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Addition of Silicon−Silicon σ-Bonds to Arynes or Bisarynes Catalyzed by a Palladium Complex

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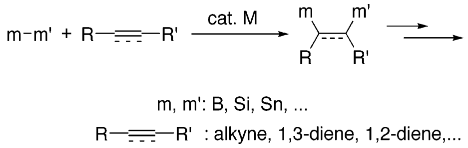
Addition reactions of the silicon−silicon σ-bonds of disilanes to the carbon−carbon triple bonds of various arynes are promoted by a palladium-1,1,3,3-tetramethylbutyl isocyanide complex to give diverse 1,2-disilylated arenes. Five-membered and benzo-condensed six-membered cyclic disilanes were applicable to the bissilylation, whereas reactions using four- or seven-membered cyclic disilanes or acyclic disilanes did not produce the desired insertion products at all. Bisarynes, containing two strained triple bonds in a molecule, could also insert into the silicon−silicon bond smoothly to afford tetrasilylated arenes in modest yields.

Introduction

The transition metal-catalyzed addition reactions of metal−metal σ-bonds to carbon−carbon unsaturated compounds (bismetalation) have attracted considerable attention as a powerful method for the straightforward synthesis of highly functionalized organometallic compounds, in which two carbon−metal bonds are generated simultaneously in a regio- and stereoselective manner.[1] The resulting organometallic compounds are convertible into complex molecular skeletons through subsequent carbon−carbon bond formation and/or introduction of a functional group by utilizing their carbon−metal bonds. Although many bismetalation reactions using various combinations of metal−metal compounds (metal: B, Si, Sn, ...) and carbon−carbon unsaturated compounds (alkyne, 1,3-diene, 1,2-diene, and simple alkene) have been accomplished thus far,[2] no report is available on such reactions with transient arynes bearing a strained carbon−carbon triple bond, despite their great potential for the synthesis of functionalized arylmetal compounds (Scheme 1).

Scheme 1



In 1998, Peña and co-workers disclosed the palladium-catalyzed trimerization of arynes, demonstrating that the use of an appropriate aryne precursor and a catalyst allows arynes to undergo transition metal-catalyzed transformations selectively.[3] Since then, a variety of catalytic reactions of arynes, including cocyclization with carbon unsaturated coumpounds,[4] bisallylation,[5] and allylalkynylation,[6] were developed to offer a novel entry for the synthesis of substituted arenes of a type that would be difficult to access by conventional methods. On the basis of these findings, we envisaged that arynes would insert into a metal−metal σ-bond by employing a suitable catalyst and a dimetallic compound.

We report herein that a palladium-1,1,3,3-tetramethylbutyl isocyanide (*t*-OctNC) complex catalyzes the insertion of arynes into the silicon−silicon σ-bonds of some cyclic disilanes to give seven- or eight-membered benzo-annulated disilacarbocycles straightforwardly.[7,8] Moreover, the reactions can be applied to bisarynes[9]

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(1) For reviews, see: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435. (b) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.

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(4) With alkyne: (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Synlett* **2000**, 1061. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944. (d) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533. With allyl chloride and/or alkyne: (e) Yoshikawa, E.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 173. (f) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280. With carbon monoxide: (g) Chatani, N.; Kamitani, A.; Oshita, M.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 12686. With 1,2-diene: (h) Hsieh, J.-C.; Rayabarapu, D. K.; Cheng, C.-H. *Chem. Commun.* **2004**, 532.

(5) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 729.

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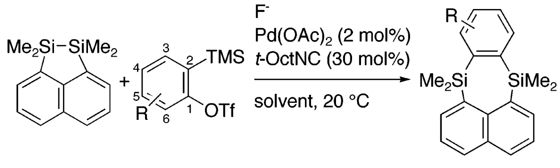
(7) A part of this work has been reported: Yoshida, H.; Ikadai, J.; Shudo, M.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2003**, *125*, 6638.

10.1021/om049276w CCC: $30.25

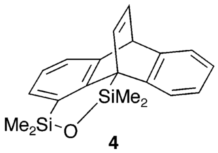
Scheme 2



1a **2** **3a**

R in **2**		F^-	solvent	time	yield (%)	product
H	**2a**	KF/18-Crown-6	THF	1.5 h	66	**3aa**
H	**2a**	CsF	MeCN	2 days	78	**3aa**
5-Me	**2b**	KF/18-Crown-6	THF	1.5 h	72	**3ab**
5-Me	**2b**	CsF	MeCN	11 days	50	**3ab**
H	**2a**	KF/18-Crown-6	THF	2 days	trace	**4**[a]

[a] The reaction was carried out without an added catalyst.



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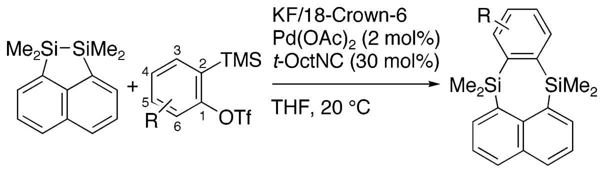
derived from biphenyl and diphenyl ether precursors, forming four carbon−silicon bonds all in one step.

Results and Discussion

Reaction Conditions for Bissilylation of Arynes. First we investigated the reaction of 1,1,2,2-tetramethyl-1,2-(1,8-naphthylene)disilane (**1a**) and benzyne (generated in situ by the action of KF/18-crown-6 on 2-(trimethylsilyl)phenyl triflate, **2a**)[10] in the presence of a palladium−*t*-OctNC complex. The latter is an excellent catalyst for the bissilylations of alkynes and alkenes as reported by Ito and co-workers.[1] As described in Scheme 2, the silicon−silicon bond of **1a** readily adds to the triple bond of benzyne to afford the seven-membered disilacarbocycle 7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadene (**3aa**) in 66% yield. The use of cesium fluoride in acetonitrile in lieu of KF/18-crown-6 in THF resulted in the formation of **3aa** in 78% yield, although the reaction required 2 days for completion. Furthermore, treatment of 4-methylbenzyne (from **2b**) with **1a** using KF/18-crown-6 gave a 72% yield of the product (**3ab**) within 1.5 h, whereas the reaction in which cesium fluoride was used resulted in a lower yield (50%) even after prolonged reaction time (11 days). In most cases, a triphenylene derived from trimerization of an aryne was formed as a byproduct. The palladium complex catalyst is crucial, since no trace of the insertion product was observed in its absence. Instead, a trace amount of compound **4** was formed through the Diels−Alder reaction of **1a** with benzyne, followed by oxidation of the Si−Si bond.

