First Isolation and Full Characterization of 2,2′-Bishalosilyl-Substituted 1,1′-Binaphthyls: Synthesis of 2,2′-Bis(fluorodimethylsilyl)-1,1′-binaphthyl and X-ray Structural Analysis of Highly Strained Disilanylene-Bridged Precursors

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Brominative Si−Si cleavage of 3,4-disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[*c*,*g*]-phenanthrene (**3a**), $LiAlH_4$ reduction of the resulting dibromide, and fluorination of the dihydride **14a** thus gave 2,2′-bis(fluorodimethylsilyl)-1,1′-binaphthyl (**7a**) in high yield as the first isolated and fully characterized 2,2′-bis(halosilyl)-1,1′-binaphthyl. Similar conversion of the more sterically hindered 3,4-disila-3,3-dimethyl-4,4-diphenyl-3,4-dihydrodibenzo[*c*,*g*]-phenanthrene (**3b**) also gave the corresponding bishydrosilane **14b**. However, subsequent fluorination did not give the desired bisfluorosilane **7b** but rather the hydrolyzed siloxane **6b**. The syntheses of the disilanylene-bridged precursors **3** were effected via bis-silylation reactions of 2,2′-dibromo-1,1′-binaphthyl (DBBN, **2**) with dihalodisilanes $ClMe_2SiSiMe_2Cl$, $ClMe_2SiSiPh_2Cl$, $FMe_2SiSiPh_2F$, and $FPh_2SiSiPh_2F$. Although $ClMe_2SiSiMe_2Cl$ predominately gave the disilanylene-bridged product **3a**, $XMe_2SiSiPh_2X$ (X = F, Cl) produced not only the disilanylene-bridged product **3b** but also the dimethylsilylene-bridged product **8a**. $FMe_2SiSiPh_2F$ served better in preparation of the desired **3b** than $ClMe_2SiSiPh_2Cl$. The sterically hindered $FPh_2SiSiPh_2F$ did not give silylation products. The X-ray structural analyses of **3a** and **3b** provided the first geometrical parameters of the 2,2′-disilanylene-bridged 1,1′-binaphthyl derivatives. In comparison with the acyclic analogues and less sterically hindered disilanylene-bridged biaryls such as 2,2′-bis(trimethylsilyl)-1,1′-binaphthyl ((±)-**1a**), (*R*)-(−)-2,2′-bis(dimethylphenylsilyl)-1,1′-binaphthyl ((*R*)-(−)-**1b**), dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene (**12**), and dithienodisilacyclohexadiene **13** the disilanylene-bridged binaphthyls **3** were found to be highly strained due to the steric repulsion of the binaphthyl groups fixed in a narrow angle.

Introduction

Lewis acids are conventionally employed in contemporary organic synthesis.[1] Not only transition metals but also electron-deficient main group elements such as boron, aluminum, and tin have been extensively utilized as Lewis acids. Silicon, which also has an electronegativity lower than most main group elements, would be the candidate for the active site of Lewis acidic reagents.[2] The rather weak Lewis acidity of the silicon atom has limited its use to electrophilic activation. However, Tamao recently reported the enhanced Lewis acidity of *ortho*-bis(fluorosilyl)benzene in which two bidentate silicon atoms chelate the basic fluoride anion which becomes attached in the rigid Si−F−Si bridging structure.[3] Kira and Corriu independently reported the bidentate and tridentate Lewis acidic behavior of 1,4-disila- and 1,3,5-trisilacyclohexanes in solution and in the solid state.[4,5] Maruoka demonstrated the first

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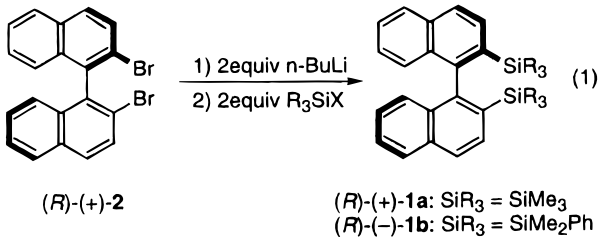
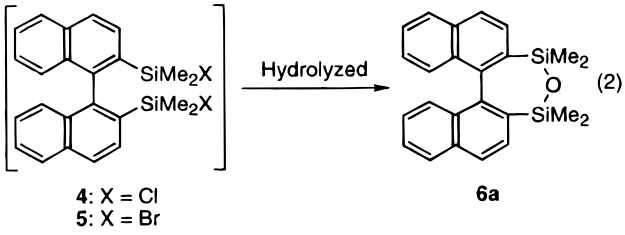
synthetic application of the bidentate Lewis acidic silicon to the allylation of aldehydes using *ortho*-phenylene bisallylsilane.[6]

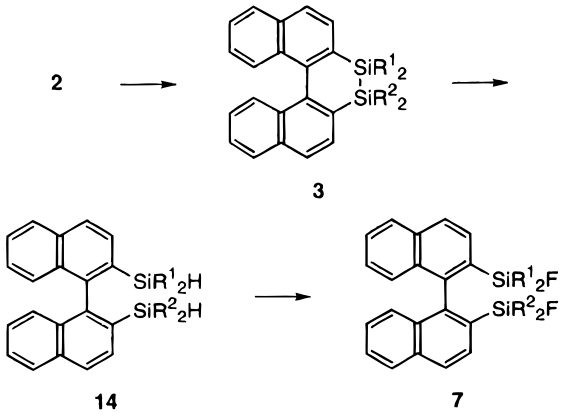
We quite recently reported the first chiral 2,2′-bis-silyl-substituted 1,1′-binaphthyls (*R*)-(+)-**1a** and (*R*)-(−)-**1b** prepared via the direct bis-silylation of chiral (*R*)-(+)-2,2′-dibromo-1,1′-binaphthyl (DBBN) ((*R*)-(+)-**2**) (eq 1).[7] Due to the suitable size for the bidentate cavity to accommodate basic substrates, the chiral bis-silyl-substituted binaphthyls **1** would be promising as novel bidentate Lewis acids for asymmetric syntheses. For the synthetic application of **1** to electrophilic activation, it is essential to enhance the Lewis acidity of the trialkylsilyl groups. It is well known that electronegative groups such as halogens enhance the Lewis acidity of silicon. In fact, recently, Lucchi and Kaufmann successively attempted the preparation of 2,2′-bis(halosilyl)-1,1′-binaphthyls **4** and **5** via the Si−Si bond cleavage of 3,4-disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene (2,2′-tetramethyldisilanylene-1,1′-binaphthyl) (**3a**) using X_2 (X = Cl, Br) or the direct bromination of (±)-**1a** using BBr_3.[8,9] In either case, the halogenation products **4** and **5** were produced. However, neither their isolation nor their synthetic application was achieved due to their highly hygroscopic nature to give the cyclic siloxane **6a** (eq 2).[8]





