Synthesis and Reactivity of Several Stable 1-Silaallenes

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Three stable 1-silapropadienes **1a**−**c** were prepared by the intermolecular addition of organolithium reagents at the carbon−carbon triple bond of fluoroalkynylsilanes **3a**,**b** followed by LiF elimination. The structure of **1a** and of the intermediate α-lithiated fluorosilane **2a** were determined by X-ray diffraction. The chemical behavior of 1-silapropadienes **1a**−**c** differs greatly depending on the substituents on the silicon atom. When two triisopropylphenyl groups were present (**1a**), typical addition reactions of the Si=C double bond were observed. Thermolysis of **1a** yielded benzosilacyclobutene **7**. For the more hindered 1-silapropadienes **1b** and **1c**, no reaction was observed with dioxygen, benzaldehyde, 2,3-dimethylbutadiene, or trimethylchlorosilane at room temperature. However, thermolysis of **1b** or treatment with excess ethanol under neutral or acidic conditions produced **8b**, the product of an intramolecular insertion of the Si=C double bond into an adjoining primary C−H bond of one *tert*-butyl group in an ortho-position of the supermesityl substituent. In the presence of EtOD and catalytic D_2SO_4, this reaction occurred very rapidly at −78 °C with over 95% incorporation of deuterium in the product.

Introduction

Compounds containing cumulated double bonds to silicon, based on their unique geometric and electronic structure, are particularly interesting and important molecules. Both 2-silaallenes $(R_2C=Si=CR_2)$[1,2] and 1-silaallenes $(R_2Si=C=CR_2)$[3−6] have been proposed as transient species in pyrolysis or photolysis reactions for several years. Whereas 2-silaallenes are still almost unknown, some progress has been made in the 1-silaallene chemistry. Very recently, a ruthenium complex of a 1-silaallene has been reported,[7] and a transient 1-silaallene derivative could be detected directly in a laser flash photolysis study.[8] In 1993, we reported for the first time the synthesis and structure of a stable, extremely hindered fluorenylidenesilene, Mes*(1-adamantyl)Si=C=C(fluorenyl) (**1d**), which was generated via an intramolecular nucleophilic addition−elimination reaction initiated by metalation of the biphenyl group[9] (Scheme 1, a). However, since sterically hindered fluorenylidenesilenes can be prepared only by a multistep synthesis with great efforts, the chemical behavior of 1-silapropadienes has hardly been investigated. An analogous but much easier route to new members of this

novel class of compounds with cumulated silicon−carbon double bonds is the intermolecular addition of organolithium compounds at sterically hindered haloalkynylsilanes followed by metal halide elimination (Scheme 1, b). This route is related to the addition−elimination reaction of chlorovinylsilanes first described by Jones[10] and later widely used in the synthesis of silenes[11−14] and germenes.[15]

We report here the synthesis and some aspects of the reactivity of stable 1-silapropadienes **1a**−**c**, which were obtained in high yields by the intermolecular addition of organolithium compounds at the carbon−carbon triple bond of phenylethynylfluorosilanes **3a**,**b** followed by lithium fluoride elimination of the intermediate vinyllithium compounds **2a**−**c** (Scheme 1, b). Moreover, for the first time we were able to characterize an α-lithiated fluorosilane species **2a**, which is formed as an intermediate in this reaction, by single-crystal X-ray diffraction. This class of compounds plays a key role in the synthesis of doubly bonded silicon compounds via the salt elimination route and has been widely used in the synthesis of silenes,[16,17] iminosilanes,[18−20] and several phospha- and arsasilenes.[21,22] In contrast to the well-characterized lithium salts of the group I5 element

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.
(1) Bertrand, G.; Manuel, G.; Mazerolles, P. *Tetrahedron* **1978**, *34*, 1951.
(2) Urbanov, M.; Volnina, E. A.; Gusel'nikov, L. E.; Bastl, Z.; Pola, J. *J. Organomet. Chem.* **1996**, *509*, 73.
(3) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumuda, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872.
(4) Ishikawa, M.; Matsuzawa, S.; Sugisawa, H.; Yano, F.; Kamitori, S.; Higuchi, T. *J. Am. Chem. Soc.* **1985**, *107*, 7706.
(5) Ishikawa, M.; Yuzuriha, Y.; Horio, T.; Kunai, A. *J. Organomet. Chem.* **1991**, *402*, C20.
(6) Ishikawa, M.; Horio, T.; Yuzuriha, Y.; Kunai, A.; Tsukihara, T.; Naitou, H. *Organometallics* **1992**, *11*, 597.
(7) Yin, J.; Klosin, J.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 3298.
(8) Kerst, C.; Rogers, C. W.; Ruffolo, R.; Leigh, W. J. *J. Am. Chem. Soc.* **1997**, *119*, 466.
(9) Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

(10) Jones, P. R.; Lim, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 2013.
(11) (a) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55. (b) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494.
(12) Auner, N. In *Organosilicon Chemistry: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1994; pp 103−13 and references therein.
(13) Yoo, B. R.; Jung, I. N.; Lee, M. E.; Kim, C. H. *Bull. Kor. Chem. Soc.* **1991**, *12*, 517.
(14) (a) Delpon-Lacaze, G.; Couret, C. *J. Organomet. Chem.* **1994**, *480*, C14. (b) Delpon-Lacaze, G.; de Battisti, C.; Couret, C. *J. Organomet. Chem.* **1996**, *514*, 59.
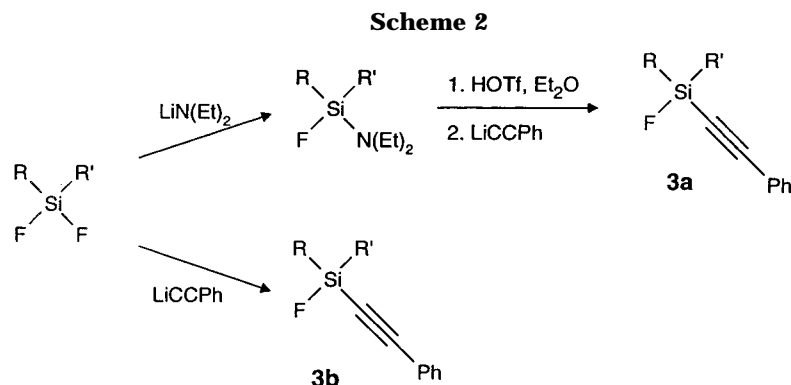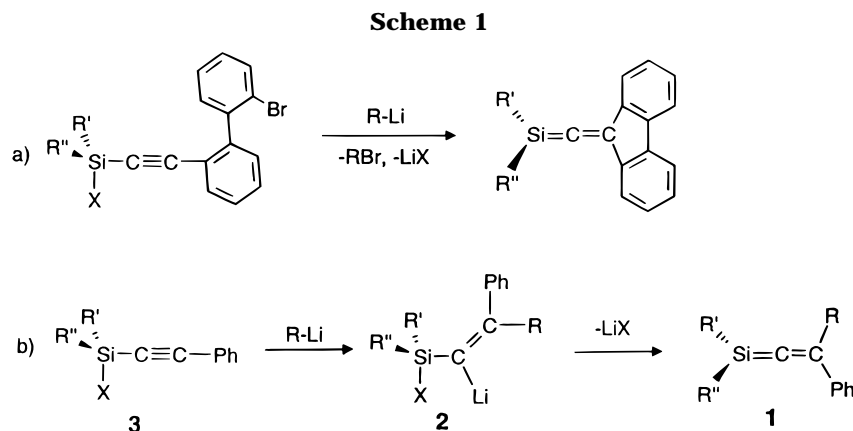(15) Couret, C.; Escudié, J.; Delpon-Lacaze, G.; Satgé, J. *Organometallics* **1992**, *11*, 3176.
(16) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.
(17) Wiberg, N.; Wagner, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 32.
(18) Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649.
(19) Walter, S.; Klingebiel, U. *Coord. Chem. Rev.* **1994**, *130*, 481.

Scheme 1

Scheme 2

3a R, R' = 2,4,6-tri-isopropylphenyl (Tip)

3b R = t-Bu, R' = 2,4,6-tri-t-butylphenyl (Mes*)

fluorosilanes, very little is known about the corresponding lithium derivatives of carbofluorosilanes. On the basis of trapping experiments, α-lithium adducts have been proposed as transient intermediates in the addition of organolithium compounds at the carbon−carbon double bonds of chlorovinylsilanes, but could never be observed directly.[23]

Results and Discussion

Preparation of Phenylethynylfluorosilanes 3a and 3b. Starting compounds for the synthesis of 1-silapropadienes **1a**−**c** are the sterically hindered alkynylfluorosilanes **3a**[24] and **3b**. **3a** could not obtained pure by direct treatment of 1,1-bis(2,4,6-triisopropylphenyl)difluorosilane[25] with 1 equiv of phenylethynyl-

lithium, since both mono- and disubstitution took place regardless of the reaction conditions. However, **3a** was obtained in high yields by using the triflate route,[26,27] in which **3a** was formed selectively in diethyl ether via the aminosilane and via the corresponding silyltriflate ethynylfluorosilane after addition of phenylethynyl-lithium (Scheme 2). **3a** exhibits a doublet at δ −25.5 ppm in the ^{29}Si NMR with a Si−F coupling constant of 279.5 Hz. Two characteristic doublets in the ^{13}C NMR at 92.5 and 107.7 ppm with C−F coupling constants of 28 and 4.5 Hz were assigned to the two carbon atoms of the alkynyl group.