Bissilylation of Arynes with 1a. We next examined the bissilylation of various arynes with **1a** using KF/18-crown-6 as a fluoride ion source (Table 1). Similar to the cases of benzyne and 4-methylbenzyne, 4-methoxy- (from **2c**), 4-phenyl- (from **2d**), and 4,5-disubstituted benzyne (from **2e** or **2f**) also gave good to high yields of the corresponding bissilylation products (entries 1−6). On the other hand, the reactions of 3-substituted benzynes (from **2g**−**2i**) and 1,2-naphthalyne (from **2j**) were rather sluggish and provided the products in 30−40% yields, probably due to the steric hindrance around the triple bond of the arynes (entries 7−10). It should be noted that 3,4-dimethoxybenzyne (from **2k**) and 3,6-dimethoxybenzyne (from **2l**) reacted smoothly with **1a** to give the insertion products in 63 and 72% yields, respectively, despite their steric congestion (entries 11 and 12). This may be attributed to the enhanced kinetic stability of the aryne induced by the two electron-withdrawing methoxy groups (−*I* effect).[11]

Table 1. Palladium-Catalyzed Bissilylation of Arynes with 1a[a]



1a **2** **3a**

entry	R in **2**	precursor	time (h)	yield (%)[b]	product
1	H	**2a**	1.5	66	**3aa**
2	5-Me	**2b**	1.5	72	**3ab**
3	4-MeO	**2c**	1.5	75	**3ac**
4	4-Ph	**2d**	3	54	**3ad**
5	4,5-Me_2	**2e**	1.5	77	**3ae**
6	4,5- $-(CH_2)_3-$	**2f**	1.5	76	**3af**
7	6-Me	**2g**	3	40	**3ag**
8	3-MeO	**2h**	3	37	**3ah**
9	6-Ph	**2i**	3	30	**3ai**
10	3,4- $-(CH)_4-$	**2j**	3	33	**3aj**
11	3,4-$(MeO)_2$	**2k**	24	63	**3ak**
12	3,6-$(MeO)_2$	**2l**	3	72	**3al**

[a] The reaction was carried out in THF (1.0 mL) at 20 °C using **1a** (0.40 mmol), **2** (0.60 mmol), KF (1.2 mmol), and 18-crown-6 (1.2 mmol) in the presence of $Pd(OAc)_2$ (8.0 μmol) and *t*-OctNC (0.12 mmol). [b] Isolated yield based on **1a**.

Bissilylation of Arynes with Benzo-Condensed Six-Membered Cyclic Disilane 1b. The present reaction was found to be also applicable to a benzo-condensed six-membered cyclic disilane (1,1,2,2-tetramethyl-1,2-(2,2′-biphenylene)disilane, **1b**), giving an eight-membered disilacarbocycle, 1,6-dihydrotribenzo[1,4]-disilocine (**3b**). As depicted in Table 2, simple benzyne, 4-substituted benzynes, and even 3-substituted benzynes afforded good to high yields of the corresponding disilocines, in contrast to the reactions with **1a** (entries 1−5). Regardless of the high reactivity of **1b** in the present bissilylation, the reaction with 3-trimethylsilyl-2-pyridyl triflate (**2n**), a 2,3-pyridyne precursor, gave none of the desired product and **1b** was recovered (entry 6).

Bissilylation of Arynes with 1,2-Disilacyclopentane 1c. A simple cyclic disilane, disilacyclopentane **1c**,

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(8) We also reported palladium-catalyzed carbostannylation and bisstannylation of arynes. For carbostannylation, see: (a) Yoshida, H.; Honda, Y.; Shirakawa, E.; Hiyama, T. *Chem. Commun.* **2001**, 1880. For bisstannylation, see: (b) Yoshida, H.; Tanino, K.; Ohshita, J.; Kunai, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5052.

(9) A referee pointed out that "bisaryne" generally contains two triple bonds in the same benzene structural framework. However, we refer to an aryne bearing two triple bonds in the same molecule as "bisaryne" in this paper.

(10) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

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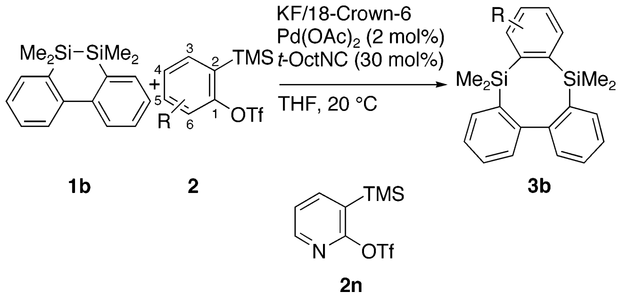
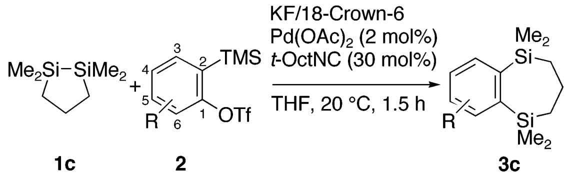
Table 2. Palladium-Catalyzed Bissilylation of Arynes with 1b[a]



entry	R in **2**	precursor	time (h)	yield (%)[b]	product
1	H	**2a**	1	81	**3ba**
2	4-Me	**2m**	1.5	63	**3bm**
3	4-MeO	**2c**	1.5	72	**3bc**
4	6-Me	**2g**	1.5	70	**3bg**
5	3-MeO	**2h**	1.5	72	**3bh**
6		**2n**	3		

[a] The reaction was carried out in THF (1.0 mL) at 20 °C using **1b** (0.40 mmol), **2** (0.60 mmol), KF (1.2 mmol), and 18-crown-6 (1.2 mmol) in the presence of $Pd(OAc)_2$ (8.0 μmol) and *t*-OctNC (0.12 mmol). [b] Isolated yield based on **1b**.

