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Synthesis, Properties, and Reactions of a Series of Stable Dialkyl-Substituted Silicon−Chalcogen Doubly Bonded Compounds

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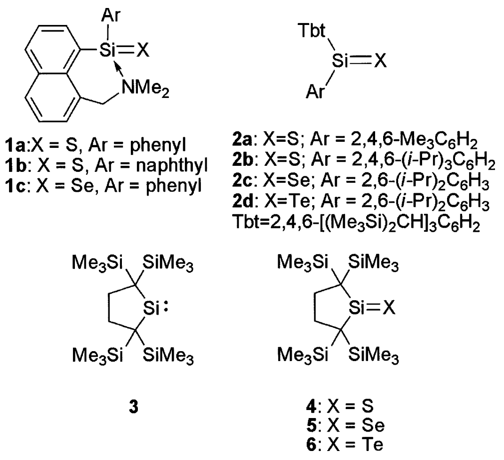
Abstract: The first dialkyl-substituted silicon−chalcogen doubly bonded compounds [$R_2Si{=}X$; R_2 = 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl, X = S (**4**), Se (**5**), and Te (**6**)] were synthesized by the reactions of an isolable dialkylsilylene R_2Si: (**3**) with phosphine sulfide, elemental selenium, and elemental tellurium, respectively. Systematic changes of characteristics of silicon−chalcogen double bonds are elucidated by X-ray analysis, UV−vis spectroscopy, and DFT calculations. In the solid state, the unsaturated silicon atom in **4**−**6** adopts planar geometry and the extent of the shortening of Si=X double bonds from the corresponding Si−X single bonds decreases in the order **4** > **5** > **6**. In the absorption spectra of **4**−**6**, $\pi \to \pi^*$ transition bands are observed distinctly in addition to $n \to \pi^*$ transition bands. Both the $n \to \pi^*$ and $\pi \to \pi^*$ transitions are red-shifted in the order **4** < **5** < **6**, and the difference between the energies of the two transitions is kept almost constant among **4**−**6**. The tendency is explained using the qualitative perturbation theory and is reproduced by the DFT calculations for model silanechalcogenones. Addition reactions of water, methanol, and isoprene to **4**−**6** are reported.

Introduction

Although heavier group-14 element−group-16 element doubly bonded compounds, metallanechalcogenones ($R_2E{=}X$: E = Si, Ge, Sn; X = S, Se, Te),[1] constitute an important class of compounds as heavier congeners of ubiquitous ketones, the synthesis and chemical properties of stable metallanechalcogenones still remain to be elucidated. As the first stable silanechalcogenones Corriu et al. reported the synthesis and characterization of diarylsilanethiones and diarylsilaneselones **1a**−**1c** that were stabilized by the intramolecular coordination of nitrogen to unsaturated silicon (Chart 1).[2] Tokitoh, Okazaki, et al. have synthesized and characterized a series of stable heavier diarylsilanechalcogenones without intramolecular extracoordination to unsaturated group-14 atoms **2a**−**2d** using the steric protection of the reactive unsaturated bonds with bulky aromatic substituents.[3] In addition to these stable silanechalcogenones, a number of stable $Ar_2E{=}X$ type compounds (E = Ge, Sn, Pb; X = S, Se, Te) have been reported so far.[4] However, all these metallanechalcogenones have aryl substituents strongly modifying the electronic properties of the E=X bonds. Among silanechalcogenones **2a**−**2d**, only the structure of silanethione **2a** has been analyzed by X-ray crystallography.[3a]

Chart 1



1a: X = S, Ar = phenyl
1b: X = S, Ar = naphthyl
1c: X = Se, Ar = phenyl

2a: X=S; Ar = 2,4,6-$Me_3C_6H_2$
2b: X=S; Ar = 2,4,6-(i-Pr)$_3C_6H_2$
2c: X=Se; Ar = 2,6-(i-Pr)$_2C_6H_3$
2d: X=Te; Ar = 2,6-(i-Pr)$_2C_6H_3$
Tbt=2,4,6-[$(Me_3Si)_2CH]_3C_6H_2$

3

4: X = S
5: X = Se
6: X = Te

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(1) For recent reviews on silicon−chalcogen doubly bonded compounds, see: (a) Tokitoh, N.; Okazaki, R. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 17, pp 1063−1103. (b) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *37*, 625−630. (c) Tokitoh, N.; Okazaki, R. *Adv. Organomet. Chem.* **2001**, *47*, 121−166.

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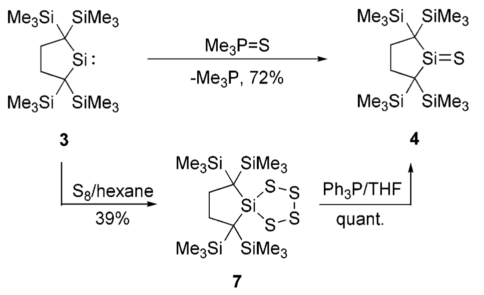
10.1021/ja065774f CCC: $33.50

Recently, we have shown that stable dialkylsilylene **3** (R_2Si:), the first isolable dialkylsilylene,[5] can be applied to the synthesis of an isolable trisilaallene ($R_2Si{=}Si{=}SiR_2$),[6a] the first stable compound with a formally sp-hybridized silicon atom and a 2-germadisilaallene.[6b] This success encourages us to apply dialkylsilylene **3** and its germanium[7a] and tin analogues[7b,c] to the synthesis of various types of heavier group-14 unsaturated compounds.[8] In this paper, we report the synthesis, properties, and some reactions of a series of the first dialkylsilanechalcogenones [$R_2Si{=}X$; X = S (**4**), Se (**5**), Te (**6**), R_2 = 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl] using **3**. Molecular structures of silanechalcogenones **4**−**6** have all been determined by X-ray crystallography to allow discussion of the systematic structural change depending on the chalcogen atoms. In contrast to diaryl-substituted silanechalcogenones **2a**−**2d**,[3] $\pi \rightarrow \pi^*$ transitions of **4**−**6** are distinctly observed in addition to the n $\rightarrow \pi^*$ transition bands.

