11096 *J. Am. Chem. Soc.* **1998,** *120,* 11096−11105

Synthesis, Structure, and Reactivity of the First Kinetically Stabilized Silanethione

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Received March 9, 1998

Abstract: Diaryltetrathiasilolanes **2a**,**b**, bearing bulky aryl groups such as 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt), mesityl (Mes), and 2,4,6-triisopropylphenyl (Tip), were obtained by thermal reaction of dihydrosilane **3a** with elemental sulfur, reaction of highly hindered disilene **4** with sulfur, or reduction of dibromosilane **6** followed by addition of sulfur. The molecular structure of **2a** was determined by X-ray crystallographic analysis. Desulfurization of **2a** at −78 °C afforded a silicon−sulfur double bond compound (silanethione **7a**). Although the formation of **7a** was confirmed by various trapping reactions, **7a** dimerized at room temperature to give 1,3,2,4-dithiadisiletane **8**, whose molecular structure was determined by X-ray crystallographic analysis. Desulfurization of **2b** afforded the first stable silanethione, Tbt(Tip)Si═S (**7b**), as yellow crystals, which were thermally stable under inert gas up to its melting point (185−189 °C) and showed λ_{max} (n→π^*) at 396 nm and $\nu_{Si=S}$ (Raman) at 724 cm^{-1}. The chemical shift of δ_{Si} 166.56 in the ^{29}Si NMR spectrum is greatly downfield-shifted, characteristic of a silathiocarbonyl unit. Comparison of the electronic spectra (n→π^*) of a series of $R^1R^2M{=}S$ (M = C, Si, Ge, Sn) compounds revealed an interesting trend: λ_{max} is significantly blue-shifted on going from M = C to M = Si, whereas λ_{max}'s for $R^1R^2M{=}S$ (M = Si, Ge, Sn) are red-shifted on increasing the atomic number of M. This trend is also found in calculated values for $H_2M{=}S$ (M = C, Si, Ge, Sn). The X-ray crystallographic analysis of **7b** revealed that there are two nonidentical silanethiones in the asymmetric unit and the silathiocarbonyl units have completely trigonal-planar geometry, with silicon−sulfur double bond lengths of 1.948(4) and 1.952(4) Å, which are about 0.2 Å shorter than the typical Si−S single bond length (ca. 9% shortening), indicating an unambiguous double bond character between silicon and sulfur. Despite the presence of two very bulky substituents on silicon, **7b** easily reacted with water, methanol, phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene to afford the corresponding adduct or cycloadduct. Theoretical calculations were carried out for the σ and π bond energies of $H_2M{=}X$ (M = C, Si, Ge, Sn, Pb; X = O, S, Se, Te) and for the single and double bond lengths of $H_3M{-}XH$ and $H_2M{=}X$, and the theoretical backgrounds of the chemistry of group 14−group 16 double bond species were discussed.

Introduction

Recently, remarkable progress has been made in the chemistry of organosilicon compounds containing multiple bonds to group 14 or group 15 elements,[1] i.e., Si═Si,[2] Si═C,[3] and Si═Pn (Pn = N, P, As).[4] These species have been isolated successfully by taking advantage of kinetic stabilization with bulky substituents. In contrast, there had been no example of the isolation using kinetic stabilization for silicon−chalcogen double-bond species until we preliminarily communicated[5a] the synthesis of the first silanethione[6] (silicon−sulfur double bond compound), though much theoretical interest has been focused on this

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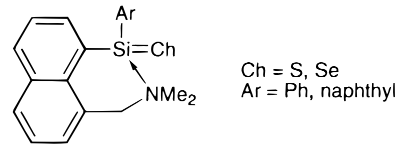
10.1021/ja980783c CCC: $15.00

fascinating class of low-coordinate organosilicon compounds.[7] The difficulty in synthesizing such a type of species is obviously due to the fact that bulky substituents for steric protection can be introduced only on the silicon atom, and hence their oligomerization cannot be efficiently prevented. Although Corriu et al. reported the isolation of thermodynamically stabilized silicon−sulfur double bond compounds and their selenium analogues **1** in 1989,[8] they found by X-ray crystallography that the Si atom of the silanethione **1** (Ar = naphthyl, Ch = S) was tetracoordinate because of the intramolecular coordination by a nitrogen lone pair and the geometry around silicon was a distorted tetrahedral. The silicon−sulfur bond length is 2.013(3) Å, which indicates only 6% shortening compared to the normal silicon−sulfur single bond (∼2.15 Å). Spectral features also suggest that **1** is not a doubly bonded compound; the chemical shift of 22.3 ppm in ^{29}Si NMR of **1** (Ar = Ph, Ch = S) is within the region of normal tetrahedral organosilicon species.



Ch = S, Se
Ar = Ph, naphthyl

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To synthesize a silanethione, it is important to choose a proper precursor and a suitable methodology, since it can be anticipated that a desired silanethione is too reactive toward atmospheric oxygen and moisture to be purified with chromatography. We have selected, therefore, a silicon-containing cyclic polysulfide as a precursor and investigated the synthesis of a silanethione via desulfurization of the polysulfide. The present paper delineates a detailed account of the synthesis of silicon-containing cyclic polysulfides and their transformation to the first stable silanethione,[5] together with the theoretical aspects of the chemistry of group 14−group 16 double bond species.

Results and Discussion

I. Theoretical Considerations. Computational Methods. Geometries were fully optimized with the nonlocal hybrid density functional method at the B3LYP level.[9] The effective core potential and basis set developed by Wadt and Hay[10] were used on Si, Ge, Sn, Pb, S, Se, and Te. The basis set [3s3p] in the triple-ζ (TZ) form was augmented by a set of d-type polarization functions (d exponents 0.45 (Si), 0.246 (Ge), 0.183 (Sn), 0.164 (Pb), 0.65 (S), 0.338 (Se), 0.237 (Te)).[11,12]

Table 1. σ and π Bond Energies (kcal mol^{-1}) for $H_2M{=}X$ Calculated at the B3LYP/TZ(d,p) Level

		X			
$H_2M{=}X$		O	S	Se	Te
$H_2C{=}X$	σ	93.6	73.0	65.1	57.5
	π	95.3	54.6	43.2	32.0
	σ + π	188.9	127.6	108.3	89.5
$H_2Si{=}X$	σ	119.7	81.6	73.7	63.2
	π	58.5	47.0	40.7	32.9
	σ + π	178.2	128.6	114.4	96.1
$H_2Ge{=}X$	σ	101.5	74.1	67.8	59.1
	π	45.9	41.1	36.3	30.3
	σ + π	147.4	115.2	104.1	89.4
$H_2Sn{=}X$	σ	94.8	69.3	64.3	56.4
	π	32.8	33.5	30.6	26.3
	σ + π	127.6	102.8	94.9	82.7
$H_2Pb{=}X$	σ	80.9	60.9	57.0	50.3
	π	29.0	30.0	27.8	24.4
	σ + π	109.9	90.9	84.8	74.7

The 6-311G(d,p) basis set was used for C, O, and H.[11] The π and σ bond energies were calculated at the B3LYP/TZ(d,p) level with the procedure proposed by Schleyer and Kost.[13] The excitation energies were calculated at the CIS[14]/TZ(d,p)//B3LYP/TZ(d,p) level. The ^{29}Si NMR chemical shifts were calculated with the GIAO[15]-B3LYP method using the B3LYP/6-31G(d)-optimized geometries; the 6-311G(3d) basis set was used for Si and S, while 6-311G(d) was used for the second row atoms. All calculations were carried out using the Gaussian 94 program.[16]

Bond Energies and Bond Lengths. When we undertook a study on the synthesis of a series of heavier element congeners of a ketone ($R^1R^2M{=}X$; M = Si, Ge, Sn, Pb; X = S, Se, Te), which we refer to as "heavy ketones", we carried out theoretical calculations on the σ and π bond energies as well as on the single and double bond lengths of $H_2M{=}X$ to study general aspects of heavy ketones. The results are shown in Tables 1 and 2. Some points of interest pertinent to the results of the calculations follow:

(1) A carbon−oxygen double bond is unique in that the σ and π bond energies are almost equal to each other. This is an energetic basis of the well-known reactivity of a carbonyl compound, i.e., addition−elimination mechanism through a tetrahedral intermediate.

(2) In all the other double bonds, the σ bond energy is much greater than the corresponding π bond energy. This indicates the high reactivity of these double bond compounds toward any kind of addition reaction, because the formation of two new σ bonds on M and X with concurrent cleavage of the π bond results in substantial overall energy gain.

(3) Every compound with a group 14−group 16 element double bond corresponds to a minimum on the potential energy surface, as confirmed from all positive eigenvalues of the Hessian matrix. This suggests that all the doubly bonded

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[6] Although "thioxosilane" is a recommended name for a silicon−sulfur double bond compound according to the nomenclature in *Chemical Abstracts* and "silylidenesulfane" is the nomenclature in conformity with IUPAC, we use here a name "silanethione" for a silicon−sulfur double bond compound instead of thioxosilane in this paper because silanethione is a common name which has been often used in the literature of organosilicon chemistry.