Table 3. Palladium-Catalyzed Bissilylation of Arynes with 1c[a]



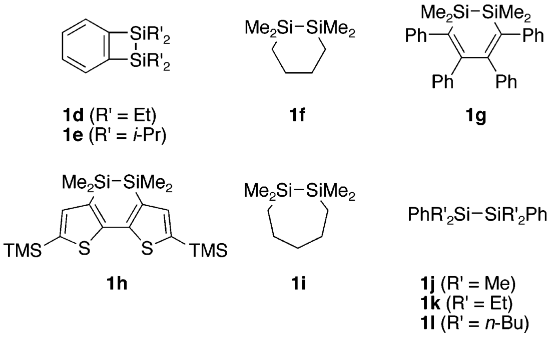
entry	R in **2**	precursor	yield (%)[b]	product
1	H	**2a**	59	**3ca**
2	5-Me	**2b**	39	**3cb**
3	4-MeO	**2c**	42	**3cc**
4	6-Me	**2g**	71	**3cg**
5	3-MeO	**2h**	73	**3ch**

[a] The reaction was carried out in THF (1.0 mL) at 20 °C using **1c** (0.40 mmol), **2** (0.60 mmol), KF (1.2 mmol), and 18-crown-6 (1.2 mmol) in the presence of $Pd(OAc)_2$ (8.0 μmol) and *t*-OctNC (0.12 mmol). [b] Isolated yield based on **1c**.

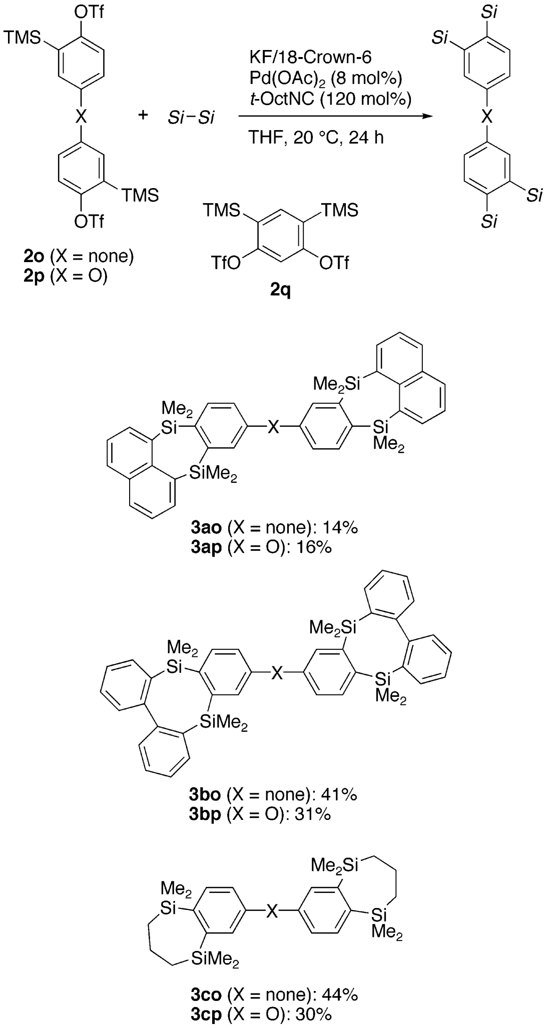
could undergo the bissilylation reaction with benzyne as well to produce tetrahydrobenzo[1,4]disilepine **3c** (Table 3). Although treatment of benzyne or 4-substituted benzyne with **1c** resulted in only moderate product yields (entries 1−3), 3-substituted aryne reacted more effectively to give the expected product in 71% or 73% yields, respectively (entries 4 and 5). At present, the reasons that the opposite reactivity trends toward substituted arynes were observed between **1a** and **1c** are unclear.

Unfortunately, a four-membered cyclic disilane, benzodisilacyclobutene (**1d** or **1e**), decomposed in the reaction with **2a**, probably through fluoride ion attack on the disilanes. No insertion product was generated in the reaction of 1,2-disilacyclohexane (**1f**), a disilacyclohexadiene (**1g**), a dithienodisilacyclohexadiene (**1h**), 1,2-disilacycloheptane (**1i**), or an acyclic disilane (**1j**−**1l**). In all cases, starting disilane did not react (Chart 1).

Chart 1



Scheme 3



Tetrasilylation Using a Bisaryne. Application of the bissilylation to arynes containing two six-membered rings with a triple bond provided tetrasilylated arenes. The reaction of **1a** with a bisaryne precursor (**2o** or **2p**) afforded a biphenyl (**3ao**) or diphenyl ether derivative (**3ap**) bearing two naphthodisilepine moieties in 14% and 16% yield, respectively, forming four carbon−silicon bonds all in one step (Scheme 3). Furthermore, higher yields (30−44%) of dibenzodisilocine- (**3bo** or **3bp**) or disilepine-condensed arenes (**3co** or **3cp**) were obtained by the use of **1b** or **1c**, whereas the reaction of **1a** with precursor **2q** did not give the insertion product at all.