Results and Discussion

Synthesis of Dialkyl-Substituted Silanechalcogenones 4−**6.** Silanethione **4** is synthesized as colorless crystals by the reaction of stable dialkylsilylene **3**[5] with trimethylphosphine sulfide in 72% yield (Scheme 1).[9] Silanethione **4** is thermally stable but very hygroscopic. When silylene **3** is treated with elemental sulfur, S_8, tetrathiasilolane **7** is obtained as a major product instead of **4**. Similarly to the synthesis of **2a** and **2b**,[3] desulfination of **7** with triphenylphosphine provides **4** almost quantitatively, but the separation of pure **4** from the side product, triphenylphosphine sulfide, is considerably difficult.

Scheme 1



Dialkyl-substituted silaneselone **5** and silanetellone **6** are prepared in good yields as pale yellow and bright orange crystals, respectively, by the direct reactions of **3** with elemental Se and Te, respectively (eq 1).[9] Both **5** and **6** are also thermally stable but hygroscopic.

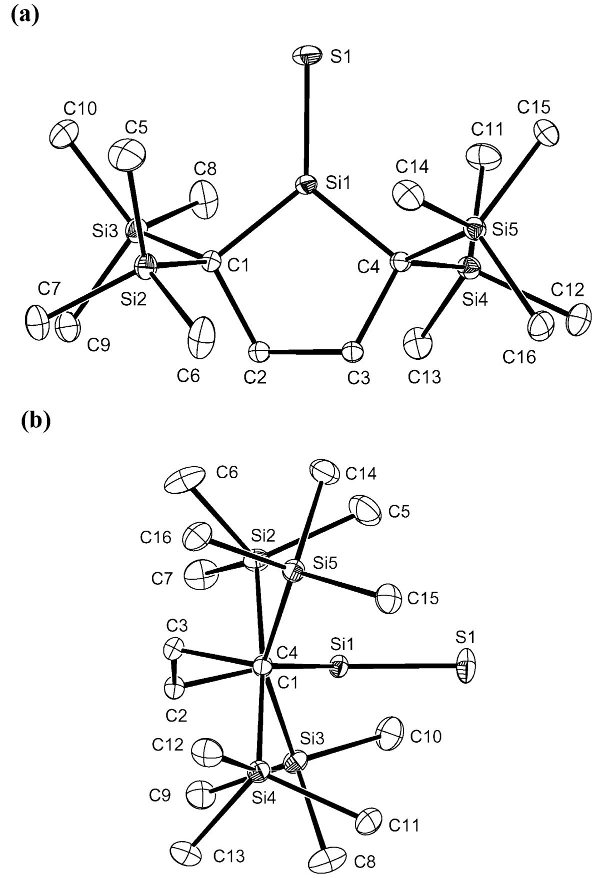
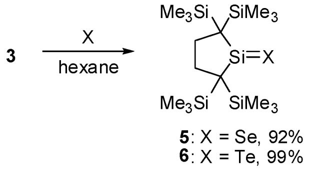


Figure 1. ORTEP drawings of dialkylsilanethione **4**: (a) top view; (b) side view. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Si1−S 1.9575(7), Si1−C1 1.855(2), Si1−C4 1.853(2). Selected bond angles (deg): C1−Si1−C4 102.09(7), S−Si1−C1 128.24(6), X−Si1−C1 128.68(6). Sum of the bond angles around Si1, 360.0°.



(1)

Molecular Structures of Silanechalcogenones 4−**6.** Molecular structures of **4**−**6** were determined by X-ray structural analysis. The ORTEP drawings of **4**−**6** are shown in Figures 1−3 together with their selected structural parameters.

Silanechalcogenones **4**−**6** are all monomeric in the crystals and have an approximate C_2 molecular symmetry with a half-chair silacyclopentane ring. There are several interesting structural characteristics among **4**−**6**. (1) Similarly to diaryl-substituted silanethione **2b**,[3a,b] the geometry around the tricoordinate silicon atom in **4**−**6** is perfectly planar with the sum of the bond angles around the silicon atom of 360.0°. (2) The Si=S double-bond distance of **4** (1.9575(7) Å) is much shorter than that of base-stabilized silanethione **1** (2.013(3) Å)[2] but comparable with that for silanethione **2b** (1.948(4) and 1.952(4) Å).[3a,b] (3) As shown in Table 1, the Si=X bond lengths in **4**−**6** are shorter than the corresponding Si−X single-bond

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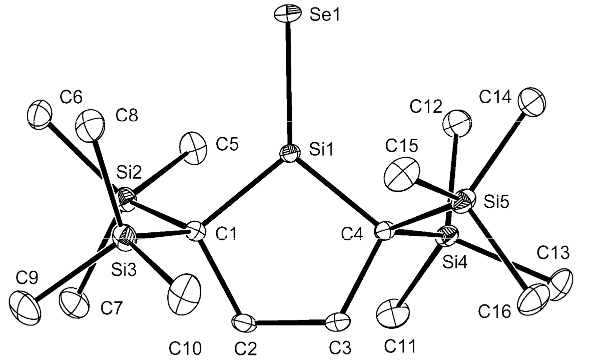


Figure 2. ORTEP drawing of dialkylsilaneselone **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Si1−Se 2.0963(5), Si1−C1 1.855(2), Si1−C4 1.853(2). Selected bond angles (deg): C1−Si1−C4 102.18(10), Se−Si1−C1 128.14(8), Se−Si1−C1 129.68(7). Sum of the bond angles around Si1, 360.0°.