The more hindered fluoroalkynylsilane **3b** could be prepared by direct addition of phenylethynyllithium to *tert*-butyl(2,4,6-tri-*tert*-butylphenyl)difluorosilane[25] in refluxing THF in reasonable yields. It was clearly identified by NMR and mass spectroscopy. In analogy to **3a**, the two carbons of the triple bond resonate as doublets at 92.5 and 107.6 ppm with C−F coupling constants of 27 and 4.5 Hz. In the ^{29}Si NMR, **3b** exhibits a doublet at δ −12.1 ppm with an Si−F coupling constant of $J = 273.4$ Hz.

Synthesis and Reaction of 2a. Addition of 1 equiv of *t*-BuLi to a solution of **3a** in diethyl ether at −78 °C resulted in the appearance of a yellow-orange color after warming up to 0 °C. In a very smooth reaction α-lithio adduct **2a** was formed almost quantitatively. In the ^{29}Si NMR spectrum, the doublet of the starting material

(20) Hemme, I.; Klingebiel, U. In *Multiply Bonded Main Group Metals and Metalloids*; West, R., Stone, F. G. S., Eds.; Academic Press, Inc.: San Diego, CA, 1996.

(21) Driess, M.; Pritzkow, H.; Rell, S.; Winkler, U. *Organometallics* **1995**, *15*, 1845.

(22) Driess, M. In *Multiply Bonded Main Group Metals and Metalloids*; West, R., Stone, F. G. S., Eds.; Academic Press, Inc.: San Diego, CA, 1996.

(23) Auner, N.; Wolff, A. *Chem. Ber.* **1993**, *126*, 575.

(24) Wiberg, N.; Wagner, G. *Chem. Ber.* **1985**, *119*, 1455. (a) X-ray structure analysis of **3a**: (C$_{38}$H$_{51}$SiF), M_r = 554.88, monoclinic, *Cc*, *a* = 10.0931(2) Å, *b* = 22.1859(4) Å, *c* = 15.5723(3) Å, β = 91.839(2)°, *V* = 3485.22(12) Å³, *Z* = 4, ρ(calcd) = 1.057 Mg m⁻³, *F*(000) = 1208, λ = 0.710 73 Å, θ = 133(2) K. The crystal was a colorless transparent prism (crystal size 0.44 × 0.36 × 0.10 mm). Intensity data were collected by the ψ scan method (2.54° < θ < 29.16°) on a Siemens P4 diffractometer equipped with a CCD area detector. From a total of 8474 measured data, 5479 were independent (R_{int} = 0.0301). The structure was solved by direct methods and refined by a full-matrix least-squares method on F^2 using the SHELXTL+ program. R1(F_{obs}) = 0.0471, wR2(F^2_{all}) = 0.1307, *S* = 1.066 for 5479 data and 380 variables. The thermal ellipsoids were drawn at the 50% probability level.

(25) Nakadaira, Y.; Oharu, K.; Sakurai, H. *J. Organomet. Chem.* **1986**, *309*, 247.

(26) Uhlig, W.; Tretner, C. *J. Organomet. Chem.* **1994**, *467*, 31.

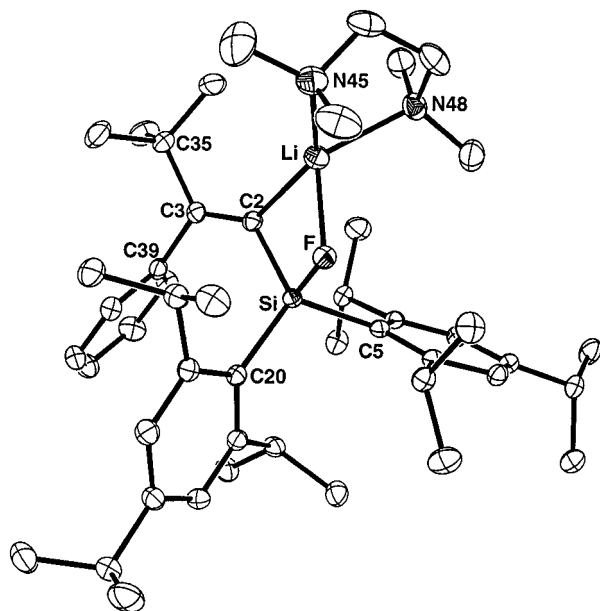(27) Uhlig, W. *Chem. Ber.* **1996**, *129*, 733.

Figure 1. Molecular structure of lithium salt **2a**. Thermal ellipsoid drawing with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si−C(2) 1.8217(12), Si−F 1.6924(7), C(2)−Li 2.184(3), F−Li 2.047(2), C(2)−C(3) 1.353(4), Si−Li 2.771(2), Si−C(5) 1.9218(12), Si−C(20) 1.9200(12), N(45)−Li 2.153(3), N(48)−Li 2.166(3), Si−C(2)−Li 87.07(8), Si−F−Li 95.16(7), F−Si−C(2) 96.42(5), F−Si−Li 47.38(5), C(2)−Si−Li 51.90(6), F−Li−C(2) 76.50(8), C(3)−C(2)−Si 133.05(10), C(3)−C(2)−Li 136.75(11).

disappeared completely and a new doublet was observed at δ +1.2 ppm with a significantly smaller Si−F coupling constant of 202.6 Hz. **2a** was clearly identified by trapping reactions and by single-crystal X-ray diffraction. The thermal ellipsoid drawing of the X-ray structure of **2a**·1TMEDA is depicted in Figure 1. In the solid state, **2a** is a monomer with the lithium atom chelated by one tetramethylethylenediamine (TMEDA) molecule. The *t*-BuLi added stereo- and regiospecifically to the carbon−carbon triple bond of **3a** to form the vinyllithium compound **2a** in the sterically less-hindered *cis* conformation. The central unit is a folded four-membered (SiCLiF)-ring with out-of-plane angles of 23.1° between the C(2)−Si−F and F−Li−C(2) planes and 23.8° between the Si−C(2)−Li and Li−F−Si planes. Steric repulsion between the bulky substituents at the silicon atom, the carbon atom C(3), and the TMEDA ligand are probably the main reason for the folding. The vinylic C(2) carbon atom is slightly pyramidalized (sums of the valence angles at C(2) = 356.9°), whereas the other carbon atom of the vinylic double bond (C(3)) is planar.

The Li−F distance is 2.047(2) Å, and the Si−C(2) bond length is 1.822(1) Å, which is typical for a silicon atom bonded to a carbon with a carbanionic character (1.79−1.82 Å).[28] A particularly interesting structural feature of **2a** is the remarkably short Si−Li distance of 2.771(2) Å, which is only 0.07−0.15 Å longer than that of an ionic Si−Li bond.[28] One TMEDA ligand seems to be unable to saturate the lithium atom electronically. Owing to the bulky substituents at the silicon and carbon atom
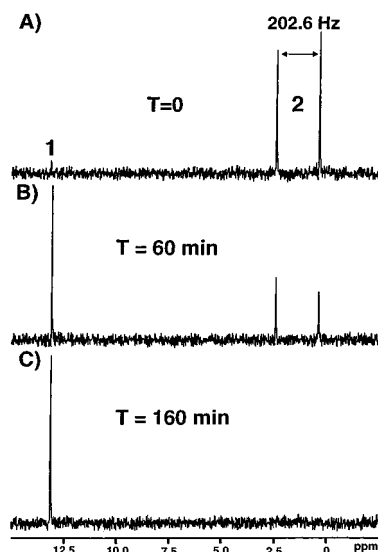
C(3), the limited space around the lithium prohibits the coordination of a second donor molecule like TMEDA. The lack of electronic saturation of the lithium atom can, thus, only be compensated by strong Li−Si interactions. Both the lithium and silicon atom can reasonably be considered as five-coordinate. As an effect of the strong coordination between the lithium and silicon atoms, the Si−F bond is unusually long (1.6924(7) Å), which also corresponds with a significantly smaller Si−F coupling constant in **2a** compared to **3a**. Similar observations were made for the lithium derivatives of aminofluorosilanes, which are all characterized by a smaller Si−F coupling constant relative to their precursor molecules.[29,30]

Ethereal solutions of **2a** are instantly decolorized on addition of protic reagents like alcohols or water. Regardless of the protic compound used in this reaction, the sole product is fluorovinylsilane **4**, which was clearly identified by multinuclear NMR and mass spectroscopy (Scheme 3). In the ^{29}Si NMR spectrum, a doublet at δ −7.2 ppm with an Si−F coupling constant of 295.4 Hz was found for **4**. A characteristic feature in the ^{1}H NMR is the signal of a vinylic proton, which resonates as a doublet at 6.13 ppm with a H−F coupling constant of 16.2 Hz. It is absent, as expected, when deuterated alcohols are used as trapping reagents.

Synthesis and Structure of 1-Silapropadiene 1a. Lithium salt **2a** is stable in diethyl ether below 0 °C and can be stored at that temperature without decomposition even for several weeks. However, when an ethereal solution of **2a** was allowed to warm up to room temperature, within in a few hours 1-silapropadiene **1a** was formed as a single product (Scheme 3).[31] This reaction was monitored by ^{29}Si NMR spectroscopy (Figure 2). The replacement of the doublet of **2a** at 1.2 ppm in the ^{29}Si NMR by a new singlet at +13.1 ppm

Figure 2. ^{29}Si NMR spectra showing the progressive lithium fluoride elimination of **2a** at room temperature. The new resonance at 13.1 ppm formed in this reaction stems from 1-silapropadiene, **1a**.

(28) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; Part 1, Chapter 3.

(29) Stalke, D.; Keweloh, N.; Klingebiel, W.; Noltemeyer, M.; Sheldrick, G. M. *Z. Naturforsch.* **1987**, *42b*, 1237.

(30) Klingebiel, U.; Stalke, D.; Vollbrecht, S. *Z. Naturforsch.* **1992**, *47b*, 27.

(31) West, R.; Trommer, M.; Powell, D. R.; Miracle, G. E. *Abstracts of Papers*, 30th Organosilicon Symposium, London, Ontario, May 30−31, 1997; p A-21.