X-ray Structures of 3aa and 3ba. The crystal structures of **3aa** and **3ba** were determined by X-ray diffraction studies. As described in Figure 1, the structure of **3aa** shows a seven-membered ring with a boatlike conformation. Bond angles of sp^2 carbons in its

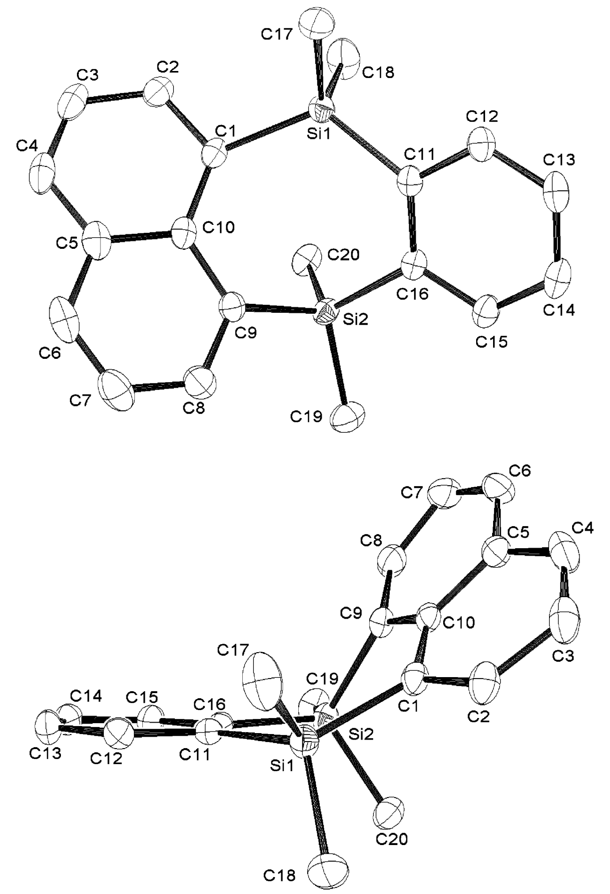


Figure 1. ORTEP drawing of the structure of **3aa**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

naphthalene moiety range from 117.7(4)° (for C5−C10−C9) to 124.0(4)° (for C1−C10−C9), being little distorted from the ideal sp^2 carbon bonding. Figure 2 shows the crystal structure of **3ba** with its eight-membered ring with a twist-boat-like conformation. The biphenyl moiety in **3ba** has turned out to be twisted with a torsion angle of 62.6(3)° (for C12−C7−C6−C1).

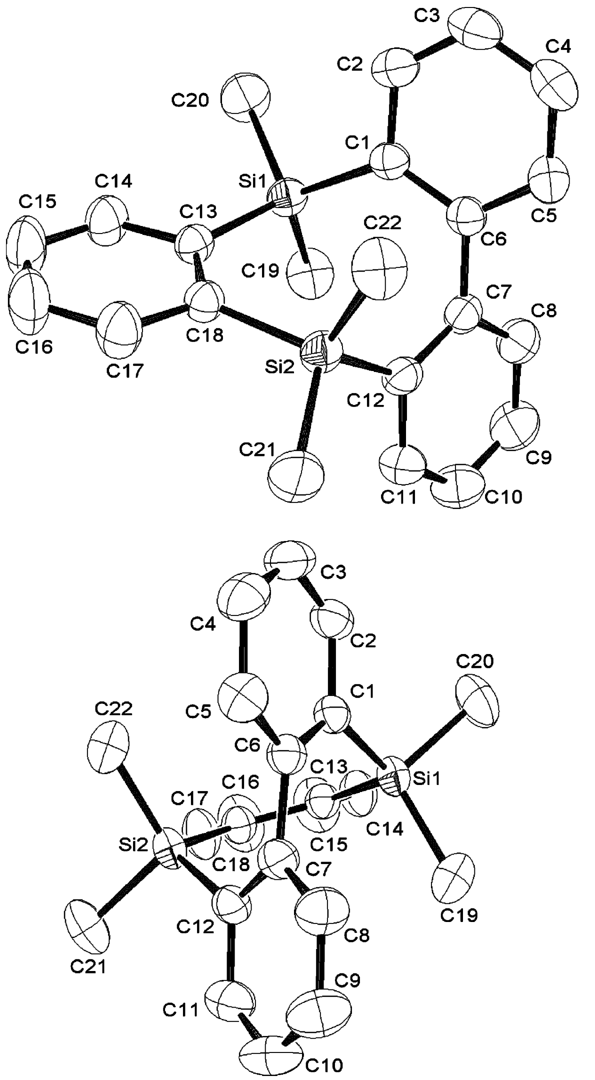
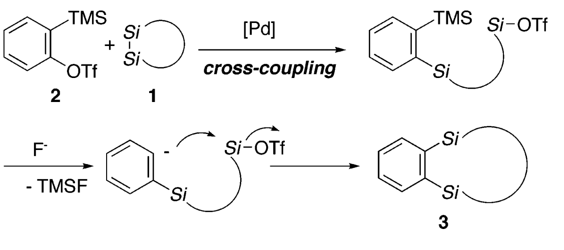


Figure 2. ORTEP drawing of the structure of **3ba**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 4



Catalytic Cycle. Because an aryl halide is known to undergo cross-coupling with a disilane in the presence of a palladium catalyst,[12] the bissilylation might proceed through a pathway that does not involve an aryne intermediate: cross-coupling of **2** at a C−OTf moiety with **1** followed by fluoride ion-induced intramolecular silicon−silicon exchange as shown in Scheme 4. Therefore, we examined the bissilylation of an unsymmetrical disilane (**1m**) with **2b** or **2m** (a 4-methylbenzyne precursor), supposing that one of the silyl moieties (SiMe$_2$ or SiEt$_2$) of **1m** is introduced into the C−OTf moiety of **2b** or **2m** preferentially according to the above-mentioned cross-coupling pathway.[13] Contrary to the supposition, both of the reactions afforded two regioisomeric products in equal ratio,[14] indicating the intermediacy of an aryne in the bissilylation (Scheme 5).