We anticipated that fluorination would be much more suitable for the activation of silyl groups. Fluorine has the highest electronegativity in the periodic table, and its steric hindrance is much smaller than other halogens. Due to its electronic and steric peculiarities, fluorine effectively enhances the Lewis acidity of silicon, allowing the formation of stable hypercoordinate complexes with various nucleophilic guests.[10] A rather stable Si−F bond would also be advantageous in synthetic operations. With the aim of developing a route to chiral bidentate Lewis acids directly bound to the 1,1′-binaphthyl skeleton, we herein report the synthetic study of novel 2,2′-bis(fluorosilyl)-1,1′-binaphthyls **7** via brominative Si−Si cleavage of the 2,2′-disilanylene-bridged 1,1′-binaphthyls **3** followed by $LiAlH_4$ reduction of the resulting dibromide and subsequent fluorination of the dihydrides **14** (Scheme 1). The precursor **3a** is the first 2,2′-disilanylene-bridged 1,1′-binaphthyl.[8] However, neither the geometrical analysis of **3a** nor the synthesis of its derivatives has been reported. The disilanylene-bridged binaphthyls **3** should open up the possibility of preparing various 2,2′-bis(fluorosilyl)-1,1′-binaphthyls **7** (Scheme 1). In addition, we were also interested in investigating the structure of **3**, which should be highly strained due to the steric repulsion of the binaphthyl groups fixed in a narrow angle. Thus, we also report the synthetic study and the X-ray structural analysis of the precursors **3**.

Scheme 1



Results and Discussion

Synthetic Study of 2,2′-Disilanylene-Bridged 1,1′-Binaphthyl. The cyclization reaction of organometallic reagents with dihalodisilanes is the conventional method for the preparation of strained disilanylene-bridged compounds. 2,2′-Tetramethyldisilanylene-1,1′-binaphthyl **3a** was prepared in 55% yield as colorless crystals via the previously reported bis-silylation of 2,2′-dibromo-1,1′-binaphthyl (DBBN, **2**) involving dilithiation followed by cyclization with $ClMe_2SiSiMe_2Cl$ (Scheme 2).[8] The identity of **3a** was confirmed by its ^1H NMR spectrum, which was consistent with the data reported in the literature.[8]

The novel $Me_2SiSiPh_2$-bridged binaphthyl **3b** was also produced as a white powder according to a similar procedure using $ClMe_2SiSiPh_2Cl$. However, the yield (8.4%) was much lower than that of the less sterically hindered **3a** (Scheme 2). Instead of the disilanylene-bridged product **3b**, the unexpected silylene-bridged product **8a** was predominantly obtained in 58% yield as a white solid. It is noteworthy that such a silylene-bridged product was not obtained during the preparation of **3a**. The first nucleophilic attack of the binaphthyl dianion occurred at the $SiMe_2Cl$ group of $ClMe_2SiSiPh_2Cl$. The second attack then occurred at the less sterically hindered $-SiMe_2-$ unit rather than the $SiPh_2Cl$ group

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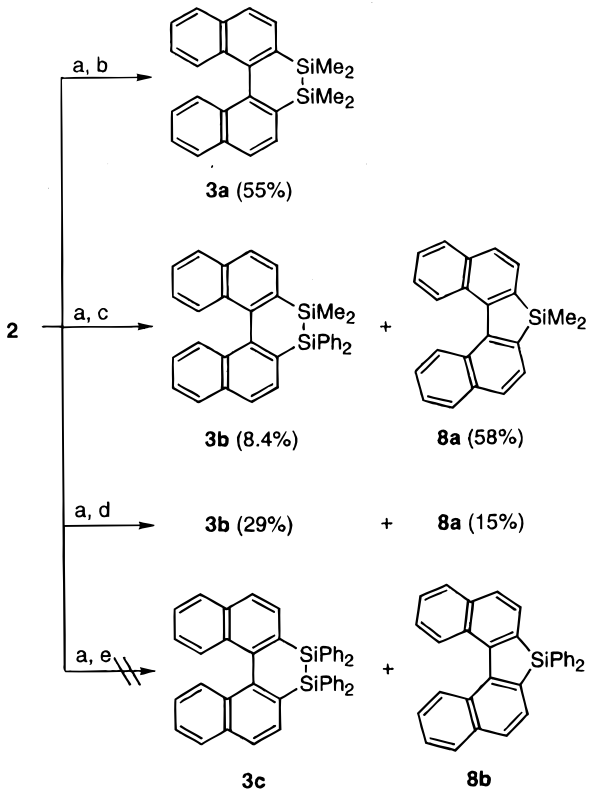
Scheme 2[a]



[a] Reagents and conditions: (a) 2.4 equiv *n*-BuLi, THF, −70 °C, 30 min. (b) 1.6 equiv $ClMe_2SiSiMe_2Cl$, −90 to −70 °C, 4 h. (c) 1.5 equiv $ClMe_2SiSiPh_2Cl$, −90 to −30 °C, 6 h. (d) 1.6 equiv $FMe_2SiSiPh_2F$, −90 to −40 °C, 6 h. (e) 1.3 equiv $FPh_2SiSiPh_2F$, −90 to −50 °C, 5 h.

to give **8a** accompanied by expulsion of the silyl anion $[ClPh_2Si]^-$. The electronic stabilization of the silyl anion by two phenyl groups no doubt promoted the facile Si−Si bond cleavage to give **8a**. The novel disilanylene-bridged binaphthyl **3b** was fully characterized and gave a satisfactory elemental analysis. The identity of **8a** was confirmed by its ^1H NMR spectrum, which was consistent with the data reported in the literature.[8] 7-Sila-7,7-dimethyl-7*H*-dibenzo[*c*,*g*]fluorene (**8a**) has a silacyclopentadiene (silole) unit in the five-membered ring.[11] The characteristic details of **8a** and the other silylene-bridged binaphthyls will be reported elsewhere. Fluorosilanes are generally better electrophilic reagents than the corresponding chlorosilanes due to their electronic and steric properties, especially in the coupling reaction with organolithium reagents.[12] Thus, we employed $FMe_2SiSiPh_2F$ instead of $ClMe_2SiSiPh_2Cl$ to improve the selectivity for the desired product **3b**. As expected, the disilanylene-bridged product **3b** was produced in 29% yield as a major product. However, even in this case, the competitive Si−Si bond cleavage occurred to give **8a** in 15% yield (Scheme 2). The alternative five-membered product **8b** was not formed in either case. Next, we further attempted the preparation of the Ph_2-$SiSiPh_2$-bridged binaphthyl **3c** using $FPh_2SiSiPh_2F$. However, no silylation product such as **3c** and **8b** was obtained. There is no doubt that the four phenyl groups of $FPh_2SiSiPh_2F$ were too bulky to allow formation of a silylation product at low temperature.

