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Synthesis, Structures, and Isomerization of 9,10-Di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes

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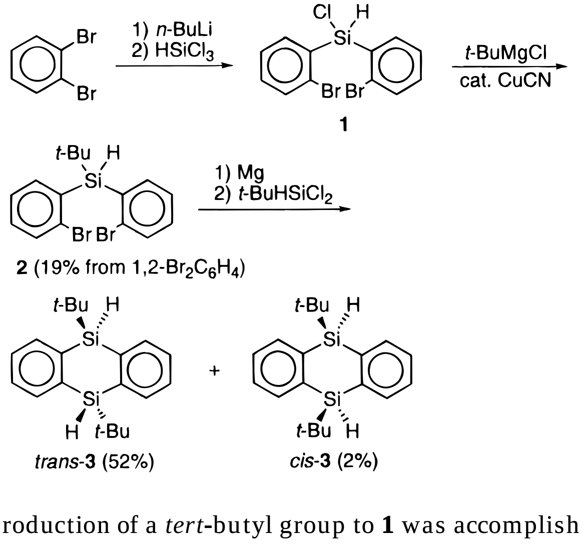
9,10-Di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes (*trans*-**3** and *cis*-**3**) were synthesized, and their structures were determined by X-ray crystallography. The trans and cis isomers have a different conformation of the disilacyclohexadiene rings: *trans*-**3** has a chair-like structure, while *cis*-**3** has a boat-like structure. On irradiation of a solution of *trans*-**3** or *cis*-**3** in the presence of di-*tert*-butyl peroxide, *trans*-**3** and *cis*-**3** isomerized to each other and reached an equilibrium to give a mixture of *cis*-**3** (81%) and *trans*-**3** (19%). The isomerization shows the inversion of the radical center of the intermediate silyl radicals, which is rare in reactions of silyl radicals. Considering the reaction mechanism, the silyl radicals derived from *trans*-**3** and *cis*-**3** are found to be relatively stable, probably due to bulky *tert*-butyl substituents.

Introduction

Since the first 9,10-dihydro-9,10-disilaanthracene was synthesized by Gilman and co-workers,[1] studies on the syntheses, structures, properties, and reactions have been developed.[2−4] One of the most interesting features of the 9,10-dihydro-9,10-disilaanthracene derivatives is their utility as potential precursors of organosilicon reactive intermediates. For example, Ando and co-workers have recently reported the formation of 9,10-dilithio- and 9,10-dipotassio-9,10-dimethyl-9,10-disilaanthracene from the 9,10-dimethyl-9,10-disilaanthracene dimer.[4] Nishiyama and co-workers and Chatgilialoglu and co-workers have recently reported the utility of 9,10-dihydro-9,10-disilaanthracene derivatives as radical reducing agents in dehalogenation and deoxygenation reactions.[5] As part of our recent investigations on organosilanes containing aromatic π systems,[6] we plan to introduce bulky substituents to the silicon atoms of 9,10-dihydro-9,10-disilaanthracene because bulky substituents are expected to stabilize reactive species kinetically. However, the syntheses of 9,10-dihydro-9,10-disilaanthracenes so far reported are limited to methyl and phenyl derivatives, and the introduction of bulky substituents has not been reported. We present herein the following new information: (1) the synthesis of *trans*- and *cis*-9,10-di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes; (2) their X-ray structures and the first example of the chair-like structure of 9,10-dihydro-9,10-disilaanthracene; (3) the isomerization of the trans and cis isomers via the inversion of the silyl radical center, indicating the considerable stability of the intermediate silyl radicals.

Results and Discussion

Synthesis of 9,10-Di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes. 9,10-Di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes (*trans*-**3** and *cis*-**3**) were synthesized by a modified procedure of Corey's method.[3] Trichlorosilane was coupled with 2 mol of (2-bromophenyl)lithium, which was prepared by the exchange reaction of 1,2-dibromobenzene with butyllithium at −110 °C,[7] to give bis(2-bromophenyl)chlorosilane (**1**). The introduction of a *tert*-butyl group to **1** was accomplished



[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1997.

