Table III. Bond Angles (deg) for Complex 3b[a]

C(1)–Ag···Ag(a)	91.9 (1)	C(1)–Ag–C(2a)	178.2 (1)
Ag(a)···Ag–C(2a)	86.4 (1)	C(1)–P–C(2)	109.4 (1)
C(1)–P–C(11)	111.7 (1)	C(2)–P–C(11)	112.1 (1)
C(1)–P–C(21)	105.2 (1)	C(2)–P–C(21)	114.0 (1)
C(11)–P–C(21)	104.3 (1)	C(3)–O(2)–C(4)	114.7 (3)
C(6)–O(4)–C(7)	117.1 (2)	Ag–C(1)–P	104.2 (1)
Ag–C(1)–C(3)	107.3 (2)	P–C(1)–C(3)	117.9 (2)
P–C(2)–C(6)	115.4 (2)	P–C(2)–Ag(a)	109.2 (1)
C(6)–C(2)–Ag(a)	110.1 (2)	O(1)–C(3)–O(2)	121.6 (2)
O(1)–C(3)–C(1)	127.1 (3)	O(2)–C(3)–C(1)	111.3 (3)
O(2)–C(4)–C(5)	106.3 (4)	O(3)–C(6)–O(4)	122.0 (2)
O(3)–C(6)–C(2)	126.7 (3)	O(4)–C(6)–C(2)	111.3 (2)
O(4)–C(7)–C(8)	108.1 (3)	P–C(11)–C(12)	122.3 (2)
P–C(11)–C(16)	119.9 (2)	C(12)–C(11)–C(16)	117.6 (3)
C(11)–C(12)–C(13)	121.5 (3)	C(12)–C(13)–C(14)	120.9 (4)
C(13)–C(14)–C(15)	119.3 (4)	C(14)–C(15)–C(16)	120.5 (4)
C(11)–C(16)–C(15)	119.9 (4)	P–C(21)–C(22)	122.7 (2)
P–C(21)–C(26)	118.2 (2)	C(22)–C(21)–C(26)	119.2 (3)
C(21)–C(22)–C(23)	119.8 (4)	C(22)–C(23)–C(24)	120.9 (3)
C(23)–C(24)–C(25)	120.3 (3)	C(24)–C(25)–C(26)	119.7 (4)
C(21)–C(26)–C(25)	120.2 (3)		

[a] Symmetry operator: (a) $1 - x, 2 - y, 1 - z$.

Mg m^{-3}; $F(000) = 472$; $\lambda(\text{Mo K}\alpha) = 0.71069$ Å; $\mu = 1.1$ mm^{-1}.

Data Collection and Reduction. A crystal, 0.55 × 0.3 × 0.15 mm, was mounted in a glass capillary. A total 4929 profile-fitted intensities[17] were registered on a Stoe-Siemens four-circle diffractometer using monochromated Mo Kα radiation ($2\theta_{max} = 50°$). An absorption correction based on ψ scans was applied, with transmission factors of 0.78–0.99. Merging equivalents gave 3526 unique reflections ($R_{int} = 0.012$), of which 3307 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, locally modified by its author, Prof. G.M. Sheldrick). Cell constants were refined from 2θ values of 54 reflections in the range 20–23°.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and refined anisotropically on F to $R = 0.025$ and $R_w = 0.027$. H atoms were included by using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00017F^2$ (235 parameters; $S = 1.8$; maximum $\Delta/\sigma = 0.002$; maximum $\Delta\rho = 0.7$ e Å^{-3}). Final atomic coordinates are given in Table I, with derived bond lengths and angles in Tables II and III, respectively.

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Supplementary Material Available: Tables of anisotropic displacement parameters and H-atom coordinates (2 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Solid-State Structures of Some Sterically Hindered Cyclopropenylsilanes

Dhananjay B. Puranik, M. Pontier Johnson, and Mark J. Fink*

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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The reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with the polysilyllithium reagents LiSiR(SiMe$_3$)$_2$ [R = SiMe$_3$, Ph, 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl] affords covalent 3-cyclopropenylsilanes, Cyp*SiR(SiMe$_3$)$_2$, in high yields (Cyp* = tri-*tert*-butylcyclopropenyl). The compounds display remarkable thermal and chemical stability. The spectroscopic properties are compared, and two X-ray crystal structures are reported. The compound Cyp*SiPh(SiMe$_3$)$_2$ crystallizes in the monoclinic system: Si$_3$C$_{27}$H$_{50}$, space group $P2_1/c$, $Z = 4$, $a = 16.382$ (5) Å, $b = 11.990$ (2) Å, $c = 15.199$ (3) Å, $\beta = 96.70$ (2)°. The compound Cyp*SiMes(SiMe$_3$)$_2$ also crystallizes in the monoclinic system: Si$_3$C$_{30}$H$_{56}$, space group $P2_1/c$, $Z = 4$, $a = 16.412$ (4) Å, $b = 10.403$ (2) Å, $c = 15.566$ (5) Å, $\beta = 104.69$ (2)°. The two structures reveal unusually long bond lengths to the central silicon atom due to strong steric interactions.

Introduction

The chemistry of 3-cyclopropenylsilanes is largely unexplored despite the potential for these compounds to serve as sources of cyclopropenyl anions[1,2] and of high energy organosilicon intermediates.[3,4] Only a few examples of 3-cyclopropenylsilanes are known. The compound 3-(trimethylsilyl)-1,2,3-triphenylcyclopropene (**1**) has been shown to undergo fluorodesilylation in both solution and the gas phase to yield the triphenylcyclopropenyl anion.[1] A similar compound, 3-(trimethylsilyl)-3-phenyl-1,2-dimethylcyclopropene (**2**), also undergoes gas-phase fluorodesilylation. Additionally, compound **2** and several closely related analogues have been demonstrated to undergo [1,5]-sigmatropic migrations of the trimethylsilyl group about the cyclopropene ring.[5]

All of the forementioned cyclopropenylsilanes have been prepared by the reaction of acetylenes with sources of α-silylcarbenes. Distressing limitations are encountered with this type of synthesis, however: the general nonavailibility of α-silylcarbene precursors[6] and the tendency of the α-silylcarbenes to undergo facile intramolecular rearrangements.[7] Our interest in highly hindered cyclo-

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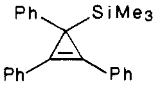
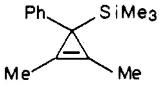
propenyltrisilanes as precursors to cyclopropenylsilylenes[3] and silacyclobutadienes[4] has prompted us to examine other methods for the synthesis of these types of compounds.

The reaction of cyclopropenium cations with anionic nucleophiles has been demonstrated to be very useful in forming cyclopropenyl linkages to carbon,[8] nitrogen,[9] phosphorus,[10] and some transition metals.[11] We have subsequently found that this strategy may be extended to silicon as well and should be useful as an alternative preparation for certain 3-cyclopropenylsilanes.

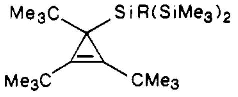
In this paper, we report the synthesis of four cyclopropenylsilanes (**3a–d**) from the reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with polysilyllithium reagents. The reactions are generally high yield and give stable crystalline products. The X-ray crystal structures for two of these highly hindered compounds have been obtained and are compared.



1



2



3a: R = SiMe$_3$
b: R = Ph
c: R = Mes (2,4,6-trimethylphenyl)
d: R = 2,4,6-triisopropylphenyl

Results and Discussion

Synthesis of Cyclopropenylsilanes. The room-temperature reaction of the polysilyllithium reagents **4a–d** with tri-*tert*-butylcyclopropenium tetrafluoroborate in THF or pentane solvents generally gives high yields of the cyclopropenylsilanes **3a–d** along with lithium tetrafluoroborate (eq 1).

$$\mathrm{Cyp^{*+}BF_4^-} + \mathrm{LiSiR(SiMe_3)_2} \rightarrow \mathrm{Cyp^*SiR(SiMe_3)_2} + \mathrm{LiBF_4} \quad (1)$$

4a: R = SiMe$_3$
4b: R = Ph
4c: R = Mes
4d: R = TIP

3a (88%)
3b (89%)
3c (81%)
3d (42%)

Cyp* = tri-*tert*-butylcyclopropenyl

TIP = 2,4,6-triisopropylphenyl

Interestingly, the yields of cyclopropenylsilanes do not appear to depend much on whether THF or pentane is used as a solvent. This observation is somewhat surprising in view of the fact that the reactions between the cyclopropenium salt and the polysilyllithium reagents are heterogeneous in pentane but are totally homogeneous in THF.

