). The mixture was allowed to warm to room temperature over 1.5 h, and then saturated NH_4Cl aq was added. Extractive workup followed by purification by preparative TLC gave **4i** (78 mg, 32%).

4i: ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 6 H), 0.11 (s, 6 H), 0.20 (s, 6 H), 0.23 (s, 6 H), 4.12 (s, 1 H), 6.68—6.74 (m, 2 H), 6.76—6.86 (m, 1 H), 7.08—7.18 (m, 2 H), 7.26—7.36 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ=−3.9, −3.8, −3.5, −2.9, 62.3, 114.6, 119.4, 127.7, 128.3, 129.1, 133.9, 139.3, 160.3. Anal. Calcd for $C_{27}H_{40}OSi_4$: C, 65.79; H, 8.18%. Found: C, 65.57; H, 8.23%.

Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)phenylthiomethane (4j). To a THF (10 mL) solution of (phenylthio)(1,1,2,2-tetramethyl-2-phenyldisilanyl)methane (1 g, 3.2 mmol), prepared from (phenylthio)methyllithium and 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane, was added *n*-butyllithium (1.6 M in hexane, 3.1 mmol) at 0 °C. After 1.5 h, 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane was added dropwise, and the mixture was stirred for 16 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl. Extractive workup followed by purification by preparative gel permeation chromatography gave **4j** (670 mg, 42%).

4j: ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 6 H), 0.11 (s, 6 H), 0.30 (s, 6 H), 0.31 (s, 6 H), 1.74 (s, 1 H), 6.84—6.88 (m, 2 H), 6.98—7.16 (m, 3 H), 7.24—7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ=−3.2, −2.9, −2.6, −1.1, 12.4, 124.2, 126.1, 127.7, 128.3, 128.4, 138.9, 139.4, 139.7. Anal. Calcd for $C_{27}H_{40}SSi_4$: C, 63.71; H, 7.92%. Found: C, 63.62; H, 7.96%.

^{1}H NMR Study of the Catalytic Cycle of the Bis-Silylation via Intramolecular Metathesis (Illustrated in Scheme 5). To a benzene-*d*$_6$ (0.5 mL) solution of **5a** (9.5 mg, 0.019 mmol) in an NMR tube was added phenylacetylene (1.9 mg, 0.019 mmol) at room temperature under an argon atmosphere. ^{1}H NMR showed clean formation of (bis-silylated alkene)palladium complex **18** after 1 min. To the mixture was added **4g** (7.2 mg, 0.019 mmol). Monitoring the reaction by ^{1}H NMR revealed that formation of **5a**, hexamethyldisilane, and bis-silylated alkene **12a** from **18** and **4g** completed after 3.5 h at room temperature. **18** was identified by comparison with the authentic sample, which was prepared by mixing isolated **12a** with bis(*t*-butyl isocyanide)palladium(0) (**2**) in benzene-*d*$_6$.

General Procedure for the Catalytic Bis-Silylation of Alkynes with 4g in the Presence of 5a. To a mixture of **4g** (152 mg, 0.40 mmol) and **5a** (4.0 mg, 8.0 µmol) in toluene (0.4 mL) was added alkynes (0.60 mmol) under an argon atmosphere. The mixture was stirred under the conditions listed in Table 3, cooled to room temperature, and then subjected to preparative TLC (for **12a**,**13**,**15**, and **19**), or bulb-to-bulb distillation (for **20**) to furnish the cyclized product.

19: ^{1}H NMR ($CDCl_3$) δ=0.34 (s, 6 H), 0.36 (s, 6 H), 0.88 (t, *J*=6.2 Hz, 3 H), 1.24—1.50 (m, 8 H), 1.96—2.08 (m, 2 H), 2.18—2.28 (m, 2 H), 2.64—2.72 (m, 4 H), 6.40 (t, *J*=1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ=−1.5, −0.7, 14.1, 22.6, 22.8, 25.7, 28.3, 28.9, 29.1, 31.7, 37.2, 141.8, 166.9; IR (neat) 2932, 1250, 860 cm^{-1}. Anal. Calcd for $C_{16}H_{32}S_2Si_2$: C, 55.75; H, 9.36%. Found: C, 55.83; H, 9.60%.

20: Mp 46.0—46.5 °C; ^{1}H NMR (C_6D_6) δ=0.44 (s, 6 H), 0.51 (s, 6 H), 0.81 (t, *J*=7.0 Hz, 3 H), 1.08—1.42 (m, 4 H), 1.56—1.72 (m, 2 H), 2.03 (s, 3 H), 2.18—2.38 (m, 6 H); ^{13}C NMR (C_6D_6) δ=−1.3, −0.6, 14.0, 22.4, 23.1, 25.7, 28.8, 31.4, 32.0, 33.5, 160.0, 160.2, 206.3; IR (neat) 2964, 1682, 1252, 1202, 836 cm^{-1}. Anal. Calcd for $C_{16}H_{30}OS_2Si_2$: C, 53.57; H, 8.43%. Found: C, 53.41; H, 8.66%.