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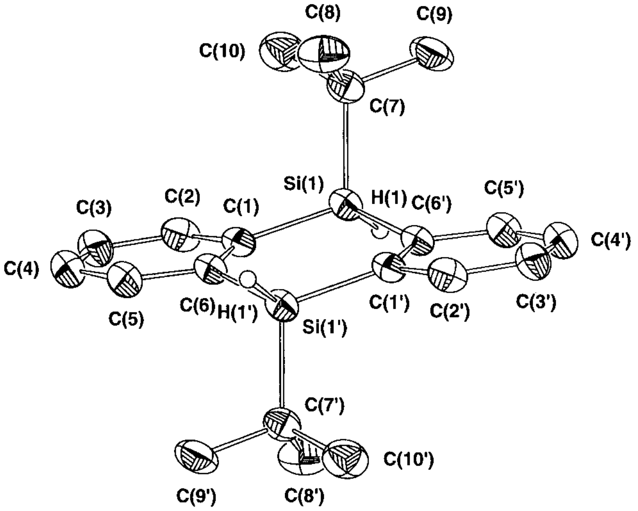

Figure 1. Molecular structure of *trans*-**3**. Thermal ellipsoids are drawn at the 30% probability level.

by use of *tert*-butylmagnesium chloride in the presence of a catalytic amount of cuprous cyanide.[8,9] Another attempt to synthesize **2** by the direct coupling of *tert*-butyldichlorosilane with 2 mol of (2-bromophenyl)lithium was unsuccessful, although it has been reported that 2 mol of (2-bromophenyl)lithium couple to methyldichlorosilane to give bis(2-bromophenyl)methylsilane in good yield.[3a] By the coupling of the di-Grignard reagent derived from **2** with *tert*-butyldichlorosilane, *trans*-**3** and *cis*-**3** were obtained in 52 and 2% yields, respectively. It is noted that *trans*-**3**, which is more strained and less stable than *cis*-**3** as mentioned below, was formed in preference to *cis*-**3**. This result is explained by the consideration that the trans orientation of two *tert*-butyl groups is favored in the final ring closure step, and therefore, the reaction is kinetically controlled.

Structures of *trans*-3 and *cis*-3. There have been some reports on X-ray crystal structures of 9,10-dihydro-9,10-disilaanthracene derivatives.[2b–e,4] 9,10-Dihydro-9,10-disilaanthracene (**4**),[2b,e] 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracene (**5**),[2b,c] and the 9,10-dimethyl-9,10-disilaanthracene dimer[4] have folded structures along the silicon atoms at the 9- and 10-positions.[10] In order to study the effect of bulky substituents on the structure of 9,10-dihydro-9,10-disilaanthracene, the structures of *trans*-**3** and *cis*-**3** were determined by X-ray crystallography. In Figures 1 and 2 the molecular structures of *trans*-**3** and *cis*-**3** are shown. Crystallographic data and selected bond lengths and angles are summarized in Tables 1–3.

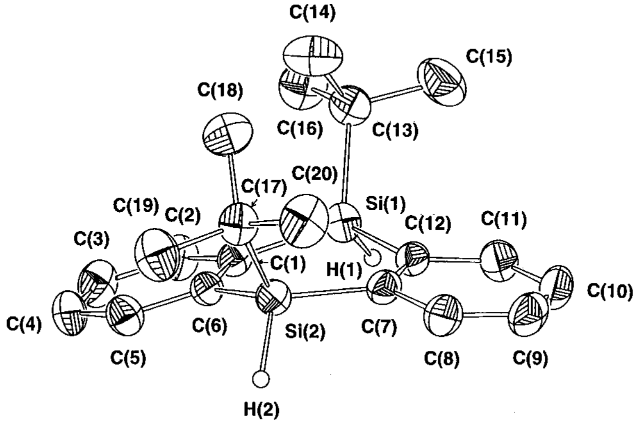

Figure 2. Molecular structure of *cis*-**3**. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Summary of Crystal Data, Data Collection, and Refinement for *trans*-3 and *cis*-3