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Table 2. Single and Double Bond Lengths (Å) at the B3LYP/TZ(d,p) Level

	X			
	O	S	Se	Te
$H_3C{-}XH$	1.421	1.835	1.979	2.165
$H_2C{=}X$	1.200	1.617	1.758	1.949
Δ^a	15.5	11.9	11.1	10.0
$H_3Si{-}XH$	1.649	2.148	2.294	2.508
$H_2Si{=}X$	1.514	1.945	2.082	2.288
Δ^a	8.1	9.4	9.3	8.7
$H_3Ge{-}XH$	1.788	2.256	2.393	2.596
$H_2Ge{=}X$	1.634	2.042	2.174	2.373
Δ^a	8.6	9.5	9.2	8.6
$H_3Sn{-}XH$	1.950	2.438	2.565	2.768
$H_2Sn{=}X$	1.802	2.222	2.346	2.543
Δ^a	7.6	8.9	8.5	8.1
$H_3Pb{-}XH$	2.025	2.502	2.628	2.819
$H_2Pb{=}X$	1.853	2.273	2.394	2.590
Δ^a	8.5	9.2	8.9	8.1

[a] Value of % reduction in a bond length defined as [(single bond length − double bond length)/single bond length] × 100.

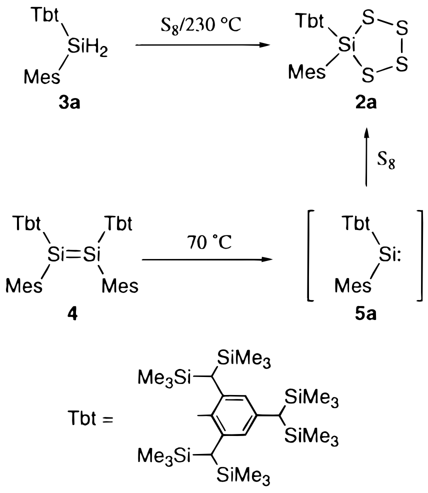
compounds in Table 1 are synthetically accessible, if one can find an appropriate synthetic methodology.

(4) The values of percent reduction listed in Table 2 increase roughly with increasing the π bond energy, although the results for M−O bond compounds are somewhat exceptional. It should be noted that the values except for C═O, C═S, and C═Se are similar to each other, being 8−10%, irrespective of the atomic numbers of constitutional elements.

Although σ and π bond energies of $H_2Si{=}S$ are smaller than those of $H_2Si{=}O$, the silicon−sulfur double bond compound is considered to be more easily synthesized, since the theoretical calculation carried out by one of the authors has predicted[17] that a silicon−sulfur double bond is kinetically more stable than a silicon−oxygen double bond. According to the natural population analysis at the B3LYP/TZ(d,p) level, the double bond ($Si^{+0.98}S^{-0.56}$) of $H_2Si{=}S$ is much less polarized than that ($Si^{+1.58}O^{-1.05}$) of $H_2Si{=}O$, the former being apparently less reactive than the latter. In addition, $H_2Si{=}S$ is calculated to be 15.0 kcal mol^{-1} more stable than its divalent isomer, H(HS)Si:, whereas $H_2Si{=}O$ is only 3.5 kcal mol^{-1} more stable than H(HO)Si:.

II. Synthesis of Tetrathiasilolanes. Although there have been several reports on the synthesis of cyclic polychalcogenides containing transition metals such as Cp_2TiS_5,[18a] Cp_2VS_5,[18b] Cp_2CSe_5,[18c] Cp_2MoS_4,[18d] Cp_2WS_4[18e] (Cp = η^5-C_5H_5), and $(N\text{-}MeIm)_2ZnSe_4$ (Im = imidazole),[18f] main group element analogues including silicon-containing cyclic polychalcogenides had been unknown until 1,2,3,4,5-tetrathiasilolane **2a** was synthesized by taking advantage of kinetic stabilization utilizing sterically bulky substituents, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt) and mesityl (Mes) groups.[5b] Compound **2a** can be obtained by thermal reaction of the corresponding diaryldihydrosilane **3a** with elemental sulfur and is quite stable toward heat and moisture (Scheme 1). It is in sharp contrast with diphenyltetrathiasilolane, which is, reportedly, stable only below −20 °C.[19] The instability of the diphenyl derivative is most likely due to its high sensitivity toward hydrolysis, which is prevented by the presence of bulky substituents (kinetic stabilization) in the case of **2a**.

Scheme 1



It should be noted that the bulkiness of the substituents on a silicon atom is an important factor in determining the type of a product which results from the reaction of a dihydrosilane with sulfur. For example, the reaction of diphenyldihydrosilane with elemental sulfur is known to give trithiatrisilane with no monomeric sulfide being formed.[20] It is clear, therefore, that the Tbt and Mes groups not only play an important role in kinetic stabilization to retard hydrolysis but also prevent oligomerization.

Although we already reported the synthesis of **2a** by the thermal reaction of **3a** with elemental sulfur, the yield was quite low (<10%), and the purification was very difficult.[5b] However, **2a** could be obtained in an excellent yield by utilizing the dissociation of extremely hindered disilene **4** into silylene **5a**.[21] When a benzene solution of **4** and sulfur was heated at 70 °C for 6 h, **2a** was formed in 94% yield (Scheme 1).

The structure of **2a** was confirmed by ^1H and ^{13}C NMR, elemental analysis, and X-ray crystallographic analysis.[22] The crystallographic data for this structure is summarized in Table 3. Selected bond lengths and angles are listed in Table 4.

We next attempted the synthesis of a tetrathiasilolane bearing a different combination of bulkier substituents, i.e., Tbt- and 2,4,6-triisopropylphenyl (Tip)-substituted tetrathiasilolane. Although the reaction of $TbtSiH_3$ with TipLi gave diaryldihydrosilane **3b** in good yield (77%), the reaction of **3b** with elemental sulfur below 240 °C resulted in the recovery of the starting material, and the reaction over 270 °C gave a complex mixture. However, the reduction of dibromosilane **6**, obtained by the bromination of **3b** with *N*-bromosuccinimide (NBS), with lithium naphthalenide followed by addition of sulfur at low temperature afforded Tbt- and Tip-substituted tetrathiasilolane **2b** in 28% yield as pale yellow crystals (Scheme 2). Compound **2b** showed satisfactory spectral and analytical data. The Raman spectrum taken for the powdered sample with a 1064-nm line

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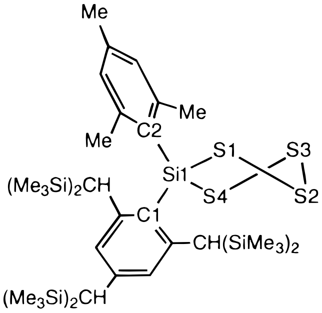
(22) For the ORTEP drawing of **2a**, see ref 5b.

Table 3. Experimental Crystallographic Data for **2a**, **7b**, and **8**

	2a	**7b**	**8**
empirical formula	$C_{36}H_{70}Si_7S_4 \cdot CHCl_3$	$C_{42}H_{82}Si_7S$	$C_{72}H_{140}Si_{14}S_2$
fw	947.30	815.77	1463.21
cryst size, mm	0.60 × 0.60 × 0.1	0.40 × 0.35 × 0.20	0.60 × 0.40 × 0.20
temp, K	298	298	298
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
unit cell dimens			
a, Å	12.292(3)	21.33(1)	17.923(3)
b, Å	13.034(2)	13.82(1)	21.672(4)
c, Å	33.532(9)	36.13(2)	24.214(4)
β, deg	91.60(1)	92.50(5)	92.99(1)
V, Å^3	5370(2)	10639(12)	9392(2)
Z	4	8	4
density (calcd), g cm^{-3}	1.172	1.018	1.035
scan type	ω	$2\theta-\omega$	$2\theta-\omega$
no. of obsd reflns	4906	5390	8548
data-to-param ratio	10.7	6.0	10.8
largest diff peak, e Å^{-3}	0.535	0.4	0.4
largest diff hole, e Å^{-3}	- 0.531	0.2	0.5
R, %	7.8	6.1	7.0
R_w, %	7.8	5.1	5.5
goodness of fit	1.04	2.35	3.91

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **2a**



S(1)−Si(1)	2.224(3)	S(4)−Si(1)	2.155(3)
S(1)−S(2)	2.051(4)	Si(1)−C(1)	1.898(6)
S(2)−S(3)	2.046(5)	Si(1)−C(2)	1.897(7)
S(3)−S(4)	2.057(3)		
S(1)−Si(1)−S(4)	100.4(1)	S(1)−Si(1)−C(1)	119.2(3)
Si(1)−S(1)−S(2)	102.9(2)	S(1)−Si(1)−C(2)	96.5(3)
S(1)−S(2)−S(3)	99.6(2)	S(4)−Si(1)−C(1)	103.4(2)
S(2)−S(3)−S(4)	97.4(2)	S(4)−Si(1)−C(2)	118.5(2)
S(3)−S(4)−Si(1)	100.3(1)	C(1)−Si(1)−C(2)	118.3(3)

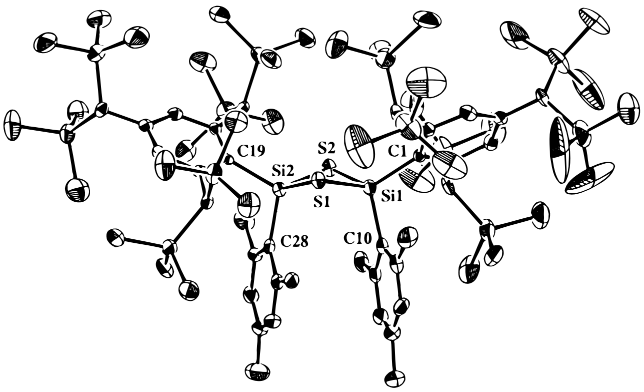


Figure 1. ORTEP drawing of [Tbt(Mes)SiS]$_2$ (**8**) with thermal ellipsoid plot (30% probability).