General Procedure for the Catalytic Bis-Silylation of Alkenes with 4g in the Presence of 5a. To a mixture of **4g** (152 mg, 0.40 mmol) and **5a** (4.0 mg, 8.0 µmol) in toluene (0.4 mL) was added alkenes (0.60 mmol) under an argon atmosphere. The mixture was stirred at 90 °C for 15 h, cooled to room temperature, and then subjected to preparative TLC (for **21a** and **22a**—**c**), or bulb-to-bulb distillation (for **21b**) to furnish the cyclized product.

21a: ^{1}H NMR ($CDCl_3$) δ=0.23 (s, 3 H), 0.31 (s, 3 H), 0.37 (s, 3 H), 0.50 (s, 3 H), 1.04 (dd, *J*=7.3 15.0 Hz, 1 H), 1.31 (dd, *J*=11.9, 15.0 Hz, 1 H), 1.96—2.06 (m, 2 H), 2.40 (dd, *J*=7.3, 11.9 Hz, 1 H), 2.56—2.80 (m, 4 H), 3.65 (s, 3 H); ^{13}C NMR (C_6D_6) δ=−3.9, −1.9, −1.4, −0.6, 12.1, 22.9, 25.6, 28.6, 28.7, 31.3, 50.9, 175.4; IR (neat) 2960, 1728, 1252, 1192, 858 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_2S_2Si_2$: C, 44.95; H, 7.55%. Found: C, 44.88; H, 7.77%.

21b: Mp 75.0—76.5 °C; ^{1}H NMR (C_6D_6) δ=0.09 (s, 3 H), 0.19 (s, 3 H), 0.31 (s, 3 H), 0.42 (s, 3H), 0.78 (dd, *J*=12.0, 14.9 Hz, 1 H), 0.92 (dd, *J*=7.6, 14.9 Hz, 1 H), 1.38—1.58 (m, 2 H), 1.72 (dd, *J*=7.6, 12.0 Hz, 1 H), 2.00—2.30 (m, 4 H); ^{13}C NMR (C_6D_6) δ=−4.0, −2.6, −1.9, −1.5, 11.8, 13.8, 21.7, 25.3, 28.5, 28.7, 122.4; IR (neat) 2964, 2220, 1420, 1256, 802 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NS_2Si_2$: C, 45.94; H, 7.36; N, 4.87%. Found: C, 45.78; H, 7.39; N, 4.70%.

22a: ^{1}H NMR (C_6D_6) δ=0.42 (s, 6 H), 0.55 (s, 6 H), 1.40—1.58 (m, 4 H), 1.73 (d, *J*=1.1 Hz, 3 H), 2.12—2.38 (m, 4 H), 4.64 (tq, *J*=6.8, 1.1 Hz, 1H); ^{13}C NMR (C_6D_6) δ=−1.8, 0.5, 12.8, 22.7, 24.9, 25.0, 26.9, 103.8, 148.1; IR (neat) 2924, 1678, 1252, 1004 cm^{-1}. Anal. Calcd for $C_{12}H_{24}OS_2Si_2$: C, 47.31; H, 7.94%. Found: C, 47.26; H, 8.20%.

22b: ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 3 H), 0.34 (s, 3 H), 0.41 (s, 3 H), 0.51 (s, 3 H), 1.02 (d, *J*=7.7 Hz, 3 H), 1.74 (dd, *J*=1.5, 1.1 Hz, 3 H), 1.80—2.16 (m, 3 H), 2.50—2.84 (m, 4 H), 4.40 (dq, *J*=5.9, 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ=−5.5, −3.4, −0.4, 1.7, 15.7, 16.8, 22.4, 22.6, 24.8, 26.6, 26.8, 113.0, 145.6; IR (neat) 2960, 1676, 1252, 832 cm^{-1}. Anal. Calcd for $C_{13}H_{26}OS_2Si_2$: C, 49.00; H, 8.22%. Found: C, 48.70; H, 8.39%.

22c: ^{1}H NMR ($CDCl_3$) δ=0.34 (s, 6 H), 0.46 (s, 6 H), 1.75

(d, J=7.4 Hz, 2 H), 1.86—2.10 (m, 2 H), 2.56—2.82 (m, 4 H), 5.71 (t, J=7.4 Hz, 1 H), 7.20—7.34 (m, 3 H), 7.46—7.54 (m, 2 H); ^{13}C NMR (CDCl$_3$) $\delta = -2.1$, 0.1, 13.3, 24.5, 24.7, 26.7, 105.7, 123.9, 127.0, 128.1, 137.6, 148.7; IR (KBr) 2968, 1682, 1254, 1080, 848 cm^{-1}. Anal. Calcd for $C_{17}H_{26}OS_2Si_2$: C, 55.68; H, 7.15%. Found: C, 55.41; H, 7.18%.