	trans-**3**	*cis*-**3**
	Crystal Data	
formula	$C_{20}H_{28}Si_2$	$C_{20}H_{28}Si_2$
fw	324.61	324.61
cryst description	colorless prisms	colorless prisms
cryst size, mm	0.3 × 0.1 × 0.3	0.25 × 0.15 × 0.25
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	10.104(1)	12.250(1)
b, Å	9.970(1)	9.890(1)
c, Å	10.455(1)	16.743(1)
β, deg	114.250(5)	102.802(4)
V, Å^3	960.3(1)	1978.1(3)
T, K	295(1)	295(1)
Z	2	4
D_{measd}, g cm^{-3}	1.127	1.094
D_{calcd}, g cm^{-3}	1.123	1.090
	Data Collection	
diffractometer	Rigaku AFC-7S	Rigaku AFC-7S
radiation (λ, Å)	Cu Kα (1.5418)	Cu Kα (1.5418)
μ, cm^{-1}	16.24	15.76
abs corr	empirical	none
T_{min}	0.756	
T_{max}	1.000	
variation of standards	none	none
2θ range, deg	5–120	5–120
range of h	0 to +11	0 to +14
range of k	0 to +11	0 to +11
range of l	−12 to +12	−19 to +19
scan type	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	0.95 + 0.30 tan θ	0.74 + 0.30 tan θ
no. of reflns measd	1628	3312
no. of indep reflns	1533	3147
no. of obsd reflns ($I > 3\sigma(I)$)	1159	1874
	Refinement	
R	0.048	0.041
R_w	0.042	0.028
weighting scheme	$w = 1/\sigma^2(F_o)$	$w = 1/\sigma^2(F_o)$
S	3.78	1.65
$(\Delta/\sigma)_{max}$	0.02	0.01
$(\Delta\rho)_{max}$, e Å^{-3}	0.22	0.16
$(\Delta\rho)_{min}$, e Å^{-3}	−0.23	−0.18
ext corr	secondary	secondary
ext coeff	2.36 × 10^{-5}	4.98 × 10^{-6}
no. of params	157	312

As shown in Figures 1 and 2, *trans*-**3** and *cis*-**3** have different structures of the 9,10-dihydro-9,10-disilaanthracene skeletons. The disilacyclohexadiene ring of *trans*-**3** has a chair-like structure. The structure is strained because the Si–C(phenyl) bonds are oriented above and below the benzene planes, with a bending angle of 9.7° (Si(1)–C(1)) and 11.4° (Si(1′)–C(6)). The *tert*-butyl groups occupy pseudoaxial positions, probably to avoid the steric repulsion with the hydrogen atoms on the benzene rings. On the other hand, the disilacy-

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(10) It has been reported that 9,9,10,10-tetraphenyl-9,10-dihydro-9,10-disilaanthracene has a planar structure, but details were not explained. See ref 2d.

Table 2. Bond Lengths (Å) and Angles (deg) for *trans*-3[a]

Bond Lengths			
Si(1)–C(1)	1.870(4)	C(3)–C(4)	1.365(6)
Si(1)–C(7)	1.901(4)	C(4)–C(5)	1.385(6)
Si(1)–C(6′)	1.852(4)	C(5)–C(6)	1.409(5)
Si(1)–H(1)	1.45(3)	C(7)–C(8)	1.533(6)
C(1)–C(2)	1.407(5)	C(7)–C(9)	1.534(6)
C(1)–C(6)	1.411(4)	C(7)–C(10)	1.525(6)
C(2)–C(3)	1.400(5)		
Bond Angles			
C(1)–Si(1)–C(7)	108.8(2)	C(3)–C(4)–C(5)	120.3(4)
C(1)–Si(1)–C(6′)	111.1(2)	C(4)–C(5)–C(6)	122.0(4)
C(1)–Si(1)–H(1)	114(1)	Si(1′)–C(6)–C(1)	122.2(3)
C(7)–Si(1)–C(6′)	108.1(2)	Si(1′)–C(6)–C(5)	118.9(3)
C(7)–Si(1)–H(1)	106(1)	C(1)–C(6)–C(5)	118.2(4)
C(6′)–Si(1)–H(1)	107(1)	Si(1)–C(7)–C(8)	109.9(3)
Si(1)–C(1)–C(2)	118.1(3)	Si(1)–C(7)–C(9)	109.8(3)
Si(1)–C(1)–C(6)	123.4(3)	Si(1)–C(7)–C(10)	111.3(3)
C(2)–C(1)–C(6)	118.2(3)	C(8)–C(7)–C(9)	109.0(4)
C(1)–C(2)–C(3)	122.2(4)	C(8)–C(7)–C(10)	108.0(4)
C(2)–C(3)–C(4)	118.9(4)	C(9)–C(7)–C(10)	108.8(4)

[a] Primed atoms are generated by the crystallographic symmetry operator (1 − *x*, −*y*, 1 − *z*).