The reaction in pentane is characterized by the loss of the yellow to orange colored silyllithium reagent over a period of 30 min and the transformation of the granular cyclopropenium salt to a sticky precipitate of lithium tetrafluoroborate. By contrast, in THF solvent the reaction is homogeneous; the colored silyllithium reagent is consumed over a 30-min period, and no precipitate is formed.

When the highly polar HMPA is used as a solvent, a much different result is obtained. Although the polysilyllithium reagents **4a–d** are very efficiently generated in HMPA solvents, the anticipated reaction of tri-*tert*-butylcyclopropenium cation with these reagents does not occur. Addition of an HMPA solution of **4b** to tri-*tert*-butylcyclopropenium tetrafluoroborate results in no reaction at room temperature. It is likely that in HMPA solvent, the respective anion and cation are sufficiently solvated to disfavor the formation of the covalent product.[12] If the solution is heated to 80 °C, tri-*tert*-butylcyclopropene and phenylbis(trimethylsilyl)silane are formed in equimolar amounts as the only volatile products. It appears that at these temperatures electron transfer[13] is the more favored reaction (eq 2), giving tri-*tert*-butylcyclopropenyl and phenylbis(trimethylsilyl)silyl radicals. Hydrogen atom abstraction by these radicals, presumably from solvent, gives the observed products.

$$\mathrm{Cyp^{*+}} + \mathrm{LiSiPh(SiMe_3)_2} \rightarrow \mathrm{Cyp^{*\bullet}} + {}^{\bullet}\mathrm{SiPh(SiMe_3)_2} + \mathrm{Li^+} \quad (2)$$

Cyp* = tri-*tert*-butylcyclopropenyl

The polysilyllithium reagents were prepared from the reaction of methyllithium[14] on the branched polysilanes **5a–d** in THF solution in accordance with the Gilman method[15] (eq 3). Although the reactions very cleanly gave the lithium reagents in all cases, the time required for complete conversion varied from 5 to 12 h.

$$\mathrm{RSi(SiMe_3)_3} + \mathrm{MeLi} \rightarrow \mathrm{LiSiR(SiMe_3)_2} + \mathrm{SiMe_4} \quad (3)$$

5a: R = SiMe$_3$ **4a–d**
5b: R = Ph
5c: R = Mes
5d: R = TIP

Mes = 2,4,6-trimethylphenyl

TIP = 2,4,6-triisopropylphenyl

The rate of formation of the silyllithium compound depends greatly with the substituent R of the polysilane with **5d** > **5c** > **5b** > **5a**. The presence of an aryl group greatly accelerates the reaction, with the more sterically hindered aryl groups giving the faster rates. The quicker formation of the aryl-substituted anions may be attributed to resonance stabilization by the aromatic ring.[16] Addi-

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Table I. Spectroscopic Data for Cyclopropenylsilanes 3a–d

		NMR[b]			
compd	MS *m/e* (%)[a]	^{1}H	^{13}C	^{29}Si	IR,[c] cm^{-1}
3a	439 (0.2, M$^+$ − Me)	0.24 (s, 27 H, SiMe$_3$)	5.0 (CH$_3$, SiMe$_3$), 31.4 (CH$_3$, *t*-Bu)	−13.7 (SiMe$_3$)	2900 (s, ν(CH))
	397 (1.7, M$^+$ − *t*-Bu)	0.91 (s, 9 H, *t*-Bu)	31.6 (q, *t*-Bu), 32.1 (CH$_3$, *t*-Bu)	−72.9 (Si)	1815 (vw, ν(C=C) of Cyp)
	207 (100, M$^+$ − (SiMe$_3$)$_3$Si)	1.26 (s, 18 H, *t*-Bu)	32.1 (unresolved, q of *t*-Bu)		1240 (vs, δ(SiMe$_3$))
	73 (28.7, SiMe$_3$)		38.9 (q, allylic, Cyp)		790 (vs, br, ν(SiMe$_3$))
	57 (33.2, *t*-Bu)		130.3 (q, C=C of Cyp)		
3b	443 (0.2, M$^+$ − Me)	0.26 (s, 18 H, SiMe$_3$)	3.3 (CH$_3$, SiMe$_3$), 31.2 (CH$_3$, *t*-Bu)	−15.01 (SiMe$_3$)	3100 (s, ν(CH)), 2960 (s, ν(CH))
	401 (0.6, M$^+$ − *t*-Bu)	0.97 (s, 9 H, *t*-Bu)	31.5 (CH$_3$, *t*-Bu), 31.5 (unresolved, q of *t*-Bu)	−38.76 (Si)	2900 (s, ν(CH))
	207 (100, C$_3$(*t*-Bu)$_3$)	1.05 (s, 18 H, *t*-Bu)	37.4 (q, allylic, Cyp), 38.2 (q, *t*-Bu)		1815 (w, ν(C=C) of Cyp)
	73 (14.4, SiMe$_3$)	7.19–7.42 (m, 5 H, Ph)	126.6 (CH, arom), 127.5 (CH, arom)		1590 (s, ν(C=C), arom)
	57 (30.1, *t*-Bu)		128.0 (q, C=C of Cyp), 138.1 (CH, arom), 138.6 (q, arom)		800 (s, ν(SiMe$_3$))
3c	485 (0.6, M$^+$ − Me)	0.26 (s, 18 H, SiMe$_3$)	6.2 (CH$_3$, SiMe$_3$), 20.7 (CH$_3$, *p*-Me)	−13.96 (SiMe$_3$)	3900 (s, ν(CH)), 2890 (s, ν(CH))
	427 (0.8, M$^+$ − SiMe$_3$)	0.96 (s, 9 H, *t*-Bu)	29.4 (CH$_3$, *o*-Me), 31.4 (CH$_3$, *t*-Bu)	−35.55 (Si)	2900 (s, ν(CH))
	207 (100, C$_3$(*t*-Bu)$_3$)	1.05 (s, 18 H, *t*-Bu)	31.4 (unresolved q of *t*-Bu)		1810 (w, ν(C=C) of Cyp)
	73 (68, SiMe$_3$)	2.17 (s, 3 H, *p*-Me, arom)	31.7 (CH$_3$, *t*-Bu), 38.3 (q, *t*-Bu)		1600 (m, ν(C=C), arom)
	57 (86, *t*-Bu)	2.52 (s, 6 H, *o*-Me, arom)	42.0 (q, allylic, Cyp), 128.1 (CH, arom)		1550 (s, ν(C=C), arom)
		6.69 (s, 2 H, arom)	129.6 (q, arom), 135.1 (q, C=C of Cyp)		1250 (s, δ(SiMe$_3$))
			137.2 (q, arom), 145.0 (q, arom)		800 (s, ν(SiMe$_3$))
3d	569 (0.2, M$^+$ − Me)	0.31 (s, 18 H, SiMe$_3$)	6.7 (CH$_3$, SiMe$_3$), 23.7 (CH$_3$, *p*-*i*-Pr)	−13.29 (SiMe$_3$)	3000 (s, ν(CH))
	511 (1.0, M$^+$ − SiMe$_3$)	0.98 (s, 9 H, *t*-Bu)	27.2 (CH$_3$, *o*-*i*-Pr), 27.5 (CH$_3$, *o*-*i*-Pr)	−38.71 (Si)	2900 (s, ν(CH))
	231 (2.0, TIPSi)[d]	1.04 (s, 18 H, *t*-Bu)	31.7 (CH$_3$, *t*-Bu), 32.1 (CH$_3$, *t*-Bu)		1820 (vw, ν(C=C) of Cyp)
	207 (100, C$_3$(*t*-Bu)$_3$)	1.15–1.25 (m, 18 H, CH(C*H*$_3$)$_2$)	32.1 (CH, *i*-Pr), 33.7 (CH, *i*-Pr)		1500 (s, ν(C=C), arom)
	73 (24, SiMe$_3$)	2.79 (m, 1 H, C*H*(CH$_3$)$_2$)	35.2 (q, *t*-Bu), 38.8 (q, *t*-Bu)		1250 (s, δ(SiMe$_3$))
	57 (40, *t*-Bu)	3.51 (m, 2 H, C*H*(CH$_3$)$_2$)	45.0 (q, allylic, Cyp), 122.5 (CH, arom)		760 (vs, br, ν(SiMe$_3$))
		6.94 (s, 2 H, arom)	130.4 (q, arom), 135.1 (q, C=C of Cyp)		
			148.3 (q, arom), 156.1 (q, arom)		