Scheme 3

Tip = 2,4,6-tri-isopropylphenyl
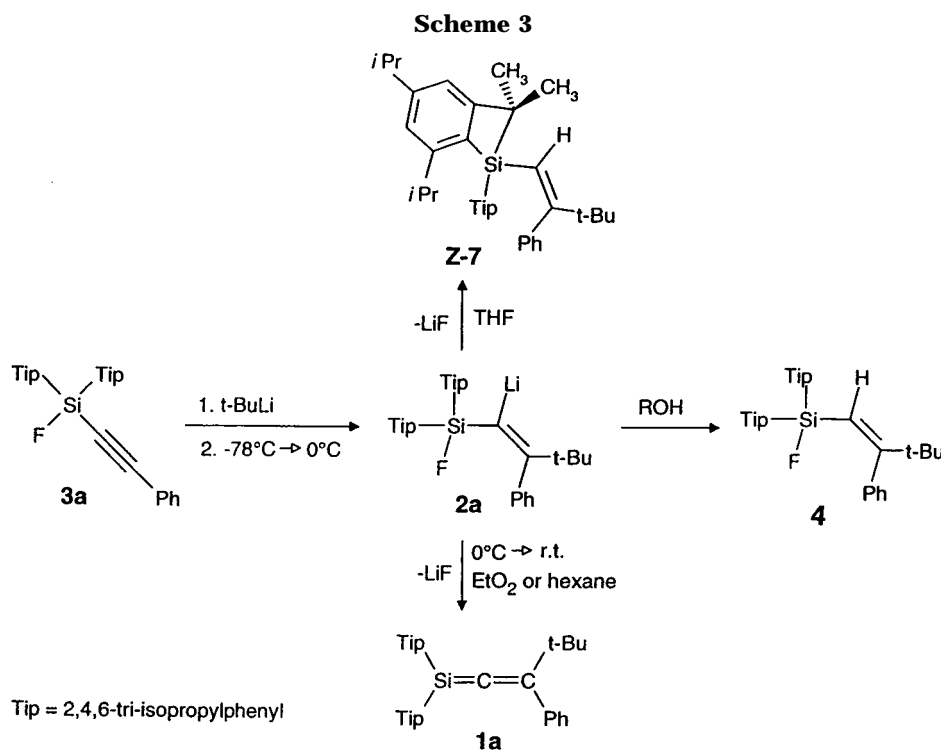
can only be rationalized by the loss of the fluoride atom in **2a**. Further evidence for the elimination of lithium fluoride was obtained from the ^{19}F NMR spectrum, in which the signal at 32.6 ppm assigned to **2a** had disappeared completely. The rate of the lithium fluoride elimination was significantly increased when the diethyl ether as the solvent of **2a** was replaced by much more nonpolar solvents like hexane. In this case, the formation of **1a** was complete within seconds at room temperature, presumably due to an increased destabilization of **2a** by the nonpolar solvent.

A thermal ellipsoid diagram of **1a** from single-crystal X-ray diffraction is shown in Figure 3. The geometry of the central Si−C1−C2 skeleton in **1a** is very similar to that found for fluorenylidenesilene **1d**.[9] The length of the Si=C double bond is 1.693(3) Å, the shortest bond distance reported for a Si=C double bond to date. A short Si=C distance is expected since the silicon is bonded to an sp-hybridized carbon atom. The slightly longer Si=C distance in **1d**, 1.704 Å, probably reflects greater steric repulsion between the substituents in that molecule. The C=C double bond distance is 1.325 Å, and the Si−C1−C2 bond angle is 172.0(3)°, compared with 173.5° for **1d**. The silicon atom in **1a** is slightly pyramidalized (sums of the valence angles at Si = 357.2(2)°), whereas the terminal sp[2] carbon is essentially planar. As a consequence of the pyrmidalization at the silicon atom, the C13−Si−C28 plane forms an angle of 163.8° with the Si−C1 double bond.

The most characteristic feature in the ^{13}C NMR spectrum of **1a** is the presence of a chemical shift at +223.6 ppm, which is assigned to the central carbon atom of the cumulated double bond. This is in good agreement with our first isolated 1-silaallene which is characterized by a strongly deshielded carbon atom at

225.7 ppm.[9] The chemical shift of the silicon atom in **1a**, +13.1 ppm, is significantly upfield compared to all known doubly-bonded silicon atoms in silenes.[32] An upfield shift as a result of complexation with THF[33] or other Lewis bases can be excluded, since neither the addition of THF nor the addition of dry pyridine to a solution of **1a** in C_6D_6 influences the chemical shift of
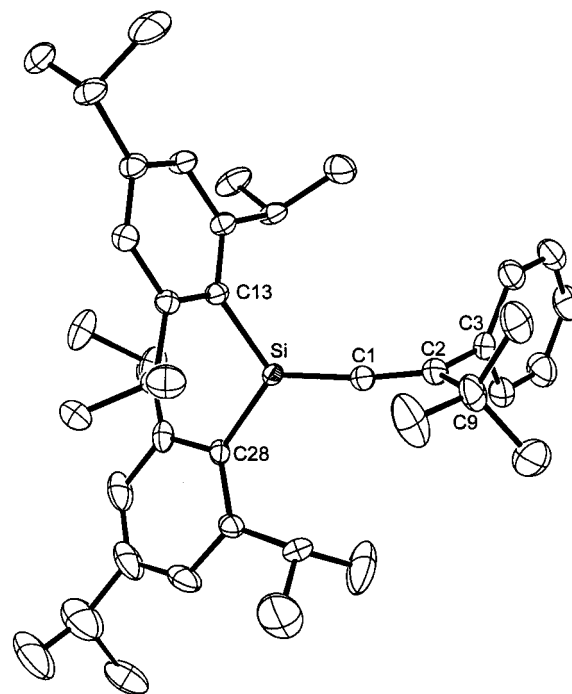

Figure 3. Molecular structure of 1-silapropadiene, **1a**. Thermal ellipsoid drawing with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si−C(1) 1.693(3), Si−C(13) 1.880(3), Si−C(28) 1.879(3), C(1)−C(2) 1.325(4), C(2)−C(3) 1.510(5), C(2)−C(9) 1.545(5), Si−C(1)−C(2) 172.0(3), C(28)−Si−C(13) 116.48(12), C(1)−Si−C(13) 115.20 (14), C(1)−Si−C(28) 125.50(14), C(1)−C(2)−C(3) 118.1(3), C(1)−C(2)−C(9) 123.5(3), C(3)−C(2)−C(9) 118.3(3).

(32) Brook, A. G.; Brook, M. A. In *Multiply Bonded Main Group Metals and Metalloids*; West, R., Stone, F. G. S., Eds.; Academic Press Inc.: San Diego, CA, 1996.
(33) Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

Scheme 4

Tip = 2,4,6-tri-isopropylphenyl
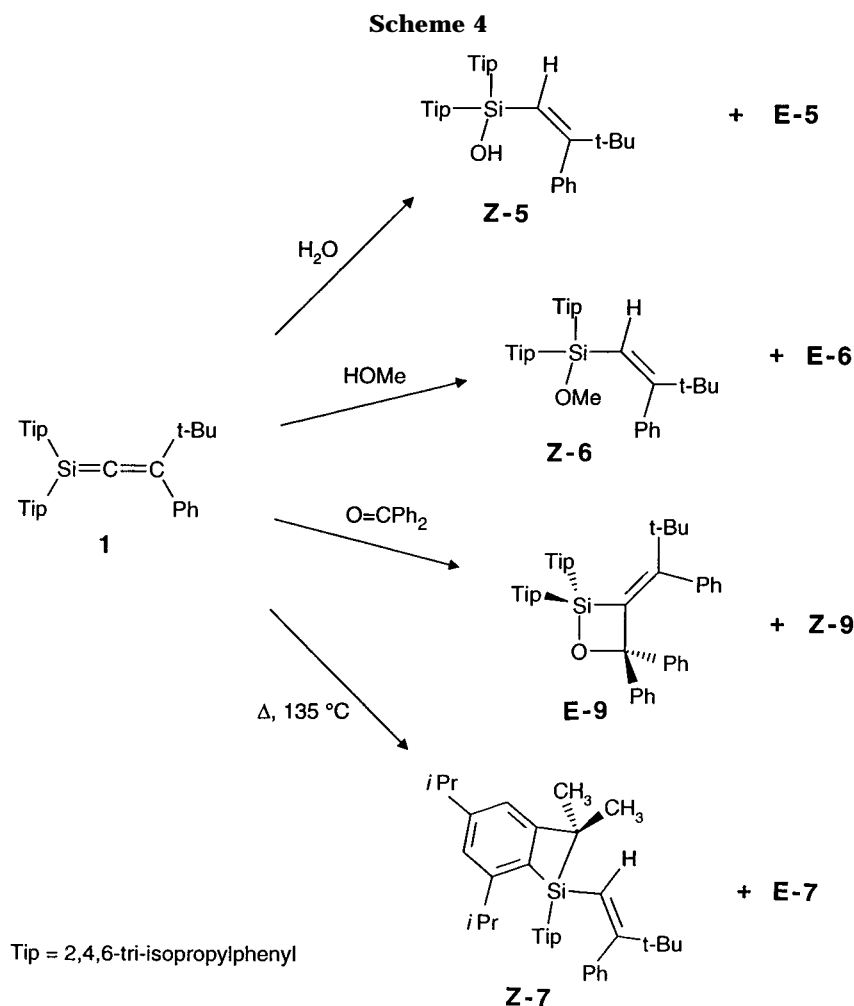
the silicon atom. According to *ab initio* calculations, this shift might be an effect of the strongly reduced polarity of the Si=C double bond in 1-silaallenes[34,35] compared to silenes.[36]

Reactions of 1-Silapropadiene 1a. Compared to other known silenes and disilenes, **1a** is relatively unreactive toward oxygen. Crystals of **1a** exposed to air decompose slowly over several hours, and solutions of **1a** could be stored at ambient temperature for more than three months in an unsealed NMR tube in C_6D_6 solution without decomposition. However, **1a** reacts instantly with water and methanol to give hydroxyvinylsilane **5** and methoxyvinylsilane **6** in almost quantitative yield (Scheme 4).