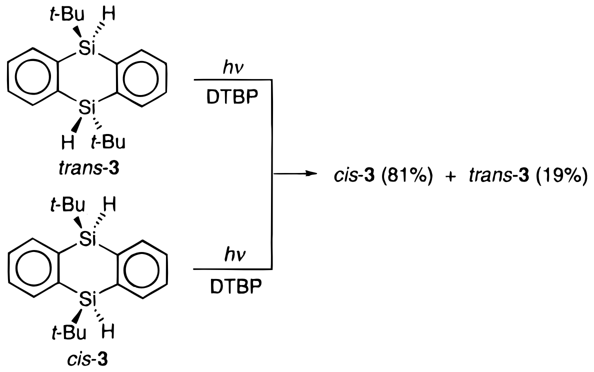
Table 3. Bond Lengths (Å) and Angles (deg) for *cis*-3

Bond Lengths			
Si(1)–C(1)	1.874(3)	C(5)–C(6)	1.393(4)
Si(1)–C(12)	1.867(3)	C(7)–C(8)	1.406(4)
Si(1)–C(13)	1.894(4)	C(7)–C(12)	1.406(4)
Si(1)–H(1)	1.46(3)	C(8)–C(9)	1.385(6)
Si(2)–C(6)	1.876(3)	C(9)–C(10)	1.370(6)
Si(2)–C(7)	1.863(3)	C(10)–C(11)	1.380(6)
Si(2)–C(17)	1.896(4)	C(11)–C(12)	1.411(5)
Si(2)–H(2)	1.45(3)	C(13)–C(14)	1.520(6)
C(1)–C(2)	1.402(4)	C(13)–C(15)	1.539(7)
C(1)–C(6)	1.402(4)	C(13)–C(16)	1.537(6)
C(2)–C(3)	1.373(5)	C(17)–C(18)	1.531(6)
C(3)–C(4)	1.368(6)	C(17)–C(19)	1.531(6)
C(4)–C(5)	1.382(5)	C(17)–C(20)	1.543(5)
Bond Angles			
C(1)–Si(1)–C(12)	110.0(2)	Si(2)–C(7)–C(8)	117.1(3)
C(1)–Si(1)–C(13)	112.9(2)	Si(2)–C(7)–C(12)	124.5(3)
C(1)–Si(1)–H(1)	110(1)	C(8)–C(7)–C(12)	118.2(3)
C(12)–Si(1)–C(13)	112.8(2)	C(7)–C(8)–C(9)	121.7(4)
C(12)–Si(1)–H(1)	108(1)	C(8)–C(9)–C(10)	119.9(4)
C(13)–Si(1)–H(1)	102(1)	C(9)–C(10)–C(11)	119.9(5)
C(6)–Si(2)–C(7)	110.0(2)	C(10)–C(11)–C(12)	121.5(4)
C(6)–Si(2)–C(17)	112.2(1)	Si(1)–C(12)–C(7)	123.8(3)
C(6)–Si(2)–H(2)	108(1)	Si(1)–C(12)–C(11)	117.4(3)
C(7)–Si(2)–C(17)	114.5(2)	C(7)–C(12)–C(11)	118.7(3)
C(7)–Si(2)–H(2)	109(1)	Si(1)–C(13)–C(14)	111.4(3)
C(17)–Si(2)–H(2)	103(1)	Si(1)–C(13)–C(15)	109.0(3)
Si(1)–C(1)–C(2)	118.0(3)	Si(1)–C(13)–C(16)	108.7(3)
Si(1)–C(1)–C(6)	124.1(2)	C(14)–C(13)–C(15)	110.4(5)
C(2)–C(1)–C(6)	117.9(3)	C(14)–C(13)–C(16)	109.1(4)
C(1)–C(2)–C(3)	122.0(4)	C(15)–C(13)–C(16)	108.1(4)
C(2)–C(3)–C(4)	120.3(4)	Si(2)–C(17)–C(18)	111.1(3)
C(3)–C(4)–C(5)	118.6(4)	Si(2)–C(17)–C(19)	110.2(3)
C(4)–C(5)–C(6)	122.6(4)	Si(2)–C(17)–C(20)	110.0(3)
Si(2)–C(6)–C(1)	124.0(3)	C(18)–C(17)–C(19)	109.7(4)
Si(2)–C(6)–C(5)	117.5(3)	C(18)–C(17)–C(20)	107.3(4)
C(1)–C(6)–C(5)	118.5(3)	C(19)–C(17)–C(20)	108.4(4)