On the basis of the above results and the accepted mechanism of the palladium-catalyzed bissilylation of other carbon unsaturated compounds,[1] a plausible catalytic cycle (cycle A) is depicted in Scheme 6. First, complex **5** is formed through oxidative addition of the

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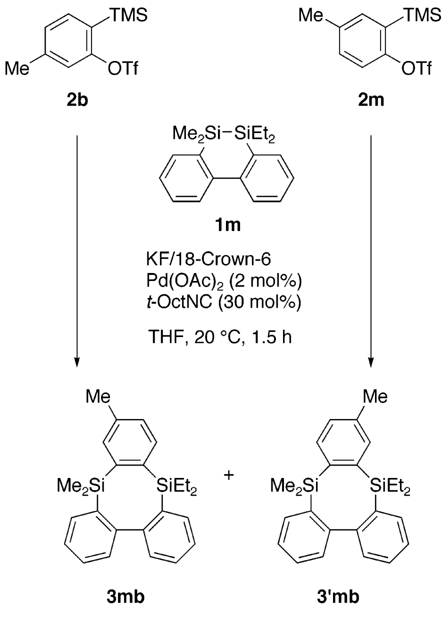
[12] (a) Matsumoto, H.; Nagashima, S.; Yoshihiro, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *85*, C1. (b) Azarian, D.; Dua, S. S.; Eabornand, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55. (c) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409. (d) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 4715. (e) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895.

[13] The palladium-catalyzed cross-coupling of benzoyl chloride with an unsymmetrical disilane, PhMe$_2$Si−SiMe$_3$, has been reported to give PhCOSiMe$_2$Ph and PhCOSiMe$_3$ in 55:21 ratio: Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974.

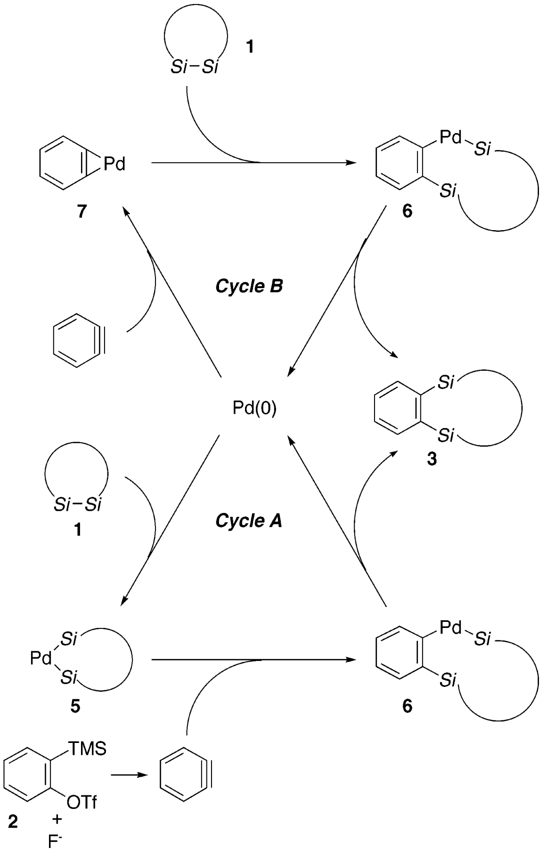
[14] Although the regioisomeric ratio of **3mb** and **3′mb** was elucidated to be 50:50 by ^{1}H NMR, we could not determine the exact position of the methyl substituent of each compound, since separation of the regioisomers was found to be difficult. Hence, the structures of **3mb** and **3′mb** have been identified on the basis of their NMR spectra, mass spectra, and elemental analysis as well as the similarity of their ^{1}H NMR spectra to that of the bissilylation product (**3ma**) arising from **1m** and benzyne (from **2a**). See Experimental Section and Supporting Information for details.

Scheme 5



2b: 33% yield (50 : 50)
2m: 23% yield (50 : 50)

Scheme 6



silicon−silicon bond of **1** to the palladium(0) complex.[15] Subsequent insertion of an in situ-generated aryne into the silicon−palladium bond of **5** produces arylpalladium complex **6**, which then undergoes reductive elimination to provide bissilylation product **3** with regeneration of the palladium(0) complex. Alternatively, formation of triphenylene as a byproduct implies that another catalytic cycle (cycle B), in which the palladium(0) complex first interacts with an aryne, is possibly operative.[16] The resulting palladacycle (**7**) furnishes bissilylation product **3** via the reaction with **1**.

Conclusion

We have demonstrated that arynes, regardless of their highly transient character, can undergo the catalytic bissilylation with cyclic disilanes in the presence of a palladium−*t*-OctNC complex to give diverse benzo-annulated disilacarbocycles straightforwardly. Moreover, the present reaction was found to be applicable to bisarynes, providing biphenyl and diphenyl ether derivatives condensed with two disilepine or disilocine moieties. The reaction using an unsymmetrical aryne and disilane produced an equal amount of regioisomeric products, which implies that the bissilylation indeed proceeds through an aryne intermediate.