X-ray Structural Analysis of 3a and 3b. The X-ray structural analyses of several 2,2′-bis-silyl-substituted 1,1′-binaphthyls were recently disclosed by Kaufmann and then by our group. Kaufmann reported the geometrical parameters of the racemic 2,2′-bis(trimethylsilyl)-1,1′-binaphthyl ((±)-**1a**) and related compounds.[9] We first determined the molecular structure and the absolute configuration of chiral (*R*)-(−)-2,2′-bis(dimethylphenylsilyl)-1,1′-binaphthyl, (*R*)-(−)-**1b**.[7] The two naphthyl groups of these acyclic 2,2′-substituted 1,1′-binaphthyls are oriented almost perpendicular to release their steric repulsion. Thus, it was easily anticipated that the disilanylene-bridged binaphthyls **3a** and **3b** would be highly strained by its geometrical restriction. The facile Si−Si bond cleavage by X_2 (X = Cl, Br) also suggests the presence of significant strain in the six-membered disilacyclohexadiene moiety.[8,13] The strained disilanylene compounds show unique reactivities such as ring-opening polymerization,[14] oxidative addition,[15] thermal or photochemical retro-Diels−Alder fragmentation,[16] photochemical extrusion of silylene,[17] and acid-catalyzed alcoholysis.[18]

Colorless single crystals of **3a** suitable for the X-ray diffraction study were obtained from a solution of the compound in dibutyl ether at −10 °C over 12 h. Single crystals of **3b** were obtained as colorless crystals by evaporating the solvent of a diethyl ether solution at room temperature over 3 days. Two alternative views of the molecular structures of **3a** and **3b** are shown in parts a and b of Figures 1 and 2, respectively. The cell constants and data collection parameters are summarized in Table 1. The important geometrical parameters are shown in Table 2 for **3a** and Table 3 for **3b**.

Around the six-membered disilacyclohexadiene moiety of the C_2 symmetrical **3a**, the Si−Si bond length (2.3238(8) Å) is within the typical Si−Si single bond length. However, the geometry of the silicon atoms is significantly deformed from the tetrahedral shape. The Si1′−Si1−C12 bond angle is expanded to 119.0(2)°, and again the Si1′−Si1−C2 bond angle in the six-membered ring is extremely narrowed to 92.47(3)°, which is very small compared to the idealized value of sp^3-hybridized silicon of 109.5°. This narrowed Si1′−Si1−C2 bond angle of the disilanylene moiety makes **3a** much more strained

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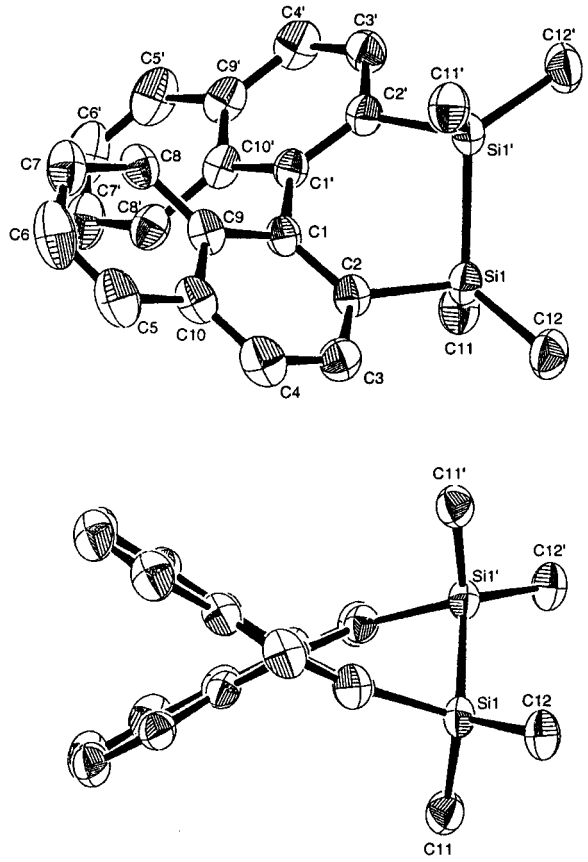


Figure 1. (a, top) Molecular structure of **3a** with thermal ellipsoids at the 30% probability level. (b, bottom) Alternative view of **3a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

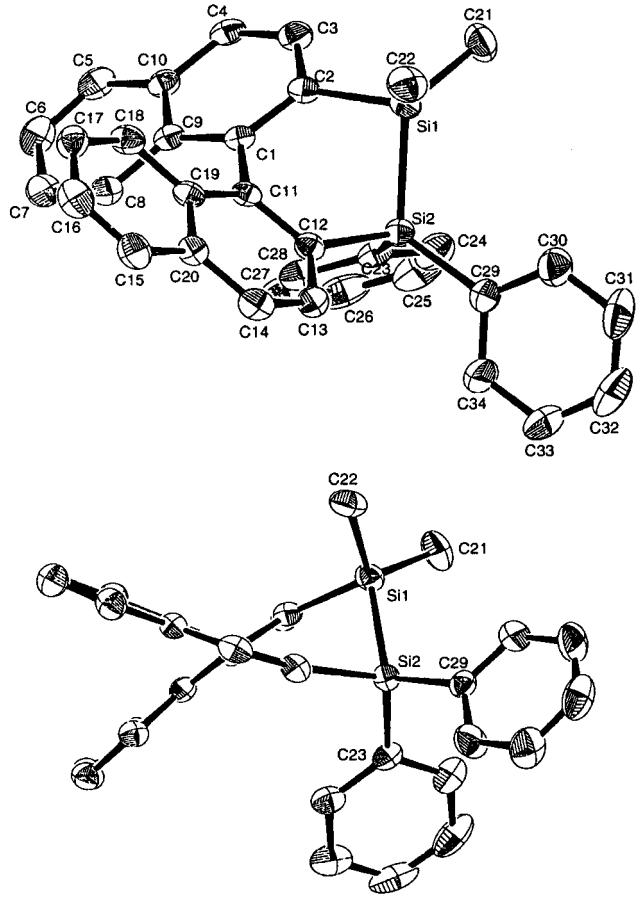
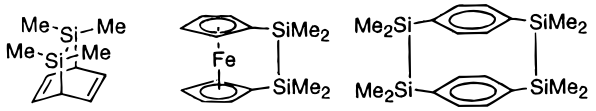