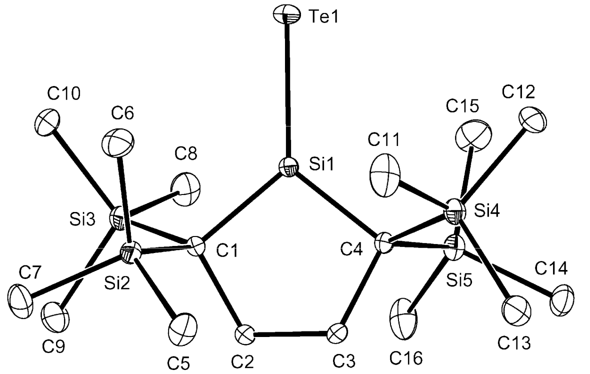


Figure 3. ORTEP drawing of dialkylsilanetellone **6**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Si1−Te 2.3210(6), Si1−C1 1.863(2), Si1−C4 1.861(2). Selected bond angles (deg): C1−Si1−C4 101.60(9), Te−Si1−C1 129.51(6), Te−Si1−C1 128.39(7). Sum of the bond angles around Si1, 360.0°.

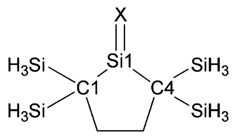
Table 1. Geometrical Parameters Around Si═X Double Bonds in **4**−**6**

compound	*d*(Si═X)/Å[a]	%Δ*d*[b]	Σ(SiI)/deg[c]
4 (X═S)	1.957(7)	9.4	360.0
5 (X═Se)	2.0963(5)	8.6	360.0
6 (X═Te)	2.3210(6)	7.6	360.0

[a] Silicon−chalcogen double-bond distance. [b] %Δ*d* = [1 − (Si═X double-bond length)/(Si−X single-bond length)] × 100%. See ref 10 for standard single-bond lengths of Si−S (2.14 Å), Si−Se (2.27 Å), and Si−Te (2.52 Å). [c] The sum of the bond angles around the unsaturated Si atom.

lengths.[10] The percent bond shortening, %Δ*d*, which is defined as [1 − (Si═X double-bond length)/(Si−X single-bond length)] × 100%,[11b] among **4**−**6** decreases in the order X = S (9.4%) > Se (8.8%) > Te (7.6%), suggesting that the Si−X π bonds weaken in the same order (Table 1).[11b]

Table 2. Calculated Structural Parameters of **4′**−**6′**[a]

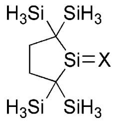


	distance/Å		angles/deg			
compound	Si1–X	Si1–C1(C4)	X–Si1–C1(C4)	C1–Si1–C4	Σρ(Si)[b]	%Δ*d*[c,d]
4′ (X═S, C_2)	1.9658	1.8749	130.332	99.335	360.0	9.9
5′ (X═Se, C_2)	2.1010	1.8775	130.430	99.140	360.0	9.7
6′ (X═Te, C_2)	2.3076	1.8821	130.604	98.793	360.0	9.1

[a] The geometry was optimized at the B3LYP/B1 level. B1 basis set: 6-31+G(d) for C and H atoms and Lanl2dzpd for Si, S, Se, Te atoms. [b] The sum of the bond angles around the tricoordinate silicon atom. [c] See the footnote of Table 1 for the definition. [d] Single-bond lengths of Si−S (2.183 Å), Si−Se (2.327 Å), and Si−Te (2.540 Å) are those calculated for the corresponding $Me_3Si{-}X{-}SiMe_3$ (X = S, Se, and Te) at the same theoretical level.

The planar geometry in silanechalcogenones **4**−**6** can be understood qualitatively by applying the CGMT (Carter−Goddard−Malrieu−Trinquier) model[12] to the R_2Si═X compounds. The CGMT model says that the bent geometry of the R_2Si═X molecule may be more stabilized due to the σ*−π interaction in the Si═X bond than the planar geometry, if $\Sigma\Delta E_{ST} > (^1/_2)(E_\sigma + E_\pi)$, where $\Sigma\Delta E_{ST}$ is the sum of the singlet−triplet energy differences of R_2Si: and the X atom and E_σ and E_π are the σ and π bond energies of the Si═X double bonds. While the ΔE_{ST} value for dialkylsilylene is ca. 25 kcal mol^{-1},[13] the ΔE_{ST} value for chalcogen atoms is negative because their ground state electronic configuration is triplet ($^3P_2$). On the other hand, the $(E_\sigma + E_\pi)$ values for R_2Si═X are even larger than 100 kcal mol^{-1}; theoretical $(E_\sigma + E_\pi)$ values are reported to be 128.6, 114.4, and 96.1 kcal mol^{-1} for H_2Si═X (X = S, Se, and Te, respectively).[1b] The $\Sigma\Delta E_{ST}$ value is far smaller than the $(^1/_2)(E_\sigma + E_\pi)$ values for all R_2Si═X compounds, and hence, the geometry around the Si atom should be planar on the basis of the above CGMT model.

DFT calculations[14] were performed for model silanechalcogenones **4′**−**6′**, where the four Me_3Si groups of **4**−**6** are replaced by four H_3Si groups. The geometry of these compounds was optimized at the B3LYP/B1 level;[15] B1 means 6-31+G(d) for C and H atoms and Lanl2dzpd for Si, S, Se, and Te atoms. The geometrical parameters for the optimized structures of **4′**−**6′** are shown in Table 2. The structural characteristics of **4**−**6** determined by X-ray crystallography are well reproduced in the



4′: X = S
5′: X = Se
6′: X = Te

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(10) The following values are used for typical single-bond distances: 2.14 Å for the Si−S bond (ref 11a), 2.27 Å the for Si−Se bond (ref 11b), and 2.52 Å for the Si−Te bond (ref 11c), respectively.