Experimental Section

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{29}Si, 53.7 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz) spectrometer using residual chloroform (^{1}H) or $CDCl_3$ (^{13}C) as an internal standard and tetramethylsilane (^{29}Si) as an external standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and H-2002L columns (benzene as an eluent). Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. THF was distilled from Na/K alloy. MeCN was distilled from phosphorus pentoxide. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum-dried at 100 °C for 12 h. 1,1,2,2-Tetramethyl-1,2-(1,8-naphthylene)disilane (**1a**),[17] 1,1,2,2-tetramethyl-1,2-(2,2′-biphenylene)disilane (**1b**),[18] 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1c**),[19] 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene (**1d**),[20] 3,4-benzo-1,1,2,2-tetraisopropyl-1,2-disilacyclobut-3-ene(**1e**),[21] 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**1f**),[19] 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclo-3,5-diene (**1g**),[22] 4,4,5,5-tetramethyl-2,7-bis(trimethylsilyl)-4,5-dithieno[3,2-*c*:2′,3′-*e*]disilacyclohexadiene (**1h**),[23] 1,1,2,2-tetramethyl-1,2-disilacycloheptane (**1i**),[19] 1,1,2,2-tetraethyl-1,2-diphenyldisilane (**1k**),[24] 1,1,2,2-tetrabutyl-1,2-diphenyldisilane (**1l**),[25] 2-(trimethylsilyl)phenyl triflate (**2a**),[10] 5-methyl-2-(trimethylsilyl)phenyl triflate (**2b**),[4f] 4-methoxy-2-(trimethylsilyl)phenyl triflate (**2c**),[7] 4-phenyl-2-(trimethylsilyl)-

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phenyl triflate (**2d**),[7] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2e**),[26] 6-(trimethylsilyl)-5-indanyl triflate (**2f**),[26] 6-methyl-2-(trimethylsilyl)phenyl triflate (**2g**),[7] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**2h**),[4a] 6-phenyl-2-(trimethylsilyl)phenyl triflate (**2i**),[27] 1-(trimethylsilyl)-2-naphthyl triflate (**2j**),[4c] 3,4-dimethoxy-2-(trimethylsilyl)phenyl triflate (**2k**),[7] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**2l**),[26] 4-methyl-2-(trimethylsilyl)phenyl triflate (**2m**),[4f] and 3-trimethylsilyl-2-pyridyl triflate (**2n**)[28] were prepared according to literature procedures. Bisaryne precursors were synthesized from the corresponding halogenated phenols ($ArX_2(OH)_2$: 3,3′-dibromo-4,4′-biphenol[29] for **2o**; 3,3′-dibromo-4,4′-dihydroxydiphenyl ether[29] for **2p**; 4,6-dichlororesorcinol (commercially available) for **2q**) in a manner similar to the preparation of **2a**.

Preparation of Disilane 1m. 1,1-Diethyl-2,2-dimethyl-1,2-(2,2′-biphenylene)disilane (**1m**) was prepared from 2,2′-dilithiobiphenyl and 1,2-dichloro-1,1-diethyl-2,2-dimethyldisilane in a manner similar to the preparation of **1b**. **1m**: ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 0.77 (q, J = 7.6 Hz, 4 H), 0.91 (t, J = 7.6 Hz, 6 H), 7.23−7.29 (m, 2 H), 7.39−7.49 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ −4.4, 2.6, 8.8, 126.4, 126.5, 129.79, 129.83, 129.9, 133.0, 133.9, 134.0, 135.7, 147.7, 147.8; ^{29}Si NMR ($CDCl_3$) δ −28.8, −20.0. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.98; H, 8.19.

Bissilylation of Arynes. General Procedure. A THF solution (1.0 mL) of 1,1,3,3-tetramethylbutyl isocyanide (0.017 g, 0.12 mmol), $Pd(OAc)_2$ (1.8 mg, 8.0 μmol), and 18-crown-6 (0.32 g, 1.2 mmol) was degassed by three freeze−thaw cycles. To this solution were added a disilane (0.40 mmol), an aryne precursor (0.60 mmol), and KF (0.070 g, 1.2 mmol), and the resulting mixture was stirred at 20 °C. After the time specified in tables, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Silica gel column chromatography (hexane as an eluent) followed by gel permeation chromatography (benzene as an eluent) gave the corresponding product. Analytical data for **3aa**−**3al**, **3ba**, **3bg**, **3bh**, **3bm**, and **3ca** have been shown in our previous paper[7] as Supporting Information, and the others are listed below.

3-Methoxy-1,1,6,6-tetramethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3bc). 3bc was isolated in 72% yield as a colorless solid: ^1H NMR ($CDCl_3$) δ −0.76 (s, 3 H), −0.74 (s, 3 H), 0.61 (s, 3 H), 0.63 (s, 3 H), 3.82 (s, 3 H), 6.88 (dd, J = 8.2, 2.7 Hz, 1 H), 7.21 (d, J = 2.7 Hz, 1 H), 7.32−7.45 (m, 6 H), 7.59 (d, J = 7.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ −1.0, −0.7, 0.2, 0.4, 54.9, 112.4, 120.8, 126.73, 126.74, 128.5, 128.6, 129.1, 129.2, 135.4, 135.5, 135.7, 137.3, 137.4, 137.9, 148.8, 151.0, 151.1, 159.2; ^{29}Si NMR ($CDCl_3$) δ −8.2, −7.4. Anal. Calcd for $C_{23}H_{26}OSi_2$: C, 73.74; H, 7.00. Found: C, 73.45; H, 7.04.

1,1,3,6,6-Pentamethyl-6,7,8,9-tetrahydro-(1*H*)-benzo[*b*][1,4]disilepine (3cb). 3cb was isolated in 39% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 0.26 (s, 6 H), 0.95−0.99 (m, 4 H), 1.90 (quintet, J = 6.6 Hz, 2 H), 2.34 (s, 3 H), 7.15 (d, J = 7.5 Hz, 1 H), 7.40 (s, 1 H), 7.50 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.24, −0.18, 18.1, 21.5, 29.7, 128.6, 134.6, 135.3, 137.2, 143.2, 146.9; ^{29}Si NMR ($CDCl_3$) δ −1.0, −0.9. Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 10.19. Found: C, 67.73; H, 10.18.