Figure 2. (a, top) Molecular structure of **3b** with thermal ellipsoids at the 30% probability level. (b, bottom) Alternative view of **3b** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

than other highly reactive disilanylene-bridged compounds such as 7,8-disilabicyclo[2.2.2]octa-2,5-diene **9** (av 96.3°),[19] ferrocenyldisilane **10** (102.8°),[20] and 1,2,9,-10-tetrasila[2.2]paracyclophane **11** (105.0°).[21] In the



9 **10** **11**

disilacyclohexadiene moiety, not only the Si1′−Si1−C1 bond angle but also the Si1−C2═C1−C1′ torsion angle is strained to the significant value of 13.2(7)°, which should be essentially fixed to 0° as a torsion angle of the planar C═C double bond geometry. It is noteworthy that this twisted structure of Si1−C2═C1−C1′ is mainly attributed to the distorted geometry of the trivalent C2 carbon directly bridged by the disilanylene group (Si1−C2/C1−C2−C3 = 10.2°). The alternative trivalent C1 carbon at the binaphthyl juncture is in the typical trigonal shape (C1′−C1/C9−C1−C2 = 2.6°). The C1−C9 ring of the naphthyl group is distorted by the strain

Table 1. Summary of Crystal Data and Intensity Collection Parameters

	3a	**3b**
empirical formula	$C_{24}H_{24}Si_2$	$C_{34}H_{28}Si_2$
fw	368.62	492.77
cryst syst	orthorhombic	monoclinic
space group	*Fdd*2 (No. 43)	$P2_1/c$ (No. 14)
a, Å	12.861(4)	8.880(5)
b, Å	34.255(2)	28.046(6)
c, Å	9.427(2)	10.807(5)
β, deg		91.69(4)
V, Å^3	4152(1)	2690(2)
Z	8	4
D_{calcd}, g/cm^3	1.179	1.217
μ(Mo Kα), mm^{-1}	0.175	0.153
$2\theta_{max}$, deg	55	55
no. of unique reflns	1355	5621
no. of used reflns ($I > 3.00\sigma(I)$)	794	1698
R	0.044	0.045
R_W	0.041	0.039

of the disilacyclohexadiene moiety in the 0.1−7.0° region (av 3.7°) of the torsion angles of the naphthyl carbon atoms. The C5−C10 ring is also slightly distorted with an average torsion angle of 2.0°. The disilacyclohexadiene moiety of the asymmetrical **3b** also shows a similar strained geometry. The Si2−Si1−C1 and Si1−Si2−C12 bond angles are extremely bent at 90.7(2)° and 92.1(2)°. The Si1−C2═C1−C11 and Si2−C12═C11−C1 are twisted with torsion angles of 11.4(7)° and 13.8-(7)°. The geometries of trivalent C2 and C12 carbons bridged by the disilanylene group are distorted by 10.7°

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Table 2. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Dihedral Angles (deg) of 3a

Bond Lengths			
Si1−Si1′	2.3238(8)	Si1−C2	1.888(4)
Si1−C11	1.87(2)	Si1−C12	1.878(6)
C1−C2	1.378(5)	C1−C1′	1.53(2)
Bond Angles			
Si1−Si1′−C2′	92.47(3)	Si1−Si1′−C11′	112.5(3)
Si1−Si1′−C12′	119.0(2)	Si1−C2−C1	121.9(4)
C1−C1′−C2′	120.3(6)		
Torsion Angles			
Si1′−Si1−C2−C1	42.2(4)	Si1−C2−C1−C1′	13.2(7)
C2−C1−C1′−C2′	54.8(9)	C9−C1−C1′−C9′	60.2(9)
Dihedral Angles			
Si1−C2/C1−C2−C3	10.2	C1′−C1/C9−C1−C2	2.6

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Dihedral Angles (deg) of 3b

Bond Lengths			
Si1−Si2	2.329(3)	Si1−C2	1.880(6)
Si1−C21	1.861(7)	Si1−C22	1.867(7)
Si2−C12	1.896(6)	Si2−C23	1.867(6)
Si2−C29	1.882(6)	C1−C2	1.390(7)
C1−C11	1.507(7)	C11−C12	1.401(7)
Bond Angles			
Si2−Si1−C2	90.7(2)	Si2−Si1−C21	119.6(2)
Si2−Si1−C22	112.6(2)	Si1−Si2−C12	92.1(2)
Si1−Si2−C23	113.8(2)	Si1−Si2−C29	119.6(2)
Si1−C2−C1	121.8(4)	C2−C1−C11	119.8(5)
Si2−C12−C13	119.6(5)	C1−C11−C12	120.7(5)
Torsion Angles			
Si1−Si2−C12−C11	43.6(4)	Si1−C2−C1−C11	11.4(7)
Si2−C12−C11−C1	13.8(7)	Si2−Si1−C2−C1	45.3(5)
C2−Si1−Si2−C12	62.9(2)	C2−C1−C11−C12	55.6(8)
C9−C1−C11−C19	61.1(7)		
Dihedral Angles			
Si1−C2/C1−C2−C3	10.7	Si2−C12/C11−C12−C13	11.5
C11−C1/C9−C1−C2	4.3	C1−C11/C19−C11−C12	1.0

for Si1−C2/C1−C2−C3 and 11.5° for Si2−C12/C11−C12−C13. These significantly strained disilacyclohexadiene moieties, especially the narrowed Si−Si−C bond angles and twisted Si−C═C−C torsion angles, imply the highly reactive Si−Si bonds of **3a** and **3b**.

The two naphthyl groups of **3a** and **3b** are oriented at average torsion angles of 57.5° and 58.4°, respectively, which are much narrower than those of the acyclic (±)-**1a** (89.60°) and (*R*)-(−)-**1b** (av 92.5°). The naphthyl groups fixed at such narrow angles should induce an intramolecular steric repulsion between the coterminous H(C8) positions. In fact, the torsion angle of the acyclic C9−C1−C1′−C9′ moiety in **3a** (60.2(9)°) is expanded outward by 5.4° more than that of the bridged C2−C1−C1′−C2′ moiety (54.8(9)°). A similar deformation of the binaphthyl group around the C1−C11 pivot is also shown in **3b** (C2−C1−C11−C12 = 55.6(8)°, C9−C1−C11−C19 = 61.1(7)°). In contrast, there is no such remarkable difference between the two torsion angles of the acyclic (*R*)-(−)-**1b**, which has the conformational flexibility to release the steric repulsion through rotation about the C1−C1′ pivot (C2−C1−C1′−C2′ = 93°, C9−C1−C1′−C9′ = 92°).[7] This remarkable expansion of the acyclic moieties of the disilanylene-bridged binaphthyl groups reflects the presence of a significant steric repulsion in the binaphthyl groups.

