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Microwave-Assisted Efficient One-Pot Synthesis of 9-Phenyl-9,10-disilatriptycene and Its Bridgehead Functionalization

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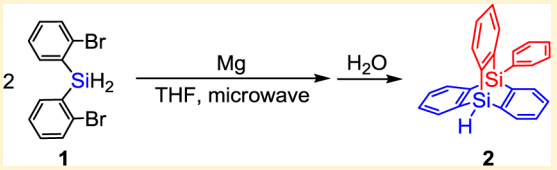
Supporting Information

ABSTRACT: 9-Phenyl-9,10-disilatriptycene (**2**) was synthesized by the reaction of bis(2-bromophenyl)silane (**1**) with magnesium in THF. On conventional heating, **2** and *cis*-9,10-diphenyl-9,10-dihydro-9,10-disilaanthracene (*cis*-**3**) were obtained in 31% and 36% yields, respectively. However, the yield of **2** was significantly increased to 71% on microwave irradiation. Theoretical calculations suggest that the intermediary Grignard reagents generated from *trans*- and *cis*-9,10-diaryl-9,10-dihydro-9,10-disilaanthracenes have quite different reactivity for construction of the 9,10-disilatriptycene skeleton. The bridgehead Si−H moiety of **2** was readily functionalized to give several 9,10-disilatriptycene derivatives.

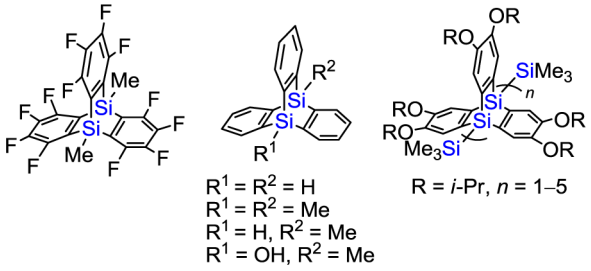


INTRODUCTION

Although several 9,10-disilatriptycenes and their oligomers have been reported for their structural interest (Scheme 1),[1−5] their preparation frequently requires harsh reaction conditions, difficult to handle reagents, or multistep reactions. Parent 9,10-disilatriptycene was obtained by pyrolysis of 9,10-dihydro-9,10-disilaanthracene in the presence of 1,2-dichlorobenzene.[2] Bickelhaupt and co-workers have demonstrated that reactions of 1,2-phenylenemagnesium derived from the corresponding organomercury reagent with trichloromethylsilane afforded 9,10-dimethyl-9,10-disilatriptycene.[3] Other 9,10-disilatriptycenes were synthesized by halogen−lithium exchange of tris(2-halogenophenyl)silanes followed by silylation of tris(2-lithiophenyl)silanes with trichlorosilane or trichloromethylsilane as a key step.[4] Tamao, Tsuji, and co-workers synthesized 9,10-disilatriptycene oligomers as a separable mixture by the reductive coupling of the corresponding 9,10-dibromo-9,10-disilatriptycene followed by silylation of the terminal bridgehead positions.[5]

We report herein efficient one-pot synthesis of 9-phenyl-9,10-disilatriptycene (**2**) from simple diarylsilane, bis(2-bromophenyl)silane (**1**), and magnesium on microwave irradiation. Detailed reaction pathways and energy profiles were analyzed by theoretical calculations. Furthermore, several 9-phenyl-9,10-disilatriptycene derivatives were synthesized by functionalization of the hydrosilane moiety of **2**.

Scheme 1

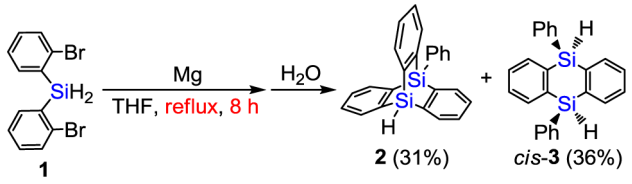


RESULTS AND DISCUSSION

Efficient One-Pot Synthesis of 9-Phenyl-9,10-disilatriptycene on Microwave Irradiation. Since **2** is constructed by two silicon atoms and four benzene rings, we designed **1** as an appropriate and easily handled precursor of **2**. Compound **1** was prepared by the reaction of 2-bromophenyllithium[6] with trichlorosilane followed by reduction with lithium aluminum hydride. When a mixture of **1** and magnesium in THF was refluxed for 8 h, **2** and *cis*-9,10-diphenyl-9,10-dihydro-9,10-disilaanthracene (*cis*-**3**) were obtained in 31% and 36% yields, respectively (Scheme 2).