Scheme 2

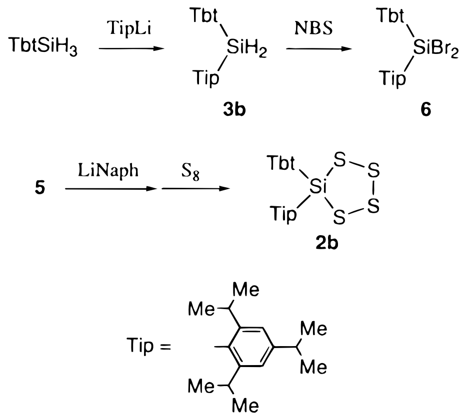


Table 5. Selected Bond Lengths (Å) and Angles (deg) of **8**

S(1)−Si(1)	2.190(3)	Si(1)−C(1)	1.922(6)
S(1)−Si(2)	2.172(3)	Si(1)−C(10)	1.926(8)
S(2)−Si(1)	2.174(3)	Si(2)−C(19)	1.922(7)
S(2)−Si(2)	2.191(3)	Si(2)−C(28)	1.915(7)
Si(1)−S(1)−Si(2)	84.4(1)	C(1)−Si(1)−C(10)	110.6(3)
Si(1)−S(2)−Si(2)	84.4(1)	S(1)−Si(2)−S(2)	90.4(1)
S(1)−Si(1)−S(2)	90.4(1)	S(1)−Si(2)−C(19)	116.4(2)
S(1)−Si(1)−C(1)	118.3(2)	S(1)−Si(2)−C(28)	113.2(2)
S(1)−Si(1)−C(10)	106.4(2)	S(2)−Si(2)−C(19)	118.2(2)
S(2)−Si(1)−C(1)	116.5(2)	S(2)−Si(2)−C(28)	107.6(2)
S(2)−Si(1)−C(10)	113.0(3)	C(19)−Si(2)−C(28)	109.8(3)

of a Nd:YAG laser in the region of 300−1800 cm^{-1} showed a characteristic Raman line at 504 cm^{-1}. For **2a**, the Raman line was observed at 505 cm^{-1}. These Raman lines are most likely assignable to the S−S stretching in the polysulfido linkages of **2a** and **2b**.

III. Silanethiones. Desulfurization of Tbt- and Mes-Substituted Tetrathiasilolane 2a. To synthesize a silanethione, we first examined the desulfurization of **2a** with triphenylphosphine. Since triphenylphosphine is soluble in hexane while triphenylphosphine sulfide is not, the purification of the reaction product was expected to be easily carried out only by filtration. When **2a** was treated with 3 molar equiv of triphenylphosphine in hexane at −78 °C, the solution turned pale yellow, suggesting the generation of silanethione **7a**. Warming up of the yellow solution to room temperature, however, gave only 1,3,2,4-dithiadisiletane **8** (90%), which probably resulted from the dimerization of silanethione **7a**. Although **8** exhibited a ^{1}H NMR spectrum which was too complicated to be assigned because of great steric congestion around the silicon atoms,[23] the molecular structure of **8** was definitively confirmed by X-ray crystallographic analysis. Figure 1 shows the ORTEP drawing of **8**. The crystallographic data for this structure are summarized in Table 3. Selected bond lengths and angles are listed in Table 5.

It is interesting that the geometry of **8** is a cis form and the central four-membered ring is folded by 35.2° with regard to the two S−Si−S planes. The two mesityl groups facing each other are almost parallel, with the dihedral angle between these two aromatic rings being 3.9°. These results can be explained in terms of steric repulsion caused by these bulky substituents, which is expected to be smaller for the folded cis form than for a trans form, which is expected to be planar.

Although silanethione **7a** immediately dimerized at room temperature to afford **8**, the yellow color of the reaction mixture

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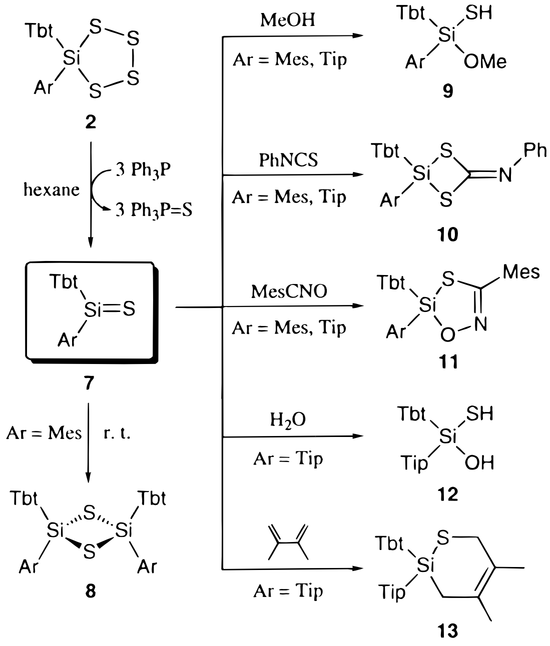
[23] For the ^{1}H NMR spectrum of **8**, see the Supporting Information.

Scheme 3



at −78 °C suggested the existence of **7a** at low temperature. To trap **7a**, methanol, phenyl isothiocyanate, and mesitonitrile oxide were added to the hexane solution of **2a** and 3 molar equiv of triphenylphosphine at −78 °C to afford the corresponding adducts (**9a**, 93%; **10a**, 72%; **11a**, 45%), along with **8** as a minor product (Scheme 3).

Desulfurization of Tbt- and Tip-Substituted Tetrathiasilolane 2b. Since it is obvious that the combination of Tbt and Mes groups is not bulky enough to prevent the dimerization of the corresponding silanethione **7a** at room temperature, desulfurization of Tbt- and Tip-substituted tetrathiasilolane **2b** was examined. When 3 molar equiv of triphenylphosphine was added to a hexane solution of **2b** at room temperature, the solution turned yellow, suggesting the formation of **7b**. Surprisingly, this yellow color did not disappear, even after refluxing for 2 h in hexane, indicating the high stability of silanethione **7b** toward dimerization. After filtration of triphenylphosphine sulfide under argon, the filtrate was concentrated in a glovebox to give quantitatively silanethione **7b** as yellow crystals (Scheme 3).[24]

Silanethione **7b** is thermally very stable under inert gas up to its melting point (185−189 °C), but it is very unstable in the air, as expected, and rapidly decomposes to afford a hydroxysilanethiol (**12**) quantitatively (Scheme 3). It is interesting that thioketones and selenoketones readily react with atmospheric oxygen in the air to form the corresponding ketones, whereas the silanethione decomposes in the air to afford a hydrolyzed compound resulting from a reaction with atmospheric moisture, indicating the very high reactivity of the Si=S bond toward water.

Reactions of Silanethione 7b. Although silanethione **7b** is thermally very stable, it has high chemical reactivities toward various reagents (Scheme 3). Methanol immediately reacted with **7b** at room temperature to afford an addition product **9b** (53%). Reactions of **7b** with phenyl isothiocyanate and mesitonitrile oxide at room temperature resulted in the ready formation of [2 + 2] and [2 + 3] cycloadducts **10b** (63%) and **11b** (54%), respectively. By contrast, 2,3-dimethyl-1,3-butadiene was very reluctant to react with **7b**. The yellow color due to **7b** did not disappear, even upon heating to 150 °C of a hexane solution of **7b** and the diene in a sealed tube. The reaction, however, proceeded at 180 °C for 3 h to afford the [2 + 4] cycloadduct **13** in 74% yield. This result demonstrates that the silanethione has a considerable extent of ene character like its carbon analogues, such as thioketones and thioaldehydes, which are known to have high reactivities in Diels−Alder reactions.[26] It is surprising that silanethione **7b** shows these high reactivities despite the extremely severe steric congestion around the Si=S group.

Table 6. M−X Stretching Frequencies (cm^{-1}) of $H_2M{=}X$ at the B3LYP/TZ(d,p) Level

	X			
$H_2M{=}X$	O	S	Se	Te
$H_2C{=}X$	1826	1087	882	755
$H_2Si{=}X$	1227	723	554	461
$H_2Ge{=}X$	942	553	387	310
$H_2Sn{=}X$	797	470	319	251
$H_2Pb{=}X$	707	414	270	207

Spectral Features of Silanethione 7b. Silanethione **7b** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, Raman, and UV spectroscopy. The chemical shift of δ_{Si} 166.56 for the silathiocarbonyl unit is highly downfield-shifted, as in the case of other silicon-containing double bond compounds.[27] The observed chemical shift is in good accordance with the values for $H_2Si{=}S$ (158.0 ppm) and $Ph_2Si{=}S$ (167.3 ppm) calculated with the GIAO−B3LYP (6-311G(3d) for Si and S and 6-311G(d) for C and H) method using the B3LYP/6-31G(d)-optimized geometries. The chemical shift of **7b** is very different from that of the thermodynamically stabilized Corriu's silanethione **1** (Ar = Ph, Ch = S) (δ_{Si} 22.3),[8] clearly indicating the genuine Si=S double bond nature of **7b** without any intra- or intermolecular coordination. The electronic spectrum of **7b** exhibited an absorption maximum at 396 nm which is assignable to the $n \rightarrow \pi^*$ transition. The Raman spectrum in the solid state showed an absorption at 724 cm^{-1}. This absorption is attributable to the Si=S stretching, as suggested from the calculated values (scaled by 0.98) of $H_2Si{=}S$ (709 cm^{-1}) at the B3LYP/TZ(d,p) level in Table 6 and $Ph_2Si{=}S$ (755 cm^{-1}) at the B3LYP/6-31G(d) level. The M−X stretching frequencies calculated for all the combinations of ketone analogues, $H_2M{=}X$ (Table 6), are roughly parallel to the corresponding bond energies ($\sigma + \pi$) shown in Table 1.