5 was characterized by multinuclear NMR spectroscopy, by mass spectroscopy, and by comparison with an authenic sample. According to ^{1}H and ^{29}Si NMR, **5** was formed in *cis* and *trans* conformations, indicated by two signals for both the vinylic proton and the silicon atom in the same ratio of about 11:1. By comparison of the NMR spectra of the hydrolysis reaction with those of an authentic sample of (**Z**)-**5**,[37] the major product was shown to have the less strained *cis* conformation.

(34) Gordon, M. S.; Koob, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 2939.
(35) Krogh-Jespersen, K. *J. Comput. Chem.* **1982**, *3*, 571.
(36) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.
(37) The authentic reference substance (**Z**)-**5** was obtained in the reaction of (**Z**)-**4** with potassium hydroxide in refluxing toluene (*vide* Experimental Section). The absolute configuration was established by single-crystal X-ray diffraction and NMR spectroscopy. A listing of the bonding parameters is available in the Supporting Information.

Methanolysis of **1a** gives methoxyvinylsilane **6** in *cis* and *trans* conformations in a ratio of about 15:1. Because of the analogy to the hydrolysis reaction, we can reasonably assume that the major isomer is formed in the *cis* conformation. As expected with CH_3OD as trapping reagent, the deuterium atom was found in the vinylic position.

Addition of benzophenone to a solution of **1a** in toluene results in the formation of two products after several hours at room temperature, indicated by the formation of two signals in the ^{29}Si NMR spectrum. The major product exhibits an absorption at δ +5.4 ppm in the ^{29}Si NMR spectrum and is the formal [2 + 2] addition product 1,2-oxasiletane (**E**)-**9**. The structure of (**E**)-**9** was solved by X-ray diffraction methods and is depicted in Figure 4. The minor compound exhibits a signal at δ +6.6 ppm in the ^{29}Si NMR spectrum and compared to (**E**)-**9** a very similar set of absorptions in the ^{13}C NMR spectrum. We, therefore, tentatively assign as the structure of the minor compound the Z-stereoisomer of **9**. In contrast to the reaction with water, the silicon atom in (**E**)-**9** is in a position *trans* to the phenyl group of the exocyclic double bond. Although (**E**)-**9** seems to be the more hindered stereoisomer, its formation can be reasonably explained by the preferential addition of benzophenone at the less-hindered side of the Si=C double bond, *cis* to the phenyl group of the C=C double bond. This would place the phenyl group in a *trans* position to the silicon atom.
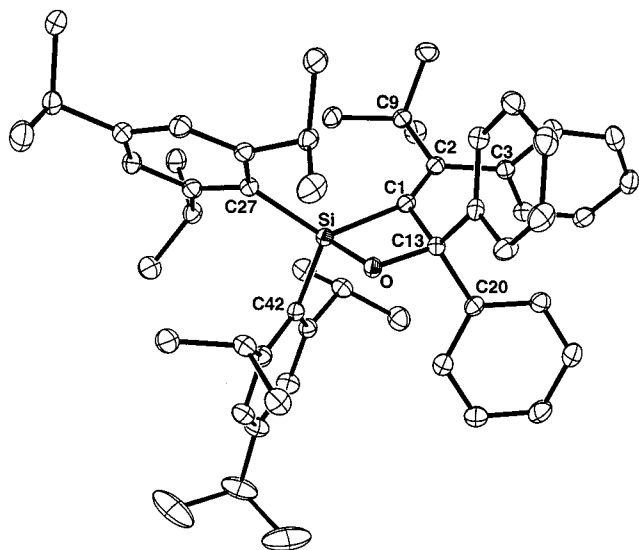
Figure 4. Molecular structure of 1,2-oxasiletane, (**E**)-**9**. Thermal ellipsoid drawing with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si−C(1) 1.9017(13), Si−O 1.6896(9), Si−C(13) 2.3788(13), C1−C(2) 1.347(2), C(1)−C(13) 1.570(2), Si−C(27) 1.9073(13), Si−C(42) 1.9045(13), O−Si−C(1) 78.58(5), O−C(13)−C(1) 97.03(9), C(13)−C(1)−Si 85.93(7), C(13)−O−Si 97.36(7), Si−C(1)−C(2) 144.90(10), C(2)−C(1)−C(13) 129.17(11), C(42)−Si−C(47) 107.76(5).

(**E**)-**9** is the first 1,2-oxasiletane with an exocyclic double bond to be characterized by an X-ray structure. The four-membered (SiOC(13)C(1))-ring is slightly folded with an out-of-plane angle of 11.4° between the Si−C1−C13 and Si−O−C13 planes. The exocyclic double bond is twisted with a twist angle of 15.6° between the Si−C1−C13 and C9−C2−C3 planes. The two carbon atoms of the exocyclic double bond are essentially planar. The Si−O bond length is 1.6895(9) Å, and the transannular Si−C13 distance is 2.3788(13) Å.

A remarkable intramolecular insertion of the Si=C double bond into one of the adjacent tertiary aliphatic C−H bonds of the isopropyl groups was observed when **1a** was heated in a sealed NMR tube at 135 °C in C_6D_6 for several hours (Scheme 4). Benzosilacyclobutane **7**, the sole product of this reaction, was characterized by NMR spectroscopy and by single-crystal X-ray diffraction. Similar to the hydrolysis reaction, the intramolecular insertion reaction does not proceed stereospecifically. According to the relative intensities for the two signals of the vinylic proton in the ¹H NMR spectrum and for the silicon atom in the ²⁹Si NMR spectrum, the *cis* and *trans* isomers of **7** were formed in a ratio of about 4.5:1. The major product is the sterically less-hindered *cis* isomer, which was identified by comparison of the NMR spectra with those of an authentic sample. This intramolecular rearrangement is related to similar reactions of other doubly bonded silicon compounds bearing a C−H bond in the ortho position of an aryl group attached to the silicon atom.[38,39]

Interestingly, the authentic sample of (**Z**)-**7** was prepared directly from lithium salt **2a**. Addition of THF
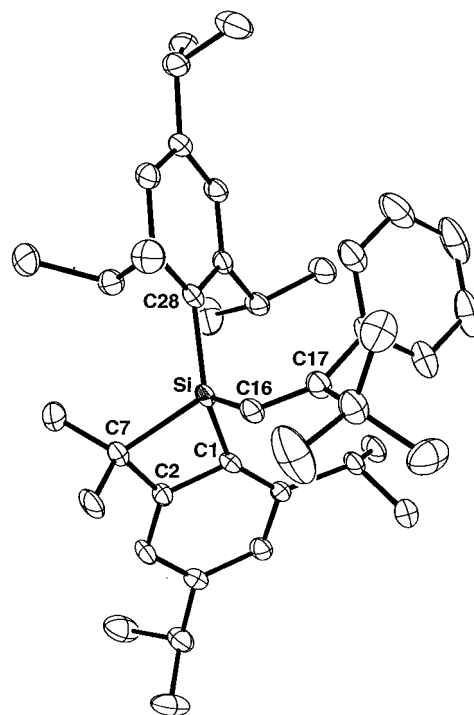

Figure 5. Molecular structure of (**Z**)-**7**. Thermal ellipsoid drawing with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si−C(1) 1.894(2), Si−C(16) 1.873(2), Si−C(7) 1.936(2), Si−C(28) 1.905(2), C(1)−C(2) 1.414(3), C(2)−C(7) 1.533(3), C(16)−C(17) 1.342(3), C(1)−Si−C(7) 76.69(10), C(2)−C(1)−Si 90.4(2), C(1)−C(2)−C(7) 107.4 (2), C(2)−C(7)−Si 85.46(13), C(17)−C(16)−Si 132.0(2).

to crystals of **2a** at −78 °C gave, after warming to room temperature, (**Z**)-**7** as the sole product (Scheme 3). The configuration of (**Z**)-**7** was established by single-crystal X-ray diffraction (Figure 5). The geometry of the silacyclobutene unit of **7** is very similar to other known benzosilacyclobutane derivatives.[40]

According to trapping experiments, **7** is formed directly from **2a**, presumably via intramolecular deprotonation of a benzylic C−H bond in the ortho position of one of the aryl groups followed by ring closure of the intermediate benzyllithium derivative.[41] This assumption is also supported by the fact that this reaction occurs stereospecifically, and thus, the possibility of the formation of **1a** as an intermediate can be excluded in THF solution. Evidently, the basicity of the vinyl anion in THF is strong enough to abstract a benzylic proton.

Synthesis and Reactions of 1-Silapropadienes 1b and 1c. The reaction of **3b** with *t*-BuLi in ether (Scheme 5) was monitored by variable-temperature ²⁹Si NMR spectroscopy. After 1 h at 0 °C, the doublet arising from **3b** was completely replaced by a singlet at δ +55.1 ppm assigned to the silicon atom in 1-silapropadiene **1b**. However, in contrast to the reaction of **3a** with *t*-BuLi, no intermediates were observed in this reaction. The rapid elimination of lithium fluoride is probably driven by significantly greater steric interactions in the vinylic intermediate **2b** compared to **2a**. The most characteristic feature in the coupled ¹³C NMR

(38) Fink, M. J.; DeYoung, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(39) Miracle, G.; West, R.; Ball, J. L.; Powell, D. R. In *Abstracts Xth International Symposium on Organosilicon Chemistry*; 1993, Poznan, Poland; 33.