clohexadiene ring of *cis*-**3** has a boat-like structure and the 9,10-dihydro-9,10-disilaanthracene ring has a folded structure with a dihedral angle of 161.0°. The *tert*-butyl groups occupy less crowded flagpole positions. The Si–C(phenyl) bond lengths (average 1.870 Å) are longer than those of *trans*-**3** (average 1.861 Å), **4** (average 1.85 Å),[2e] and **5** (average 1.86 Å).[2c] The Si–C–C bond angles of the disilacyclohexadiene rings (average 124.1°) are larger than those of *trans*-**3** (average 122.8°), **4** (average 122°),[2e] and **5** (average 123°).[2c] Furthermore, C(alkyl)–Si–C(phenyl) bond angles (average 113.1°) are larger than those of *trans*-**3** (average 108.5°) and **5** (average 110.8°).[2c] These structural features of *cis*-**3** seem to be favorable for reducing the steric repulsion among the *tert*-butyl groups.[11]

Other information on the structures was obtained by temperature-dependent ^{1}H NMR measurements. In a solution, *trans*-**3** has the possibility of interconversion between two chair-like conformations. However, the ^{1}H NMR spectrum of *trans*-**3** did not change significantly in the temperature range from 20 to −85 °C, where only one kind of *tert*-butyl signal was observed. It is reasonable to assume that the chair-like structure of *trans*-**3** is rigid in a solution. In the ^{1}H NMR spectrum of *cis*-**3**, only one kind of *tert*-butyl signal was observed from 20 to −85 °C and no significant change was observed in this temperature range, indicating that the boat-like structure is also rigid in a solution. These results are in contrast with that reported for 9,9,10,10-tetramethyl-9,10-dihydro-9,10-disilaanthracene, in which the disilacyclohexadiene ring has a planar structure in a solution.[3a]

Photoisomerization of *trans*-3 and *cis*-3 in the Presence of Di-*tert*-butyl Peroxide. UV irradiation of a solution of *trans*-**3** in pentane in the presence of di-*tert*-butyl peroxide (DTBP) gave a mixture of *cis*-**3** (81%) and *trans*-**3** (19%). A similar isomerization also occurred in the case of *cis*-**3** under these conditions to afford a mixture of *cis*-**3** (81%) and *trans*-**3** (19%). These results show that *trans*-**3** and *cis*-**3** isomerize to each other to reach an equilibrium. The isomerization proceeds in the presence of a catalytic amount of DTBP. For example, the isomerization of *trans*-**3** with 0.05 equiv of DTBP led to a mixture of *cis*-**3** (39%) and *trans*-**3** (61%). However, to make the reaction reach equilibrium sufficiently, 1 equiv of DTBP was used. In order to gain more information about the reaction mechanism, the isomerization was carried out with the use of C_6D_{12} as the solvent. When a solution of *trans*-**3** in C_6D_{12} was irradiated in the presence of 1 equiv of DTBP, a mixture of *cis*-**3** (81%) and *trans*-**3** (19%) was obtained and the analysis of the products by ^{1}H NMR showed that deuterium atoms were not incorporated into *cis*-**3** and *trans*-**3**.



From these results, a mechanism for the isomerization is proposed, as shown in Scheme 1. Silyl radicals *trans*-**3**$^{\bullet}$ and *cis*-**3**$^{\bullet}$ are formed from *trans*-**3** and *cis*-**3**, respectively, by hydrogen abstraction with a *tert*-butoxy

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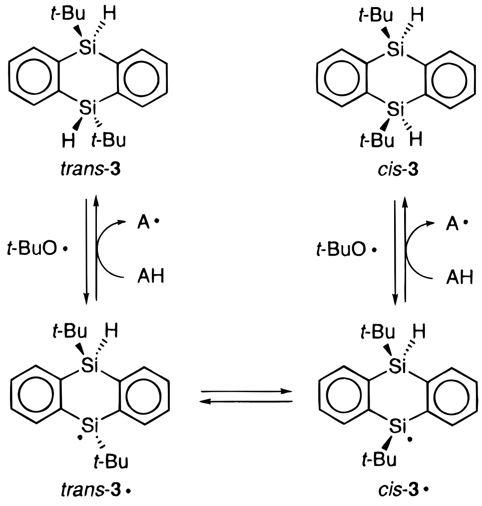
[11] In MM2 calculations, the optimized structures of *trans*-**3** and *cis*-**3** reproduce X-ray structures very well.[23] The calculations show that *cis*-**3** is more stable by 2.5 kcal mol^{-1} than *trans*-**3**.