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(24) Similar dechalcogenation reactions were also applied to the syntheses of thioaldehyde TbtCHS,[25a] germanethione Tbt(Tip)Ge=S,[25b] and germaneselone Tbt(Tip)Ge=Se.[25c]

(25) (a) Tokitoh, N.; Takeda, N.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 7907. (b) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (c) Matsumoto, T., Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316.

(26) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1390. (b) Schönberg, A.; König, B. *Chem. Ber.* **1968**, *101*, 725. (c) Ohnishi, Y.; Akasaki, Y.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3307. (d) Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487. (e) Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 922. (f) Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947. (g) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Penny, D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556. (h) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976.

(27) The ^{29}Si NMR chemical shifts of some low-coordinate organosilicon compounds follow: $Mes_2Si{=}SiMes_2$, 63.6;[28a] (*E*)-Tbt(Mes)Si=Si(Tbt)Mes, 66.49;[21] $(Me_3Si)_2Si{=}C(OSiMe_3)$(*t*-Bu), 41.4;[28b] Tip(*t*-Bu)Si=PAr (Ar = 2,4,6-tri-*tert*-butylphenyl), 175.9;[28c] $Tip_2Si{=}AsSi(i\text{-}Pr)_3$, 179.0.[28d]

(28) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. (b) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994. (c) Smit, C. N.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011. (d) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *31*, 1022.

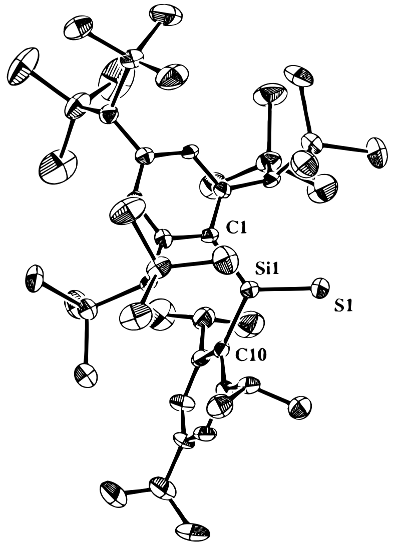
Table 7. Electronic Spectra (n→π*) of Doubly Bonded Compounds between Group 14 Elements and Sulfur

observed[a]		calcd[e]		
	λ_{max}/nm		λ_{max}/nm	$\Delta\epsilon_{n\pi^*}$/eV[f]
Tbt(H)C=S (**14**)	587[b]	$H_2C{=}S$	460	10.81
Tbt(Tip)Si=S (**7b**)	396	$H_2Si{=}S$	352	10.27
Tbt(Tip)Ge=S (**15**)	450[c]	$H_2Ge{=}S$	367	9.87
Tbt(Tip)Sn=S (**16**)	473[d]	$H_2Sn{=}S$	381	9.22
		$H_2Pb{=}S$	373	9.11

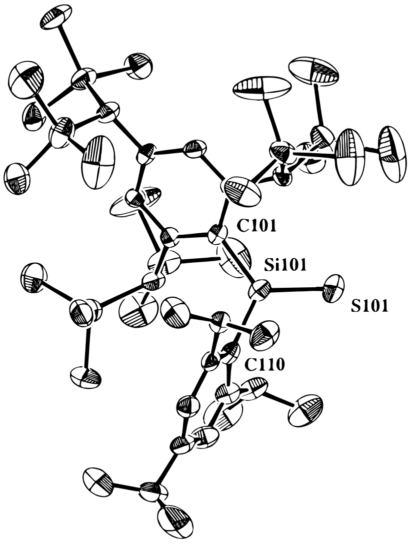
[a] In hexane. [b] Reference 25a. [c] Reference 25b. [d] Reference 32. [e] CIS/TZ(d,p)//B3LYP/TZ(d,p). [f] $\epsilon_{LUMO(\pi^*)} - \epsilon_{HOMO(n)}$.

Since a series of $R^1R^2M{=}S$ (M = C, Si, Ge, Sn) compounds are now available, we can compare their electronic spectra (n→π*) systematically.[29] In Table 7 are listed observed spectra of these compounds along with calculated spectra of $H_2M{=}S$ (M = C, Si, Ge, Sn, Pb) at the CIS/TZ(d,p)//B3LYP/TZ(d,p) level. One can see an interesting change in the observed λ_{max} depending on the difference in group 14 elements: λ_{max} is greatly blue-shifted on going from thione **14** to silanethione **7b**, whereas λ_{max}'s for **7b**, germanethione **15**, and stannanethione **16** are red-shifted on increasing the atomic number of the group 14 elements. This trend is also found in calculated values for $H_2M{=}S$ (M = C, Si, Ge, Sn). In a crude approximation, the n→π* excitation energy is expressed as $\Delta\epsilon_{n\pi^*} - J_{n\pi^*} + 2K_{n\pi^*}$. As Table 7 shows, the energy difference between n and π* orbitals decreases upon going from $H_2C{=}S$ to the heavier analogues, suggesting a shorter wavelength absorption for $H_2C{=}S$. However, the π* orbital in $H_2C{=}S$ is much less polarized (thereby less localized onto C), leading to a larger value of the Coulomb repulsion integral $J_{n\pi^*}$. Consequently, $H_2C{=}S$ (as well as **14**) has a long-wavelength absorption, as in the case of H_2CO vs H_2SiO.[31]

Molecular Structure of Silanethione 7b. As single crystals of **7b** suitable for X-ray crystallography were obtained by recrystallization from hexane in a glovebox, we carried out an X-ray structural analysis in order to obtain the structural features of this new doubly bonded system. It has been revealed that there are two nonidentical silanethiones in the asymmetric unit. Figure 2 shows the ORTEP drawings (molecules 1 and 2) of silanethione **7b**. The crystallographic data for these structures are summarized in Table 1. Selected bond lengths and angles are listed in Table 8.



Molecule 1



Molecule 2

Figure 2. ORTEP drawing of Tbt(Tip)Si=S (**7b**) with thermal ellipsoid plot (30%probability).

Table 8. Selected Bond Lengths (Å) and Angles (deg) of **7b**

molecule 1		molecule 2	
S(1)−Si(1)	1.948(4)	S(101)−Si(101)	1.952(4)
Si(1)−C(1)	1.894(8)	Si(101)−C(101)	1.872(9)
Si(1)−C(10)	1.867(9)	Si(101)−C(110)	1.88(1)
S(1)−Si(1)−C(1)	125.0(3)	S(101)−Si(101)−C(101)	125.3(4)
S(1)−Si(1)−C(10)	116.3(3)	S(101)−Si(101)−C(110)	116.9(3)
C(1)−Si(1)−C(10)	118.6(4)	C(101)−Si(101)−C(110)	117.5(4)

The data indicate that there is neither intra- nor intermolecular interaction between the silathiocarbonyl unit and the other part of the molecule; the shortest intermolecular distance between the silicon and sulfur centers is 8.2 Å. The molecular structure of molecule 1 is different from that of molecule 2 in the following points: (i) the different dihedral angles between the Tbt and Tip aromatic ring planes and the silathiocarbonyl plane (molecule 1, 41.8° for Tbt ring and 67.8° for Tip ring; molecule 2, 138.6° for Tbt ring and 112.2° for Tip ring) and (ii) the different direction of *p*-bis(trimethylsilyl)methyl of the Tbt group. There is little difference, however, in the geometry around the central silicon atom between the two molecules. The silathiocarbonyl unit of **7b** has a completely trigonal-planar geometry in both molecules as in $H_2Si{=}S$ (C_{2v}),[17] the sum of the bond angles around the silicon atom being 359.9° for molecule 1 and 359.7° for molecule 2. Dihedral angles between the trigonal plane and the two aryl planes suggest that there is little conjugation between the aromatic ring and the silathiocarbonyl group. The silicon−sulfur bond lengths are 1.948(4) (molecule 1) and 1.952(4) Å (molecule 2). These values are significantly shorter than that of 2.013(3) Å reported for Corriu's compound[5] and rather close to the 1.945 Å found for $H_2Si{=}S$ (Table 2).[33] The Si−S bond length of **7b** is ca. 0.2 Å (9%) shorter than the typical Si−S single bond length.[34] This bond shortening, which is comparable to that of 0.203 Å (9.4%) for

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(29) We have not succeeded in observing the electronic spectrum of a plumbanethione, $R^1R^2Pb{=}S$, because it undergoes 1,2-migration reaction to give a heteroleptic plumbylene $R^1Pb(SR^2)$, which is thermodynamically more stable.[30]

(30) Kano, N.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 4237.

(31) Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1986**, *128*, 507.

(32) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065.

$H_2Si{=}S$ (Table 2), confirms that **7b** has a distinct double bond between Si and S.

IV. Conclusion. The first genuine silanethione Tbt(Tip)-$Si{=}S$ (**7b**) was synthesized by the desulfurization of the corresponding tetrathiasilolane **2b**, and its structure was established by X-ray crystallographic analysis. The structural features of **7b** were very similar to those of a ketone with a trigonal-planar geometry, although the extent of reduction in the bond length from the corresponding single bond (ca. 9%) is considerably smaller than that of a ketone (ca. 15%), indicating weaker bonding in **7b**. Although **7b** is stabilized by two extremely bulky substituents on silicon toward dimerization, it can undergo facile addition or cycloaddition reactions across the $Si{=}S$ bond with some relatively small reagents, suggesting its high reactivity. These findings lead us to conclude that a silanethione, a heavier element homologue of a ketone (heavy ketone), is essentially the same as a ketone with regard to the structure but has much higher reactivity than a ketone because of a great difference between its σ (82 kcal mol^{-1}) and π (47 kcal mol^{-1}) bond energies.