References

1) a) T. D. Tilley, in "The Silicon-Heteroatom Bond," ed by S. Patai and Z. Rappoport, John Wiley & Sons, Chichester (1991), Chap. 9; b) S. Murai and N. Chatani, *J. Synth. Org. Chem. Jpn.*, **51**, 421 (1993).

2) a) H. Okinoshima, K. Yamamoto, and M. Kumada, *J. Organomet. Chem.*, **86**, C27 (1975); b) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Am. Chem. Soc.*, **97**, 932 (1975); c) K. Tamao, T. Hayashi, and M. Kumada, *J. Organomet. Chem.*, **114**, C19 (1976); d) H. Watanabe, M. Kobayashi, K. Higuchi, and Y. Nagai, *J. Organomet. Chem.*, **186**, 51 (1980); e) H. Matsumoto, I. Matsubara, T. Kato, K. Shono, H. Watanabe, and Y. Nagai, *J. Organomet. Chem.*, **199**, 43 (1980); f) H. Watanabe, M. Kobayashi, M. Saito, and Y. Nagai, *J. Organomet. Chem.*, **216**, 149 (1981); g) C. W. Carlson and R. West, *Organometallics*, **2**, 1801 (1983); h) D. Seyferth, E. W. Goldman, and J. Escudié, *J. Organomet. Chem.*, **271**, 337 (1984); i) H. Yamashita, M. Catellani, and M. Tanaka, *Chem. Lett.*, **1991**, 241; j) W. Finckh, B. Tang, A. Lough, and I. Manners, *Organometallics*, **11**, 2904 (1992); k) T. Kusukawa, Y. Kabe, and W. Ando, *Chem. Lett.*, **1993**, 985; l) F. Ozawa, M. Sugawara, and T. Hayashi, *Organometallics*, **13**, 3237 (1994).

3) a) Y. Ito, M. Suginome, and M. Murakami, *J. Org. Chem.*, **56**, 1948 (1991); b) M. Murakami, H. Oike, M. Sugawara, M. Suginome, and Y. Ito, *Tetrahedron*, **49**, 3933 (1993); c) M. Murakami, M. Suginome, K. Fujimoto, and Y. Ito, *Angew. Chem., Int. Ed. Engl.*, **32**, 1473 (1993); d) See also: A. Sekiguchi, M. Ichinohe, C. Kabuto, and H. Sakurai, *Organometallics*, **14**, 1092 (1995).

4) a) M. Murakami, P. G. Andersson, M. Suginome, and Y. Ito, *J. Am. Chem. Soc.*, **113**, 3987 (1991); b) M. Murakami, M. Suginome, K. Fujimoto, H. Nakamura, P. G. Andersson, and Y. Ito, *J. Am. Chem. Soc.*, **115**, 6487 (1993); c) M. Suginome, A. Matsumoto, K. Nagata, and Y. Ito, *J. Organomet. Chem.*, **499**, C1 (1995); d) M. Suginome, Y. Yamamoto, K. Fujii, and Y. Ito, *J. Am. Chem. Soc.*, **117**, 9608 (1995).

5) Bis-silylation of ethene and norbornene was achieved by using platinum catalyst: T. Hayashi, T. Kobayashi, A. M. Kawamoto, H. Yamashita, and M. Tanaka, *Organometallics*, **9**, 280 (1990).

6) a) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *Chem. Lett.*, **1975**, 887; b) K. Tamao, S. Okazaki, and M. Kumada, *J. Organomet. Chem.*, **146**, 87 (1978); c) H. Matsumoto, K. Shono, K. Wada, I. Matsubara, H. Watanabe, and Y. Nagai, *J. Organomet. Chem.*, **199**, 185 (1980); d) H. Watanabe, M. Saito, N. Sutou, K. Kishimoto, J. Inose, and Y. Nagai, *J. Organomet. Chem.*, **225**, 343 (1982); e) H. Sakurai, Y. Eriyama, Y. Kamiyama, and Y. Nakadaira, *J. Organomet. Chem.*, **264**, 229 (1984); f) Y. Tsuji, R. M. Lago, S. Tomohiro, and H. Tsuneishi, *Organometallics*, **11**, 2353 (1992).