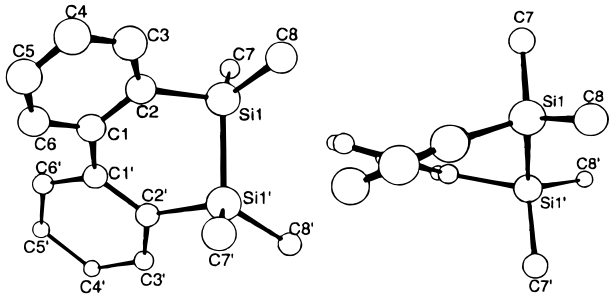
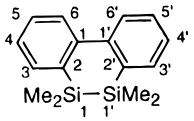
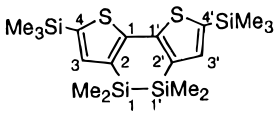


Figure 3. (a, left) B3LYP/6-31G (d) optimized structure of **12**. (b, right) Alternative view of **12**. Hydrogen atoms are omitted for clarity.

For further structural investigation of the highly strained and sterically repulsed **3a** and **3b**, we compared the geometry of the tetramethyldisilanylene-bridged **3a** with those of other biaryl analogues, dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene (**12**) and dithienodisilacyclohexadiene (**13**), in which their biaryl groups are less sterically hindered than the binaphthyl group. The synthesis and photochemical reaction of **12** were studied by Sakurai.[15] However, the geometry has not been reported. Thus, we determined the optimized geometry of **12** at the B3LYP/6-31G(d) level of theory using the Gaussian 98 programs (Figure 3).[22] The selected geometrical parameters of **12** are summarized in Table 4. The synthesis and X-ray structural analysis of the bithiophene analogue **13** was reported by Kunai and Ohshita last year.[23] Table 5 shows the most important geometrical parameters of **3a**, **12**, and **13**.



12



13

The Si−Si bond lengths of three disilanylene-bridged biaryls are similar to the typical Si−Si single bond length. However, the other geometrical parameters suggest that **3a** is extremely strained, more so than **12** and **13**. The Si1−Si1′−C2′ bond angle of **3a** (92.5°) is much more narrowed than those of **12** (96.5°) and **13** (100.5°). The torsion angle of Si1−C2═C1−C1′ in **12** (8.0°) is obviously more planar than that of **3a** (13.2°). The disilanylene-bridged C2 carbon of **12** is near the idealized trigonal shape (Si1−C2/C1−C2−C3 = 5.0°). Though the naphthyl rings of **3a** are significantly distorted as mentioned above, the phenyl groups of **12** are almost planar rings in which the torsion angles of

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), Torsion Angles (deg), and Dihedral Angles (deg) of 12

Bond Lengths			
Si1−Si1′	2.332	Si1−C2	1.904
Si1−C7	1.901	Si1−C8	1.900
C1−C2	1.423	C1−C1′	1.503
Bond Angles			
Si1−Si1′−C2′	96.5	Si1−Si1′−C7′	112.3
Si1−Si1′−C8′	117.4	Si1−C2−C1	122.5
C1−C1′−C2′	124.0		
Torsion Angles			
Si1′-Si1−C2−C1	37.6	Si1−C2−C1−C1′	8.0
C2−C1−C1′−C2′	42.0	C6−C1−C1′−C6′	39.7
Dihedral Angles			
Si1−C2/C1−C2−C3	5.0	C1′−C1/C6−C1−C2	1.2

Table 5. Selected Geometrical Parameters of 3a, 12, and 13

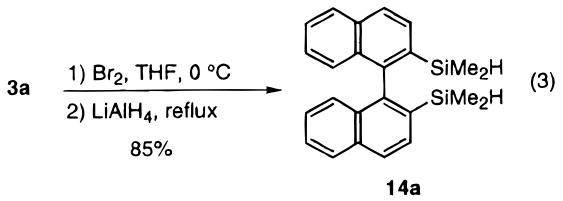
compound	Si−Si[c]	Si1−Si1′−C2′[d]	C2−C1−C1′−C2′[d]
3a[a]	2.324	92.5	54.8
12[a]	2.332	96.5	42.0
13[b]	2.320	100.5	20.2

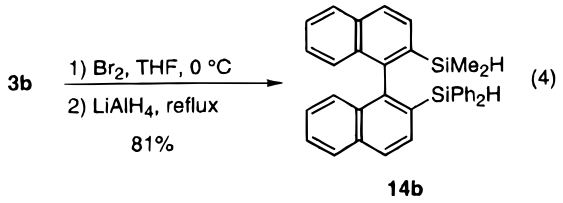
[a] This work. [b] Ref 23. [c] Angstroms. [d] Degrees.

the phenyl carbon atoms range from 0.3° to 1.7° (av 1.0°). Kunai and Ohshita also reported the absence of any strain in dithienodisilacyclohexadiene **13**.[23] The C2−C1−C1′−C2′ torsion angle of **3a** (54.8°) is remarkably expanded in order to release the steric repulsion in the distorted binaphthyl group more than those of the less sterically hindered **12** (42.0°) and **13** (20.2°). It is noteworthy that the Si1−Si1′−C2′ bond angles become narrow and strained as the C2−C1−C1′−C2′ torsion angles are expanded to release the steric repulsion between the two aryl groups. Namely, the significant strain in the disilacyclohexadiene moiety of the disilanylene-bridged binaphthyls **3** is induced by the release of the steric repulsion between the two naphthyl groups.

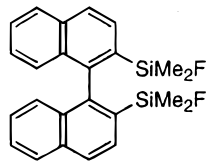
Synthetic Study of 2,2′-Bis(fluorosilyl)-1,1′-binaphthyl. Recently, Ishikawa and Kunai reported the synthesis of fluorosilanes by fluorination of the corresponding hydrosilanes using a reagent composed of $CuCl_2$, KF, and CuI under mild conditions.[24] Because hydrosilanes are not sensitive to air and moisture, we investigated the synthesis of 2,2′-bis(fluorodimethylsilyl)-1,1′-binaphthyl (**7a**) and 2-fluorodimethylsilyl-2′-fluorodiphenylsilyl-1,1′-binaphthyl (**7b**) via the fluorination of corresponding bishydrosilyl compounds **14a** and **14b**, which are hydrogenation products of **3a** and **3b**, respectively.

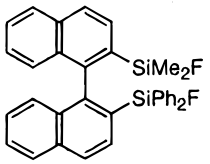
2,2′-Bis(dimethylhydrosilyl)-1,1′-binaphthyl (**14a**) was prepared in 85% yield as a colorless oil via the previously reported procedure involving the facile bromination of **3a** followed by the hydrogenation of the dibromide with $LiAlH_4$ (eq 3).[8] The identity of **14a** was confirmed by its ^1H NMR spectrum, which was consistent with the data reported in the literature.[8] Novel 2-dimethylhydrosilyl-2′-diphenylhydrosilyl-1,1′-binaphthyl (**14b**) was also obtained in 81% yield as a colorless oil from **3b** according to a similar procedure (eq 4).