(40) (a) Weidenbruch, M.; Brand-Roth, B.; Pohl, S.; Sack, W. *J. Organomet. Chem.* **1989**, *379*, 217. (b) Weidenbruch, M.; Pan, Y.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1990**, *123*, 795.

(41) Turnblom, E. W.; Boettcher, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1975**, *97*, 1766.

Scheme 5

Scheme 6

b   R = t-Bu
c   R = Ph
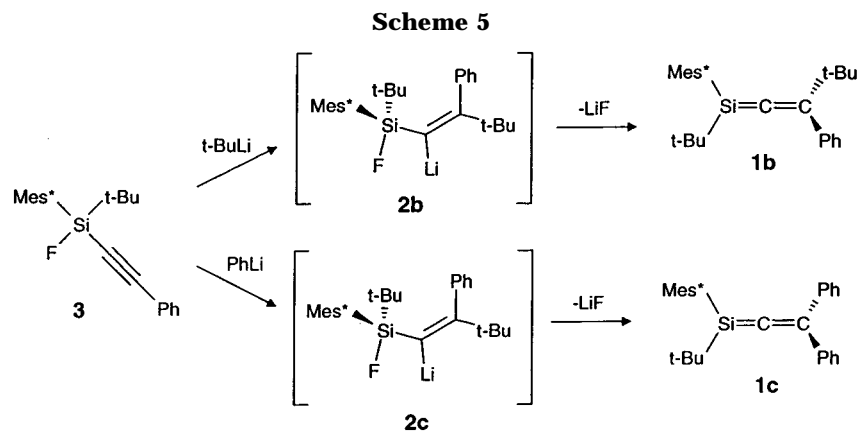
spectrum of **1b** is a deshielded singlet at δ +216.3 ppm with ^{29}Si side bands of 142.4 Hz, which was assigned to the central carbon atom of **1b**. Attempts to obtain crystals of **1b** were unsuccessful.

In contrast to **1a**, the silicon atom in **1b** is so hindered that no reactions were observed by ^{29}Si NMR spectroscopy, even after 12 h in the presence of oxygen, benzaldehyde, 2,3-dimethylbutadiene, or trimethylchlorosilane. However, when a sample of **1b** was heated to 90 °C overnight in a sealed, degassed NMR tube in ether, rearrangement to **8**, the product of net insertion of the Si=C double bond into an adjoining primary aliphatic C−H bond, was observed (Scheme 5). To our surprise, in the presence of excess ethanol, the same rearrange-

Figure 6. Molecular structure of **8b**. Thermal ellipsoid drawing with hydrogen atoms omitted for clarity. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si−C(1) 1.911(7), Si−C(8) 1.886(8), Si−C(19) 1.924(8), C(2)−C(7) 1.517(11), C(7)−C(8) 1.553(10), C(23)−C(24) 1.333(11), C(1)−Si−C(8) 92.7(3), Si−C(1)−C(2) 108.0(5), C(2)−C(7)−C(8) 108.9 (6), Si−C(8)− C(7) 107.6(5), Si−C(23)−C(24) 130.9(6).

ment took place at room temperature with a half-life of several hours. When excess ethanol containing ca. 0.05 equiv of H_2SO_4 (based on **1b**) was added, the rearrangement to **8** occurred rapidly upon mixing at −78 °C. The X-ray crystal structure of **8** is shown in Figure 6.

When ca. 0.05 equiv of D_2SO_4 and excess deuterated ethanol (based on **1b**) were added to a solution of **1b**, rearrangement to **8b** occurred with greater than 95% incorporation of deuterium in the vinylic position, as determined by ^{1}H NMR and high-resolution mass spectrometry. This suggests that the mechanism of this acid-catalyzed rearrangement involves protonation of the central carbon atom to give a highly reactive silicenium ion, which undergoes subsequent electrophilic substitution by a proton from an adjoining primary carbon atom. In the X-ray structure of **8b**, the vinylic proton is *cis* to the *tert*-butyl group. This could arise if protonation of the central carbon atom occurred on the more hindered side, *cis* to the *tert*-butyl group, placing the phenyl group rather than the *tert*-butyl group into close proximity with the substituents on silicon in **8b**.

The reaction of **3b** with phenyllithium to give **1c** (Scheme 6) occurred much more slowly than the reaction with *t*-BuLi, requiring 3 days at room temperature to reach 95% completion when a 3-fold excess of a solution of phenyllithium was added to neat **3b**. A ^{29}Si chemical shift of δ +58.7 ppm was assigned to the silicon atom in **1c**, and a characteristically deshielded chemical shift of δ +227.9 ppm was assigned to the central carbon atom. Small traces of uncharacterized side products were observed by ^{29}Si NMR, which became more prominent when the reaction was run at higher temperatures. **1c** was also more sensitive to decomposition than **1b**. 1-Silapropadiene **1c** underwent rearrangement in ethanol to give **8c** (Scheme 6), similar to **1b** but more rapidly, with a half-life of only a few seconds at room temperature. The rearrangement of **1c** may be faster because
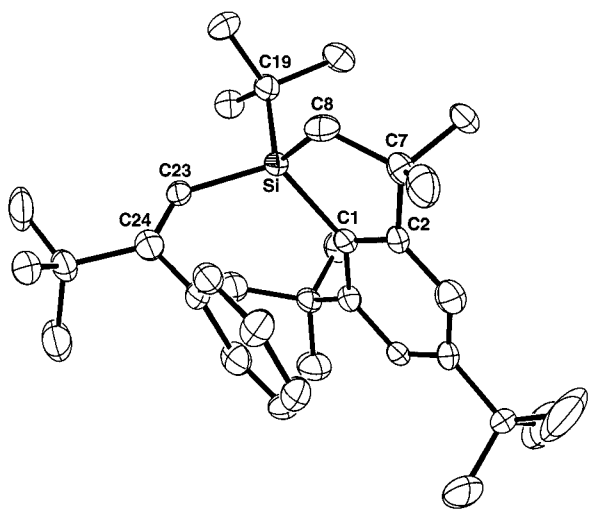
protonation occurs *cis* to a phenyl group, in a less sterically protected environment.

Conclusions

The intermolecular addition of organolithium compounds at the carbon−carbon triple bond of fluorophenylethynylsilanes followed by LiF elimination provides an important route to new members of the 1-silaallene family, which are now easily available in high yields. Moreover, it was possible to characterize an α-lithiated fluorosilane species by X-ray diffraction as an intermediate in this reaction, which was formed in a stereospecific addition of *t*-BuLi to the carbon−carbon triple bond of a fluorophenylethynylsilane.

Qualitatively, the reactivity of the Si−C double bond in 1-silaallenes is significantly reduced compared to those in silenes. The 1-silaallenes are much more stable in air and in the case of our first isolated, sterically extremely protected fluorenylidenesilene[9] even stable in the presence of water or alcohols. The reduced reactivity is consistent with early *ab initio* calculations predicting a strongly reduced polarity of the allenic Si=C double bond. However, sterically less protected silapropadienes exhibit reactivity characteristic of the silicon−carbon double bond.[8] A more detailed study of the chemical behavior of 1-silaallenes is now under way.

Experimental Section

[1]H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra were recorded on a Bruker AC-300 and/or Bruker AM-500 spectrometer. Chemical shifts are given relative to external standards (^{1}H, ^{13}C, and [29]Si, tetramethylsilane; ^{19}F NMR, C_6F_6). All ^{29}Si NMR spectra were measured on a Bruker AM-500 spectrometer by using an INVGATE pulse sequence. High-resolution electron-impact ionization mass spectrometry was performed on an MS80 Kratos spectrometer.

All reactions were carried out under an atmosphere of dry nitrogen or argon in flame-dried glassware. *tert*-Butyl(2,4,6-tri-*tert*-butylphenyl)difluorosilane and bis(2,4,6-triisopropylphenyl)difluorosilane were prepared as described in the literature.[25] Bis(2,4,6-triisopropylphenyl)(*N,N*-diethylamino)fluorosilane was obtained from equivalent amounts of bis(2,4,6-triisopropylphenyl)difluorosilane and lithium diethylamide in refluxing THF.

Bis(2,4,6-triisopropylphenyl)phenylethynylfluorosilane (3a). Two equivalents of freshly distilled trifluoromethanesulfonic acid (6.85 g, 45.64 mmol) in 50 mL of diethyl ether were added to a solution of bis(2,4,6-triisopropylphenyl)(*N,N*-diethylamino)fluorosilane (12 g, 22.82 mmol) in 150 mL of diethyl ether at room temperature. After 30 min of stirring, the mixture was heated to reflux for 15 min. The precipitated ammonium salt was filtered off, and 1 equiv of lithium phenylacetylide (prepared from 2.4 g of phenylacetylene (23.5 mmol) dissolved in 50 mL of THF and 14.5 mL of a 1.6 M solution of *n*-BuLi (23.2 mmol) in hexane) was added dropwise at −78 °C. The mixture was stirred for 12 h at room temperature. The yellow-brown-colored solution was evaporated to dryness under reduced pressure. Bulb-to-bulb distillation (160−165 °C, 0.02 Torr) and subsequent recrystallization from 2-methoxyethanol gave **3a** as colorless crystals. Yield: 10.3 g (81.3%). Mp (2-methoxyethanol): 122 °C. ^{1}H NMR (300 MHz, CDCl₃, TMS): δ 7.48−7.26 (m, 5H), 7.0 (s, 4H), 3.68 (sept, [3]*J*(H,H) = 6.62 Hz, 4H), 2.84 (sept, [3]*J*(H,H) = 6.62 Hz, 2H), 1.22 (d, [3]*J*(H,H) = 6.62 Hz, 12H), 1.11 (d, [3]*J*(H,H) = 6.62 Hz, 12H), 1.08 (d, 6.62 Hz, [3]*J*(H,H) = 12 Hz). ^{13}C NMR (125.8 MHz, CDCl₃, TMS): δ 154.9, 151.1, 131.9, 129.0, 128.8 (d, [2]*J*(C,F) = 15.9 Hz), 128.3, 122.7, 121.6, 107.7 (d, [3]*J*(C,F) = 4.5 Hz), 92.5 (d, [2]*J*(C,F) = 28 Hz), 34.3, 33.25, 33.21, 24.4,

23.83, 23.81. ^{29}Si NMR (99.4 MHz, CDCl₃, TMS): δ −25.5 (d, [1]*J*(Si,F) = 279.5 Hz). ^{19}F NMR (282.2 MHz, CDCl₃, C₆D₆): δ 19.6. MS (EI): *m/z* 554 (32, M⁺), 511 (47, M⁺ − 43), 424 (36, M⁺ − 130), 350 (100, M⁺ − 204). Anal. Calcd for C₃₈H₅₁SiF: C, 82.25; H, 9.26. Found: C, 82.12; H, 9.26.