7) a) Y. Ito, S. Nishimura, and M. Ishikawa, *Tetrahedron Lett.*, **28**, 1293 (1987); b) Y. Ito, T. Matsuura, and M. Murakami, *J. Am. Chem. Soc.*, **110**, 3692 (1988); c) Y. Ito, M. Suginome, T. Matsuura, and M. Murakami, *J. Am. Chem. Soc.*, **113**, 8899 (1991).

8) a) T. Hayashi, Y. Matsumoto, and Y. Ito, *Tetrahedron Lett.*, **29**, 4147 (1988); b) T. Hayashi, Y. Matsumoto, and Y. Ito, *J. Am. Chem. Soc.*, **110**, 5579 (1988).

9) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Organomet. Chem.*, **131**, 147 (1977).

10) T. Kusukawa, Y. Kabe, B. Nestler, and W. Ando, *Organometallics*, **14**, 2556 (1995).

11) M. Suginome, H. Oike, and Y. Ito, *J. Am. Chem. Soc.*, **117**, 1665 (1995).

12) U. Schubert, *Angew. Chem., Int. Ed. Engl.*, **33**, 419 (1994).

13) Y. Pan, J. T. Mague, and M. J. Fink, *Organometallics*, **11**, 3495 (1992).

14) M. Murakami, T. Yoshida, and Y. Ito, *Organometallics*, **13**, 2900 (1994).

15) M. Murakami, M. Suginome, and Y. Ito, *J. Synth. Org. Chem. Jpn.*, **53**, 509 (1995).

16) Preliminary communication: M. Suginome, H. Oike, and Y. Ito, *Organometallics*, **13**, 4148 (1994).

17) C. Eaborn, R. W. Griffiths, and A. Pidcock, *J. Organomet. Chem.*, **225**, 331 (1982).

18) Formation of 5-membered bis(organosilyl)palladium complexes in the reaction of 4-membered disilanes with phosphine–palladium complexes was reported, though they were not fully characterized. a) D. Seyferth, E. W. Goldman, and J. Escudié, *J. Organomet. Chem.*, **271**, 337 (1984); b) A. Naka, M. Hayashi, S. Okazaki, and M. Ishikawa, *Organometallics*, **13**, 4994 (1994).

19) Bis(organosilyl)palladium complexes have been synthesized by other methods. a) H. Yamashita, T. Kobayashi, T. Hayashi, and M. Tanaka, *Chem. Lett.*, **1990**, 1447; b) U. Shubert and C. Müler, *J. Organomet. Chem.*, **373**, 165 (1989); c) M. D. Curtis and J. Greene, *J. Am. Chem. Soc.*, **100**, 6362 (1978); d) T. R. Bierschenk, M. A. Guerra, T. J. Juhlke, S. B. Larson, and R. J. Lagow, *J. Am. Chem. Soc.*, **109**, 4855 (1987); e) M. A. Guerra and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, **1990**, 65.

20) The longest Si-Si bond has been reported to be 2.70 Å in hexa-*t*-butyldisilane. N. Wiberg, H. Schuster, A. Simon, and K. Peters, *Angew. Chem., Int. Ed. Engl.*, **25**, 79 (1986).

21) Unusually short Si–Si distances in some 4-membered rings were also reported. a) E. A. Zarate, C. A. Tessier-Youngs, and W. J. Youngs, *J. Am. Chem. Soc.*, **110**, 4068 (1988); b) E. K. Pham and R. West, *Organometallics*, **9**, 1517 (1990); c) R. H. Heyn and T. D. Tilley, *J. Am. Chem. Soc.*, **114**, 1917 (1992); d) T. Ohtaki and W. Ando, *Chem. Lett.*, **1994**, 1061.

22) To our best knowledge, these are the first successful examples for 1,2-bis-silylation of acrylate and acrylonitrile.

23) M. Kumada, K. Tamao, T. Takubo, and M. Ishikawa, *J. Organomet. Chem.*, **9**, 43 (1967).

24) M. Ishikawa, H. Sakamoto, and T. Tabuchi, *Organometallics*, **10**, 3137 (1991).

25) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).

26) H. Sakurai, T. Kishida, A. Hosomi, and M. Kumada, *J. Organomet. Chem.*, **8**, 65 (1966).

27) J. R. Hwu, J. M. Wetzel, J. S. Lee, and R. J. Butcher, *J. Organomet. Chem.*, **453**, 21 (1993).

28) K. Shiina, *J. Organomet. Chem.*, **310**, C57 (1986).

29) D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1131.

30) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Am. Chem. Soc.*, **91**, 6994 (1969).

31) Tables of final atomic coordinates, thermal parameters, bond distances, and bond angles are deposited as Document No. 69004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

32) J. J. Eisch, J. E. Galle, A. Piotrowski, and M.-R. Tsai, *J. Org. Chem.*, **47**. 5051 (1982).