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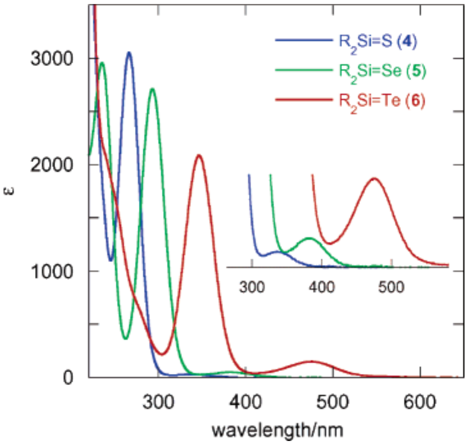

Figure 4. UV−vis spectra of **4**−**6** in hexane at room temperature. The inset shows a part magnified vertically.

Table 3. UV−Vis Absorption Maxima Observed for **4**−**6**[a]

compound	transition[b]	λ_{max}/nm (ϵ)	$\Delta\nu(\pi\pi^*–n\pi^*)$/cm^{-1}[c]
4 (X═S)	$n \to \pi^*$	336 (17)	7900
	$\pi \to \pi^*$	266 (3000)	
5 (X═Se)	$n \to \pi^*$	383 (39)	8100
	$\pi \to \pi^*$	293 (2700)	
6 (X═Te)	$n \to \pi^*$	476 (140)	7900
	$\pi \to \pi^*$	346 (2100)	

[a] In hexane. [b] Assignment based on the molar absorptivity. [c] $\Delta\nu(\pi\pi^* - n\pi^*) = \nu(\pi \to \pi^*) - \nu(n \to \pi^*)$.

optimized structures of model compounds **4′**−**6′**. The geometry around the unsaturated silicon is perfectly planar in **4′**−**6′**, and %Δ*d* of the Si═X double bond decreases slightly in the order X = S (9.9) > Se (9.7) > Te (9.1).

UV−Vis Spectra. Compounds **4**−**6** clearly show strong and weak absorption bands assignable to the $\pi \to \pi^*$ and $n \to \pi^*$ transitions in the UV−vis region as shown in Figure 4. The absorption maxima and the extinction coefficients of **4**−**6** are summarized in Table 3. Both the $n \to \pi^*$ and $\pi \to \pi^*$ transition bands of **4**−**6** are red-shifted,[16] but the differences in the transition energies between the $n \to \pi^*$ and $\pi \to \pi^*$ bands [$\Delta\nu(\pi\pi^* - n\pi^*)$] are nearly constant with the increasing atomic number of the chalcogen atom.

The $\pi \to \pi^*$ and $n \to \pi^*$ bands of dialkylsilanethione **4** appear at 266 nm (ϵ 3000) and 336 nm (ϵ 17). The $n \to \pi^*$ band appears at a shorter wavelength with a smaller absorptivity than that of diarylsilanethione **2b** [λ_{max} (ϵ), 396 nm (100)],[3a] indicating large perturbation of aryl substituents to the π^* orbital of the Si═S bond in **2b**. The substituent effects on the $n \to \pi^*$ transition are parallel to those observed between acetone and benzophenone (λ_{max}/nm (ϵ) is 279 (13) and 340 (180) for acetone and benzophenone).[19] The $n \to \pi^*$ transition bands of silaneselone **5** (383 nm) and silanetellone **6** (476 nm) are also significantly blue-shifted from the corresponding bands of **2c** (509 nm) and **2d** (593 nm).[3c]

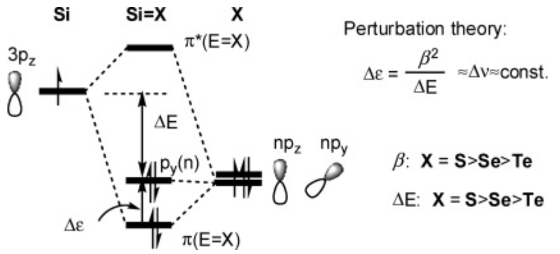

Figure 5. Qualitative orbital interaction diagram between $3p_z$ on silicon and np_z on X in $R_2Si═X$.

Table 4. UV−Vis Absorption Maxima Calculated for **4′**−**6′**[a]

compound	transition	λ_{max}/nm (f)[b]	$\Delta\nu(\pi\pi^* – n\pi^*)$[c]/cm^{-1}
4′ (X═S)	$n \to \pi^*$	369.5 (0.000)	11430
	$\pi \to \pi^*$	259.8 (0.119)	
5′ (X═Se)	$n \to \pi^*$	416.9 (0.000)	11090
	$\pi \to \pi^*$	285.1 (0.129)	
6′ (X═Te)	$n \to \pi^*$	506.7 (0.000)	10620
	$\pi \to \pi^*$	329.4 (0.136)	

[a] TD/B3LYP/B1 level. B1 basis set: 6-31 + G(d) for C and H atoms and LANL2DZpd for Si, S, Se, and Te atoms. [b] Oscillator strength. [c] $\Delta\nu(\pi\pi^* - n\pi^*) = \nu(\pi \to \pi^*) - \nu(n \to \pi^*)$.