1-Lithio-1,1-bis(2,4,6-triisopropylphenyl)fluorosilyl-2-phenyl-3,3-dimethylbut-1-ene (2a). A 1.6 M solution of *t*-BuLi in hexane (0.58 mL) was slowly added to a solution of 0.5 g of **3a** (0.90 mmol) in 15 mL of diethyl ether at −78 °C. The mixture was stirred for 30 min at −78 °C. On warming up to 0 °C, the solution turns yellow-orange. It was stirred at that temperature for an additional 30 min. This ethereal solution of **2a** was used directly, without further purification, as the starting material for the preparation of **4**, **1**, (***Z***)-**5**, and (***Z***)-**7**. Crystals of **2a**·TMEDA were obtained by the following procedure: 3 equiv of TMEDA were added at −78 °C to the ethereal solution of **2a**. The mixture was concentrated under reduced pressure at 0 °C to a volume of about 5 mL. The clear, yellow-orange-colored solution was stored at −5 °C. After 8 h, yellow-orange crystals formed. The compound was clearly identified by single-crystal diffraction. ^{29}Si NMR (99.4 MHz, Et₂O/C₆D₆): δ 1.2 (d, *J* = 202.6 Hz). ^{19}F NMR (282.2 MHz, Et₂O/C₆D₆): δ 32.6.

1,1-Bis(2,4,6-triisopropylphenyl)fluorosilyl-2-phenyl-3,3-dimethylbut-1-ene (4). Dry methanol (2 mL) was added to an ethereal solution of **2a** (*vide above*) at 0 °C. The orange-yellow-colored solution instantly turned colorless. The solvents were removed under reduced pressure. Bulb-to-bulb distillation (170−180 °C/0.02 Torr) and recrystallization from 2-methoxyethanol furnished **4** as a white solid. Yield: 0.45 g (89.9%). Mp (2-methoxyethanol): 110−111 °C. ^{1}H NMR (300 MHz, CDCl₃): δ 7.22−7.08 (m, 5H), 6.94 (s, 4H), 6.13 (d, [2]*J*(F,H) = 16.2 Hz, 1H), 3.33 (sept, [3]*J*(H,H) = 6.6 Hz, 4H), 2.81 (sept, [3]*J*(H,H) = 6.6 Hz, 2H), 1.20 (d, [3]*J*(H,H) = 6.6 Hz, 12H), 1.11 (s, 9H), 1.01 (d, [3]*J*(H,H) = 6.6 Hz, 12H), 0.96 (d, [3]*J*(H,H) = 6.6 Hz, 12H). ^{13}C NMR (125.8 MHz, CDCl₃): δ 165.1 (d, *J* = 2.5 Hz), 154.3, 150.3, 147.8, 131.6, (d, *J* = 14.4 Hz), 128.9, 126.7, 126.2, 122.0 (d, *J* = 10.7 Hz), 121.5, 38.6, 34.3, 33.0, 32.9, 29.6, 24.5, 24.4, 23.9. ^{29}Si NMR (99.4 MHz, CDCl₃): δ −7.2 (d, 295.4 Hz). ^{19}F NMR (282.2 MHz, CDCl₃): δ 14.0 (d, 16.3 Hz). MS (EI): *m/z* 613 (5, M⁺), 670 (7, M⁺ − 43), 409 (100, M⁺ − 204). Anal. Calcd for C₄₂H₆₁SiF: C, 82.29; H, 10.03. Found: C, 81.94; H, 9.99.

1,1-Bis(2,4,6-triisopropylphenyl)-3-*tert*-butyl-3-phenyl-1-sila-1,2-propadiene (1a). A solution of **2a** in diethyl ether (*vide above*) was concentrated to dryness under vacuum. Dry hexane (10 mL) was added at 0 °C to the remaining yellow lithium salt **2a**. After the mixture was warmed up to room temperature, it was stirred for an additional 30 min. According to ^{13}C and ^{29}Si NMR spectroscopy, the conversion of **2a** to **1a** proceeded in 100% yield. This solution was used directly without further purification as the starting material for the reaction of **1a** with water and MeOH. Crystals of **1a** were obtained by the following procedure: the lithium fluoride was filtered off, and the filtrate was concentrated under reduced pressure until 3 mL of hexane remained. After this was cooled for 24 h at −10 °C, colorless crystals were obtained. The structure of **1a** was established by single-crystal diffraction.[31] ^{1}H NMR (300 MHz, C₆D₆, TMS): δ 1.12−1.18 (m, 42H), 1.39 (s, 9H), 2.74 (sept, [3]*J*(H,H) = 7.0 Hz, 2H), 3.72 (sept, [3]*J*(H,H) = 6.70 Hz, 4H), 7.08 (s, 4H), 7.06−7.37 (m, 5H). ^{13}C NMR (125.8 MHz, C₆D₆, TMS): δ 223.6 (Si=C), 155.3, 153.0, 151.7, 144.5, 130.4, 129.1, 127.4, 126.2, 121.6, 38.1, 34.9, 30.4, 24.7, 24.5, 23.9. ^{29}Si NMR (99.4 MHz, C₆D₆, TMS): δ 13.1. MS (EI): *m/z* 593 (16, M⁺), 389 (11, M⁺ − 204), 57 (100).

1,1-Bis(2,4,6-triisopropylphenyl)hydroxysilyl-2-phenyl-3,3-dimethylbut-1-ene (5). Water (2 mL) was added to a solution of **1a** in hexane (*vide above*) at 0 °C. The solvents were removed under reduced pressure. Bulb-to-bulb distillation (190 °C/0.02 Torr) and recrystallization from 2-methoxyethanol furnished **5** as a colorless solid. According to the ^{1}H,

^{13}C, and ^{29}Si NMR spectra, a mixture of (*Z*)-**5** and (*E*)-**5** in a ratio of about 11:1 was formed. Yield: 0.39 g (70.8%).

(*Z*)-**5** was clearly identified by comparison of the NMR spectra of the hydrolysis reaction of **1a** with those of an authentic sample of (*Z*)-**5**, which was obtained stereospecifically by the following procedure. Water (2 mL) was added to an ethereal solution of **2a** (*vide* above) at 0 °C. The solvents were removed under reduced pressure. After addition of 0.4 g (7.13 mmol) of potassium hydroxide and 10 mL of dry toluene, the mixture was heated under reflux for 10 h. The solvents were removed under reduced pressure. Bulb-to-bulb distillation (190 °C/0.02 Torr) and recrystallization from 2-methoxyethanol gave (*Z*)-**5** as colorless crystals. Mp (2-methoxyethanol): 153 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.95 (d, 12H, ^{3}J(H,H) = 7.0 Hz), 0.99 (d, 12H, ^{3}J(H,H) = 7.0 Hz), 1.10 (s, 9H), 1.18 (d, 12H, ^{3}J(H,H) = 7.0 Hz), 2.79 (sept, 2H, ^{3}J(H,H) = 7.0 Hz), 3.50 (sept, 4H, ^{3}J(H,H) = 7.0 Hz), 6.25 (s, 1H), 6.91 (s, 4H), 7.19−7.34 (m, 5H). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 162.3, 153.9, 149.4, 142.2, 134.0, 129.3, 127.7, 127.1, 124.8, 121.4, 38.5, 34.2, 32.6, 29.5, 24.4, 23.9. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ −16.3. MS (EI): *m*/*z* 611 (8, M$^+$), 583 (37, M$^+$ − 18), 407 (100, M$^+$ − 204).

The ^{1}H and ^{13}C NMR spectra of the two stereoisomers are very similar. Since (*E*)-**5** was formed only as a minor product in the hydrolysis reaction, it could not be characterized completely. The following absorptions were assigned to (*E*)-**5**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.85 (s, vinylic proton). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 154.1, 149.9, 133.9, 128.9, 124.9, 121.8, 38.7, 32.3. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ −15.0.