In order to confirm the reaction mechanism, the reaction mixture was hydrolyzed with D_2O. Compounds **2**-*d* and *cis*-**3**-d_2 were obtained in 34% and 25% yields, respectively, in which deuterium atoms were incorporated into the 2-position of the

Scheme 2



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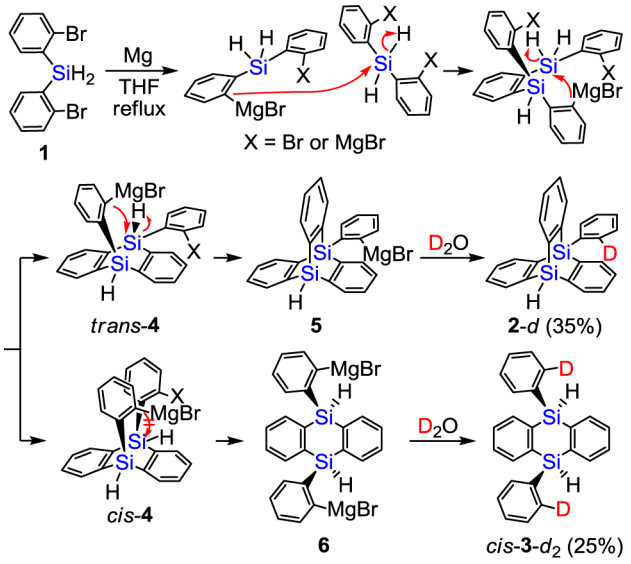
phenyl groups. Thus a plausible reaction mechanism is illustrated in Scheme 3.

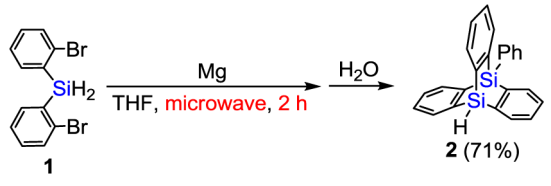
Scheme 3



Initially, successive intermolecular and intramolecular nucleophilic attack of Grignard reagents to hydrosilanes gave a cis−trans mixture of **4**. Subsequent intramolecular nucleophilic substitution in *trans*-**4** constructed a 9,10-disilatriptycene skeleton to provide **5**, which gave **2** (or **2**-*d*) after hydrolysis. A similar reaction of *cis*-**4** (or **6**) to **5** is unfavorable due to steric repulsion between two benzene rings on the same side of the silacycle, and hydrolysis of **6** furnished *cis*-**3** (or *cis*-**3**-d_2) after hydrolysis.

The reaction was carried out at room temperature for selective formation of *trans*-**4**, but the product ratio did not change: **2** and *cis*-**3** were obtained in 24% and 30% yields, respectively. Interestingly, when the reaction was carried out on microwave irradiation, the yield of **2** dramatically increased to 71% (Scheme 4). Compound *cis*-**3** was not obtained under

Scheme 4



these reaction conditions. This procedure could be applied for gram-scale synthesis of **2**, and we obtained 1.88 g of **2** in one batch. This reaction was also carried out without microwave irradiation in refluxing dibutyl ether for 1 day and in THF at 150 °C in a sealed tube for 22 h. However, the yield of **2** is not high (52% and 51% yields, respectively). Therefore, microwave irradiation is a convenient way to synthesize **2**. To the best of our knowledge, this is the first application of microwave irradiation for construction of caged organosilicon compounds.[7−15]

Theoretical Calculations of Reaction Pathways. The microwave-assisted synthesis of **2** is interesting from the viewpoint of the reaction mechanism. The difference of the activation energies of the rate-determining steps leading to **2** and *cis*-**3** seems to be small because the product ratio of **2** and *cis*-**3** is almost the same at room temperature and in refluxing THF. With microwave irradiation, the organomagnesium moiety of *cis*-**4** can attack the silicon atom on the opposite side to give **2**. To confirm this idea, we calculated the reaction pathways from *trans*- and *cis*-**4** to **2**. The results are summarized in Figure 1, and the schematic models of transition states and intermediates are shown in Figures 2 and 3.

The reaction of *trans*-**4** proceeds in two steps. The first step is the addition of the organomagnesium moiety to the silicon atom on the opposite side to give pentacoordinate silicate **8** as an intermediate.[16] The intermediate **8** has a nearly ideal trigonal bipyramidal structure: the bond angle between two apical bonds is 178.8°, and the sum of three equatorial bond angles is 360.0° (Figure 2). In the second step, the hydrogen atom and the phenyl group rotate,[17,18] and the hydrogen atom is eliminated to give **2**. On the other hand, the reaction of *cis*-**4** proceeds in one step. The transition state *cis*-**7** is formed by the addition of the organomagnesium moiety to the silicon atom. During the descent, the hydrogen atom on the silicon atom is eliminated to give **2**. In this elimination process, the hydrogen atom and the phenyl group rotate[17,18] via two kinds of pentacoordinate structures, **10** and **11**. As **10** and **11** are deformed, they do not exist in energy minima, but exist in the course of the descent.