[a] Electron ionization, 70 eV. [b] CDCl$_3$ solvent, δ (ppm) from TMS reference. [c] CCl$_4$ solution. [d] Triisopropylphenyl.

tional evidence for π delocalization in the aryl-substituted anions are their tendency to be much more highly colored than the tris(trimethylsilyl)silyl anion in THF solution. The aryl-substituted anions are orange (**4b** and **4c**) to deep red (**4d**) in color whereas (tris(trimethylsilyl)silyl)lithium is light yellow.[17]

The relative rates of formation of the aryl silyl anions, in turn, appear to reflect relief in steric strain in going from the polysilane to the silyl anion, with the more hindered derivatives reacting the quickest.

Finally, the arylpolysilanes **5b–d** were synthesized by the reductive coupling of trichlorosilanes with trimethylchlorosilane using Mg in HMPA (eq 4). These coupling conditions generally gave higher yields than with Li in THF, which sometimes led to significant amounts of byproducts in which the aryl ring had been reduced.[18]

$$\mathrm{RSiCl_3 + 3Me_3SiCl \xrightarrow[HMPA]{Mg} RSi(SiMe_3)_3 + 3MgCl_2} \tag{4}$$

Chemical and Spectroscopic Properties. The cyclopropenylsilanes **3a–d** are white solids with a waxy appearance. Although the arylcyclopropenylsilanes **3b–d** form easily deformable crystals, no discernible single crystals of **3a** have yet been produced. The cyclopropenylsilanes are indefinitely stable under ambient conditions and even survive treatment with mild aqueous acids.

The cyclopropenylsilanes display considerable thermal stability. All of the cyclopropenylsilanes survive in refluxing xylenes (bp 137–144 °C) over a 12 h period. In the solid state, compounds **3c** and **3d** melt at 165 and 156 °C, respectively, without decomposition. Melting of the derivatives **3a** and **3b** occurs at higher temperatures, 337 and 288 °C, respectively, with only some decomposition.

The spectroscopic data for compounds **3a–d** are summarized in Table I. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra are totally consistent with the proposed structures. In the ^{13}C spectrum, the allylic resonances of the cyclopropene ring appear in the range of 39–45 ppm and the olefinic resonances between 128 and 135 ppm. These chemical shifts are not significantly different from 1,2,3-tri-*tert*-butylcyclopropene which has corresponding resonances at 36 and 127 ppm.[19] The ^{29}Si spectra of these compounds show trimethylsilyl resonances between −13 and −15 ppm. The central silicon has a resonance in the range of −35 to −38 ppm for the cases where two trimethylsilyl groups are pendant and is −73 ppm for the case (**3a**) where three trimethylsilyl groups are attached. The chemical shift values of this silicon are normal for branched polysilanes

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(16) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989–6992.

(17) The spectroscopic properties of this series of anions will be discussed in detail in a future paper.

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(19) Tri-*tert*-butylcyclopropene: ^{13}C NMR (δ, C$_6$D$_6$) 29.8 (CH$_3$, *t*-Bu), 30.2 (CH$_3$, *t*-Bu), 30.9 (q, *t*-Bu), 32.3 (q, *t*-Bu), 35.5 (CH, allylic), 123.29 (q, C=C).

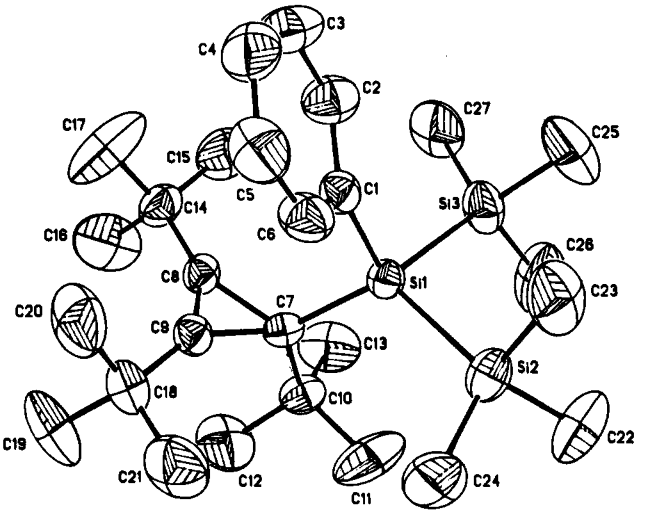

Figure 1. ORTEP diagram depicting molecule **3b**. Thermal ellipsoids are at the 50% probability level.

with the appropriate degree of substitution by trimethylsilyl groups[20] and do not appear particularly sensitive to the presence of the cyclopropene ring.

A distinguishing feature in the infrared spectrum of these cyclopropenylsilanes is a weak olefinic stretching vibration in the range of 1810–1820 cm^{-1}. This nominally "inactive" vibration is characteristic of the cyclopropene ring system.[21]

The mass spectra of **3a–d** are typified by the absence of a parent ion and an intense base peak of 207 amu corresponding to the aromatic tri-*tert*-butylcyclopropenium cation. Other intense mass fragments are present at 57 and 73 amu, belonging to *tert*-butyl and trimethylsilyl cations, respectively. The highest observed mass for these compounds correspond to the parent ion minus one methyl group.

X-ray Structure for 3b. A preliminary account of the X-ray structure of this molecule has appeared.[3] The molecular geometry is shown by the ORTEP in Figure 1. Positional parameters, bond lengths, and valence bond angles are listed in Tables II, IV, and V, respectively.

The most conspicuous structural features found for **3b** are bond length deformations around the central silicon atom, Si1. The silicon–carbon bond length to the cyclopropene ring is 1.940 (4) Å, fully 0.5 Å longer than the typical value of 1.89 Å.[22] Although the silicon–carbon bond to the phenyl group is more typical, 1.893 (5) Å, the silicon–silicon bonds are longer than normal with values of 2.396 (2) and 2.398 (2) Å.[23] The long bond lengths about Si1 are likely the consequence of severe steric interactions of the large groups attached to this atom, in particular the tri-*tert*-butylcyclopropenyl ring.

The cyclopropene ring forms a dihedral angle of 44.2° with the phenyl group. The bond lengths and endocyclic bond angles for the cyclopropene ring are not very different than for cyclopropene itself[24] which has C—C and C=C bond lengths of 1.51 and 1.30 Å, respectively. The unique endocyclic angle for cyclopropene is 50.8°. The carbon–carbon bond lengths of the *tert*-butyl substituents are also in the normal range except for the C7–C10 bond length of the allylic *tert*-butyl group which is 1.565 (6) Å. This long bond length is not surprising since the *tert*-butyl group is geminally related to the large polysilyl moiety.