Interestingly, $\Delta\nu(\pi\pi^* - n\pi^*)$ values are approximately constant among **4**−**6**; the values are 7900, 8100, and 7900 cm^{-1} for **4**, **5**, and **6**, respectively (Table 3). The tendency may be understood qualitatively using perturbation MO theory. As shown in Figure 5, the π and π* orbitals of $R_2Si═X$ (X = S, Se, and Te) are constructed by the overlap between the silicon $3p_z$ and chalcogen np_z orbitals. The stabilization energy of the π orbital from the np orbitals of X ($\Delta\epsilon$) is estimated by second-order perturbation theory to be

$$\Delta\epsilon = \beta^2/\Delta E \qquad (2)$$

The terms β and ΔE are the resonance integral and the energy difference between the Si $3p_z$ and X np_z orbitals, respectively, where ΔE is taken to be positive. With increasing atomic number of X, both the β^2 value and ΔE are expected to decrease, because the $3p_z$−np_z overlap decreases and the energy level of np_z is elevated. Because $\Delta\nu(\pi\pi^* - n\pi^*)$ corresponds to $\Delta\epsilon$ qualitatively, the constant $\Delta\nu(\pi\pi^* - n\pi^*)$ values among **4**−**6** suggest that the effects of X on β^2 and ΔE compensate each other. Although it is interesting to examine whether such a relationship is applicable to a series of $R_2C═X$ type compounds, there are no appropriate UV−vis data available for the carbon series. Notably, the $\Delta\nu(\pi\pi^* - n\pi^*)$ value in an alkanethione is known to be much larger than that of an alkanone, which is responsible for the fluorescence from the S_2 states of alkanethiones;[20] the $\Delta\nu$ $(\pi\pi^* - n\pi^*)$ values are 17 300 and 21 200 cm^{-1} for acetone and adamantanethione, respectively.[21] The large difference in the $\Delta\nu(\pi\pi^* - n\pi^*)$ values suggests that, in the two $R_2C═X$ compounds, the effects of X on β^2 and ΔE do not compensate each other; i.e., the β^2 term is less sensitive to X than the ΔE term.

The results of TDDFT[22] calculations for **4′**−**6′** are shown in Table 4. The calculated $n \to \pi^*$ and $\pi \to \pi^*$ band maxima for **4′**−**6′** are not completely in accord with the corresponding

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(16) A similar red-shift of $n \to \pi^*$ transition bands was observed for aryl-substituted silanechalcogenones (ref 3), the corresponding germanechalcogenones (refs 4a−e), and stannanechalcogenones (refs 4f−j), and chalcogenones (refs 17 and 18).

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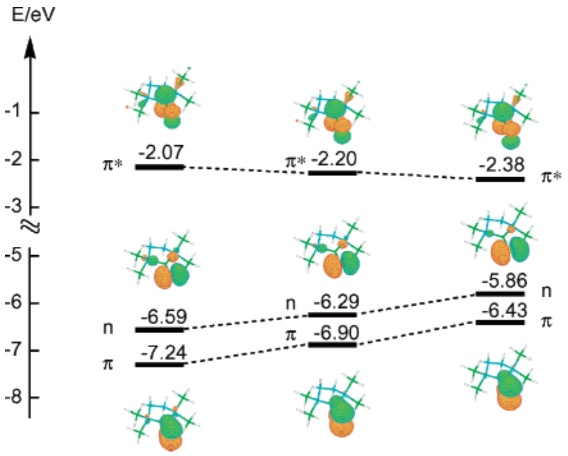


Figure 6. Kohn−Sham orbitals and their energy levels of **4′**−**6′** calculated at the B3LYP/B1 level. B1 basis set: 6-31+G(d) for C and H atoms and Lanl2dzpd for Si, S, Se, and Te atoms.

maxima observed for **4**−**6**. The theoretical n → π* band maxima are at longer wavelengths than the experimental one, while the theoretical π → π* bands are at shorter wavelengths than the experimental one. The theoretical wave numbers ν_c (cm^{-1}) are linearly correlated with the corresponding experimental wave numbers ν_e by the following equations (eqs 3 and 4; correlation coefficients for both of the two lines are 1.00).

$$\nu_c(\mathrm{n} \rightarrow \pi^*) = 0.836\nu_e(\mathrm{n} \rightarrow \pi^*) + 2160 \qquad (3)$$

$$\nu_c(\pi \rightarrow \pi^*) = 0.933\ \nu_e(\pi \rightarrow \pi^*) + 3350 \qquad (4)$$

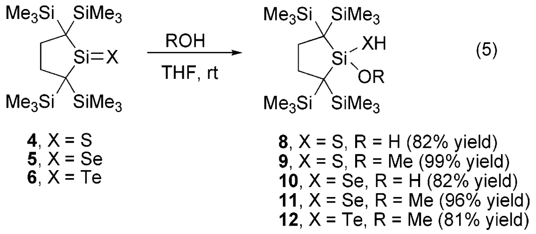
Theoretical results for **4′**−**6′** reproduce the qualitative characteristics of the absorptions among **4**−**6**: both the n → π* and π → π* transition bands are red-shifted from **4′** to **6′** but the $\Delta\nu(\pi\pi^* - \mathrm{n}\pi^*)$ values are almost constant with increasing atomic number of the chalcogen atom.

Figure 6 shows Kohn−Sham orbitals[23] and their energy levels of model silanechalcogenones **4′**−**6′**. The n and π orbital levels become higher in the order **4′** < **5′** < **6′**, but the energy difference ($\Delta\epsilon$) between the n and π orbitals is almost constant among **4′**−**6′**; $\Delta\epsilon$ values are 0.65, 0.61, and 0.57 eV for **4′**, **5′**, and **6′**, respectively. On the other hand, the π* orbital level lowers in the order **4′** > **5′** > **6′**, but the change is relatively small among them. These MO features are in good accord with the results of the qualitative MO analysis discussed above and also with the red-shifted n → π* and π → π* transition bands with increasing atomic number of the chalcogen atom and almost constant $\Delta\nu(\pi\pi^* - \mathrm{n}\pi^*)$ values among **4**−**6**.