Scheme 1



AH = *trans*-**3** or *cis*-**3**, A• = *trans*-**3**• or *cis*-**3**•

radical. The silyl radicals isomerize to each other via inversion of the radical center and abstract a hydrogen atom from the starting material *trans*-**3** or *cis*-**3** to yield *trans*-**3** and *cis*-**3** and regenerate the silyl radicals.[12] Therefore, the isomerization proceeds by a radical chain mechanism. By kinetic treatment of the isomerization in Scheme 1, assuming the steady state of the intermediate silyl radicals, the difference of the free energy of *trans*-**3** and *cis*-**3** is expressed as[13]

$$\Delta G = -RT \ln([trans\text{-}\mathbf{3}]/[cis\text{-}\mathbf{3}]) \qquad (1)$$

From this equation, *cis*-**3** is found to be slightly more stable by 0.8 kcal mol^{-1} than *trans*-**3** at 20 °C. This result is in accord with the considerations mentioned above.

The isomerization of *trans*-**3** and *cis*-**3** is interesting from the viewpoint of the stereochemistry of silyl radicals. The pyramidal structures of silyl radicals have been well-demonstrated.[14] Since there is a high energy barrier in the inversion process,[15] silyl radicals have been reported to react usually with the retention of configuration.[16] In the case of silyl radicals *trans*-**3**$^•$ and *cis*-**3**$^•$, abstraction of a hydrogen atom is slow enough to compete with the isomerization of the silyl radicals. This fact shows that the silyl radicals are relatively stable, probably due to bulky *tert*-butyl substituents.

Experimental Section

All reactions were carried out under an argon atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Pentane was distilled from sodium. 1,2-Dibromobenzene (Wako), butyllithium in hexane (Kanto), cuprous cyanide (Wako), and magnesium turnings (Wako) were purchased. Trichlorosilane was obtained from Toshiba Silicone Co., Ltd., and distilled before use. *tert*-Butylmagnesium chloride[17] and *tert*-butyldichlorosilane[18] were prepared by published procedures. DTBP was purified by a published procedure.[19]

^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained with a JEOL JNM-A500 spectrometer. IR spectra were recorded on a Perkin-Elmer model 1600 spectrophotometer. UV spectra were obtained with a JASCO Ubest-50 spectrophotometer. Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. Elemental analyses were performed by the Institute of Physical and Chemical Research.

Synthesis of Bis(2-bromophenyl)chlorosilane (1). A solution of butyllithium in hexane (1.63 M, 68 mL) was added dropwise to a solution of 1,2-dibromobenzene (25.1 g, 106 mmol) in diethyl ether (300 mL) and THF (240 mL) at −110 °C. After the addition was completed, the mixture was stirred for additional 1 h and a solution of trichlorosilane (9.45 g, 69.8 mmol) in diethyl ether (30 mL) was added dropwise to the mixture at −110 °C. After the mixture was stirred for an additional 2 h, the resulting mixture was allowed to warm gradually to room temperature. The solvents were evaporated, and the residue was dissolved in hexane (160 mL) and filtered. Distillation of the filtrate under reduced pressure gave crude **1** (14.9 g, 89% purity). Although the analytically pure sample of **1** could be obtained by recrystallization from hexane twice, the loss of **1** was large and crude **1** was used in the following reactions without further purification. Mp: 54−55 °C. ^{1}H NMR (CD_2Cl_2): δ 5.92 (s, 1H), 7.39 (td, 2H, $J = 7.4$, 2.2 Hz), 7.42 (td, 2H, $J = 7.4$, 1.7 Hz), 7.59 (dd, 2H, $J = 7.4$, 1.7 Hz), 7.68 (dd, 2H, $J = 7.4$, 2.2 Hz). ^{13}C NMR (CD_2Cl_2): δ 127.5, 130.0, 133.0, 133.4, 133.8, 138.2. ^{29}Si NMR (CD_2Cl_2): δ −10.4. IR (NaCl): 3050, 2180, 1580, 1550, 1450, 1410, 1130, 1100, 1020, 790, 740 cm^{-1}. MS: *m/z* 374 (M^+($^{79}Br_2{}^{35}Cl$), 10), 295 ($^{79}Br^{35}Cl$, 14), 259 (^{79}Br, 21), 215 (^{35}Cl, 100), 152 (34), 139 (41). Anal. Calcd for $C_{12}H_9Br_2ClSi$: C, 38.28; H, 2.41. Found: C, 38.35; H, 2.36.