Table II. Positional Parameters for Compound 3b

atom	x	y	z	B(eq), Å^2
Si1	0.78321 (7)	0.0427 (1)	0.74101 (8)	2.78 (5)
Si2	0.88824 (8)	0.0298 (1)	0.6442 (1)	4.21 (7)
Si3	0.7619 (1)	0.2402 (1)	0.7479 (1)	4.71 (7)
C1	0.8393 (3)	−0.0012 (4)	0.8516 (3)	3.2 (2)
C2	0.8313 (3)	0.0516 (5)	0.9314 (3)	4.8 (3)
C3	0.8696 (4)	0.0133 (6)	1.0114 (4)	6.0 (3)
C4	0.9175 (4)	−0.0804 (6)	1.0138 (4)	5.8 (3)
C5	0.9277 (4)	−0.1342 (5)	0.9372 (4)	5.7 (3)
C6	0.8898 (3)	−0.0941 (5)	0.8574 (3)	4.5 (2)
C7	0.6870 (2)	−0.0525 (4)	0.7219 (3)	2.7 (2)
C8	0.6506 (3)	−0.0965 (4)	0.8039 (3)	3.0 (2)
C9	0.6907 (3)	−0.1697 (4)	0.7645 (3)	3.1 (2)
C10	0.6266 (3)	−0.0312 (4)	0.6359 (3)	3.6 (2)
C11	0.6731 (4)	−0.0174 (7)	0.5573 (4)	7.5 (4)
C12	0.5665 (4)	−0.1286 (6)	0.6154 (4)	6.8 (3)
C13	0.5750 (4)	0.0714 (6)	0.6478 (4)	6.1 (3)
C14	0.5993 (3)	−0.0718 (5)	0.8770 (3)	4.2 (2)
C15	0.5939 (5)	0.0519 (6)	0.8939 (4)	7.3 (4)
C16	0.5142 (4)	−0.1175 (8)	0.8537 (5)	9.5 (5)
C17	0.6388 (5)	−0.1242 (9)	0.9613 (5)	10.2 (5)
C18	0.7154 (3)	−0.2907 (4)	0.7588 (4)	4.1 (2)
C19	0.6372 (4)	−0.3627 (5)	0.7403 (5)	7.5 (4)
C20	0.7615 (4)	−0.3295 (5)	0.8464 (5)	6.9 (4)
C21	0.7692 (4)	−0.3098 (5)	0.6866 (5)	6.9 (4)
C22	0.8727 (4)	0.1256 (6)	0.5465 (4)	7.3 (4)
C23	0.9886 (3)	0.0718 (6)	0.7083 (5)	6.5 (3)
C24	0.9057 (4)	−0.1112 (6)	0.5978 (4)	6.4 (3)
C25	0.8642 (4)	0.3051 (5)	0.7825 (5)	7.8 (4)
C26	0.7214 (5)	0.3053 (6)	0.6385 (5)	7.8 (4)
C27	0.6918 (4)	0.2921 (5)	0.8280 (5)	6.8 (4)

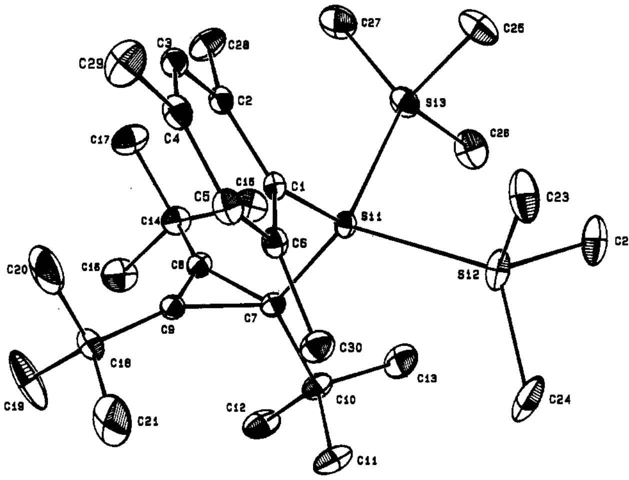

Figure 2. ORTEP diagram depicting molecule **3c**. Thermal ellipsoids are at the 25% probability level.

X-ray Structure for 3c. A single-crystal X-ray structure for **3c** was undertaken in order to present a comparison with **3b** and to examine the structural consequences of increased steric bulk about the central silicon atom. The structure solution showed threefold rotational disorder about the exocyclic carbon–carbon bond of one of the vinylic *tert*-butyl groups. The three discrete conformers were identifiable by residual electron density in the Fourier maps and have been successfully modeled to give a satisfactory refinement (see Experimental Section). An ORTEP drawing of the major conformer is shown in Figure 2. Positional parameters, bond lengths, and bond angles are in Tables III, IV, and V, respectively. The atoms corresponding to the two minor orientations of the disordered *tert*-butyl group are indicated by the letters B and

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[20] Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845–4850.

[21] Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53–127.

[22] Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkenson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2.

[23] Compare with a typical value of 2.34 Å.[22]

[24] Most recent microwave structure: Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1890–1891.

Table III. Positional Parameters for Compound 3c

atom	*x*	*y*	*z*	*B*(eq), Å^2
Si1	0.29670 (5)	0.24731 (7)	0.84306 (4)	3.07 (1)
Si2	0.44918 (5)	0.2254 (1)	0.85827 (6)	5.57 (2)
Si3	0.26499 (7)	0.03657 (9)	0.78994 (6)	5.03 (2)
C1	0.2687 (2)	0.3867 (3)	0.7760 (1)	2.97 (5)
C2	0.2006 (2)	0.3828 (3)	0.7153 (1)	3.29 (6)
C3	0.1890 (2)	0.4786 (3)	0.6640 (2)	3.72 (6)
C4	0.2424 (2)	0.5820 (3)	0.6697 (2)	4.13 (7)
C5	0.3055 (2)	0.5919 (3)	0.7304 (2)	4.17 (7)
C6	0.3191 (2)	0.4990 (3)	0.7834 (2)	3.61 (6)
C7	0.2461 (2)	0.2803 (3)	0.9219 (1)	3.37 (6)
C8	0.1501 (2)	0.2627 (3)	0.9093 (2)	3.72 (6)
C9	0.1742 (2)	0.3800 (3)	0.9105 (1)	3.60 (6)
C10	0.3010 (2)	0.2581 (3)	0.9986 (2)	4.79 (8)
C11	0.3672 (2)	0.3634 (4)	1.0204 (2)	6.8 (1)
C12	0.2474 (3)	0.2614 (5)	1.0526 (2)	6.7 (1)
C13	0.3437 (3)	0.1276 (4)	1.0039 (2)	7.2 (1)
C14	0.0775 (2)	0.1702 (4)	0.9065 (2)	4.88 (8)
C15	0.1089 (3)	0.0324 (4)	0.9222 (2)	6.8 (1)
C16	0.0312 (2)	0.2068 (5)	0.9629 (2)	7.3 (1)
C17	0.0150 (2)	0.1798 (4)	0.8344 (2)	6.6 (1)
C18	0.1481 (0)	0.5201 (0)	0.9102 (0)	5.1 (0)
C19	0.0893 (0)	0.5418 (0)	0.9544 (0)	11.9 (0)
C19B	0.0583 (0)	0.5213 (0)	0.8648 (0)	7.6 (0)
C19C	0.0625 (0)	0.5293 (0)	0.9336 (0)	4.5 (0)
C20	0.1137 (0)	0.5667 (0)	0.8333 (0)	13.2 (0)
C20B	0.1476 (0)	0.5510 (0)	0.9862 (0)	7.2 (0)
C20C	0.1250 (0)	0.5840 (0)	0.8340 (0)	4.0 (0)
C21	0.2216 (0)	0.6100 (0)	0.9357 (0)	10.7 (0)
C21B	0.1878 (0)	0.6102 (0)	0.8678 (0)	5.6 (0)
C21C	0.2240 (0)	0.5880 (0)	0.9586 (0)	4.0 (0)
C22	0.4908 (3)	0.0569 (4)	0.8707 (3)	8.2 (1)
C23	0.4714 (2)	0.2808 (4)	0.7730 (2)	7.7 (1)
C24	0.5273 (2)	0.3076 (5)	0.9330 (3)	8.9 (1)
C25	0.3209 (3)	0.0230 (4)	0.7171 (2)	7.4 (1)
C26	0.3068 (3)	−0.0917 (3)	0.8595 (2)	7.2 (1)
C27	0.1558 (3)	−0.0273 (4)	0.7477 (3)	7.7 (1)
C28	0.1353 (2)	0.2785 (4)	0.7026 (2)	5.52 (9)
C29	0.2317 (3)	0.6806 (3)	0.6112 (2)	6.3 (1)
C30	0.3873 (2)	0.5313 (3)	0.8484 (2)	5.18 (9)