Experimental Section

General Procedure. All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H+2H columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. Flash column chromatography (FCC) was performed with silica gel BW 300 (Fuji Davison Chemical). Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254 Art. 7747. The ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), and ^{29}Si NMR (53.5 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a Bruker AM-500 or JEOL EX-270 spectrometer using $CHCl_3$ or C_6H_6 as an internal standard or tetramethylsilane as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-mesityl-1,2,3,4,5-tetrathiasilolane (2a). (a) Thermal Reaction of Diaryldihydrosilane 3a with Sulfur. Diaryldihydrosilane **3a**^{21b} (668 mg, 0.95 mmol) was mixed with S_8 (2.5 g) and heated to 230 °C for 22 min. Most excess sulfur was removed by recrystallization from chloroform. The residue was separated with DCC (silica/hexane) and GPLC. Solid material thus obtained was dissolved into CH_2Cl_2, to which was added approximately the same volume of ethanol. Evaporation of CH_2Cl_2 at room temperature under reduced pressure gave **2a** (35 mg, 4%) as pale yellow crystals. **2a**: mp 179−181 °C; ^{1}H NMR ($CDCl_3$, 340 K) δ 0.03 (s, 36H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.09 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.39 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.24 (s, 3H, Mes-*p*-Me), 2.29 (br s, 2H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.53 (s, 6H, Mes-*o*-Me), 6.43 (br s, 2H, Tbt-*m*-C*H*), 6.78 (s, 2H, Mes-*m*-C*H*); ^{13}C NMR ($CDCl_3$, 340 K) δ 0.99 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.85 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 20.86 (q, Mes-*p*-Me), 25.77 (q, Mes-*o*-Me), 29.21 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.36 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 121.74 (s, Tbt-*p*-C), 123.67 (d, Tbt-*m*-*C*H), 128.98 (d, Tbt-*m*-*C*H), 130.39 (d, Mes-*m*-*C*H), 133.63 (s), 140.14 (s), 142.28 (s), 146.92 (s), 154.17 (s, Tbt-*o*-C); FT-Raman spectrum in solid (excitation, Nd:YAG laser, 1064 nm) 505 cm^{-1}. Anal. Calcd for $C_{36}H_{70}Si_7S_4$: C, 52.23; H, 8.52; S, 15.49. Found: C, 52.36; H, 8.29; S, 14.92.

(b) Reaction of Disilene 4 with Sulfur. To a solution of **4**^{21b} (51 mg, 0.036 mmol) in THF (4 mL) was added sulfur (28 mg, 0.11 mmol), and the solution was heated under reflux for 6 h. After removal of the solvent, the residue was chromatographed (GPLC) to afford **2a** (56 mg, 94%) as pale yellow crystals.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-(2,4,6-triisopropylphenyl)silane (3b). To a solution of TipLi, prepared from TipBr^{35} (4.0 g, 14 mmol) and *t*-BuLi (1.59 M in pentane, 17 mL) at −78 °C in THF (40 mL), was added a THF solution (80 mL) of 2,4,6-tris[bis(trimethylsilyl)methyl]phenylsilane^{21b} (4.56 g, 8.82 mmol) at −78 °C. The solution was stirred for 10 h, during which time it was warmed to room temperature. To this solution was added a saturated aqueous solution of NH_4Cl, and the organic layer was separated. The water layer was extracted with 50 mL of hexane, and the organic layer was dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from ethanol to afford **3b** (4.75 g, 77%) as colorless crystals. **3b**: mp 169−171 °C; ^{1}H NMR ($CDCl_3$) δ −0.06 (s, 18H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.02 (s, 18H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.04 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.22 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.24 (d, *J* = 7 Hz, 12H, Tip-*o*-CH*Me*$_2$), 1.34 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.08 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.35 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.86 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.31 (sept, *J* = 7 Hz, 2H, Tip-*o*-C*H*Me$_2$), 5.10 (s, 2H, Si*H*$_2$), 6.25 (br s, 1H, Tbt-*m*-C*H*), 6.43 (br s, 1H, Tbt-*m*-C*H*), 7.01 (s, 2H, Tip-*m*-C*H*); ^{13}C NMR ($CDCl_3$) δ 0.83 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.88 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.20 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 23.93 (q, Tip-*p*-CH*Me*$_2$), 24.78 (q, Tip-*o*-CH*Me*$_2$), 28.46 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 28.60 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.53 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 33.41 (d, Tip-*p*-*C*HMe$_2$), 34.53 (d, Tip-*o*-*C*HMe$_2$), 120.57 (d, Tip-*m*-*C*H), 122.52 (d, Tbt-*m*-*C*H), 125.41 (s, Tbt-*p*-C), 127.41 (d, Tbt-*m*-*C*H), 128.22 (s), 143.93 (s), 150.46 (s), 151.34 (s, Tbt-*o*-C) 151.45 (s, Tbt-*o*-C), 155.27 (s, Tip-*o*-C). Anal. Calcd for $C_{42}H_{84}Si_7$: C, 64.20; H, 10.78. Found: C, 64.00; H, 10.97.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-(dibromo)(2,4,6-triisopropylphenyl)silane (6). A solution of **3b** (3.21 g, 4.09 mmol), NBS (2.0 g, 11.2 mmol), and a catalytic amount of benzoyl peroxide in benzene (80 mL) was heated under reflux for 1 h. After removal of the solvent, the crude reaction products were dissolved in hexane. The filtrate, after removal of the solvent, was roughly purified by DCC (hexane), followed by recrystallization from ethanol to afford **6** (1.87 g, 49%) as colorless crystals. **6**: mp 240−242 °C; ^{1}H NMR ($CDCl_3$, 340 K) δ 0.07 (br s, 36H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.08 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.16 (br d, 6H, Tip-*o*-CH*Me*$_2$), 1.22 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.23 (br d, 6H, Tip-*o*-CH*Me*$_2$), 1.37 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.28 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.85 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.81 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 3.93 (sept, *J* = 6 Hz, 2H, Tip-*o*-C*H*Me$_2$), 6.43 (br s, 2H, Tbt-*m*-C*H*), 7.04 (s, 2H, Tip-*m*-C*H*); ^{13}C NMR ($CDCl_3$, 340 K) δ 1.05 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 2.45 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 23.58 (q, Tip-*p*-CH*Me*$_2$), 23.96 (q, Tip-*o*-CH*Me*$_2$), 27.26 (q, Tip-*o*-CH*Me*$_2$), 27.76 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.20 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 32.81 (d, Tip-*p*-*C*HMe$_2$), 34.32 (d, Tip-*o*-*C*HMe$_2$), 123.36 (d, Tip-*m*-*C*H), 123.47 (d, Tbt-*m*-*C*H), 126.19 (s, Tbt-*p*-C), 129.48 (d, Tbt-*m*-*C*H), 130.66 (s), 145.97 (s), 151.58 (s), 151.72 (s, Tbt-*o*-C) 154.02 (s, Tip-*o*-C). Anal. Calcd for $C_{42}H_{82}Si_7Br_2\cdot H_2O$: C, 52.46; H, 8.81; Br, 16.62. Found: C, 52.43; H, 8.81; Br, 16.75.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiasilolane (2b). To a solution of **6** (475 mg, 0.50 mmol) in THF (10 mL) was added at −78 °C lithium naphthalenide (2.7 mL), prepared from lithium dispersion (209 mg, 30.1 mmol) and naphthalene (2.93 g, 22.9 mmol) in THF (39 mL), and the mixture was stirred for 20 min. To this solution was added elemental sulfur (130 mg, 0.51 mmol) at −78 °C, the mixture was stirred for 10 min, and then a saturated aqueous solution of NH_4Cl was added. The solution was stirred for 1 h, during which time it was warmed to room temperature. The organic layer was separated, and the water layer was extracted with 50 mL of hexane. The organic layers were put together and dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was roughly purified by GPLC and FCC (hexane), followed by recrystallization from ethanol to afford **2b** (127

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(33) Upon replacement of two hydrogens in $H_2Si{=}S$ by two phenyl groups, it was calculated that the Si−S bond is elongated only by 0.01 Å at the B3LYP/6-31G(d) level.

(34) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, pp 227−304.

(35) Miller, A. R.; Curtin, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 1860.

mg, 28%). **2b**: Pale yellow crystals, mp 207−209 °C; ^{1}H NMR (CDCl$_3$, 340 K) δ 0.05 (br s, 36H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.08 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.16 (br s, 12H, Tip-*o*-CH*Me*$_2$), 1.22 (d, J = 6.9 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.38 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.29 (br s, 2H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.83 (sept, J = 6.9 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.89 (br s, 2H, Tip-*o*-C*H*Me$_2$), 6.42 (br s, 2H, Tbt-*m*-C*H*), 7.02 (s, 2H, Tip-*m*-C*H*); ^{13}C NMR (CDCl$_3$) δ 1.09 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 2.56 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 23.61 (q, Tip-*p*-CH*Me*$_2$), 24.76 (q, Tip-*o*-CH*Me*$_2$), 27.70 (q, Tip-*o*-CH*Me*$_2$), 28.50 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.23 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 34.29 (d, Tip-*p*-*C*HMe$_2$), 35.03 (d, Tip-*o*-*C*HMe$_2$), 123.41 (d, Tip-*m*-*C*H), 123.61 (s, Tbt-*p*-C), 123.84 (d, Tbt-*m*-*C*H), 129.52 (d, Tbt-*m*-*C*H), 130.67 (s), 146.06 (s), 150.95 (s), 153.54 (s, Tbt-*o*-C), 154.04 (s, Tip-*o*-C); FT-Raman spectrum in solid (excitation, Nd:YAG laser, 1064 nm) 504 cm^{-1}. Anal. Calcd for $C_{42}H_{82}Si_7S_4$: C, 55.32; H, 9.06; S, 14.06. Found: C, 55.30; H, 9.30; S, 13.50.