Expectedly, the activation energies of the addition of the organomagnesium moiety to the silicon atom are quite different in *trans*-**4** and *cis*-**4**. The activation energy is 5.1 kcal mol^{-1} in the case of *trans*-**4**, while that of *cis*-**4** is remarkably high (22.8 kcal mol^{-1}). In the case of *trans*-**4**, the organomagnesium moiety easily approaches the silicon atom to form pentacoordinate silicate **8**. On the other hand, in the case of *cis*-**4**, nucleophilic attack of the organomagnesium moiety to the silicon atom seems unfavorable because of the steric repulsion between the two aryl groups. Furthermore, in a THF solution, coordination of THF to magnesium atoms would increase the activation barrier from *cis*-**4** to *cis*-**7** because of the increased steric hindrance around the nucleophilic carbon atoms.

The difference in the activation energies was analyzed by the activation strain analysis proposed by Bickelhaupt and coworkers.[19] According to this analysis, an activation energy ($\Delta E^{\ddagger}$) is expressed by the sum of a strain energy $\Delta E^{\ddagger}_{\text{strain}}$ and an interaction energy $\Delta E^{\ddagger}_{\text{int}}$ (eq 1). In order to apply the activation state analysis to our reaction, the reactant **4** is separated into two radical fragments, **4A** and **4B**, and the transition state **7** is separated into two radical fragments, **7A** and **7B** (Scheme 5). These fragments have the same geometries as the corresponding moieties in **4** and **7**.

$$\Delta E^{\ddagger} = \Delta E^{\ddagger}_{\text{strain}} + \Delta E^{\ddagger}_{\text{int}} \quad (1)$$

The strain energy $\Delta E^{\ddagger}_{\text{strain}}$ shows how the transition state is strained compared with the reactant. This energy can be evaluated by comparing the energies of the two fragments **4A** and **4B** of the reactant and those of the two fragments **7A** and **7B** of the transition state (eq 2). The interaction energy $\Delta E^{\ddagger}_{\text{int}}$ shows how the transition state is stabilized by the interaction between the two fragments. This energy can be evaluated by considering the energies of **4**, **4A**, **4B**, **7**, **7A**, and **7B** according to eq 3.

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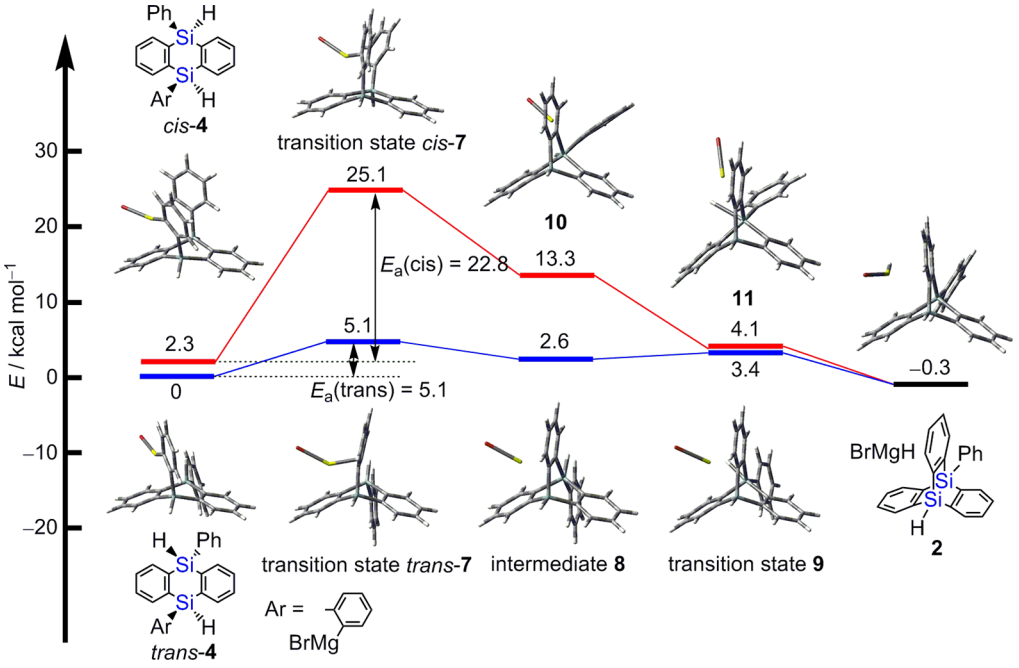

Figure 1. Energy diagram for the reaction of *trans*-**4** and *cis*-**4** to **2** calculated at the B3LYP/6-31+G(d) level.