Table IV. Non-Hydrogen Bond Lengths (Å) for Structures 3b and 3c[a]

		distance	
atom 1	atom 2	**3b**	**3c**
Si1	C1	1.893 (5)	1.932 (4)
Si1	C7	1.940 (4)	1.959 (4)
Si2	C22	1.871 (6)	1.874 (6)
Si2	C23	1.880 (6)	1.874 (6)
Si2	C24	1.867 (7)	1.887 (6)
Si3	C25	1.867 (7)	1.886 (6)
Si3	C26	1.887 (7)	1.905 (5)
Si3	C27	1.874 (6)	1.893 (6)
C1	C2	1.388 (7)	1.409 (5)
C1	C6	1.384 (7)	1.417 (5)
C2	C3	1.380 (7)	1.396 (6)
C2	C28		1.502 (6)
C3	C4	1.370 (9)	1.374 (6)
C4	C5	1.358 (8)	1.368 (6)
C4	C29		1.513 (6)
C5	C6	1.382 (7)	1.393 (6)
C6	C30		1.504 (6)
C7	C8	1.536 (6)	1.542 (6)
C7	C9	1.546 (6)	1.544 (6)
C7	C10	1.565 (6)	1.560 (6)
C8	C9	1.284 (6)	1.281 (6)
C8	C14	1.499 (6)	1.522 (6)
C9	C18	1.511 (7)	1.519 (4)
C10	C11	1.500 (7)	1.526 (7)
C10	C12	1.537 (7)	1.535 (7)
C10	C13	1.516 (7)	1.520 (7)
C14	C15	1.509 (8)	1.527 (7)
C14	C16	1.503 (8)	1.538 (7)
C14	C17	1.505 (8)	1.523 (7)
C18	C19	1.543 (7)	1.467 (0)
C18	C20	1.524 (8)	1.544 (0)
C18	C21	1.504 (8)	1.507 (0)
Si1	Si2	2.396 (2)	2.455 (2)
Si1	Si3	2.398 (2)	2.426 (2)

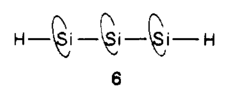
[a] Estimated standard deviations in the least significant figure are given in parentheses.

C appended to the atom labels with B being the more abundant of the two minor conformers.

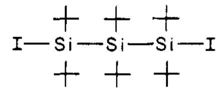
The overall structure of **3c** is similar to that of **3b**. The bond distances and angles of the cyclopropene ring are not unusual. As for the case of **3b**, the longest exocyclic carbon–carbon bond is to the allylic *tert*-butyl substituent (1.565 (6) Å). The cyclopropene ring in **3c** forms a dihedral angle of 54.0 (2)° with the aromatic ring.

The most interesting comparison between the structures lies in the bond distances about the central silicon atom. The mesityl group is more sterically demanding than the phenyl ring due to the presence of ortho methyl substituents. As a consequence, the lengthening of the bonds about Si1 are more pronounced in **3c** than for **3b**. The long silicon–carbon bond exocyclic to the cyclopropene ring is 1.959 (4) Å in **3c** compared to 1.940 (4) Å for **3b**. More striking is the lengthening of the silicon–carbon bond to the aromatic ring; increasing from a typical value of 1.893 (5) Å in **3b** to a value of 1.932 (2) Å in **3c**. The silicon–silicon bonds are also significantly longer in **3c**, having values of 2.426 (2) and 2.455 (2) Å. In addition, a large decrease in the Si2–Si1–Si3 bond angle is observed in going from **3b** (102.09 (7)°) to **3c** (93.97 (6)°). This angle compression is also consistent with the increased bulk of the aromatic substituent in **3c**.

Comparison with Other Trisilanes. The X-ray structures of compounds **6**[25] and **7**[26] represent the only previously reported structures for linear trisilanes. A comparison of silicon–silicon bond lengths and the central Si–Si–Si valence bond angles of **6** and **7** with those of **3b** and **3c** is presented in Table VI.

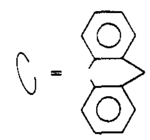


6



$$\mathrm{I{-}\overset{+}{\underset{+}{Si}}{-}\overset{+}{\underset{+}{Si}}{-}\overset{+}{\underset{+}{Si}}{-}I}$$

7



The silicon–silicon bond lengths of all the trisilanes except for **6** are longer than the usual value of 2.34 Å. This is readily explainable by the strong vicinal repulsion of groups across the silicon–silicon bond in these compounds. On one extreme, the heavily *tert*-butylated derivative **7** possesses one of the longest silicon–silicon bonds known (2.644 (1) Å). Compound **6**, on the other hand, likely represents a "normal" trisilane. This molecule should be free of large steric interactions since the the non-hydrogen substituents are pinned back in a ring structure. It is therefore not surprising that the silicon–silicon bond lengths and central bond angle in **6** should assume typical values. Compounds **3b** and **3c** are intermediate cases; the sterically larger substituents are located on the central silicon atom with only methyl groups on the terminal silicon atoms. The result is an elongated silicon–silicon bond but not to the extent displayed by **7** which has large

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(25) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* 1987, *6*, 1595–1596.

(26) Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 79–80.