1,1-Bis(2,4,6-triisopropylphenyl)methoxysilyl-2-phenyl-3,3-dimethylbut-1-ene (6). Dry methanol (2 mL) was added to a solution of **1a** in hexane (*vide* above) at 0 °C. The solvents were removed under reduced pressure. Bulb-to-bulb distillation (170−180 °C/0.02 Torr) furnished **6** as a white solid. According to the ^{1}H, ^{13}C and ^{29}Si NMR spectra, a mixture of (*Z*)-**6** and (*E*)-**6** was formed in a ratio of about 15:1. Yield: 0.44 g (78%). (*Z*)-**6**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.28−7.17 (m, 5H), 6.9 (s, 4H), 6.19 (s, vinylic proton), 3.52 (sept, ^{3}J(H,H) = 6.6 Hz, 4H), 2.80 (sept, ^{3}J(H,H) = 6.6 Hz, 2H), 2.44 (s, 3H), 1.18 (d, ^{3}J(H,H) = 6.6 Hz, 12H), 1.07 (s, 9H), 0.95 (d, ^{3}J(H,H) = 6.6 Hz, 12H), 0.93 (d, ^{3}J(H,H) = 6.6 Hz, 12H). MS (EI): *m*/*z* 624 (2, M$^+$), 581 (6, M$^+$ − 43), 420 (100, M$^+$ − 204). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 162.7, 154.5, 149.5, 142.8, 132.2, 129.6, 126.6, 125.8, 125.0, 121.5, 50.9, 38.7, 34.2, 32.5, 29.9, 24.5, 24.4, 24.0, 23.9. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ −14.1. Anal. Calcd for C$_{43}$H$_{64}$OSi: C, 82.62; H, 10.32. Found: C, 82.37; H, 10.71.

The ^{1}H and ^{13}C NMR spectra of the two stereoisomers are very similar. Since (*E*)-**6** was formed only as a minor product, it could not be characterized completely. The following absorptions were assigned to (*E*)-**6**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.83 (s, vinylic proton). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 162.3, 154.8, 149.6, 142.8, 132.2, 129.6, 126.6, 125.9, 124.9, 121.7, 50.9, 38.7, 34.3, 32.7, 29.9, 24.5, 24.4, 24.0, 23.9. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ −16.5.

2,2-Bis(2,4,6-triisopropylphenyl)-3-(3,3-dimethyl-2-phenylbut-1-ylidene)-4,4-diphenyl-1,2-oxasiletane (9). A solution of **1a** in hexane (*vide* above) was concentrated to dryness under reduced pressure. The residue was taken up in 10 mL of toluene, and a solution of 180 mg of benzophenone (0.99 mmol) in 10 mL of dry toluene was added at 0 °C. After the mixture was warmed up to room temperature, the reaction was followed by GC. After 8 h, the conversion of **1a** was complete. The solvent was removed under reduced pressure. According to the ^{29}Si NMR spectrum of the crude product, a mixture of (*E*)-**9** and (*Z*)-**9** in a ratio of about 6:1 was formed. Recrystallization from dry benzene furnished (*E*)-**9** as colorless crystals. Yield: 0.15 g (22%). (*E*)-**9**. Mp (benzene): 215 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.60−6.76 (m, 19H), 3.54 (sept, ^{3}J(H,H) = 6.6 Hz, 2H), 3.01−2.69 (m, 4H), 1.28 (s, 9H), 1.26−0.88 (m, 36H). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 159.9, 156.0, 155.4, 154.0, 151.1, 150.8, 150.1, 146.5, 146.0, 145.8, 138.2,

137.8, 134.0, 133.0, 131.0, 129.8, 128.3, 126.9, 126.5, 125.8, 125.3, 122.5, 122.2, 122.1, 121.6, 92.7, 39.4, 36.2, 34.4, 34.2, 33.8, 32.6, 31.9, 30.3. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ +5.4. MS (EI): *m*/*z* 775 (45, M$^+$), 718 (6, M$^+$ − 57), 615 (38, M$^+$ − 160), 593 (30, M$^+$ − 182), 388 (100). HRMS (EI): *m*/*z* calcd for C$_{55}$H$_{70}$SiO 774.5196, found 774.5191.

The ^{1}H and ^{13}C NMR spectra of the two stereoisomers are very similar. Since (*Z*)-**9** was formed only as a minor product, it could not be characterized completely. The following absorptions were assigned to (*Z*)-**9**. ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 159.2, 155.5, 155.3, 154.3, 151.1, 150.3, 150.0, 146.6, 146.5, 138.1, 133.9, 132.4, 128.5, 121.6, 121.5, 121.3, 93.6, 40.2, 35.9, 34.3, 34.0, 32.2. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ +6.6.

1-(2,4,6-Triisopropylphenyl)-4,6-diisopropyl-1-(2-phenyl-3,3-dimethylbut-1-enyl)-2,2-dimethylsilacyclobutane (7). A solution of 200 mg of **1a** in 1 mL of C$_6$D$_6$ was placed in an NMR tube. The tube was sealed under vacuum and heated up to 135 °C for several hours. The reaction was followed by ^{1}H, ^{13}C, and ^{29}Si NMR. After 7 h, the starting material had completely disappeared. According to the ^{1}H, ^{13}C, and ^{29}Si NMR spectra, a mixture of (*Z*)-**7** and (*E*)-**7** in a ratio of 4.5:1 was formed.

(*Z*)-**7** was clearly identified by comparison of the NMR spectra with those of an authentic sample of (*Z*)-**7**, which was obtained stereospecifically by the following procedure. A solution of **2a** in diethyl ether (*vide* above) was concentrated to dryness under vacuum. Dry THF (10 mL) was added at −78 °C to the remaining yellow lithium salt **2a**. After the mixture was warmed up to room temperature, it was stirred for an additional 30 min. **2a** was concentrated to dryness under reduced pressure. After this was cooled for 24 h at −10 °C, colorless crystals were obtained. Bulb-to-bulb distillation (165 °C/0.02 Torr) and recrystallization furnished (*Z*)-**7** as colorless crystals. Yield: 0.48 g (90%). The configuration of **7** was established by single-crystal diffraction. (*Z*)-**7**. Mp (2-methoxyethanol): 129 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.05−6.65 (m, 9H), 6.22 (s, 1H), 2.85 (sept, ^{3}J(H,H) = 6.6 Hz, 4H), 2.71 (sept, ^{3}J(H,H) = 6.6 Hz, 1H), 1.49 (s, 3H), 1.29−1.17 (m, 30H), 1.15 (s, 3H), 1.0 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.4, 162.1, 154.2, 152.0, 149.6, 141.3, 138.4, 131.4, 129.2, 126.3, 126.0, 122.4, 121.4, 120.4, 116.5, 38.4, 34.6, 34.3, 33.3, 30.8, 29.6, 27.5, 26.8, 24.7, 24.1, 23.9, 23.0. ^{29}Si NMR (99.4 MHz, CDCl$_3$): δ −12.0. MS (EI): *m*/*z* 553 (5, M$^+$), 550 (11, M$^+$ − 43), 536 (55, M$^+$ − 57), 389 (100, M$^+$ − 204). Anal. Calcd for C$_{42}$H$_{60}$Si: C, 85.06; H, 10.20. Found: C, 83.03; H, 10.38.

The ^{1}H and ^{13}C NMR spectra of the two isomers are very similar. Since (*E*)-**7** was formed only as a minor product in the thermolysis of **1a**, it could not be characterized completely. The following absorptions were assigned to (*E*)-**7**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.85 (s, vinylic proton). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 166.9, 162.2, 152.0, 149.7, 141.2, 138.3, 131.6, 129.2, 126.8, 126.2, 122.4, 121.4, 116.6. ^{29}Si NMR (99.4 MHz, C$_6$D$_6$): δ −13.3.

***tert*-Butyl(2,4,6-tri-*tert*-butylphenyl)phenylethynylfluorosilane (3b).** To a solution of phenylacetylene (1.6 g, 16 mmol) in THF (30 mL) at 0 °C was added *n*-BuLi (9.4 mL, 1.6 M in hexane, 15 mmol), followed by *tert*-butyl(2,4,6-tri-*tert*-butylphenyl)difluorosilane[25] (5.0 g, 13.6 mmol). The mixture was stirred at reflux for 2 h, then the solvent was stripped off. The product was taken up in pentane, washed with water, dried with MgSO$_4$, and concentrated under vacuum. Fractional vacuum bulb-to-bulb distillation gave **3b** as a highly viscous colorless oil (3.72 g, 8.25 mmol, 61%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.48 (br s, 2H), 7.36−7.32 (m, 2H), 6.99−6.88 (m, 3H), 1.61 (br s, 18H), 1.26 (s, 9H), 1.17 (d, J = 1.94 Hz, 9H). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 151.2, 132.2, 129.1, 128.5, 124.5, 124.3, 123.1, 122.4, 107.6 (d, ^{3}J(C,F) = 4.45 Hz), 92.5 (d, ^{1}J(C,F) = 27.33 Hz), 39.7, 34.6, 33.8, 31.2, 28.9, 23.4. ^{19}F NMR (282.2 MHz, C$_6$D$_6$): δ 20.2. ^{29}Si NMR (99.4 MHz, C$_6$D$_6$): δ −12.2 (d, ^{1}J(Si,F) = 274.66 Hz). HRMS (EI): *m*/*z* calcd for C$_{30}$H$_{43}$FSi 450.3118, found 450.3144.