^{29}Si NMR. The isotropic ^{29}Si chemical shifts of the unsaturated silicon atoms in dialkylsilanechalcogenones **4**, **5**, and **6** appear at 216.0, 227.7, and 229.5 ppm, respectively. Expectedly, the chemical shifts are at a much lower field than those of donor-stabilized silanethione **1a** (X = S; 22.3 ppm)[2] and donor-free diarylsilanechalcogenones **2b**−**2d**,[3] indicative of the less perturbed nature of the double bonds; the ^{29}Si resonances for **2b**, **2c**, and **2d** have been reported to be 166.6, 174, and 171 ppm, respectively. The ^{29}Si chemical shift is not remarkably different among **4**−**6** but lower-field shifted from **4** to **5** to **6**. The GIAO calculations of the unsaturated ^{29}Si resonances of **4′** and **5′** gave 217 and 241 ppm, respectively.

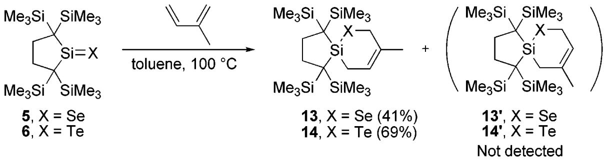
Reactions of 4−**6.** Silanechalcogenones **4**−**6** are thermally stable and are intact for 1 week at 80 °C in benzene-d_6.

Tokitoh, Okazaki, et al. have reported that silanethione **2a** and silaneselone **2b** react with water and methanol to give the corresponding adducts.[3] Similarly, silanechalcogenones **4**−**6** react with water and methanol to give the corresponding adducts in high yields, while the reaction of silanetellone **6** with water gave a complex mixture (eq 5).



(5)

Silanethione **2a** reacts with 2,3-dimethylbutadiene at 180 °C to give the corresponding [2 + 4] cycloadduct.[3] Silanechalcogenones **4**−**6** do not react with 2,3-dimethylbutadiene even at 180 °C in toluene, but **5** and **6** react with isoprene in toluene at 100 °C to give the corresponding [2 + 4] cycloadducts in a regiospecific manner; no regioisomers **13′** and **14′** are detected in the reaction mixtures.



(6)

The reaction of silanethione **4** with isoprene under similar conditions does not give the corresponding cycloadduct. Instead, the corresponding 1,3-dithiadisiletane was obtained after a prolonged reaction time but in very low yield (4%). Due to the shorter Si═S bond distance than Si═Se and Si═Te bonds, the reaction of **4** with isoprene may meet more severe steric strain at the cyclic transition state.

No reactions take place between **4**−**6** and 2,6-dimethylphenylisocyanide or 4-(*N*,*N*-dimethylamino)pyridine at 60 °C in benzene-d_6 for 3 days.

Conclusion

A systematic study of the synthesis, structure, spectroscopic properties, and reactions of a series of dialkyl-substituted silanechalcogenones ($R_2Si{=}X$; X = S, Se, and Te) has revealed an interesting dependence of the properties of the Si═X double bonds on X. As predicted by the CGMT model, unsaturated silicon atoms in **4**−**6** adopt planar geometry. The Si═X double-bond lengths lengthen on going from **4** to **6**, but their bond shortening %Δ*d* decreases in the same order. Both n → π* and π → π* transitions red-shift in the order **4** < **5** < **6** with a constant difference of the two transition frequencies, suggesting that the effect of the decrease in the resonance integral between the silicon 3pz and chalcogen npz orbital with increase of the atomic number of X compensates the effect of the lift of the npz orbital level with the increase.

The reactivity of **4**−**6** is similar to that of diarylsilanechalcogenones[3] but more sensitive to the steric hindrance around the unsaturated silicon atom. Compounds **4**−**6** do not react with 2,3-dimethylbutadiene even at 180 °C in toluene, but **5** and **6**

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react with isoprene in toluene at 100 °C to give the corresponding [2 + 4] cycloadducts in a regiospecific manner.

Experimental Section

All operations were performed in flame-dried glassware under an atmosphere of dry argon. All solvents were distilled from appropriate drying agents before use. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (79 MHz) NMR were recorded on a Bruker Avance 400 NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are referenced to residual ^{1}H and ^{13}C of the solvents, benzene-d_6 (^{1}H δ 7.15 and ^{13}C δ 128.0). ^{29}Si NMR chemical shifts are given in ppm relative to externally referenced tetramethylsilane (δ_{Si} 0). Mass spectra and high-resolution mass spectral data were obtained on a JEOL JMS MS-600W mass spectrometer. UV−vis spectra were recorded on a Hewlett-Packard HP8453 spectrometer. Dialkylsilylene **3** and triphenylphosphine sulfide were prepared by the procedure according to the literature.[5,26] Elemental selenium and tellurium are commercially available.

1. Synthesis of [1,1,4,4-Tetrakis(trimethylsilyl)butane-1,1-diyl]-silanethione (4). In a Schlenk flask (10 mL) equipped with a magnetic stir bar, dialkylsilylene **3** (510 mg, 1.37 mmol) and trimethylphosphine sulfide (149 mg, 1.38 mmol) were placed, and then THF (5 mL) was transferred into the mixture. After stirring the mixture for 6 h at room temperature, the color of the solution disappeared. Removal of volatiles in vacuo gave a colorless solid. ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies of the solid indicated that silanethione **4** formed as a single product. Recrystallization from hexane gave pure **4** in 72% yield. **4**: colorless crystals; mp 63−64 °C; ^{1}H NMR (C_6D_6, δ) 0.29 (s, 36H), 1.82 (s, 4H); ^{13}C NMR (C_6D_6, δ) 2.1 (SiMe$_3$), 28.4 (C), 31.3 (CH$_2$); ^{29}Si NMR (C_6D_6, δ) 1.0 (SiMe$_3$), 216.8 (Si═S); MS (70 eV, EI) m/z (%) 404 (4, M$^+$), 389 (26), 73 (100); UV−vis (hexane) λ_{max}/nm (ϵ) 266 (3000), 336 (17); HRMS calcd for $C_{16}H_{40}SSi_5$, 404.1697; found, 404.1687.