Table V. Intramolecular Bond Angles (deg) for 3b and 3c

			angle	
atom 1	atom 2	atom 3	**3b**	**3c**
C1	Si1	C7	105.7 (2)	109.2 (2)
C22	Si2	C23	106.0 (3)	104.7 (3)
C22	Si2	C24	105.6 (3)	99.8 (3)
C23	Si2	C24	106.0 (3)	107.5 (3)
C25	Si3	C26	106.7 (3)	109.4 (3)
C25	Si3	C27	106.1 (3)	103.4 (3)
C26	Si3	C27	104.8 (3)	101.3 (3)
Si1	C1	C2	124.4 (4)	123.5 (3)
Si1	C1	C6	120.3 (4)	121.1 (3)
C2	C1	C6	115.3 (4)	115.3 (3)
C1	C2	C3	112.7 (5)	121.1 (4)
C1	C2	C28		122.7 (4)
C3	C2	C28		115.8 (4)
C2	C3	C4	119.7 (5)	122.2 (4)
C3	C4	C5	119.7 (5)	117.1 (4)
C3	C4	C29		121.4 (5)
C5	C4	C29		121.5 (4)
C4	C5	C6	120.0 (6)	122.5 (4)
C1	C6	C5	122.7 (5)	121.0 (4)
C1	C6	C30		124.2 (4)
C5	C6	C30		114.7 (4)
Si1	C7	C8	117.8 (3)	118.3 (3)
Si1	C7	C9	118.7 (3)	117.7 (3)
Si1	C7	C10	116.9 (3)	118.4 (3)
C8	C7	C9	49.3 (3)	49.0 (2)
C8	C7	C10	117.8 (4)	117.0 (3)
C9	C7	C10	119.2 (4)	118.2 (4)
C7	C8	C9	65.8 (3)	65.6 (3)
C7	C8	C14	146.8 (4)	147.0 (4)
C9	C8	C14	147.3 (5)	147.0 (4)
C7	C9	C8	64.9 (3)	65.4 (3)
C7	C9	C18	147.8 (4)	148.2 (3)
C8	C9	C18	146.9 (4)	145.9 (4)
C7	C10	C11	110.7 (4)	111.1 (4)
C7	C10	C12	111.9 (4)	111.5 (4)
C7	C10	C13	109.9 (4)	110.0 (4)
C11	C10	C12	107.1 (5)	106.4 (5)
C11	C10	C13	110.3 (5)	109.8 (5)
C12	C10	C13	106.7 (5)	107.9 (5)
C8	C14	C15	111.7 (4)	111.4 (4)
C8	C14	C16	109.8 (4)	110.1 (4)
C8	C14	C17	109.0 (5)	109.2 (4)
C15	C14	C16	109.1 (6)	107.0 (5)
C15	C14	C17	107.0 (6)	111.2 (5)
C16	C14	C17	110.1 (6)	107.9 (4)
C9	C18	C19	109.0 (4)	111.9 (2)
C9	C18	C20	110.6 (4)	109.7 (1)
C9	C18	C21	111.8 (4)	113.1 (2)
C19	C18	C20	107.8 (5)	113 (0)
C19	C18	C21	109.0 (5)	107 (0)
C20	C18	C21	108.5 (5)	101 (0)
Si2	Si1	Si3	102.09 (7)	93.97 (6)
Si2	Si1	C1	102.6 (1)	102.2 (1)
Si2	Si1	C7	120.0 (1)	123.0 (1)
Si3	Si1	C1	107.1 (2)	113.5 (1)
Si3	Si1	C7	117.9 (1)	114.1 (2)
Si1	Si2	C22	114.0 (2)	115.5 (2)
Si1	Si2	C23	108.2 (2)	106.5 (2)
Si1	Si2	C24	116.3 (2)	121.5 (2)
Si1	Si3	C25	107.1 (2)	107.4 (2)
Si1	Si3	C26	114.1 (2)	109.1 (2)
Si1	Si3	C27	117.4 (2)	125.5 (2)

[a] Numbers in parenthesises are estimated standard deviations of the least significant digit.

Table VI. Comparison of Selected Bond Lengths and Angles in Linear Trisilanes

compd	d(Si–Si), Å	θ(Si–Si–Si), deg
6[a]	2.342 (2), 2.358 (2)	114.2 (1)
3b[b]	2.396 (2), 2.398 (2)	102.09 (7)
3c[b]	2.426 (2), 2.455 (2)	93.97 (6)
7[c]	2.581 (1), 2.644 (1)	115.8 (1)

[a] Reference 25. [b] This work. [c] Reference 26.

substituents on both the central and terminal silicon atoms.

The central Si–Si–Si bond angle also appears to depend on the relative size of substituents on the trisilane, the groups attached to the central silicon atom being the most important. In the case of **3b** and **3c**, the two smaller trimethylsilyl substituents are compressed by the larger aromatic and cyclopropenyl groups around the central silicon atom and consequently the Si–Si–Si angle is considerably reduced from tetrahedral. The reduction of this bond angle from 102.09 (7) to 93.97 (6)° as the phenyl substituent in **3b** is replaced by the larger mesityl group in **3c** is consistent with this picture. Interestingly, the bond angle in compound **7**, which is the most sterically crowded of the trisilanes, is almost the same as the "normal" trisilane **6**. This is explainable with the condition that even though all four groups around the central silicon atom are large, their mutual repulsions are not very different. Specifically, the tendency of the two large *tert*-butyl groups in **7** to reduce the Si–Si–Si angle is counteracted by a resultingly large 1,3 repulsion between the two di-*tert*-butyliodosilyl groups.

The X-ray results clearly indicate that the structural features of the silicon backbone in trisilanes are very sensitive to the size of the appended groups. In principle, it should be possible to alter the structural features in a predictable manner by the judicious choice of substituents.

Conclusion

The direct reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with a number of polysilyllithium reagents provides a facile synthesis for some very hindered cyclopropenylpolysilanes. The extension of this reaction with other cyclopropenium cations and sources of silyl anions is currently under investigation.

Experimental Section

All operations involving syntheses were performed under a blanket of nitrogen and Schlenk techniques were used as required. All glassware was oven dried at 150 °C before use. Reagents were purchased from Aldrich, Lancaster, or Petrarch Chemical Companies and used without further purification. Pentane was deolefinized with concentrated sulfuric acid, dried with anhydrous magnesium sulfate, and distilled from either CaH_2 or $LiAlH_4$. Tetrahydrofuran and diethyl ether were distilled over sodium–benzophenone prior to use. Benzene was distilled over CaH_2. HMPA was distilled over anhydrous BaO and stored over 3A molecular sieves. Tri-*tert*-butylcyclopropenium tetrafluoroborate,[27] 2,2-bis(trimethylsilyl)hexamethyltrisilane[28] (**5a**), and 1-bromo-2,4,6-triisopropylbenzene[29] were prepared by literature procedures.

All NMR spectra were recorded on a IBM-Bruker AF-200 200-MHz instrument. Multiplicities in the ^{13}C NMR were assigned by using either INEPT or DEPT techniques. ^{29}Si spectra were recorded by using a refocussed INEPT sequence. Reactions were monitored on a HP gas chromatograph (5880 series) or a Hewlett-Packard series 5995C GC–MS in total ion mode. Infrared spectra were recorded on a Perkin-Elmer Model 683 infrared spectrophotometer. Mass spectra were obtained on a Hewlett-Packard 5995 series GC–MS using electron impact ionization at 70eV. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points are uncorrected.

Synthesis of Polysilanes. 2-Phenyl-2-(trimethylsilyl)hexamethyltrisilane (5b). A 1-L, 4-neck flask, a mechanical stirrer, a reflux condenser, and an addition funnel were assembled

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under nitrogen. This was then charged with crushed Mg (25.0 g, 1.04 mol), 127 mL of Me_3SiCl (108.8 g, 1 mol), and 340 mL of dry HMPA. The mixture was heated to 95 °C, and then phenyltrichlorosilane (50 mL, 66.5 g, 0.31 mol), was added dropwise with moderate stirring. The reaction that ensued was slightly exothermic, and the flask needed to be cooled occasionally with an ice bath. After 2 h, the addition was complete and the mixture was stirred at 95 °C for 16 h. The reaction mixture was allowed to cool and, with rapid stirring, quenched with 200 mL of hexane followed by 120 mL of 7% HCl solution. After the solution was stirred for 1 h, the hexane layer was separated and dry chromatographed over a silica gel column (60–220 mesh) with hexane as an eluent. The hexane was rotary evaporated to yield a brown viscous oil.

Vacuum distillation (137–146 °C, 0.5 mmHg) of this material yielded 32 g of **5b** as a white waxy solid (22% yield): ^1H NMR (δ, $CDCl_3$) 0.15 (s, 27 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (δ, $CDCl_3$) 1.31 (CH_3, $SiMe_3$), 127.44 (CH, Ph), 127.80 (CH, Ph), 135.49 (q, Ph), 136.65 (CH, Ph); ^{29}Si NMR (δ, $CDCl_3$) 0.24 ($SiMe_3$), −63.27 (Si); MS (*m/e*, rel intensity) 324 (M^+, 20.2), 309 ($M^+ - Me$, 8.1), 251 ($M^+ - SiMe_3$, 9.6), 236 ($M^+ - SiMe_4$, 12.9), 174 ($M^+ - PhSiMe_3$, 64.2), 135 (50.7), 73 ($SiMe_3$, 100); mp 81 °C (lit.[30] mp 84–85°C).