Desulfurization of 2a with Triphenylphosphine. To a mixture of **2a** (50 mg, 0.060 mmol) and triphenylphosphine (48 mg, 0.18 mmol) was added hexane (5 mL) at −78 °C, and the solution was stirred for 2 h, during which time it was warmed to room temperature. After removal of the solvent, the crude reaction products were chromatographed by GPLC to afford (*Z*)-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadisiletane (**8**) (35 mg, 90%), together with triphenylphosphine sulfide (47 mg, 100%). **8**: Colorless crystals (from ethanol), mp > 300 °C. As mentioned in the text, **8** showed a very complicated ^{1}H NMR spectrum at room temperature, which is shown in the Supporting Information. Anal. Calcd for $C_{72}H_{140}Si_{14}S_2$: C, 59.10; H, 9.64; S, 4.38. Found: C, 59.35; H, 9.59; S, 4.50.

Reaction of 7a with Methanol. To a mixture of **2a** (50 mg, 0.060 mmol) and triphenylphosphine (48 mg, 0.18 mmol) was added hexane (5 mL) at −78 °C, and the solution was stirred for 10 min. To this solution was added methanol (0.1 mL, 2.5 mmol), and the mixture was stirred for 2 h, during which time it was warmed to room temperature. After removal of the solvent, the crude reaction products were chromatographed by GPLC to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)methoxysilanethiol (**9a**) (43 mg, 93%), together with **8** (3 mg, 6%) and triphenylphosphine sulfide (52 mg, 95%). **9a**: Colorless crystals (from ethanol), mp 197−199 °C; ^{1}H NMR (CDCl$_3$) δ −0.07 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.06 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.03 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.00 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.04 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.64 (s, 1H, S*H*), 1.30 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.22 (s, 3H, Mes-*p*-Me), 2.45 (s, 6H, Mes-*o*-Me), 2.52 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.63 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 3.40 (s, 3H, O*Me*), 6.22 (br s, 1H, Tbt-*m*-C*H*), 6.36 (br s, 1H, Tbt-*m*-C*H*), 6.76 (s, 2H, Tip-*m*-C*H*); ^{13}C NMR (CDCl$_3$) δ 0.87 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.16 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.21 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.46 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.50 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 20.91 (q, Mes-*p*-Me), 25.30 (q, Mes-*o*-Me), 27.40 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 27.56 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.46 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 49.53 (q, O*Me*), 122.96 (d, Tbt-*m*-*C*H), 127.10 (s, Tbt-*p*-C), 128.08 (d, Tbt-*m*-*C*H), 129.90 (d, Tbt-*m*-*C*H), 132.99 (s), 139.55 (s), 143.77 (s), 144.84 (s), 151.72 (s, Tbt-*o*-C), 152.01 (s, Tbt-*o*-C). Anal. Calcd for $C_{37}H_{74}Si_7OS{\cdot}1.5H_2O$: C, 56.21; H, 9.82; S, 4.06. Found: C, 56.22; H, 9.64; S, 4.49.

Reaction of 7a with Phenyl Isothiocyanate. To a mixture of **2a** (147 mg, 0.18 mmol) and triphenylphosphine (140 mg, 0.53 mmol) was added hexane (3 mL) at −78 °C, and the solution was stirred for 10 min. To this solution was added phenyl isothiocyanate (0.04 mL, 0.33 mmol), and the mixture was stirred for 2 h, during which time it was warmed to room temperature. After removal of the solvent, the crude reaction products were chromatographed by GPLC to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-mesityl-4-phenylimino-1,3,2-dithiasiletane (**10a**) (110 mg, 72%), together with **8** (7 mg, 5%) and triphenylphosphine sulfide (152 mg, 97%). **10a**: Colorless crystals (from hexane), mp 145 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.04 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.02 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.01 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.00 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.06 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.36 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.28 (s, 3H, Mes-*p*-Me), 2.51 (s, 6H, Mes-*o*-Me), 2.71 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.80 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 6.33 (s, 1H, Tbt-*m*-C*H*), 6.46 (s, 1H, Tbt-*m*-C*H*), 6.87 (s, 2H, Tip-*m*-C*H*), 6.95 (d, J = 8 Hz, 2H, Ph-*o*-C*H*), 7.09 (t, J = 7 Hz, 1H, Ph-*p*-C*H*), 7.29 (dd, J = 8, 7 Hz, 2H, Ph-*m*-C*H*); ^{13}C NMR (CDCl$_3$) δ 0.86 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.06 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.32 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 21.04 (q, Mes-*p*-Me), 25.42 (q, Mes-*o*-Me), 28.71 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 28.96 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.08 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 121.20 (d), 121.90 (s, Tbt-*p*-C), 123.48 (d, Tbt-*m*-*C*H), 124.49 (d), 128.61 (d, Tbt-*m*-*C*H), 128.83 (d), 129.86 (d), 133.87 (s), 140.60 (s), 142.04 (s), 147.28 (s), 148.40 (s), 148.59 (s), 153.57 (s, Tbt-*o*-C), 153.87 (s, Tbt-*o*-C). Anal. Calcd for $C_{43}H_{75}Si_7NS_2{\cdot}0.5H_2O$: C, 58.97; H, 8.75; N, 1.60; S, 7.32. Found: C, 58.80; H, 8.88; N, 1.57; S, 7.38.

Reaction of 7a with Mesitonitrile Oxide. To a mixture of **2a** (72 mg, 0.087 mmol) and triphenylphosphine (68 mg, 0.26 mmol) was added hexane (5 mL) at −78 °C, and the solution was stirred for 10 min. A hexane solution of mesitonitrile oxide (16 mg, 0.099 mmol) was added to the solution, and the mixture was stirred for 2 h, during which time it was warmed to room temperature. After removal of the solvent, the crude reaction products were roughly chromatographed by GPLC and purified by PTLC (hexane/CH$_2$Cl$_2$ = 2:1) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4-dimesityl-1,3,5,2-oxathiazasilole (**11a**) (35 mg, 45%), together with **8** (6.1 mg, 10%) and triphenylphosphine sulfide (77 mg, 98%). **11a**: Colorless crystals (from ethanol), mp 283−285 °C; ^{1}H NMR (CDCl$_3$) δ −0.12 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.08 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.069 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.071 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.11 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.38 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.05 (br s, 6H, Mes-*o*-Me), 2.23 (s, 3H, Mes-*p*-Me), 2.24 (s, 3H, Mes-*p*-Me), 2.51 (s, 6H, Mes-*o*-Me), 2.54 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.60 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 6.35 (br s, 1H, Tbt-*m*-C*H*), 6.48 (br s, 1H, Tbt-*m*-C*H*), 6.75 (s, 2H, Mes-*m*-C*H*), 6.80 (s, 2H, Mes-*m*-C*H*); ^{13}C NMR (CDCl$_3$) δ 0.55 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.81 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.86 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.95 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.43 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.69 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 19.35 (q, Mes-*o*-Me), 21.05 (q, Mes-*p*-Me), 21.10 (q, Mes-*p*-Me), 24.18 (q, Mes-*o*-Me), 29.14 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 29.55 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.97 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 122.79 (s, Tbt-*p*-C), 122.99 (d, Tbt-*m*-*C*H), 128.08 (d, Tbt-*m*-*C*H), 128.30 (d, Mes-*m*-*C*H), 128.96 (s), 129.48 (d, Mes-*m*-*C*H), 133.90 (s), 136.88 (s), 139.02 (s), 140.08 (s), 142.10 (s), 146.61 (s), 152.64 (s, Tbt-*o*-C), 152.78 (s, Tbt-*o*-C), 160.16 (s, *C*=N). Anal. Calcd for $C_{46}H_{81}Si_7NSO$: C, 61.88; H, 9.14; N, 1.57; S, 3.59. Found: C, 61.83; H, 9.40; N, 1.71; S, 3.49.

Synthesis and Isolation of Silanethione 7b. To a mixture of **2b** (74 mg, 0.082 mmol) and triphenylphosphine (64 mg, 0.24 mmol) was added hexane (2 mL) at room temperature, and the solution was refluxed for 1 h. After filtration of triphenylphosphine sulfide under argon, the filtrate was concentrated to afford a yellow solid, which contained 86% of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)thioxosilane (**7b**) (66 mg, 100%) and 14% of triphenylphosphine sulfide (2.3 mg). Pure **7b** was obtained by recrystallization from hexane. **7b**: Pale yellow crystals, mp 185−189 °C; ^{1}H NMR (C$_6$D$_6$ at 360 K) δ 0.15 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.19 (s, 36H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.19 (d, J = 6.9 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.40 (d, J = 6.5 Hz, 12H, Tip-*o*-CH*Me*$_2$), 1.50 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.76 (sept, J = 6.9 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.46 (br s, 2H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 3.51 (sept, J = 6.5 Hz, 2H, Tip-*o*-C*H*Me$_2$), 6.58 (br s, 2H, Tbt-*m*-CH), 7.05 (s, 2H, Tip-*m*-CH); ^{13}C NMR (C$_6$D$_6$) δ 1.13 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.49 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.83 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 22.53 (q, Tip-*p*-CH*Me*$_2$), 24.00 (q, Tip-*o*-CH*Me*$_2$), 27.67 (q, Tip-*o*-CH*Me*$_2$), 30.33 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.98 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.98 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 34.88 (d, Tip-*o*-*C*HMe$_2$), 38.13 (d, Tip-*p*-*C*HMe$_2$), 121.93 (d, Tbt-*m*-CH), 123.87 (d, Tbt-*m*-CH), 131.22 (d, Tip-*m*-CH), 139.03 (s, Tbt-*p*-C), 148.35 (s), 151.00 (s), 151.16 (s), 151.26 (s, Tbt-*o*-C), 152.77 (s, Tbt-*o*-C), 153.01 (s, Tip-*o*-C); ^{29}Si NMR (C$_6$D$_6$) δ 2.44, 3.23, 166.56. UV (hexane) $\lambda_{\max}$ 396 nm (ϵ 100); FT-Raman spectrum in solid (excitation, Nd:YAG laser, 1064 nm) 724 cm^{-1} ($\nu_{\mathrm{Si=S}}$); high-resolution FAB-MS, observed *m*/*z* 815.4672, calcd for $C_{42}H_{82}Si_7S$ *m*/*z* 815.4600.