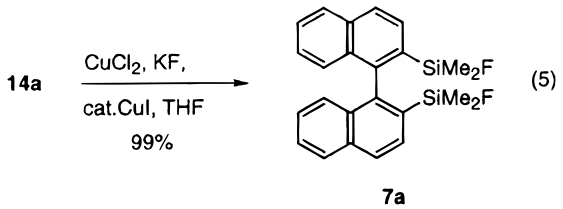


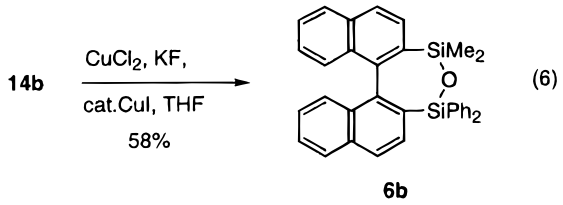


The fluorination of **14a** proceeded smoothly to give 2,2′-bis(fluorodimethylsilyl)-1,1′-binaphthyl (**7a**) (eq 5). After filtration of the inorganic products, the crude product was subjected to immediate flash chromatography to afford pure **7a** in almost quantitative yield. The NMR data and the elemental analysis were consistent with both the identity and purity of **7a**. This novel bisfluorosilane **7a** is the first isolated and fully characterized 2,2′-bis(halosilyl)-1,1′-binaphthyl derivative. In contrast to the highly hygroscopic nature of the chlorine and bromine analogues **4** and **5**, **7a** was stable during the open-column chromatography. We also attempted to prepare the asymmetrical bisfluorosilyl binaphthyl **7b** by a similar procedure. The bishydrosilane **14b** completely disappeared and two products were detected in the reaction mixture by GC−MS spectroscopy which showed molecular ion peaks of $M^+ = 508$ and 512. However, formation of the desired bisfluorosilane **7b** ($M^+ = 530$) was not confirmed. After workup, the siloxane **6b** was obtained in 58% yield (eq 6).









Experimental Section

General Comments. ^1H (499.9 MHz) and ^{13}C (125.7 MHz) NMR spectra were measured on a Varian Unity 500 plus NMR

(24) Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1996**, *15*, 2478.

spectrometer. ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker AVANCE 300 NMR spectrometer. ^{1}H (200 MHz) NMR spectra were measured on a Varian Gemini 200H NMR spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (^{1}H δ 7.24 ppm; ^{13}C δ 77.0 ppm) relative to Me_4Si at δ 0.00 ppm. ^{29}Si chemical shifts were referred to Me_4Si (^{29}Si δ 0.00 ppm) as an external standard. Low- and high-resolution mass spectra were obtained on a JEOL GCmate mass spectrometer. Melting points are uncorrected and were measured on a Yanaco MP-500D melting point apparatus. Density functional theory (B3LYP/6-31G(d)) calculation was performed on a Silicon Graphics Indigo2000 workstation. Medium-pressure liquid chromatography (MPLC) was done on a JASCO PRC-50 using a silica gel-packed column. GLC analysis was conducted by using a Shimadzu 14A gas chromatography with a DB-1HT 0.32 mm × 30 m capillary column. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl prior to use. Hexane and toluene were distilled and stored over molecular sieves prior to use. 2,2′-Dibromo-1,1′-binaphthyl (DBBN, **2**), $ClMe_2SiSiPh_2Cl$, and $ClPh_2SiSiPh_2Cl$ were prepared according to published procedures.[7,25] All reactions were carried out under nitrogen.

$FMe_2SiSiPh_2F$. To antimony trifluoride (2.37 g, 13.3 mmol) was added a solution of $ClMe_2SiSiPh_2Cl$ (4.04 g, 13.0 mmol) in hexane (10 mL), and the reaction mixture was stirred for 10 min at room temperature, then heated to reflux for an additional 1 h. The crude product was adsorbed onto silica gel and chromatographed as quickly as possible (silica gel, hexane) to afford $FMe_2SiSiPh_2F$ (3.33 g, 12.0 mmol) in 92% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.48 (d, J = 8.8 Hz, 6H), 7.3−7.7 (m, 10H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 0.83 (d, $^{2}J_{C-F}$ = 10.8 Hz), 128.3, 130.7, 133.7 (d, $^{2}J_{C-F}$ = 13.1 Hz), 134.0 (d, $^{3}J_{C-F}$ = 2.4 Hz); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 28.99 (dd, J_{Si-F} = 305.1, 34.9 Hz), 3.24 (dd, J_{Si-F} = 312.3, 33.2 Hz); MS, *m*/*z* (%) 278 (M^+, 5), 201 (80), 182 (31), 181 (34), 135 (100); HRMS found, 278.0772; calcd for $C_{14}H_{16}F_2Si_2$, 278.0759.

$FPh_2SiSiPh_2F$.[26] To antimony trifluoride (2.46 g, 13.8 mmol) was added a solution of $ClPh_2SiSiPh_2Cl$ (2.53 g, 5.82 mmol) in toluene (10 mL), and the reaction mixture was stirred for 20 min at room temperature, then heated to reflux for an additional 30 min. The crude product was adsorbed onto silica gel and chromatographed with hexane as quickly as possible to afford $FPh_2SiSiPh_2F$ (1.60 g, 3.98 mmol) in 68% yield as a colorless solid: mp 82 °C (lit.[26] 77 °C); ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 7.38 (dd, J = 7.5, 7.5 Hz, 8H), 7.46 (tt, J = 7.5, 2.0 Hz, 4H), 7.57 (dd, J = 7.5, 2.0 Hz, 8H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 128.3, 130.9, 133.2 (dd, $^{2}J_{C-F}$ = 8.8 Hz, $^{3}J_{C-F}$ = 6.5 Hz), 134.4 (dd, $^{3}J_{C-F}$ = 1.5 Hz, $^{4}J_{C-F}$ = 1.5 Hz); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 2.27 (dd, J_{Si-F} = 313.5, 34.6 Hz); MS, *m*/*z* (%) 402 (M^+, 2), 259 (85), 201 (47), 182 (100), 181 (95); HRMS found, 402.1078; calcd for $C_{24}H_{20}F_2Si_2$, 402.1072.