Kugelrohr distillation (190 °C, 0.5 Torr) of the pot residue yielded 9 g (0.02 mol, 11% yield) of $[PhSi(SiMe_3)_2]_2$ as the only other volatile product: ^1H NMR (δ, $CDCl_3$) 0.12 (s, 36 H), 7.14–7.39 (m, 10 H); ^{13}C NMR (δ, $CDCl_3$) 2.01 (CH_3, $SiMe_3$), 127.7 (CH, Ph), 136.6 (CH, Ph), 137.4 (CH, Ph); ^{29}Si NMR (δ, $CDCl_3$) −12.2 ($SiMe_3$), −71.0 (Si); MS (*m/e*, rel intensity) 487 (0.1, $M^+ - Me$), 429 (0.1, $M^+ - SiMe_3$), 352 (14.5, $M^+ - PhSiMe_3$), 278 (100), 251 (27.9, $PhSi(SiMe_3)_2$), 177 (36.3), 135 (66.1), 73 (77.1, $SiMe_3$); IR (KBr, cm^{-1}), 2960 (s), 2920 (s), 1550 (s), 1465 (w), 1250 (s), 1000 (m), 730–840 (br, s).

2-Mesityl-2-(trimethylsilyl)hexamethyltrisilane (5c). Over a 2-h period, 175 mL of *n*-BuLi (1.6 M) was added to a degassed solution of bromomesitylene (50 g, 0.25 mol) in 100 mL of ether. The mixture was stirred overnight. GC analysis showed only 50% conversion, and another 90 mL (1.6 M) of *n*-BuLi was added. After complete conversion, the ether was removed under vacuum, leaving a dry white mass of mesityllithium.

A suspension of the mesityllithium in 75 mL of dry benzene was added dropwise to a solution of 120 mL of $SiCl_4$ (77.8 g, 1.04 mol) and 100 mL of dry benzene heated to 65 °C. After the addition was completed, the mixture was kept at 65 °C for 48 h. After the mixture was cooled to room temperature, the excess $SiCl_4$ and benzene were removed under vacuum, leaving crude mesityltrichlorosilane[31] as a solid.

A solution of the mesityltrichlorosilane in 100 mL of THF was added dropwise over a 2-h period via an addition funnel to a mixture of 18 g of Mg (0.75 mol), 125 mL of HMPA, and 100 mL (86 g, 0.79 mol) of Me_3SiCl heated to 50–60 °C in a 500-mL flask equipped with a mechanical stirrer and reflux condenser. After the addition, the mixture was heated to 90–95 °C for 36 h. The mixture was then allowed to cool and, with rapid stirring, quenched with 200 mL of hexane followed by 100 mL of 7% aqueous HCl solution. The hexane layer was separated followed by the addition of another 200 mL of hexane. The hexane layer was next washed with 100-mL portions of water and saturated NaCl solution and then dry chromatographed to yield a pale brown viscous material. Vacuum distillation (160–170 °C, 0.4–0.5 mm) gave 27 g of **5c** (24% based on the bromomesitylene): mp 78–80 °C; ^1H NMR (δ, $CDCl_3$) 0.22 (s, 27 H, $SiMe_3$), 2.21 (s, 3 H, *p*-Me), 2.44 (s, 6 H, *o*-Me), 6.79 (s, 2 H); ^{13}C NMR (δ, $CDCl_3$) 3.54 (CH_3, $SiMe_3$), 20.72 (CH_3, *p*-Me), 27.64 (CH_3, *o*-CH_3), 128.16 (CH, arom), 131.33 (q, arom), 136.80 (q, arom), 144.67 (q, arom); ^{29}Si NMR (δ, $CDCl_3$) −79.34 (Si), −11.47 ($SiMe_3$); MS (*m/e*, rel intensity) 366 (M^+, 11.3), 293 ($M^+ - SiMe_3$, 21.7), 219 ($M^+ - MesSi$, 100), 119 (Mes, 7.3), 73 ($SiMe_3$, 95.6). Anal. Calcd for $C_{18}H_{38}Si_4$: C, 58.93; H, 10.44. Found: C, 58.72; H, 10.57.

2-(2,4,6-Triisopropylphenyl)-2-(trimethylsilyl)hexamethyltrisilane (5d). Following the previous procedure, 14 g of 1-bromo-2,4,6-triisopropylbenzene (0.05 mol) gave 9 g of **5d** (40% yield based on the bromide) as a white solid after recrystallization from hot EtOH: mp 88–90 °C; ^1H NMR (δ, $CDCl_3$) 0.21 (s, 27 H), 1.15–1.22 (d, 18 H), 2.82 (m, 1 H), 3.40 (m, 2 H), 6.94 (s, 2 H); ^{13}C NMR (δ, $CDCl_3$) 3.58 (CH_3, $SiMe_3$), 23.81 (CH_3, *i*-Pr), 26.64 (CH_3, *i*-Pr), 33.69 (CH, *i*-Pr), 35.87 (CH, *i*-Pr), 121.43 (CH, arom), 129.54 (q, arom), 147.96 (q, arom), 155.90 (q, arom); ^{29}Si NMR (δ, $CDCl_3$) −83.15 (Si), −11.63 ($SiMe_3$); MS (*m/e*, rel intensity) 450 (M^+, 0.23), 435 ($M^+ - CH_3$, 0.3), 377 ($M^+ - SiMe_3$, 46), 303 ($M^+ - 2SiMe_3$, 63), 243 (56.3), 229 (51.89), 73 (100). Anal. Calcd for $C_{24}H_{50}Si_4$: C, 63.92; H, 11.16. Found: C, 63.06, H, 11.31.

Synthesis of Cyclopropenylsilanes. 2-(3-Tri-*tert*-butylcyclopropenyl)-2-mesitylhexamethyltrisilane (3c). 2-Mesityl-2-(trimethylsilyl)hexamethyltrisilane (**5c**) (1.128 g, 3.08 mmol) was dissolved in 20 mL dry THF, and the solution was purged with nitrogen. To this solution was added 2.8 mL methyllithium (1.25 M, 3.31 mmol), and the solution was stirred for 12 h at room temperature. The orange solution was cannulated into a suspension of 0.952 g (3.13 mmol) tri-*tert*-butylcyclopropenium fluoroborate in dry, degassed pentane. After 10 min, the yellow color disappeared and the solution became homogeneous. Stirring was continued for 12 h, after which the solution was evaporated to dryness. The residue was extracted with 150 mL of hexane, filtered, and dry chromatographed through silica gel (60–230 mesh) with an additional 50 mL of hexane. Removal of hexane yielded 1.24 g of **3c** as a white crystalline solid product (81% based on silane), mp 165–170 °C. Anal. Calcd for $C_{30}H_{56}Si_3$: C, 71.91; H, 11.26. Found: C, 71.74; H, 11.23.

In a similar manner, the other cyclopropenylsilanes were synthesized.

2-(3-Tri-*tert*-butylcyclopropenyl)-2-(2,4,6-triisopropylphenyl)hexamethyltrisilane (3d). 2-(2,4,6-Triisopropylphenyl)-2-(trimethylsilyl)hexamethyltrisilane (**5d**) (3.02 g, 6.72 mmol) and 2.17 g (2.18 mmol) of the fluoroborate salt were reacted for 48 h to give 1.65 g (42% yield) of **3d** as a white crystalline solid. The product was purified by recrystallization from hexane/methanol (1:2); mp 156–158 °C. Anal. Calcd for $C_{36}H_{68}Si_3$: C, 73.87; H, 11.73. Found: C, 73.78; H, 11.42.

2-(3-Tri-*tert*-butylcyclopropenyl)-2-phenylhexamethyltrisilane (3b). 2-Phenyl-2-(trimethylsilyl)hexamethyltrisilane (**5b**) (1.43 g, 3.129 mmol) and 1.37 g (4.64 mmol) of the fluoroborate gave 1.80 g of **3b** (89% yield) as a white crystalline product, mp 336–338 °C. Anal. Calcd for $C_{27}H_{50}Si_3$: C, 70.75; H, 10.91. Found C: 70.93; H, 10.84.