Reaction of 7b with Water. When the yellow solid of **7b** containing 14% triphenylphosphine sulfide (16 mg, 0.017 mmol) was exposed to the air, the color gradually disappeared within 3 h. Purification with GPLC afforded {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)hydroxysilanethiol (**12**) (14.3 mg, 100%). **12**: Colorless crystals (from hexane), mp 113−115 °C; ^{1}H NMR (CDCl$_3$, 500

MHz) δ −0.26 (br s, 18H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.04 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.13 (br s, 18H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.84 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.04 (s, 1H, SH), 1.19 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.22 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.28 (d, *J* = 7 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.29 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 1.39 (d, *J* = 6 Hz, $_3$H, Tip-*o*-CH*Me*$_2$), 1.98 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.66 (s, 1H, OH), 2.82 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.11 (sept, *J* = 6 Hz, 1H, Tip-*o*-C*H*Me$_2$), 3.56 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 4.33 (sept, *J* = 6 Hz, 1H, Tip-*o*-C*H*Me$_2$), 6.27 (br s, 1H, Tbt-*m*-CH), 6.40 (br s, 1H, Tbt-*m*-CH), 6.95 (s, 1H, Tip-*m*-CH), 7.03 (s, 1H, Tip-*m*-CH); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.85 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.01 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.44 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.74 (q, Tbt-*o*-CH-(Si*Me*$_3$)$_2$), 1.77 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 2.03 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 22.37 (q, Tip-*o*-CH*Me*$_2$), 23.74 (q, Tip-*p*-CH*Me*$_2$), 23.80 (q, Tip-*p*-CH*Me*$_2$), 24.98 (q, Tip-*p*-CH*Me*$_2$), 25.98 (q, Tip-*o*-CH*Me*$_2$), 27.07 (q, Tip-*o*-CH*Me*$_2$), 27.43 (d, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 28.06 (d, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 30.04 (d, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 30.56 (d, Tip-*o*-*C*HMe$_2$), 33.58 (d, Tip-*o*-*C*HMe$_2$), 34.34 (d, Tip-*p*-*C*HMe$_2$), 121.25 (d, Tip-*m*-CH), 123.02 (d, Tip-*m*-CH), 123.34 (d, Tbt-*m*-CH), 128.19 (d, Tbt-*m*-CH), 128.42 (s, Tbt-p), 133.58 (s), 144.50 (s), 150.35 (s, Tbt-o), 150.65 (s), 150.98 (s, Tbt-o), 153.47 (s, Tip-o), 154.06 (s, Tip-o); high-resolution FAB-MS, observed *m/z* 832.4615, calcd for $C_{42}H_{84}Si_7OS$ *m/z* 832.4628.

Reaction of 7b with Methanol. To a mixture of **2b** (73 mg, 0.080 mmol) and triphenylphosphine (63 mg, 0.24 mmol) was added hexane (2 mL) at room temperature, and the solution was refluxed for 1 h. To this solution was added methanol (0.16 mL, 4.0 mmol) at room temperature, and the mixture was stirred for 1 h. After removal of the solvent, the crude reaction products were chromatographed roughly by GPLC and purified by PTLC (hexane/CH_2Cl_2 = 20:1) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)-methoxysilanethiol (**9b**) (36 mg, 53%), together with triphenylphosphine sulfide (52 mg, 81%). **9b**: Colorless crystals (from hexane), mp 182−185 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.18 (br s, 18H, Tbt-*o*-CH-(Si*Me*$_3$)$_2$), 0.03 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.15 (br s, 18H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.73 (s, 1H, SH), 0.88 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.18 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.197 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.207 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.29 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 1.30 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.94 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.80 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.33 (sept, *J* = 6 Hz, 1H, Tip-*o*-C*H*Me$_2$), 3.43 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 3.66 (s, 3H, OMe), 3.82 (sept, *J* = 6 Hz, 1H, Tip-*o*-C*H*Me$_2$), 6.24 (br s, 1H, Tbt-*m*-CH), 6.36 (br s, 1H, Tbt-*m*-CH), 6.95 (s, 1H, Tip-*m*-CH), 7.01 (s, 1H, Tip-*m*-CH); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.90 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.77 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 2.10 (q, Tbt-*o*-CH-(Si*Me*$_3$)$_2$), 23.14 (q, Tip-*o*-CH*Me*$_2$), 23.73 (q, Tip-*p*-CH*Me*$_2$), 24.77 (q, Tip-*o*-CH*Me*$_2$), 26.61 (q, Tip-*o*-CH*Me*$_2$), 27.06 (q, Tip-*o*-CH*Me*$_2$), 27.24 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 28.61 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.06 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 30.40 (d, Tip-*o*-*C*HMe$_2$), 32.77 (d, Tip-*o*-*C*HMe$_2$), 34.24 (d, Tip-*p*-*C*HMe$_2$), 51.23 (q, OMe), 121.45 (d), 123.02 (d), 123.21 (d), 127.97 (d), 129.72 (s), 133.50 (s), 143.93 (s), 150.38 (s), 151.16 (s, Tbt-o), 151.42 (s, Tbt-o), 154.03 (s, Tip-o), 154.27 (s, Tip-o); high-resolution FAB-MS, observed *m/z* 846.4782, calcd for $C_{43}H_{86}Si_7OS$ *m/z* 846.4784. Anal. Calcd for $C_{43}H_{86}Si_7OS \cdot 2H_2O$: C, 58.43; H, 10.26; S, 3.63. Found: C, 58.66; H, 9.96; S, 3.81.

Reaction of 7b with Phenyl Isothiocyanate. To a mixture of **2b** (70 mg, 0.077 mmol) and triphenylphosphine (76 mg, 0.29 mmol) was added hexane (5 mL) at room temperature, and the solution was refluxed for 10 min. To this solution was added phenyl isothiocyanate (0.02 mL, 0.17 mmol), and the mixture was stirred for 1 h. After removal of the solvent, the crude reaction products were roughly chromatographed by GPLC and purified by PTLC (hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-dithiasiletane (**10b**) (46 mg, 63%), together with triphenylphosphine sulfide (67 mg, 99%). **10b**: Colorless crystals (from hexane), mp 142−145 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.06 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), −0.05 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.02 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.05 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 0.11 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.12 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.16 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.20 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.22 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.28 (d, *J* = 6 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.34 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.35 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.86 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 3.16 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 3.19 (sept, *J* = 6 Hz, 2H, Tip-*o*-C*H*Me$_2$), 6.31 (s, 1H, Tbt-*m*-CH), 6.51 (s, 1H, Tbt-*m*-CH), 6.93 (d, *J* = 8 Hz, 2H, Ph-*o*-CH), 7.03 (br d, 2H, Tip-*m*-CH), 7.08 (t, *J* = 7 Hz, 1H, Ph-*p*-CH), 7.29 (dd, *J* = 8, 7 Hz, 2H, Ph-*m*-CH); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.97 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.81 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.90 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 23.26 (q, Tip-*o*-CH*Me*$_2$), 23.37 (q, Tip-*o*-CH*Me*$_2$), 23.76 (q, Tip-*o*-CH*Me*$_2$), 27.82 (q, Tip-*o*-CH*Me*$_2$), 27.95 (q, Tip-*o*-CH*Me*$_2$), 28.56 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 28.66 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 30.96 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 34.39 (d, Tip-*p*-*C*HMe$_2$), 35.56 (d, Tip-*o*-*C*HMe$_2$), 35.73 (d, Tip-*o*-*C*HMe$_2$), 121.23 (d), 122.73 (d), 122.76 (d), 123.86 (d, Tbt-*m*-CH), 124.05 (s, Tbt-p), 124.32 (d), 128.84 (d), 129.24 (d, Tbt-*m*-CH), 131.97 (s), 146.59 (s), 148.69 (s), 149.04 (s), 151.18 (s), 152.58 (s, Tbt-o), 152.79 (s, Tbt-o), 153.17 (s, Tip-o), 153.95 (s, Tip-o); high-resolution FAB-MS, observed *m/z* 950.4784, calcd for $C_{49}H_{88}Si_7NS_2$ *m/z* 950.4743. Anal. Calcd for $C_{49}H_{88}Si_7NS_2 \cdot 0.5H_2O$: C, 61.31; H, 9.24; N, 1.46; S, 6.68. Found: C, 61.08; H, 9.34; N, 1.89; S, 6.77.