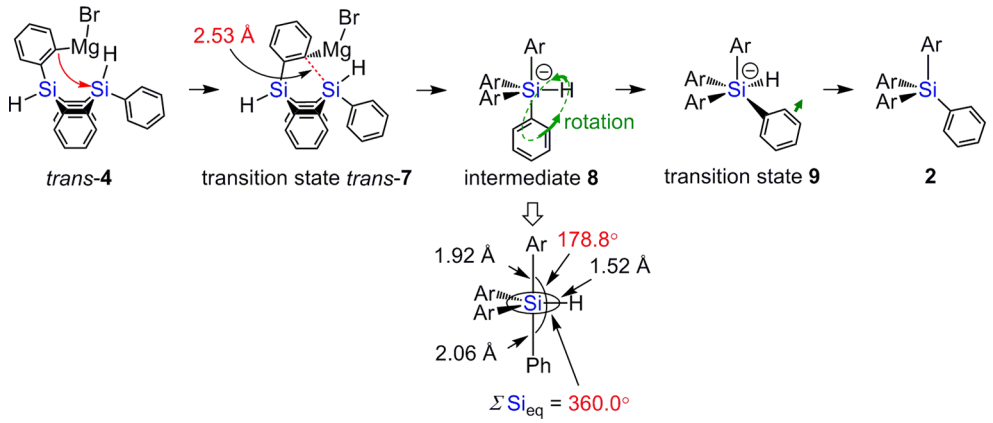

Figure 2. Reaction pathway from *trans*-**4** to **2** and structural parameters of the intermediate **8** calculated at the B3LYP/6-31+G(d) level.

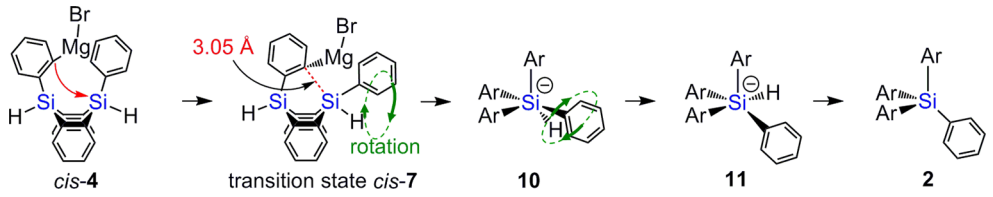

Figure 3. Reaction pathway from *cis*-**4** to **2** calculated at the B3LYP/6-31+G(d) level.

$$\Delta E^{\ddagger}_{\text{strain}} = [E(\mathbf{7A}) + E(\mathbf{7B})] - [E(\mathbf{4A}) + E(\mathbf{4B})]$$
$$= [E(\mathbf{7A}) - E(\mathbf{4A})] + [E(\mathbf{7B}) - E(\mathbf{4B})] \quad (2)$$

$$\Delta E^{\ddagger}_{\text{int}} = [E(\mathbf{7}) - E(\mathbf{7A}) - E(\mathbf{7B})] - [E(\mathbf{4}) - E(\mathbf{4A}) - E(\mathbf{4B})] \quad (3)$$

We calculated the energies of **4A**, **4B**, **7A**, and **7B** by using the same geometries of these fragments in **4** and **7**. The results are summarized in Table 1. The $\Delta E^{\ddagger}_{\text{strain}}$ from *cis*-**4** to *cis*-**7** (24.6 kcal mol^{-1}) is much higher than that from *trans*-**4** to *trans*-**7** (7.2 kcal mol^{-1}), whereas the ΔE_{int}'s from *cis*-**4** to *cis*-**7** (−1.8 kcal mol^{-1}) and from *trans*-**4** to *trans*-**7** (−2.1 kcal mol^{-1}) are almost the same. These results show that the large activation energy from *cis*-**4** to *cis*-**7** is ascribed to large strain in the transition state. These results are in accord with the above discussion about the steric repulsion between two aryl groups of *cis*-**7**.

Bridgehead Functionalizations. The hydrogen atom on the bridgehead silicon atom of **2** can be readily converted to a variety of functional groups (Scheme 6). The reaction of **2** with phenyllithium and *tert*-butyllithium gave the phenyl derivative **12** and the *tert*-butyl derivative **13** in 83% and 41% yields, respectively. Hydrolysis of **2** with aqueous sodium hydroxide

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Scheme 5

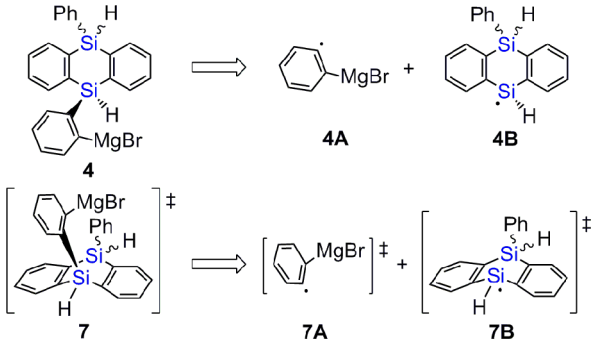
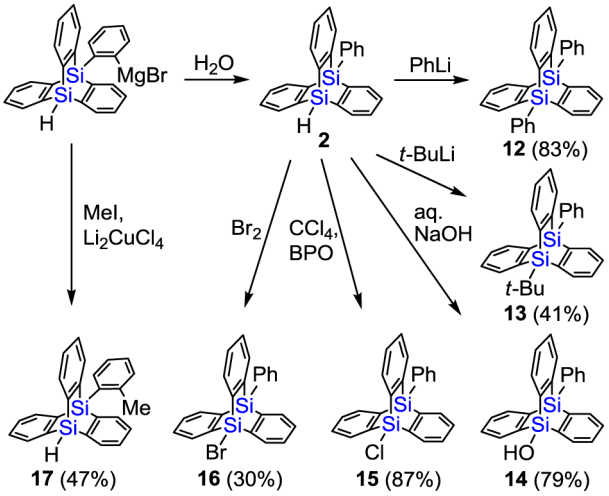