Table 1. Crystallographic Data for 1a, 2a, (Z)-7, 8b, and (E)-9

	1a	**2a**	**(Z)-7**	**8b**	**(E)-9**
formula	$C_{42}H_{60}Si$	$C_{48}H_{76}FLiN_2Si$	$C_{42}H_{60}Si$	$C_{34}H_{52}Si$	$C_{55}H_{70}SiO$
fw	592.99	735.14	592.99	488.85	775.20
cryst size (mm³)	$0.46 \times 0.40 \times 0.24$	$0.52 \times 0.44 \times 0.28$	$0.48 \times 0.32 \times 0.10$	$0.4 \times 0.3 \times 0.2$	$0.48 \times 0.42 \times 0.38$
a (Å)	31.9855(12)	11.103037(2)	19.1204(5)	13.982(4)	18.1971(5)
b (Å)	12.0682(4)	11.8678(2)	19.6814(6)	16.841(9)	15.4724(4)
c (Å)	21.9138(6)	19.2126(3)	10.2646(3)	26.031(7)	16.8628(5)
α (deg)	90	87.280(2)	90	90	90
β (deg)	114.684(2)	86.519(2)	95.171(2)	90	96.459(2)
γ (deg)	90	69.337(2)	90	90	90
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/c$
vol (Å³)	7686.0(4)	2363.62(7)	3847.0(2)	6130(4)	4717.7(2)
D_{calcd} (g cm⁻³)	1.025	1.033	1.024	1.059	1.091
Z	8	2	4	8	4
temp (K)	133(2)	133(2)	133(2)	133(2)	133(2)
abs coeff (mm⁻¹)	0.086	0.085	0.086	0.791	0.086
min/max trans	0.678/0.894	0.854/0.965	0.600/0.942	0.764/0.928	
no. of reflns collected	14557	22855	32494	4940	20224
no. of indep reflns	6660	10039	6777	4129	10042
no. of obsd reflns	4938	8127	4884	2595	7901
no. of params	400	478	388	346	514
θ range (deg)	1.83–25.00	1.96–28.18	1.49–25	3.40–56.99	1.73–28.27
R1 (%)	0.0710	0.0381	0.0617	0.1076	0.0390
wR2 (%)	0.0978	0.0956	0.1540	0.2998	0.1050

1-*tert*-Butyl-1-(2,4,6-tri-*tert*-butylphenyl)-3-*tert*-butyl-3-phenyl-1-silapropadiene (1b). To a dry 5 mm in diameter NMR tube attached to a vacuum/argon line was added **3b** (340 mg, 0.75 mmol) in toluene-d_8 (0.3 mL) and diethyl ether (0.3 mL). The tube was immersed in a dry-ice bath, and *tert*-butyllithium in pentane (1.7 M, 0.60 mL, 1.0 mmol) was added. The tube was sealed under a dynamic vacuum, and the reaction was followed by variable-temperature ^{29}Si NMR. A signal corresponding to the product was observable after 30 min at −30 °C. Reaction was complete by the time the NMR tube had been warmed to 0 °C for 1 h. No intermediate products were observed. **1b**. ^{1}H NMR (300 MHz): δ 7.44 (s, 1H), 7.39 (s, 1H), 7.13−6.96 (m, 5H), 1.65 (s, 9H), 1.26 (s, 9H), 1.23 (s, 9H), 1.16 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (75.40 MHz): δ 216.3, 158.3, 157.5, 156.5, 151.5, 143.8, 128.8, 127.4, 125.6, 122.3, 121.3, 121.2, 39.7, 38.8, 38.5, 35.1, 34.3, 33.9, 31.4, 31.1, 31.0, 22.8. ^{29}Si NMR (99.4 MHz): δ 55.1.

Reactions of 1b with 1,3-Dimethylbutadiene, Benzaldehyde, Trimethylchlorosilane, and Oxygen Gas. To different samples of **1b**, prepared in NMR tubes with an excess of *t*-BuLi as described above, were added 1,3-dimethylbutadiene (1.0 mL), benzaldehyde (1.0 mL), trimethylchlorosilane (1.0 mL), and oxygen gas (an excess was bubbled in under atmospheric pressure). The tubes were then sealed and analyzed after 12 h by ^{29}Si NMR. In each case, no reaction was observed.

1,5,7-Tri-*tert*-butyl-1-((Z)-3,3-dimethyl-2-phenylbut-1-enyl)-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*b*]silole (8b). 8b was prepared by three routes: (a) warming an NMR sample of **1b** to 90 °C overnight (considerable discoloration of the reaction medium occurs, but no significant impurities are observed by NMR); (b) treating a sample of **1b** (0.31 mmol), prepared in an NMR tube, with dry, degassed ethanol (0.01 mL, 2.9 mmol) overnight (slight discoloration occurred, but no impurities were observed); and (c) treating a sample of **1b** (0.31 mmol) with dry, degassed ethanol (0.01 mL, 2.9 mmol) containing H_2SO_4 (reaction occurred upon mixing at −78 °C without side products). In methods a and b, the samples of **1b** were prepared as described above in an NMR tube with an excess of *t*-BuLi. In method c, **1b** was prepared with less than 1 equiv of *t*-BuLi, and some starting material remained. When deuterated ethanol was used in method b, approximately 50% incorporation of deuterium occurred in the vinyl position, as determined by HRMS and ^{1}H NMR, and when deuterated ethanol and D_2SO_4 were used in method c, greater than 95% incorporation of deuterium occurred. In each case, the product was isolated by recrystallization from ethanol. Mp 88−90 °C

(EtOH). ^{1}H NMR (300 MHz, C_6D_6): δ 7.55 (d, 1H, $J = 1.56$ Hz), 7.18 (d, 1H, $J = 1.56$ Hz), 6.94−6.89 (m, 5H), 6.44 (s, 1H), 1.58 (s, 9H), 1.32 (s, 3H), 1.31 (s, 9H), 1.11 (s, 9H), 1.10 (s, 9H), 0.98 (s, 3H), 0.70 (AB, $n_A = 0.81$, $n_B = 0.58$, $J_{AB} = 15.75$ Hz). ^{13}C NMR (75.40 MHz, C_6D_6): δ 166.55, 163.90, 155.70, 152.03, 141.96, 130.18, 129.78, 127.31, 126.49, 122.59, 121.95, 119.07, 41.36, 38.87, 37.46, 35.52, 35.14, 34.87, 33.86, 31.52, 30.09, 30.08, 24.83, 19.01. ^{29}Si NMR (99.4 MHz, C_6D_6): δ 7.10. HRMS (EI): m/z calcd for $C_{34}H_{52}Si$ 488.3838, found 488.3841.

1-*tert*-Butyl-1-(2,4,6-tri-*tert*-butylphenyl)-3,3-diphenyl-1-silapropadiene (1c). A sample of **3b** was weighed (118 mg, 0.263 mmol) into an NMR tube to which a sealed capillary tube containing benzene-d_6 had been added. A solution of phenyllithium (1.5 M in 70% cyclohexane and 30% diethyl ether, 0.6 mL, 0.9 mmol) was added, the contents of the tube were frozen under liquid nitrogen and degassed, and the tube was sealed under dynamic vacuum. The sample was warmed to room temperature, shaken to dissolve **1b**, and monitored by ^{29}Si NMR. Approximately 72 h at room temperature were necessary for the reaction to reach 95% completion. ^{1}H NMR (300 MHz, C_6D_6): δ 7.40 (s, 2H), 7.11−6.90 (m, 10H), 1.20 (s, 18H), 1.13 (s, 9H), 0.95 (s, 9H). ^{13}C NMR (75.40 MHz, C_6D_6): δ 227.9, 158.0, 141.9, 136.7, 132.2, 129.1, 127.8, 127.0, 121.6, 117.8, 39.0, 38.8, 34.1, 33.8, 31.4, 23.2. ^{29}Si NMR (99.36 MHz, C_6D_6): δ 55.1 ppm.

1,5,7-Tri-*tert*-butyl-1-(2,2-diphenylethenyl)-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*b*]silole (8c). A sample of **1c** prepared in an NMR tube as described above from **3b** (157 mg, 0.348 mmol) and PhLi (0.72 mmol) kept at room temperature for 72 h was cracked open and poured into a flask containing 50 mL of ethyl alcohol. The dark orange color disappeared within a few seconds upon mixing. The solvent was removed, and the product was taken up in pentane and filtered to remove the salts. The product was purified by preparative thin layer chromatography using hexane with 2% ethyl acetate as the eluent. ^{1}H NMR (300 MHz, C_6D_6): δ 7.574 (d, $J = 1.84$ Hz), 7.375−7.367 (m, 1H), 7.346 (d, $J = 1.47$ Hz), 7.251 (d, $J = 1.84$ Hz), 7.074−6.835 (m, 9H), 1.531 (s, 9H), 1.352 (s, 3H), 1.340 (s, 3H), 1.333 (s, 9H), 1.194 (s, 9H), 0.986 (s, 2H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 164.08, 157.99, 155.64, 152.45, 150.34, 146.01, 142.30, 130.74, 130.37, 128.86, 128.41, 128.30, 128.11, 127.91, 127.49, 122.38, 119.55, 41.50, 37.48, 35.79, 34.94, 33.76, 31.83, 31.56, 30.20, 25.07, 19.24. ^{29}Si NMR (99.4 MHz, C_6D_6): δ 7.37.

Crystal Structure Determinations. Intensity data for **1a**, **2a**, **(Z)-7**, and **(E)-9** were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα

radiation (λ = 0.710 73 Å) and a CCD area detector. These data sets were collected with completeness ratios greater than 95% in the range θ < 24° and were corrected for absorption using an empirical absorption correction. Intensity data for **8b** were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) and a scintillation point detector. For **8b**, ω scans were used to collect data in the ranges $-15 \leq h \leq 3$, $0 \leq k \leq 18$, $0 \leq l \leq 28$. No absorption correction was applied to the data for **8b**. The structures of all compounds were solved by direct methods and refined by full-matrix least-squares refinement on F^2 (SHELXTL, version 5). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in all structures were refined using a riding model with isotropic displacement parameters set at 1.2 times the isotropic equivalent U of the bonded atom for non-methyl groups and 1.5 times U_{eq} for methyl groups. One *tert*-butyl group in **8b** was found to be disordered and modeled in two orientations with occupancies of 0.759(9) for C(12)−C(14) and 0.205(9) for C(12′)−C(14′). Details of data collection and refinement are given in Table 1.

Supporting Information Available: Tables of atomic coordinates and U values, bonding parameters, and anisotropic displacement parameters and ORTEP and packing diagrams for **1a**, **2a**, **3a**, (*Z*)-**5**, (*Z*)-**7**, **8b**, and (*E*)-**9**, ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **1a**, **1b**, **1c**, **2a**, **3b**, **5**, **8b**, and **8c**, and ^{29}Si NMR spectrum of **9** (127 pages). Ordering information is given on any current masthead page.