Reaction of 7b with Mesitonitrile Oxide. To a mixture of **2b** (85 mg, 0.093 mmol) and triphenylphosphine (97 mg, 0.37 mmol) was added hexane (5 mL) at room temperature, and the solution was refluxed for 30 min. A hexane solution of mesitonitrile oxide (26 mg, 0.16 mmol) was added to the solution, and the mixture was stirred for 1 h. After removal of the solvent, the crude reaction products were roughly chromatographed by GPLC and purified by PTLC (hexane/CH_2Cl_2 = 10:3) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-mesityl-1,3,5,2-oxathiazasilole (**11b**) (49 mg, 54%), together triphenylphosphine sulfide (109 mg, 100%). **11b**: Colorless crystals (from ethanol), mp 207−209 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.06 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.02 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.05 (s, 9H, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 0.06 (s, 9H, Tbt-*o*-CH-(Si*Me*$_3$)$_2$), 0.08 (s, 18H, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.05 (d, *J* = 5 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.18 (d, *J* = 5 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.20 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me*$_2$), 1.23 (d, *J* = 5 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.25 (d, *J* = 5 Hz, 3H, Tip-*o*-CH*Me*$_2$), 1.35 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)$_2$), 2.11 (s, 6H, Mes-*o*-Me), 2.24 (s, 3H, Mes-*p*-Me), 2.50 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.83 (sept, *J* = 7 Hz, 1H, Tip-*p*-C*H*Me$_2$), 2.91 (s, 1H, Tbt-*o*-C*H*(SiMe$_3$)$_2$), 2.99 (sept, *J* = 5 Hz, 1H, Tip-*o*-C*H*Me$_2$), 3.72 (sept, *J* = 5 Hz, 1H, Tip-*o*-C*H*Me$_2$), 6.37 (s, 1H, Tbt-*m*-CH), 6.49 (s, 1H, Tbt-*m*-CH), 6.81 (s, 2H, Mes-*m*-CH), 6.94 (s, 1H, Tip-*m*-CH), 7.02 (s, 1H, Tip-*m*-CH); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 1.11 (q, Tbt-*p*-CH(Si*Me*$_3$)$_2$), 1.22 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.62 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.67 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 1.91 (q, Tbt-*o*-CH(Si*Me*$_3$)$_2$), 20.30 (q), 21.07 (q), 23.74 (q), 23.81 (q), 24.32 (q), 24.79 (q), 26.60 (q), 28.43 (q), 28.69 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 29.05 (d, Tbt-*o*-*C*H(SiMe$_3$)$_2$), 31.04 (d, Tbt-*p*-*C*H(SiMe$_3$)$_2$), 32.36 (d, Tip-*o*-*C*HMe$_2$), 34.31 (d, Tip-*o*-*C*HMe$_2$), 35.43 (d, Tip-*p*-*C*HMe$_2$), 122.51 (d, Tip-*m*-CH), 122.58 (d, Tip-*m*-CH), 123.77 (s), 124.13 (d, Tbt-*m*-CH), 128.58 (d, Mes-*m*-CH), 128.83 (s), 129.44 (d, Tbt-*m*-CH), 132.00 (s), 137.01 (s), 138.84 (s), 146.20 (s), 151.15 (s), 152.73 (s), 153.42 (s), 153.62 (s, Tbt-o), 154.43 (s, Tbt-o), 159.07 (s, Tip-o). Anal. Calcd for $C_{52}H_{93}Si_7NOS \cdot H_2O$: C, 62.77; H, 9.62; N, 1.41; S, 3.22. Found: C, 63.07; H, 9.33; N, 1.61; S, 3.46.

Reaction of 7b with 2,3-Dimethyl-1,3-butadiene. To a mixture of **2b** (116 mg, 0.13 mmol) and triphenylphosphine (123 mg, 0.47 mmol) in a dry 12-mm Pyrex glass tube were placed 2,3-dimethyl-1,3-butadiene (0.035 mL, 0.31 mmol) and hexane (1.5 mL) at room temperature. After five freeze−pump−thaw cycles, the tube was evacuated and sealed. The solution was heated at 180 °C for 3 h, during which time the yellow color of the solution disappeared. After removal of the solvent, the crude reaction products were roughly chromatographed by GPLC and purified by PTLC (hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-dimethyl-1-silacyclohex-4-ene (**13**) (85 mg, 74%), together with triphenylphosphine sulfide (119 mg, 100%). **13**: Colorless crystals (from ethanol), mp 179−181 °C; ^{1}H NMR (CDCl$_3$, 500 MHz, 340 K) δ 0.02 (s, 18H, Tbt-*o*-CH(Si*Me*$_3$)2), 0.07 (s, 9H, Tbt-*p*-CH(Si*Me*$_3$)2), 0.08 (s, 9H, Tbt-*p*-CH(Si*Me*$_3$)2), 0.09 (s, 18H, Tbt-*o*-CH(Si*Me*$_3$)2), 1.03 (br s, 3H, Tip-*o*-CH*Me*2), 1.11 (br s, 3H, Tip-*o*-CH*Me*2), 1.12 (br s, 3H, Tip-*o*-CH*Me*2), 1.19 (d, *J* = 7 Hz, 6H, Tip-*p*-CH*Me2*), 1.20 (br s, 3H, Tip-*o*-CH*Me*2), 1.33 (s, 1H, Tbt-*p*-C*H*(SiMe$_3$)2), 1.45 (s, 3H), 1.78 (s, 3H), 2.18 (d, J = 14 Hz, 1H, SC*H*2), 2.29 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)2), 2.42 (d, J = 14 Hz, 1H, SC*H*2), 2.79 (sept, J = 7 Hz, 1H, Tip-*p*-C*H*Me2), 2.86 (br s, 1H, Tip-*o*-C*H*Me2), 3.06 (d, J = 14 Hz, 1H, SiC*H*2), 3.18 (br s, 1H, Tbt-*o*-C*H*(SiMe$_3$)2), 3.30 (d, J = 14 Hz, 1H, SiC*H*2), 4.19 (br s, 1H, Tip-*o*-C*H*Me2), 6.37 (br s, 2H, Tbt-*m*-CH), 6.92 (br s, 1H, Tip-*m*-CH), 6.94 (br s, 1H, Tip-*m*-CH); ^{13}C NMR (CDCl$_3$, 125 MHz, 340 K) δ 1.11 (q, Tbt-*p*-CH(Si*Me$_3$*)2), 1.25 (q, Tbt-*p*-CH(Si*Me$_3$*)2), 2.40 (q, Tbt-*o*-CH(Si*Me$_3$*)2), 2.58 (q, Tbt-*o*-CH(Si*Me$_3$*)2), 20.44 (q), 21.49 (q), 23.70 (q), 23.72 (q), 25.40 (q), 25.73 (t, SCH2), 26.34 (q), 26.84 (t, SiCH2), 28.08 (d, Tbt-*o*-*C*H(SiMe$_3$)2), 30.61 (d, Tbt-*o*-*C*H(SiMe$_3$)2), 31.48 (d, Tbt-*p*-*C*H(SiMe$_3$)2), 32.98 (d, Tip-*o*-*C*HMe2), 33.12 (d, Tip-*o*-*C*HMe2), 34.19 (d, Tip-*p*-*C*HMe2), 122.42 (d, Tbt-*m*-CH), 123.45 (s, Tbt-p), 124.05 (d, Tip-*m*-CH), 128.71 (d, Tbt-*m*-CH), 128.81 (s), 129.26 (d, Tip-*m*-CH), 131.62 (s), 132.37 (s), 143.40 (s), 149.59 (s), 151.08 (s, Tbt-o), 151.20 (s, Tbt-o), 153.60 (s, Tip-o), 155.70 (s, Tip-o); high-resolution FAB-MS, observed *m*/*z* 896.5317, calcd for $C_{48}H_{92}Si_7S$ *m/z* 896.5305. Anal. Calcd for $C_{48}H_{92}Si_7S\cdot H_2O$: C, 62.94; H, 10.34; S, 3.50. Found: C, 63.29; H, 10.20; S, 4.15.

X-ray Data Collection. Single crystals of **2a** and **8** were grown by the slow evaporation of a saturated solution in ethanol and chloroform at room temperature, and single crystals of **7b** were grown by the slow evaporation of a saturated solution in hexane at room temperature in a glovebox. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) (for **2a**) and a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) (for **8** and **7b**). The structure of **2a** was solved by direct method with MULTAN 78[36] and refined by the full matrix least-squares method. The structures of **8** and **7b** were solved by direct methods with SHELXS-86[37] and refined by the full matrix least-squares method. All the non-hydrogen atoms were refined anisotropically. The final cycle of the least-squares refinement was based on 4906 (for **2a**), 8548 (for **8**), and 5390 (for **7b**) observed reflections [$I > 3\sigma|I|$] and 460 (for **2a**), 792 (for **8**), and 901 (for **7b**) variable parameters with R (R_w) = 0.078 (0.078) (for **2a**), 0.070 (0.055) (for **8**), and 0.061 (0.051) (for **7b**). The crystal data for these molecules are summarized in Table 3.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 05236102) from the Ministry of Education, Science, Sports and Culture, Japan. H.S. is grateful to the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We also thank Professor Y. Furukawa, Waseda University, for the measurement of the FT-Raman spectra of **2a**, **2b**, and **7b**. Thanks are due to Central Glass, Shin-etsu Chemical, and Tosoh Akzo Co., Ltd. for the generous gifts of tetrafluorosilane, chlorosilanes, and alkyllithiums, respectively.

Supporting Information Available: ^{1}H NMR spectral chart of **8** and tables listing atomic coordinates, temperature factors, bond lengths and angles, and torsion angles for **7b** and **8** (108 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA980783C

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