2. Synthesis of Silanethione 4 via Tetrathiasilolane 7. In an NMR tube, silylene **3** (64 mg, 0.17 mmol) and elemental sulfur (40 mg, 0.16 mmol as S$_8$) were placed, and then deoxygenated and dry benzene-d_6 (0.5 mL) was transferred to the tube using a vacuum line, and the mixture was kept at room temperature for 6 h. Filtration of the mixture to remove residual sulfur, evaporation in vacuo, and purification by GPC (toluene) gave compound **7** as yellow crystals in 39% yield (33 mg, 0.07 mmol). **7**: mp 143 °C; ^{1}H NMR (C_6D_6, δ) 0.25 (s, 36H), 1.85 (s, 4H); ^{13}C NMR (C_6D_6, δ) 4.6 (SiMe$_3$), 15.4 (C), 33.6 (CH$_2$); ^{29}Si NMR (C_6D_6, δ) 5.2 (SiMe$_3$), 70.3 (Si); MS (70 eV, EI) m/z (%) 436 (38, M$^+$ − 64), 421 (66), 389 (32), 73 (100). Anal. Calcd for $C_{16}H_{40}S_4Si_5$: C, 38.34; H, 8.04. Found: C, 38.19; H, 8.12. The structure was confirmed by X-ray crystallography (vide infra).

The reaction of tetrathiasilolane **7** with triphenylphosphine at room temperature for 6 h gave silanethione **4** quantitatively. However, this method for the synthesis of **4** is not recommended because repeated recrystallization is needed to remove the less volatile byproduct, triphenylphosphine sulfide.

3. Synthesis of [1,1,4,4-Tetrakis(trimethylsilyl)butane-1,1-diyl]-silaneselone (5). In a Schlenk flask (30 mL) equipped with a magnetic stir bar, silylene **3** (413 mg, 1.11 mmol) and elemental selenium (97.5 mg, 1.23 mmol) were placed, and then dry hexane (10 mL) was transferred into the mixture. After the mixture was stirred at room temperature for 2 min, the color of the mixture turned from yellow to greenish-yellow. Removal of excess selenium by decantation and solvent in vacuo from the reaction mixture gave pure silaneselone **5** (463 mg, 1.02 mmol, 92% yield) as greenish-yellow crystals. **5**: mp 91−92 °C; ^{1}H NMR (C_6D_6, δ) 0.31 (s, 36H), 1.85 (s, 4H); ^{13}C NMR (C_6D_6, δ) 2.2, 32.4, 32.5; ^{29}Si NMR (C_6D_6, δ) −0.2 (Me$_3$Si), 227.7 (Si═Se); MS (EI, 70 eV) m/z (%) 452 (10.6, M$^+$), 437 (24.7), 379 (4.9), 73 (100); UV−vis (hexane) λ_{max}/nm (ϵ) 293 (2700), 383 (39); HRMS calcd for $C_{16}H_{40}SeSi_5$, 452.1142; found, 452.1164.

4. Synthesis of [1,1,4,4-Tetrakis(trimethylsilyl)butane-1,1-diyl]-silanetellone (6). In a Schlenk flask (30 mL) equipped with a magnetic stir bar, silylene **3** (245 mg, 0.66 mmol) and elemental tellurium (88 mg, 0.68 mmol) were placed. Then dry hexane (10 mL) was transferred into the mixture. After the mixture was stirred at room temperature for 3 min, the color of the mixture turned from yellow to orange. Removal of excess tellurium by decantation and solvent in vacuo provided pure silanetellone **6** (326 mg, 0.651 mmol, 99% yield) as orange crystals. **6**: mp 123−124 °C; ^{1}H NMR (C_6D_6, δ) 0.33 (s, 36H), 1.91 (s, 4H); ^{13}C NMR (C_6D_6, δ) 2.5, 34.5, 39.8; ^{29}Si NMR (C_6D_6, δ) −2.6 (Me$_3$Si), 229.5 (Si═Te); MS (EI, 70 eV) m/z (%) 502 (10.3, M$^+$), 487 (6.3), 429 (6.2), 376 (4.2), 73 (100); UV−vis (hexane) λ_{max}/nm (ϵ) 346 (2100), 476 (140). Anal. Calcd for $C_{16}H_{40}Si_5Te$: C, 38.39; H, 8.06. Found: C, 38.45; H, 8.05.

5. Reaction of Silanethione 4 with Water. Degassed THF (2 mL) was introduced into silanethione **4** (154 mg, 0.38 mmol) in a Schlenk tube equipped with a magnetic stir bar. When water (0.2 mL) was added to the solution by syringe, the yellow color of the solution disappeared immediately. After stirring the mixture for 3 h, solvents were removed in vacuo. Hydroxysilanethiol **8** was obtained in 82% yield. **8**: colorless crystals; mp 98 °C; ^{1}H NMR (C_6D_6, δ) 0.21 (s, 1H, SH), 0.24 (s, 18H), 0.28 (s, 18H), 1.65 (s, 1H, OH), 1.82−1.89 (m, 4H); ^{13}C NMR (C_6D_6, δ) 3.9 (SiMe$_3$), 4.0 (SiMe$_3$), 14.7 (C), 32.2 (CH$_2$); ^{29}Si NMR (C_6D_6, δ) 2.4 (SiMe$_3$), 3.8 (SiMe$_3$), 32.2 (Si); MS (70 eV, EI) m/z (%) 407 (11, M$^+$ − 15), 391 (45), 375 (45), 73 (100). Anal. Calcd for $C_{16}H_{42}OSSi_5$: C, 45.43; H, 10.01. Found: C, 45.80; H, 9.82.