Synthesis of Bis(2-bromophenyl)-*tert*-butylsilane (2). A solution of crude **1** (14.9 g, 89% purity) in THF (70 mL) was added dropwise to a mixture of *tert*-butylmagnesium chloride in diethyl ether (1.65 M, 26.4 mL), cuprous cyanide (35.5 mg, 0.40 mmol), and THF (250 mL) at room temperature. The resulting mixture was refluxed for 3 h. After hydrolysis with a small amount of aqueous sodium hypochlorite, the solvents were removed by evaporation. The residue was dissolved in dichloromethane (100 mL) and filtered. The filtrate was washed with water, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvents were evaporated, and the residue was separated by column chromatography (silica gel, hexane). The fraction containing **2** was recrystallized from methanol−pentane (1:1) to give **2** (4.11 g, 19% from 1,2-dibromobenzene) as colorless crystals. Mp: 68−69 °C. ^{1}H NMR (CD_2Cl_2): δ 1.22 (s, 9H), 5.05 (s, 1H), 7.26 (ddd, 2H, $J =$ 7.9, 7.3, 1.8 Hz), 7.32 (td, 2H, $J = 7.3$, 1.2 Hz), 7.55 (dd, 2H, $J = 7.9$, 1.2 Hz), 7.62 (dd, 2H, $J = 7.3$, 1.8 Hz). ^{13}C NMR (CD_2Cl_2): δ 19.2, 28.3, 126.7, 131.60, 131.63, 133.3, 136.6, 138.1. ^{29}Si NMR (CD_2Cl_2): δ −8.5. IR (KBr): 3090, 2900, 2870, 2160, 1490, 1450, 1150, 1110, 1030, 810, 760 cm^{-1}. MS: *m/z* 396 (M^+($^{79}Br_2$), 0.3), 339 ($^{79}Br_2$, 35), 259 (^{79}Br, 53), 181 (19), 152 (15). Anal. Calcd for $C_{16}H_{18}Br_2Si$: C, 48.26; H, 4.56. Found: C, 48.39; H, 4.55.

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(12) A reviewer has commented that intramolecular exchange of the radical sites is possible. We think that the possibility of intramolecular hydrogen transfer in *trans*-**3**$^•$ and *cis*-**3**$^•$ cannot be denied completely. If the Si−H bond of *trans*-**3**$^•$ and *cis*-**3**$^•$ is cleaved and the hydrogen bonds to the silyl radical center on the opposite side, *trans*-**3**$^•$ and *cis*-**3**$^•$ are formed from *trans*-**3**$^•$ and *cis*-**3**$^•$, respectively. Therefore, the intramolecular hydrogen transfer would not affect the derivation of eq 1.

(13) For a derivation of this equation, see the Supporting Information.

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Synthesis of 9,10-Di-*tert*-butyl-9,10-dihydro-9,10-disilaanthracenes (*trans*-3 and *cis*-3). The di-Grignard reagent of **2** was prepared by adding a solution of **2** (3.50 g, 8.79 mmol) in THF (30 mL) dropwise to a mixture of magnesium turnings (0.47 g, 19 mmol) and THF (2 mL) and refluxing the resulting mixture for 3 h. To the di-Grignard reagent was added a solution of *tert*-butyldichlorosilane (1.38 g, 8.78 mmol) in THF (50 mL) dropwise at room temperature, and the mixture was refluxed for 10 h. After hydrolysis with aqueous ammonium chloride, diethyl ether (200 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over anhydrous sodium sulfate. The solvents were evaporated, and the residue was recrystallized from methanol to give *trans*-**3** (1.43 g) as colorless crystals. The filtrate was subjected to recycle-type HPLC (ODS, methanol) to give *trans*-**3** (0.066 g) and *cis*-**3** (0.064 g, 2%) as colorless crystals. The total yield of *trans*-**3** is 52%.