Table 1. Activation Energies[a] Calculated at the B3LYP/6-31+G(d) Level

reaction process	E(7A) − E(4A)	E(7B) − E(4B)	$\Delta E^{\ddagger}_{strain}$	E(7) − E(7A) − E(7B)
trans-4 to *trans*-7	3.8	3.4	7.2	−105.0
cis-4 to *cis*-7	3.4	21.2	24.6	−104.8
reaction process	E(4) − E(4A) − E(4B)		$\Delta E^{\ddagger}_{int}$	$\Delta E^{\ddagger}$
trans-4 to *trans*-7	−103.0		−2.1	5.1
cis-4 to *cis*-7	−103.0		−1.8	22.8

[a]kcal mol^{-1}.

Scheme 6



gave silanol **14** in 79% yield. Previously, the transformation of 9-methyl-9,10-disilatriptycene to silanol was performed by iodination with iodine monochloride followed by hydrolysis.[4] Compound **2** was chlorinated with carbon tetrachloride in the presence of benzoyl peroxide (BPO) to give chlorosilane **15** in 87% yield, and bromination of **2** with bromine gave bromosilane **16** in 30% yield. Furthermore, modification of the 2-position of the phenyl group of **2** could be achieved by using the Grignard reagent formed in the microwave-assisted synthesis of **2** before hydrolysis. This Grignard reagent was treated with iodomethane in the presence of a catalytic amount of dilithium tetrachlorocuprate(II) to give the tolyl derivative **17** in 47% yield.

CONCLUSION

9-Phenyl-9,10-disilatriptycene (**2**) was synthesized by the reaction of bis(2-bromophenyl)silane (**1**) with magnesium in THF on microwave irradiation. Since the bridgehead hydrogen atom of **2** can be converted to other functional groups, **2** would be a new entry of organosilicon functional materials. These studies are now in progress.

EXPERIMENTAL SECTION

Reactions. All reactions using air-sensitive compounds were carried out under an argon atmosphere. Microwave-assisted reactions were carried out with a Biotage Initiator microwave synthesizer. Diethyl ether and THF were distilled from sodium benzophenone ketyl. Hexane was distilled from lithium aluminum hydride. Carbon tetrachloride and dichloromethane were distilled from calcium hydride. Other solvents were distilled. Butyllithium in hexane (Kanto), *tert*-butyllithium in pentane (Kanto), 1,2-dibromobenzene (Tosco), trichlorosilane (TCI), lithium aluminum hydride (Kanto), magnesium turnings (Wako), deuterium oxide (Aldrich), bromobenzene (Kanto), benzoyl peroxide (Kanto), bromine (Kanto), iodomethane (Kanto), lithium chloride (Kanto), and copper(II) chloride (Kishida) were purchased and used without further purification.

Measurements. ^{1}H (500 MHz), ^{13}C (126 MHz), and ^{29}Si (99 MHz) NMR spectra were measured with a JEOL JNM-LA500 spectrometer. The ^{29}Si (119 MHz) NMR spectrum was measured with a JEOL JNM-ECA600 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8700 spectrophotometer. Mass spectra were recorded on JEOL JMS-SX102 and Hitachi M-2500 mass spectrometers. High-resolution mass spectra were recorded on a Hitachi M-2500 mass spectrometer. Elemental analyses were performed in the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Japan.

Synthesis of Bis(2-bromophenyl)silane (1). A solution of butyllithium in hexane (1.60 mol L^{-1}, 41.7 mL) was added dropwise to a solution of 1,2-dibromobenzene (15.0 g, 63.6 mmol) in diethyl ether (120 mL) and THF (120 mL) below −110 °C. After the mixture was stirred for 1 h, a solution of trichlorosilane (5.61 g, 41.4 mmol) in diethyl ether (38 mL) was added dropwise to the mixture below −110 °C. The mixture was stirred for 30 min and allowed to warm gradually to room temperature. After the solvent was exchanged with hexane, the mixture was filtered to remove insoluble materials, and the filtrate was evaporated. The crude product was dissolved in diethyl ether (50 mL), and the solution was added to a mixture of lithium aluminum hydride (0.686 g, 18.1 mmol) in diethyl ether (200 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h. The reaction mixture was hydrolyzed with dilute hydrochloric acid and extracted with dichloromethane. The organic layer was washed with aqueous sodium chloride, dried over anhydrous magnesium sulfate, and evaporated to afford crude **1**. Pure **1** (5.49 g, 50%) was isolated by column chromatography on silica gel (eluent: hexane) as a colorless solid.