Preparation of 3,4-Disila-3,3,4,4-tetramethyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene (3a) via the Bis-silylation of DBBN (2) with $ClMe_2SiSiMe_2Cl$.[8] To a solution of DBBN (**2**) (1.01 g, 2.45 mmol) in THF (15 mL) was added a hexane solution of *n*-BuLi (4.0 mL, 1.54 M, 6.2 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of $ClMe_2SiSiMe_2Cl$ (740 mg, 3.96 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was warmed to −70 °C and stirred for an additional 4 h. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, hexane) to give **3a** as an orange solid, which was recrystallized from dibutyl ether at −10 °C over 12 h to give colorless crystals (497 mg, 1.35 mmol) in 55% yield: mp 201−204 °C (lit.[8] 199−203 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.35 (s, 6H), 0.48 (s, 6H), 6.90 (d, J = 8.6 Hz, 2H), 7.10 (ddd, J = 8.6, 6.5, 1.3 Hz, 2H), 7.39 (ddd, J = 8.2, 6.5, 1.3 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.82−7.92 (m, 4H); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −25.52; MS, *m*/*z* (%) 368 (M^+, 67), 353 (17), 309 (34), 295 (100).

Preparation of 3,4-Disila-3,3-dimethyl-4,4-diphenyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene (3b) via the Bis-silylation of DBBN (2) with $ClMe_2SiSiPh_2Cl$. To a solution of **2** (518 mg, 1.25 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (2.0 mL, 1.50 M, 3.0 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of $ClMe_2SiSiPh_2Cl$ (602 mg, 1.94 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was stirred at −60 °C for 4 h and then allowed to warm to −30 °C over 2 h until the dark red color completely faded and an orange precipitate almost disappeared. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in chloroform and chromatographed on silica gel with hexane. The crude product was subjected to MPLC (hexane) to afford **3b** (51.8 mg, 0.105 mmol) in 8.4% yield as a white powder and **8a** (226 mg, 0.729 mmol) in 58% yield as a white solid, respectively.

Preparation of 3,4-Disila-3,3-dimethyl-4,4-diphenyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene (3b) via the Bis-silylation of DBBN (2) with $FMe_2SiSiPh_2F$. To a solution of **2** (502 mg, 1.21 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (2.1 mL, 1.50 M, 3.2 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of $FMe_2SiSiPh_2F$ (539 mg, 1.93 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was stirred at −70 °C for 4 h and then allowed to warm to −40 °C over 2 h until the dark red color completely faded and an orange precipitate almost disappeared. A saturated aqueous solution of NH_4Cl was added, and the mixture was extracted with Et_2O. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in dichloromethane and chromatographed on silica gel with hexane. The crude product was crystallized from Et_2O to afford **3b** (134 mg, 0.272 mmol) as a white powder. The residue was subjected to MPLC (hexane) to afford the additional **3b** (41.3 mg, 0.084 mmol) and **8a** (58.2 mg, 0.187 mmol). Total yields of **3b** and **8a** are 29% and 15%, respectively.

3,4-Disila-3,3-dimethyl-4,4-diphenyl-3,4-dihydrodibenzo[*c*,*g*]phenanthrene (3b): mp 244−247 °C; ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 0.03 (s, 3H), 0.58 (s, 3H), 6.72−6.77 (m, 2H), 6.95 (tt, J = 7.5, 1.0 Hz, 1H), 7.01−7.18 (m, 6H), 7.36 (ddd, J = 7.9, 6.5, 1.0 Hz, 1H), 7.38−7.48 (m, 6H), 7.51−7.55 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −5.1, −4.0, 125.4, 125.50, 125.55, 126.1, 126.6, 126.9, 127.0, 127.11, 127.14, 127.9, 128.0, 128.2, 128.4, 129.4, 129.6, 131.6, 132.0, 132.2, 132.7, 132.8, 132.9, 134.2, 134.51, 134.53, 135.2, 136.7, 144.1, 144.9; ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −24.60, −24.61; MS, *m*/*z* (%) 492 (M^+, 61), 357 (100), 197 (29), 135 (40); HRMS found 492.1727, calcd for $C_{34}H_{28}Si_2$ 492.1730. Anal. Calcd for $C_{34}H_{28}Si_2$: C, 82.87; H, 5.73. Found: C, 82.63; H, 6.11.

7-Sila-7,7-dimethyl-7*H*-dibenzo[*c*,*g*]fluorene (8a): mp 36−38 °C (lit.[8] a colorless oil); ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ 0.46 (s, 6H), 7.34−7.38 (m, 2H), 7.47−7.51 (m, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −3.33, 124.26, 125.74, 127.82, 127.90, 128.26, 128.48, 129.72, 135.73, 139.87, 147.12; ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 3.02; MS, *m*/*z* (%) 310 (M^+, 100), 295 (40); HRMS found, 310.1175; calcd for $C_{22}H_{18}Si$, 310.1178.

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Bis-silylation of DBBN (2) with $FPh_2SiSiPh_2F$. To a solution of **2** (501 mg, 1.21 mmol) in THF (5 mL) was added a hexane solution of *n*-BuLi (2.0 mL, 1.54 M, 3.08 mmol) at −70 °C, and the reaction mixture was stirred for 30 min. After the reaction mixture was cooled to −90 °C, a solution of $FPh_2SiSiPh_2F$ (692 mg, 1.72 mmol) in THF (5 mL) was added slowly. After the addition was complete, the reaction mixture was stirred at −70 °C for 1 h and then allowed to warm to −50 °C over 4 h until the dark red color completely faded and an orange precipitate almost disappeared. Further workup as in the preparation of **3b** gave a crude product which was subjected to MPLC (cyclohexane) to afford 1,1′-binaphthyl (14.7 mg, 0.058 mmol) as a single isolated product. The residue was a complex mixture.

Preparation of 2,2′-Bis(dimethylhydrosilyl)-1,1′-binaphthyl (14a).[8] To a solution of **3a** (0.105 g, 0.285 mmol) in THF (2 mL) was added bromine (26 μL, 0.504 mmol) at 0 °C. After 10 min, excess $LiAlH_4$ (95 mg, 2.5 mmol) was added at 0 °C, stirred for 30 min, then heated to reflux for 6 h. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **14a** (89.9 mg, 0.243 mmol) in 85% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ -0.32 (d, J = 3.9 Hz, 6H), −0.01 (d, J = 3.9 Hz, 6H), 3.76 (qq, J = 3.9, 3.9 Hz, 2H), 7.05−7.20 (m, 4H), 7.43 (ddd, J = 8.2, 6.6, 1.5 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H).