***trans*-3.** Mp: 157−158 °C. ^{1}H NMR (CD_2Cl_2): δ 0.77 (s, 18H), 4.77 (s, 2H), 7.45 (dd, 4H, $J = 5.3, 3.3$ Hz), 7.76 (dd, 4H, $J = 5.3, 3.3$ Hz). ^{13}C NMR (CD_2Cl_2): δ 18.5, 27.6, 128.4, 136.2, 140.7. ^{29}Si NMR (CD_2Cl_2): δ −16.8. IR (KBr): 3050, 2930, 2850, 2130, 1120, 800, 740, 720 cm^{-1}. UV (λ_{max} in hexane): 271 nm (ϵ 570). MS: m/z 324 (M$^+$, 5), 267 (100), 239 (31), 225 (94), 209 (20). Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69. Found: C, 73.61; H, 8.69.

***cis*-3.** Mp: 94−95 °C. ^{1}H NMR (CD_2Cl_2): δ 1.09 (s, 18H), 4.70 (s, 2H), 7.45 (dd, 4H, $J = 5.5, 3.4$ Hz), 7.78 (dd, 4H, $J = 5.5, 3.4$ Hz). ^{13}C NMR (CD_2Cl_2): δ 18.8, 28.7, 128.5, 137.1, 140.8. ^{29}Si NMR (CD_2Cl_2): δ −16.2. IR (KBr): 3060, 2930, 2850, 2120, 1120, 790, 740 cm^{-1}. UV (λ_{max} in hexane): 260 (sh, ϵ 480), 267 (700), 272 (730), 278 nm (580). MS: m/z 324 (M$^+$, 4), 267 (100), 239 (22), 225 (88), 211 (19). Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69. Found: C, 73.85; H, 8.70.

X-ray Structure Determinations of *trans*-3 and *cis*-3. Colorless crystals of *trans*-**3** were obtained from a hexane solution by slow evaporation. Colorless crystals of *cis*-**3** were obtained from a methanol solution by slow evaporation. A crystal specimen was sealed in a glass capillary and used for data collection on a Rigaku AFC-7S diffractometer using graphite-monochromated Cu Kα radiation. Cell parameters were refined by the least-squares method using 25 reflections with $54.7 < 2\theta < 56.7°$ (*trans*-**3**) and $45.3 < 2\theta < 52.6°$ (*cis*-**3**). Intensity data were collected in the range of $5 < 2\theta < 120°$ by the $\omega-2\theta$ scan technique at room temperature. Three standard reflections were measured after every 150 reflections, showing no decay. The data were corrected for Lorentz and polarization effects. In the case of *trans*-**3**, an empirical absorption correction based on a ψ scan was also applied. The structure was solved by direct methods using MULTAN88.[20] Non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic thermal parameters using teXsan.[21] A secondary extinction correction was applied in the least-squares method. All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Atomic scattering factors were taken from ref 22. All calculations were carried out on a Silicon Graphics INDY computer. Details of crystal data, data collection, and refinement are listed in Table 1.

Photoisomerization of *trans*-3 and *cis*-3 in the Presence of DTBP. In a quartz tube, *trans*-**3** (10.0 mg, 3.08×10^{-2} mmol) and a solution of DTBP in pentane (3.09×10^{-2} M, 1 mL) were placed. After bubbling argon, the mixture was irradiated with a 400 W medium-pressure mercury lamp. The reaction was monitored by GC until the reaction reached equilibrium. The ^{1}H NMR spectrum of the products showed that the ratio of *cis*-**3**:*trans*-**3** is 81:19. Similarly, irradiation of a mixture of *cis*-**3** (10.0 mg, 3.08×10^{-2} mmol) and a solution of DTBP in pentane (3.09×10^{-2} M, 1 mL) with a 400 W medium-pressure mercury lamp afforded a mixture of *cis*-**3** and *trans*-**3** (81:19).

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Supporting Information Available: Tables of the experimental details, atomic coordinates, thermal parameters, and bond lengths and angles for *trans*-**3** and *cis*-**3** and a derivation of eq 1 (30 pages). Ordering information is given on any current masthead page.

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