1. Mp: 48 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.10 (s, 2H, $^{1}J_{Si-H}$ = −213.0 Hz), 7.30−7.34 (m, 4H), 7.55−7.59 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 126.9, 131.3, 132.2, 132.3, 134.0, 138.9. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −33.3. IR (KBr): 3040, 2920, 2170, 1420, 1130, 1110, 1020, 940, 840, 750, 740, 600 cm^{-1}. MS (EI, 70 eV): m/z 342 (M^+(^{79}Br^{81}Br), 35), 340 (M^+(^{79}Br$_2$), 17), 264 (^{79}Br^{81}Br, 61), 262 (^{79}Br$_2$, 36), 261 (^{79}Br^{81}Br, 80), 259 (^{79}Br$_2$, 47), 181 (100), 152 (33), 105 (71). Anal. Calcd for $C_{12}H_{10}Br_2Si$: C, 42.13; H, 2.95. Found: C, 42.53; H, 3.20.

Coupling of 1 with Magnesium on Conventional Heating. A solution of **1** (3.00 g, 8.77 mmol) in THF (5 mL) was added to a mixture of magnesium turnings (0.487 g, 20.0 mmol) and THF (1 mL) at room temperature, and the mixture was refluxed for 8 h. The reaction mixture was hydrolyzed with water and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from toluene to give **2** (0.492 g, 31%) as colorless crystals. The filtrate was separated by column chromatography on silica gel (eluent: hexane−diethyl ether (1:1)) to give *cis*-**3** (0.583 g, 36%) as a colorless oil. The spectral data of *cis*-**3** are identical with those reported in the previous literature.[20]

2. Mp: 275 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.59 (s, 1H, $^{1}J_{Si-H}$ = −218.5 Hz), 7.18−7.24 (m, 6H), 7.68−7.69 (m, 3H), 7.73 (d, 3H, J

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= 7.0 Hz), 7.85−7.86 (m, 3H), 8.26−8.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.30, 127.35, 127.49, 128.7, 130.9, 132.8, 133.2, 136.7, 144.3, 144.4. ^{29}Si NMR (119 MHz, $CDCl_3$): δ −38.5, −36.8. IR (KBr): 3040, 2180, 1430, 1120, 1100, 750, 740, 730 cm^{-1}. MS (EI, 70 eV): *m*/*z* 362 (M^+, 87), 284 (100), 257 (29). Anal. Calcd for $C_{24}H_{18}Si_2$: C, 79.50; H, 5.00. Found: C, 79.21; H, 5.30.

Coupling of 1 with Magnesium on Conventional Heating and Hydrolysis with D_2O. The reaction of **1** (0.503 g, 1.47 mmol) with magnesium turnings (0.080 g, 3.3 mmol) in THF (3 mL) was carried out according to the similar procedure described above. After the reaction was completed, the reaction mixture was hydrolyzed with D_2O. Compounds **2**-*d* (0.092 g, 34%) and *cis*-**3**-d_2 (0.068 g, 25%) were obtained. Incorporation of deuterium atoms was confirmed by mass analysis. Deuterated positions were determined by ^{1}H and ^{13}C NMR spectroscopy as follows: (1) decrease of integration compared with those of **2** or *cis*-**3** (ca. 1/2) was observed in the 2-protons of the phenyl groups; (2) $^1J_{C-D}$ splitting was observed in the ^{13}C NMR spectra.

2-*d*. Mp: 275 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.62 (s, 1H, $^1J_{Si-H}$ = −218.5 Hz), 7.20−7.27 (m, 6H), 7.70−7.71 (m, 3H), 7.76 (d, 3H, *J* = 7.0 Hz), 7.87−7.89 (m, 3H), 8.28−8.30 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.4, 127.5, 127.6, 128.8 (d, $^1J_{C-D}$ = 15.6 Hz), 131.0, 132.9, 133.3, 136.8, 144.5, 144.6. MS (EI, 70 eV): *m*/*z* 363 (M^+, 100), 284 (92), 258 (23), 85 (49), 83 (74). HRMS (EI, 70 eV): calcd for $C_{24}H_{17}DSi_2$ 363.1009, found 363.1006.

cis-**3**-d_2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.58 (s, 2H, $^1J_{Si-H}$ = −200.5 Hz), 7.33−7.36 (m, 4H), 7.41−7.44 (m, 2H), 7.46−7.48 (m, 4H), 7.56−7.57 (m, 2H), 7.76−7.77 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 128.1 (d, $^1J_{C-D}$ = 15.5 Hz), 128.3, 129.1, 129.9, 134.0, 135.9, 140.6. MS (EI, 70 eV): *m*/*z* 366 (M^+, 34), 288 (55), 287 (100), 286 (59), 258 (28). HRMS (EI, 70 eV): calcd for $C_{24}H_{18}D_2Si_2$ 366.1228, found 366.1227.

Coupling of 1 with Magnesium at Room Temperature. A mixture of **1** (2.03 g, 5.93 mmol), magnesium turnings (0.301 g, 12.4 mmol), and THF (15 mL) was stirred at room temperature for 1 day. The reaction mixture was hydrolyzed with water and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from toluene to give **2** (0.258 g, 24%) as colorless crystals. The filtrate was separated by column chromatography on silica gel (eluent: hexane−diethyl ether (1:1)) to give *cis*-**3** (0.324 g, 30%) as a colorless oil.