Preparation of 2-Dimethylhydrosilyl-2′-diphenylhydrosilyl-1,1′-binaphthyl (14b). To a solution of **3b** (0.134 g, 0.272 mmol) in THF (5 mL) was added bromine (22 μL, 0.426 mmol) at 0 °C. After 10 min, excess $LiAlH_4$ (102 mg, 2.69 mmol) was added at 0 °C, stirred for 30 min, then heated to reflux for 6 h. The crude product was subjected to flash chromatography (silica gel, hexane) to afford **14b** (109.3 mg, 0.221 mmol) in 81% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ −0.32 (d, J = 4.0 Hz, 3H), −0.07 (d, J = 4.0 Hz, 3H), 3.75 (qq, J = 4.0, 4.0 Hz, 1H), 4.51 (s, 1H), 6.91−6.98 (m, 2H), 7.07−7.10 (m, 4H), 7.18−7.26 (m, 3H), 7.29−7.40 (m, 4H), 7.45−7.50 (m, 3H), 7.69 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −3.8, −3.0, 125.7, 126.0, 126.1, 126.7, 126.8, 127.0, 127.1, 127.2, 127.5, 127.8, 127.9, 129.0, 129.5, 130.0, 131.4, 132.4, 133.0, 133.45, 133.50, 133.8, 133.9, 135.3, 135.5, 135.9, 145.0, 147.3 (two sp^2 carbons missing due to overlap); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −19.67, −22.47; MS, *m*/*z* (%) 494 (M^+, 4), 435 (100), 357 (80); HRMS found, 494.1884; calcd for $C_{34}H_{30}Si_2$, 494.1886. Anal. Calcd for $C_{34}H_{30}Si_2$: C, 82.54; H, 6.11. Found: C, 82.65; H, 6.38.

Preparation of 2,2′-Bis(fluorodimethylsilyl)-1,1′-binaphthyl (7a). To a dried mixture of $CuCl_2$ (132.2 mg, 0.981 mmol), KF (42.7 mg, 0.725 mmol), and a catalytic amount of CuI (12.6 mg, 6.62 μmol) was added a solution of **14a** (83.0 mg, 0.224 mmol) in THF (5 mL), and the reaction mixture was stirred for 4 h at room temperature. After inorganic products were separated by flash chromatography (silica gel, 10% chloroform/hexane) and solvent was removed under reduced pressure as quickly as possible, the crude product was adsorbed onto silica gel and chromatographed as quickly as possible (silica gel, 10% chloroform/hexane) to afford **7a** (90.2 mg, 0.222 mmol) in 99% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ −0.31 (d, J = 7.5 Hz, 6H), −0.18 (d, J = 8.0 Hz, 6H), 7.15 (d, J = 8.5 Hz, 2H), 7.20−7.25 (m, 2H), 7.44−7.48 (m, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −0.38 (d, $^2J_{C-F}$ = 15.5 Hz), 0.06 (d, $^2J_{C-F}$ = 15.5 Hz), 126.3, 127.0, 127.2, 127.6, 127.9, 129.5, 133.2, 134.1, 135.2 (d, $^2J_{C-F}$ = 15.5 Hz), 144.4 (d, $^3J_{C-F}$ = 3.0 Hz); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 20.75 (d, $^1J_{Si-F}$ = 276.7 Hz); MS, *m*/*z* (%) 406 (M^+, 17), 295 (82), 77 (100); HRMS found, 406.1385; calcd for $C_{24}H_{24}F_2Si_2$, 406.1384. Anal. Calcd for $C_{24}H_{24}F_2Si_2$: C, 70.89; H, 5.95. Found: C, 70.76; H, 5.93.

Fluorination of 14b. To a dried mixture of $CuCl_2$ (166.9 mg, 1.24 mmol), KF (79.8 mg, 1.373 mmol), and a catalytic amount of CuI (9.6 mg, 5.04 μmol) was added a solution of **14b** (57.6 mg, 0.117 mmol) in THF (10 mL), and the reaction mixture was stirred for 4 h at room temperature. After inorganic products were separated by flash chromatography (silica gel, 10% chloroform/hexane) and solvent was removed under reduced pressure as quickly as possible, the crude product was adsorbed onto silica gel and chromatographed as quickly as possible (silica gel, 10% chloroform/hexane) to afford pure **6b** (34.4 mg, 67.7 μmol) in 58% yield as a white powder: mp 240−242 °C; ^{1}H NMR ($CDCl_3$, 499.9 MHz) δ −0.48 (s, 3H), 0.66 (s, 3H), 6.58−6.60 (m, 2H), 6.73 (tt, J = 7.5, 1.0 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.95−6.99 (m, 2H), 7.03−7.07 (m, 2H), 7.14 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.27 (ddd, J = 8.5, 6.5, 1.0 Hz, 1H), 7.37−7.46 (m, 5H), 7.54−7.58 (m, 3H), 7.61−7.65 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ −0.3, −0.2, 125.4, 125.7, 125.9, 126.1, 126.5, 127.1, 127.2, 127.508, 127.510, 127.9, 127.97, 128.04, 128.9, 130.0, 131.5, 132.6, 133.1, 133.5, 133.6, 133.7, 134.0, 134.8, 135.25, 135.26, 136.8, 144.6, 146.3 (one sp^2 carbon missing due to overlap); ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ 7.4 (−$SiMe_2$− and −$SiPh_2$−); MS, *m*/*z* (%) 508 (M^+, 100), 493 (47), 415 (64); HRMS found, 508.1672; calcd for $C_{34}H_{28}OSi_2$, 508.1679. Anal. Calcd for $C_{34}H_{28}OSi_2$: C, 80.27; H, 5.55. Found: C, 80.52; H, 5.60.

X-ray Crystallography. Single crystals of **3a** were obtained from a solution of the compound in dibutyl ether at −10 °C over 12 h. Single crystals of **3b** were obtained as colorless crystals by evaporating the solvent of a diethyl ether solution at room temperature over 3 days. Diffraction data were collected on a Rigaku Denki AFC7S diffractometer with a rotation anode (50 kV, 30 mA) using graphite-monochromated Mo Kα (λ = 0.7107 Å). The data were collected at a temperature of 23 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. The structures were solved by direct methods[27] and expanded using Fourier techniques.[28] The cell constants and data collection parameters are summarized in Table 1. For compound **3a**, the non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically; the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 794 observed reflections ($I > 3.00\sigma(I)$) and 131 variable parameters and converged (least parameter shift was 6.12 times its esd) with unweighted and weighted agreement factors: $R = 0.043$, $R_w = 0.041$, and R1 = 0.000 for $I > 3.00\sigma(I)$ data. For compound **3b**, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1698 observed reflections ($I > 3.00\sigma(I)$) and 325 variable parameters and converged (least parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors: $R = 0.045$, $R_w = 0.039$, and R1 = 0.045 for $I > 3.00\sigma(I)$ data. Neutral atom scattering were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in F_{calc};[30] the values for Df' and Df'' were those of Creagh and McAuley.[31] The values for the mass attenuation coefficients

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are those of Creagh and Hubbell.[32] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[33]

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Supporting Information Available: Tables of final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles of **3a** and **3b** and NMR spectra of **3b**, **7a**, and **14b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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