3-Methoxy-1,1,6,6-tetramethyl-6,7,8,9-tetrahydro-(1*H*)-benzo[*b*][1,4]disilepine (3cc). 3cc was isolated in 42% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H), 0.26 (s, 6 H), 0.96 (q, J = 7.0 Hz, 4 H), 1.90 (quintet, J = 7.0 Hz, 2 H), 3.80 (s, 3 H), 6.86 (dd, J = 8.0, 2.5 Hz, 1 H), 7.15 (d, J = 2.5 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.4, −0.1, 18.0, 18.1, 18.2, 54.8, 112.4, 120.9, 136.1, 137.5, 148.9, 159.0; ^{29}Si NMR ($CDCl_3$) δ −1.3, −0.3. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.16. Found: C, 63.48; H, 9.15.

1,1,2,6,6-Pentamethyl-6,7,8,9-tetrahydro-(1*H*)-benzo[*b*][1,4]disilepine (3cg). 3cg was isolated in 71% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.30 (s, 6 H), 0.38 (s, 6 H), 1.05−1.14 (m, 4 H), 1.92 (quintet, J = 7.0 Hz, 2 H), 2.53 (s, 3 H), 7.15 (d, J = 7.5 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 1 H), 7.47 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.4, 0.6, 16.8, 17.5, 19.0, 24.2, 127.4, 130.3, 132.2, 143.8, 146.0, 148.6; ^{29}Si NMR ($CDCl_3$) δ −2.9, −1.6. Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.64; H, 9.72.

2-Methoxy-1,1,6,6-tetramethyl-6,7,8,9-tetrahydro-(1*H*)-benzo[*b*][1,4]disilepine (3ch). 3ch was isolated in 73% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.26 (s, 12 H), 1.007 (t, J = 7.2 Hz, 2 H), 1.010 (t, J = 7.2 Hz, 2 H), 1.86 (quintet, J = 7.2 Hz, 2 H), 3.78 (s, 3 H), 6.80 (d, J = 8.2 Hz, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 7.30 (t, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.8, 0.4, 17.1, 17.7, 18.6, 54.9, 110.0, 127.3, 129.3, 135.2, 149.7, 164.4; ^{29}Si NMR ($CDCl_3$) δ −2.8, −1.8. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.16. Found: C, 63.51; H, 9.09.

1,1-Diethyl-6,6-dimethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3ma). 3ma was isolated in 28% yield as a colorless solid: ^1H NMR ($CDCl_3$) δ −0.70 (s, 3 H), −0.63 to −0.54 (m, 1 H), −0.22 to −0.13 (m, 1 H), 0.54 (t, J = 7.6 Hz, 3 H), 0.68 (s, 3 H), 1.03 (t, J = 7.6 Hz, 3 H), 1.16−1.26 (m, 1 H), 1.38−1.47 (m, 1 H), 7.34−7.40 (m, 4 H), 7.44−7.47 (m, 4 H), 7.62−7.72 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −0.9, 0.5, 3.7, 4.0, 7.6, 7.7, 126.7, 126.8, 127.6, 127.8, 128.4, 128.9, 129.0, 129.1, 134.2, 134.7, 135.15, 135.22, 135.9, 137.9, 145.2, 147.3, 151.1, 151.7; ^{29}Si NMR ($CDCl_3$) δ −8.0, −3.4; MS m/z 372 (M^+). Anal. Calcd for $C_{24}H_{28}Si_2$: C, 77.35; H, 7.57. Found: C, 77.31; H, 7.63.

A Mixture of 1,1-Diethyl-4,6,6-trimethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3mb) and 1,1-Diethyl-3,6,6-trimethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]disilocine (3′mb). The ratio of two isomers was determined to be 50:50 by integration of SiMe in ^1H NMR. For the mixture: ^1H NMR ($CDCl_3$) δ −0.74 (s, 3 H, $SiCH_3$), −0.73 (s, 3 H, $SiCH_3$), −0.69 to −0.56 (m, 2 H, $SiCH_2CH_3$), −0.26 to −0.16 (m, 2 H, $SiCH_2CH_3$), 0.50−0.55 (m, 6 H, $SiCH_2CH_3$), 0.64 (s, 3 H, $SiCH_3$), 0.65 (s, 3 H, $SiCH_3$), 0.99−1.03 (m, 6 H, $SiCH_2CH_3$), 1.12−1.24 (m, 2 H, $SiCH_2CH_3$), 1.34−1.46 (m, 2 H, $SiCH_2CH_3$), 2.37 (s, 6 H, $ArCH_3$), 7.16−7.22 (m, 2 H, ArH), 7.32−7.64 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) δ −0.9, −0.8, 0.5, 3.70, 3.73, 4.1, 7.59, 7.62, 7.7, 21.51, 21.54, 126.67, 126.69, 126.74, 126.8, 128.41, 128.44, 128.5, 128.7, 128.89, 128.93, 128.94, 128.98, 129.02, 134.4, 134.8, 135.16, 135.22, 135.4, 135.6, 135.9, 136.0, 137.1, 137.4, 137.9, 138.1, 141.5, 143.7, 145.2, 147.3, 151.09, 151.14, 151.7, 151.8; ^{29}Si NMR ($CDCl_3$) δ −8.2, −8.1, −3.6, −3.5; MS m/z 386 (M^+). Anal. Calcd for $C_{25}H_{30}Si_2$: C, 77.65; H, 7.82. Found: C, 77.45; H, 7.76.

Tetrasilylation Using Bisarynes. General Procedure. To a THF solution (2.0 mL) of 1,1,3,3-tetramethylbutyl isocyanide (0.050 g, 0.36 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), 18-crown-6 (0.32 g, 1.2 mmol), a disilane (1.2 mmol), and a bisaryne precursor (0.3 mmol) was added KF (0.070 g, 1.2 mmol), and the resulting mixture was stirred at 20 °C for 24 h. The mixture was passed through a short column of silica gel (benzene as an eluent) and concentrated. Gel permeation chromatography (benzene as an eluent) gave the corresponding product.