Coupling of 1 with Magnesium on Microwave Irradiation. Compound **1** (5.00 g, 14.6 mmol), magnesium turnings (0.750 g, 30.9 mmol), and THF (8 mL) were placed in a glass tube, and the glass tube was sealed. The mixture was heated at 100 °C for 1 h and then at 180 °C for 1 h with stirring during microwave irradiation. The reaction mixture was hydrolyzed with aqueous ammonium chloride and washed with aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from toluene to give **2** (1.88 g, 71%).

Theoretical Calculations of the Reaction Pathways. All theoretical calculations were performed using Gaussian 09 (revision A.02[21] for *trans*-**4**, *cis*-**4**, *trans*-**7**, and *cis*-**7** and revision C.01[22] for other compounds). The optimized structures and frequencies were calculated at the B3LYP/6-31+G(d) level. The intrinsic reaction coordinate (IRC) calculations were carried out to confirm the connectivity of the transition state and two minima, the reactant and the product, for each reaction. All calculations were carried out on Prime Monarch and Galleria computers and a PRIMERGY system of the Research Center for Computational Science, Japan. For details, see the Supporting Information.

Synthesis of 9,10-Diphenyl-9,10-disilatriptycene (12). A solution of phenyllithium in THF, prepared by the reaction of bromobenzene (0.140 g, 0.89 mmol) with butyllithium in hexane (1.60 mol L^{-1}, 0.6 mL) in THF (2 mL), was added dropwise to a solution of **2** (0.068 g, 0.19 mmol) in THF (20 mL) at −40 °C, and the mixture was stirred at −40 °C for 2 h. After the solvent was evaporated, the residue was dissolved in dichloromethane, and insoluble materials were filtered off. The filtrate was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from benzene to give **12** (0.068 g, 83%) as colorless crystals.

12. Mp: >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21−7.25 (m, 6H), 7.72−7.76 (m, 6H), 7.80−7.83 (m, 6H), 8.32−8.36 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.3, 127.7, 128.9, 131.0, 133.0, 136.9, 145.3. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −38.8. IR (KBr): 3040, 1430, 1110, 1100, 730, 700, 670 cm^{-1}. MS (EI, 70 eV): *m*/*z* 438 (M^+, 71), 360 (100). Anal. Calcd for $C_{30}H_{22}Si_2$: C, 82.14; H, 5.06. Found: C, 82.21; H, 5.20.

Synthesis of 9-*tert*-Butyl-10-phenyl-9,10-disilatriptycene (13). A solution of *tert*-butyllithium in pentane (1.60 mol L^{-1}, 0.45 mL) was added dropwise to a solution of **2** (0.051 g, 0.14 mmol) in THF (20 mL) at −40 °C, and the mixture was allowed to warm gradually to room temperature. After the solvents were evaporated, the residue was passed through a short column on silica gel (eluent: hexane−dichloromethane (1:1)). The eluate was evaporated. The residue was washed with a small amount of hexane and recrystallized from benzene to give **13** (0.024 g, 41%) as colorless crystals.

13. Mp: 283 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.84 (s, 9H), 7.18 (td, 3H, *J* = 7.2, 1.3 Hz), 7.22 (td, 3H, *J* = 7.2, 1.3 Hz), 7.68−7.69 (m, 3H), 7.74 (m, 3H), 8.01 (d, 3H, *J* = 7.2 Hz), 8.26−8.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.3, 28.8, 126.99, 127.03, 127.8, 128.8, 130.9, 133.16, 133.18, 137.0, 144.8, 146.2. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −39.1, −31.8. IR (KBr): 3030, 1520, 1120, 1040, 830, 760, 730 cm^{-1}. MS (EI, 70 eV): *m*/*z* 418 (M^+, 56), 361 (100), 257 (64). HRMS (EI, 70 eV): calcd for $C_{28}H_{26}Si_2$ 418.1571, found 418.1567.

Synthesis of 9-Hydroxy-10-phenyl-9,10-disilatriptycene (14). A mixture of **2** (0.051 g, 0.14 mmol), aqueous sodium hydroxide (5.0 mol L^{-1}, 1 mL), and THF (10 mL) was stirred at room temperature for 1 h. Aqueous ammonium chloride was added, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was recrystallized from benzene to give **14** (0.042 g, 79%) as colorless crystals.