2-(3-Tri-*tert*-butylcyclopropenyl)-2-(trimethylsilyl)hexamethylsilane (3a). 2,2-Bis(trimethylsilyl)hexamethyltrisilane (**5a**) (0.36 g, 1.12 mmol) and 0.40 g (1.36 mmol) of the fluoroborate salt gave 0.54 g of **3a** (88% yield) as a white crystalline product, mp 286–290 °C. Anal. Calcd for $C_{24}H_{54}Si_4$: C, 63.43; H, 11.80. Found: C, 63.53; H, 11.89.

Attempted Pyrolysis of 3a–d in Refluxing Xylene. A 15–20-mg quantity of cyclopropenylsilane was dissolved in dry degassed xylene and refluxed under nitrogen for 12 h. Analysis by both ^1H NMR and GC–MS revealed no volatile decomposition products. The mass recovery of starting material was 80–90% in all cases.

Treatment of 3a–d with Aqueous Hydrochloric Acid. A 15–20-mg quantity of cyclopropenylsilane was stirred for 12 h in 5 mL of 10% HCl in MeOH. Removal of the solvent followed by analysis by ^1H NMR and GC–MS revealed no decomposition products. Mass recovery was 80–90%.

Reaction of Tri-*tert*-butylcyclopropenium Tetrafluoroborate and 4b in HMPA. Dropwise addition of 1.5 M MeLi (0.45 mL, 0.68 mmol) to 0.20 g (0.62 mmol) of **5b** in a degassed solution consisting of 2 mL of HMPA and 2 mL of THF yielded the red-orange silyllithium **4b** after a period of 25 min. The solution of silyllithium was cannulated into a suspension of 0.22 g (0.75 mmol) of tri-*tert*-butylcyclopropenium tetrafluoroborate in 2 mL of diethyl ether. The red-brown color remained unaltered after 1 h of stirring. Heating at 70 °C resulted in a slight increase in color intensity; however, after 48 h no visible change had occurred in the appearance of the mixture. The reaction was quenched by 20 mL hexane followed by 20 mL of 5% aqueous HCl solution. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Removal of the solvent by rotary evaporation yielded a red oil. The oil was identified as a 1:1 mixture of tri-*tert*-butylcyclopropene and phenylbis(tri-

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Table VII. Experimental Crystallographic Data for Compounds 3b and 3c

	3b	3c
formula	$Si_3C_{27}H_{50}$	$Si_3C_{30}H_{56}$
mol wt	458.95	500.59
cryst dimens, mm	0.30 × 0.25 × 0.20	0.53 × 0.26 × 0.53
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
cell dimens		
a, Å	16.382 (5)	16.412 (4)
b, Å	11.990 (2)	10.403 (2)
c, Å	15.199 (3)	15.566 (5)
α, deg		
β, deg	96.70 (2)	104.69 (2)
γ, deg		
V, Å^3	2965	3231.3 (2)
Z	4	4
ρ(calcd), g cm^{-3}	1.03	1.029
radiatn	Cu Kα (λ = 1.54178 Å)	Mo Kα (λ = 0.71069 Å)
2θ range, deg	0–118	1–53°
scan type	ω–2θ	$\omega/2\theta$
scan angle	1.25 + 0.3 tan θ	0.8 + 0.2 tan θ
scan speed, deg min^{-1}	10–32	1.6–16
total data collected	4696	6919
unique data	4507	6447
obsd data with $I_0 > 3\sigma_I$	3397	4145
μ, cm^{-1}	14.8	1.6
transmissn coeff	1.0–0.89	0.99–0.98
F(000)	1016	1112
R	7.1	5.4[a]
R_w	10.0[c]	8.4[b]

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma(F^2)$. [c] $\sum w(|F_o| - |F_c|^2$, $w = 4F_o^2/\sigma^2(F_o^2)$.

methylsilyl)silane by GC–MS and comparison with independently synthesized compounds.

X-ray Structure Determinations: General Data. Difrangible crystals of **3b** and **3c** were obtained by slow evaporation of hexane solutions at room temperature. Data collection and refinement parameters used for the two structure determinations are summarized in Table VII.

X-ray Crystal Structure Determination of 3b. The data for structure **3b** were collected on a Rigaku AFC6R diffractometer equipped with Cu Kα radiation and a graphite monochromater. The measured reflections were $-18 < h < 18$, $0 < k < 13$, and $0 < l < 16$. Lorentz–polarization and empirical corrections were performed on the data.[32] The structure was solved by direct methods using the TEXSAN software package. Refinement was by full-matrix least squares; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and held positionally invariant; isotropic thermal parameters were all tied to a single variable. The maximum shift in the last least-squares cycle was 0.05σ; the highest peak in the final difference Fourier map was 0.38 e/Å^3. A small secondary extinction coefficient (6.77×10^{-6}) was necessary. Final residuals are given in Table VII.

X-ray Structure Determination of 3c. Intensity data for **3c** were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromater. Data were obtained by ω–2θ scans of variable rate with a maximum scan time of 45 s ($0 < h < 20$, $0 < k < 13$, $-24 < l < 24$). Three standard reflections were monitored every 200 reflections and showed a slight (1.8%) linear decrease in intensity of the standards over the period of the data collection. The data was corrected for Lorentz–polarization, background, and absorption effects.[33] The absorption correction was based on Ψ scans of reflections near $\chi = 90°$. The space group $P2_1/c$ was uniquely determined by systematic absences. Other details of the experiment are given in Table VII.

The structure was solved by direct methods (MULTAN) and refined as a full matrix. The remaining atoms were located in a series of difference Fourier maps and refined anisotropically. One *tert*-butyl group attached to the vinylic carbon atom C9 exhibited a slight degree of rotational disorder. Three discrete rotamers were observed in the difference Fourier map. Partial occupancies were assigned on the basis of an average value of the relative peak heights and were held invariant. The major conformer consisted of C19, C20, and C21 with a relative occupancy of 0.60. The other conformers were C19B, C20B, C21B (relative occupancy, 0.23) and C19C, C20C, C21C (relative occupancy, 0.17). Except for C21C which was placed in a calculated position, all other carbons atoms in the conformers were placed in observed positions, refined anisotropically, and then held positionally and thermally invariant. Hydrogen atoms were placed in a combination of observed and calculated positions. Some hydrogen atoms were refined isotropically before being held invariant. The final least-squares cycle converged with a maximum shift of 0.05σ with final residual values of $R = 5.4$ and $R_w = 8.4$. The highest peak in the difference Fourier map was 0.479 e/Å^3 in the vincinity (<1.0 Å) of the C21 and C21B carbon atoms in the disordered *tert*-butyl group.

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Registry No. **3a**, 118714-38-8; **3b**, 109242-63-9; **3c**, 109242-64-0; **3d**, 118714-39-9; **4a**, 4110-02-5; **4b**, 109242-61-7; **4c**, 109242-62-8; **4d**, 118714-37-7; **5a**, 4098-98-0; **5b**, 4235-65-8; **5c**, 83241-99-0; **5d**, 118714-40-2; $Cyp^{*+}BF_4^-$, 60391-90-4; Me_3SiCl, 75-77-4; $PhSiCl_3$, 98-13-5; $[PhSi(SiMe_3)_2]_2$, 118714-41-3; $(Me_3C_6H_2)SiCl_3$, 17902-75-9; 1-bromo-2,4,6-triisopropylbenzene, 21524-34-5; tri-*tert*-butylcyclopropene, 23438-08-6; phenylbis(trimethylsilyl)silane, 4099-01-8.

Supplementary Material Available: Complete listings of positional parameters including hydrogens, general temperature factors, valence bond lengths and angles, torsion angles, and intermolecular contacts and selected lists of least-squares planes for **3b** and **3c** (44 pages); listings of calculated and observed structure factors for **3b** and **3c** (65 pages). Ordering information is given on any current masthead page.

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[32] Computations were carried out on a VAX based TEXRAY computer system with the TEXSAN software package by the Molecular Structure Corp.

[33] Calculations were performed on a PDP 11/73 M computer using the Enraf-Nonius Structure Determination Package. Atom scattering factors were corrected for the effects of anamolous dispersion.