9,9′-Bi[7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiadenyl] (3ao). 3ao was isolated in 14% yield as a colorless solid: ^1H NMR ($CDCl_3$) δ 0.64 (s, 12 H), 0.65 (s, 12 H), 7.47 (td, J = 7.8, 1.5 Hz, 4 H), 7.66 (dd, J = 7.6, 1.9 Hz, 2 H), 7.85 (d, J = 7.8 Hz, 6 H), 7.93 (d, J = 7.8 Hz, 4 H), 7.97 (d, J = 1.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.8, 2.1, 124.3, 127.2, 127.3, 130.96, 130.99, 132.6, 133.6, 134.3, 135.3, 135.4, 139.1, 139.2, 140.8, 141.2, 144.1, 145.8; ^{29}Si NMR ($CDCl_3$) δ −7.3, −7.1; HRMS calcd for $C_{40}H_{42}Si_4$, M^+, 634.2364; found, m/z 634.2369.

Bis(7,7,12,12-tetramethyl-7,12-dihydro-7,12-disilapleiaden-9-yl) Ether (3ap). 3ap was isolated in 16% yield as a

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colorless solid: ^{1}H NMR (CDCl$_3$) δ 0.54 (s, 12 H), 0.57 (s, 12 H), 6.99 (dd, J = 8.2, 2.7 Hz, 2 H), 7.42−7.47 (m, 6 H), 7.68 (d, J = 8.0 Hz, 2 H), 7.83 (d, J = 7.5 Hz, 4 H), 7.87 (d, J = 7.0 Hz, 2 H), 7.90 (d, J = 7.0 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 1.8, 2.1, 118.4, 124.2, 124.3, 124.4, 130.95, 131.04, 133.6, 135.3, 135.7, 138.9, 139.2, 139.3, 140.7, 147.8, 157.1; ^{29}Si NMR (CDCl$_3$) δ −7.4, −7.1. Anal. Calcd for $C_{40}H_{42}OSi_4$: C, 73.79; H, 6.50. Found: C, 73.76; H, 6.52.

3,3′-Bi[1,1,6,6-tetramethyl-1,6-dihydrotribenzo[*b,e,g*]-[1,4]disilocinyl] (3bo). 3bo was isolated in 41% yield as a colorless solid: ^{1}H NMR (CDCl$_3$) δ −0.80 (s, 6 H), −0.79 (s, 6 H), 0.57 (s, 12 H), 7.24−7.35 (m, 12 H), 7.45−7.55 (m, 6 H), 7.64 (d, J = 7.7 Hz, 2 H), 7.75−7.77 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.8, 0.3, 126.8, 128.3, 128.6, 129.3, 133.1, 133.2, 134.6, 135.50, 135.54, 137.4, 137.5, 140.7, 140.8, 145.65, 145.68, 147.5, 151.11, 151.14; ^{29}Si NMR (CDCl$_3$) δ −7.7, −7.5; HRMS calcd for $C_{44}H_{46}Si_4$, M$^+$, 686.2677; found, *m/z* 686.2663.

Bis(1,1,6,6-tetramethyl-1,6-dihydrotribenzo[*b,e,g*][1,4]-disilocin-3-yl) Ether (3bp). 3bp was isolated in 31% yield as a colorless solid: ^{1}H NMR (CDCl$_3$) δ −0.71 (brs, 12 H), 0.59 (s, 3 H), 0.61 (s, 3 H), 0.64 (s, 6 H), 6.95 (dt, J = 8.2, 2.7 Hz, 2 H), 7.35−7.42 (m, 14 H), 7.61−7.64 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ −1.0, −0.7, 0.2, 0.5, 117.69, 117.73, 124.6, 124.7, 126.8, 128.6, 128.7, 129.2, 129.3, 135.4, 135.5, 135.8, 137.2, 137.7, 140.9, 149.5, 151.0, 151.2, 156.6, 156.7; ^{29}Si NMR (CDCl$_3$) δ −8.0, −7.5; HRMS calcd for $C_{44}H_{46}OSi_4$, M$^+$, 702.2626; found, *m/z* 702.2639.

3,3′-Bi[1,1,6,6-tetramethyl-6,7,8,9-tetrahydro-(1*H*)-benzo-[*b*][1,4]disilepinyl] (3co). 3co was isolated in 44% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.29 (s, 24 H), 0.99−1.03 (m, 8 H), 1.89−1.96 (m, 4 H), 7.52 (dd, J = 7.8, 2.1 Hz, 2 H), 7.67 (d, J = 7.8 Hz, 2 H), 7.77 (d, J = 2.1 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.3, −0.2, 18.0, 18.1, 126.6, 133.5, 134.9, 140.5, 145.7, 147.5; ^{29}Si NMR (CDCl$_3$) δ −0.6, −0.3. Anal. Calcd for $C_{26}H_{42}Si_4$: C, 66.68; H, 9.07. Found: C, 66.58; H, 9.32.

Bis(1,1,6,6-tetramethyl-6,7,8,9-tetrahydro-(1*H*)-benzo-[*b*][1,4]disilepin-3-yl) Ether (3cp). 3cp was isolated in 30% yield as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 12 H), 0.26 (s, 12 H), 0.97−1.01 (m, 8 H), 1.92 (quintet, J = 6.6 Hz, 4 H), 6.91 (dd, J = 8.1, 2.6 Hz, 2 H), 7.29 (d, J = 2.6 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.4, −0.1, 17.9, 18.0, 18.1, 117.6, 124.8, 136.1, 140.8, 149.5, 156.4; ^{29}Si NMR (CDCl$_3$) δ −0.9, −0.2. Anal. Calcd for $C_{26}H_{42}OSi_4$: C, 64.66; H, 8.77. Found: C, 64.42; H, 8.77.

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Supporting Information Available: ^{1}H NMR spectra of **3ma** and a mixture of **3mb** and **3′mb**. Full crystallographic data for **3aa** and **3ba** including tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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