14. Mp: >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.55 (s, 1H), 7.21 (td, 3H, *J* = 7.4, 1.3 Hz), 7.27 (td, 3H, *J* = 7.4, 1.3 Hz), 7.68−7.71 (m, 3H), 7.72−7.74 (m, 3H), 7.87−7.89 (m, 3H), 8.27−8.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.1, 127.4, 127.5, 128.9, 131.0, 131.1, 132.7, 136.9, 145.1, 145.3. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −40.9, −30.1. IR (KBr): 3060, 3050, 1430, 1100, 1050, 920, 880, 750, 730, 700, 680 cm^{-1}. MS (EI, 70 eV): *m*/*z* 378 (M^+, 100), 377 (100), 300 (43), 257 (19), 255 (28). Anal. Calcd for $C_{24}H_{18}OSi_2 \cdot H_2O$: C, 72.68; H, 5.08. Found: C, 72.69; H, 4.81.

Synthesis of 9-Chloro-10-phenyl-9,10-disilatriptycene (15). Benzoyl peroxide (0.061 g, 0.25 mmol) was added to a solution of **2** (0.201 g, 0.554 mmol) in carbon tetrachloride (5 mL). The mixture was refluxed for 4 days. The solvent was evaporated. The residue was washed with a small amount of hexane and recrystallized from toluene to give **15** (0.191 g, 87%) as colorless crystals.

15. Mp: 169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10−7.14 (m, 3H), 7.17−7.20 (m, 3H), 7.57−7.59 (m, 3H), 7.65−7.67 (m, 3H), 7.82−7.86 (m, 3H), 8.16−8.18 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.8, 128.0, 128.5, 129.0, 131.3, 131.5, 132.7, 136.8, 143.1, 144.4. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −40.6, −14.8. IR (KBr): 3050, 1420, 1120, 1040, 860, 750, 710, 690, 590, 570 cm^{-1}. MS (EI, 70 eV): *m*/*z* 398 (M^+(^{37}Cl), 44), 396 (M^+(^{35}Cl), 100), 320 (^{37}Cl, 35), 318 (^{35}Cl, 76), 255 (33). Anal. Calcd for $C_{24}H_{17}ClSi_2$: C, 72.61; H, 4.32. Found: C, 72.62; H, 4.46.

Synthesis of 9-Bromo-10-phenyl-9,10-disilatriptycene (16). Bromine (0.114 g, 0.713 mmol) was added dropwise to a solution of **2** (0.248 g, 0.684 mmol) in dichloromethane at room temperature. The mixture was stirred for 8 h at room temperature. The reaction mixture was evaporated, and the residue was recrystallized from toluene to give **16** (0.090 g, 30%) as colorless crystals.

16. Mp: 218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24−7.36 (m, 6H), 7.72−7.78 (m, 6H), 7.95−7.98 (m, 3H), 8.28−8.32 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 127.8, 128.2, 128.7, 130.2, 132.5, 132.7, 133.9, 136.8, 144.2, 144.3. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −50.8, −16.9. IR (KBr): 3050, 1410, 1180, 1030, 850, 780, 700, 680 cm^{-1}. MS (EI, 70 eV): *m*/*z* 442 (M^+(^{81}Br), 100), 440 (M^+(^{79}Br), 91), 364

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(^{81}Br, 65), 362 (^{79}Br, 63), 255 (40), 180 (32). HRMS (EI, 70 eV): calcd for $C_{24}H_{17}BrSi_2$ 440.0050, found 440.0043.

Synthesis of 9-(2-Tolyl)-9,10-disilatriptycene (17). A mixture of **1** (6.02 g, 17.6 mmol), magnesium turnings (0.900 g, 37.0 mmol), and THF (6 mL) in a sealed tube was heated at 100 °C for 2 h and then at 150 °C for 4 h with stirring on microwave irradiation. The resulting Grignard reagent was added dropwise to a solution of iodomethane (2.01 g, 14.2 mmol), lithium chloride (0.068 g, 1.6 mmol), and copper(II) chloride (0.112 g, 0.83 mmol) in THF (20 mL) at room temperature. The mixture was stirred at room temperature for 8 h. The solvent was evaporated, the residue was dissolved in diethyl ether, and insoluble materials were filtered off. The filtrate was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was recrystallized from toluene to give **17** (1.56 g, 47%) as colorless crystals.

17. Mp: 240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 5.48 (s, 1H, $^1J_{Si-H}$ = −218.0 Hz), 7.07−7.13 (m, 6H), 7.37−7.40 (m, 2H), 7.49 (td, 1H, J = 7.5, 1.3 Hz), 7.64−7.66 (m, 3H), 7.74−7.76 (m, 3H), 8.45 (d, 1H, J = 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.8, 125.8, 127.4, 127.6, 128.5, 131.1, 131.2, 133.2, 133.4, 137.1, 144.55, 144.61, 146.3. ^{29}Si NMR (99 MHz, $CDCl_3$): δ −38.5, −35.9. IR (KBr): 3040, 2980, 2170, 1420, 1160, 1100, 840, 790 cm^{-1}. MS (EI, 70 eV): m/z 376 (M^+, 100), 298 (27), 285 (45), 284 (83), 257 (22). HRMS (EI, 70 eV): calcd for $C_{25}H_{20}Si_2$ 376.1102, found 376.1100.

■ ASSOCIATED CONTENT

Supporting Information

Spectral data for new compounds and details of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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