6. Reaction of Silanethione 4 with Methanol. In a similar manner to the reaction of **4** with water, the reaction of **4** (55 mg, 0.14 mmol) with methanol (3 mL) in THF gave the corresponding methanol adduct **9** (59 mg, 0.14 mmol) in 99% yield. **9**: colorless crystals; mp 90 °C; ^{1}H NMR (C_6D_6, δ) 0.21 (s, 18H, Me$_3$Si), 0.28 (s, 18H, Me$_3$Si), 0.30 (s, 1H, SH), 1.83−1.96 (m, 4H, CH$_2$), 3.24 (s, 3H, OCH$_3$); ^{13}C NMR (C_6D_6, δ) 3.9 (Me$_3$Si), 4.4 (Me$_3$Si), 15.9 (C), 32.5 (CH$_2$), 51.0 (OCH$_3$); ^{29}Si NMR (C_6D_6, δ) 2.6 (Me$_3$Si), 3.5 (Me$_3$Si), 31.1 (Si); MS (EI, 70 eV) m/z (%) 422 (M$^+$, 74), 405 (M$^+$ − OH, 68), 389 (M$^+$ − SH, 50), 73 (Me$_3$Si$^+$, 100). Anal. Calcd for $C_{17}H_{44}OSSi_5$: C, 46.72; H, 10.15. Found: C, 46.91; H, 10.20.

7. Reaction of Silaneselone 5 with Water. In a similar manner to the reaction of **4** with water, the reaction of **5** (88 mg, 0.19 mmol) with water in THF gave the corresponding water adduct **10** (75 mg, 0.16 mmol) in 82% yield. **10**: colorless crystals; mp 89−90 °C; ^{1}H NMR (C_6D_6, δ) −1.58 (s, 1H, SeH), 0.24 (s, 18H, Me$_3$Si), 0.29 (s, 18H, Me$_3$Si), 1.81−1.95 (m, 4H, CH$_2$), 1.98 (s, 1H, OH); ^{13}C NMR (C_6D_6, δ) 4.0 (Me$_3$Si), 4.2 (Me$_3$Si), 15.6 (C), 32.5(CH$_2$); ^{29}Si NMR (C_6D_6, δ) 2.5 (Me$_3$Si), 4.0 (Me$_3$Si), 29.4 (Si); MS (EI, 70 eV) m/z (%) 453 (M$^+$ − OH, 1.4), 389 (M$^+$ − SeH, 15), 373 [M$^+$ − SeH(OH), 84], 73 (Me$_3$Si$^+$, 100). Anal. Calcd for $C_{16}H_{42}OSeSi_5$: C, 40.90; H, 9.01. Found: C, 40.77; H, 8.76.

8. Reaction of Silaneselone 5 with Methanol. In a similar manner to the reaction of **4** with water, the reaction of **5** (83 mg, 0.18 mmol) with methanol (5 mL) in THF gave the corresponding methanol adduct **11** (85 mg, 0.18 mmol) in 96% yield. **11**: colorless crystals; mp 106−107 °C; ^{1}H NMR (C_6D_6, δ) −1.56 (s, 1H, SeH), 0.22 (s, 18H, Me$_3$Si), 0.30 (s, 18H, Me$_3$Si), 1.88−1.91 (m, 4H, CH$_2$), 3.21 (s, 3H, OMe); ^{13}C NMR (C_6D_6, δ) 4.0 (Me$_3$Si), 4.5 (Me$_3$Si), 16.8 (C), 32.7 (CH$_2$), 52.0 (OCH$_3$); ^{29}Si NMR (C_6D_6, δ) 2.7 (Me$_3$Si), 3.6 (Me$_3$Si), 29.9 (Si); MS (EI, 70 eV) m/z (%) 453 (M$^+$ − MeOH, 13), 403 (M$^+$ − SeH, 100), 73 (Me$_3$Si$^+$, 16). Anal. Calcd for $C_{17}H_{44}OSeSi_5$: C, 42.19; H, 9.16. Found: C, 42.10; H, 9.00.

9. Reaction of Silanetellone 6 with Methanol. In a similar manner to the reaction of **4** with water, the reaction of **6** (49 mg, 0.097 mmol) with methanol (5 mL) in THF gave the corresponding methanol adduct **12** (42 mg, 0.079 mmol) in 81% yield. **12**: colorless crystals; mp 97−

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101 °C (decomp); ^{1}H NMR (C_6D_6, δ) −6.20 (s, 1H, TeH), 0.22 (s, 18H, Me_3Si), 0.30 (s, 18H, Me_3Si), 1.84−1.98 (m, 4H, CH_2), 3.16 (s, 3H, OCH_3); ^{13}C NMR (C_6D_6, δ) 4.1 (Me_3Si), 4.7 (Me_3Si), 18.1 (C), 33.2 (CH_2), 54.5 (OCH_3); ^{29}Si NMR (C_6D_6, δ) 2.5 (Me_3Si), 3.8 (Me_3Si), 21.1 (Si); MS (EI, 70 eV) *m/z* (%) 532 (M^+, 6.4), 403 ($M^+ -$ TeH, 81), 389 ($M^+ -$ TeMeH, 44), 73 (Me_3Si^+, 100); HRMS (ESI negative mode) calcd for $C_{17}H_{43}OSi_5{}^{130}Te^-$ $[M - H]^-$, 533.1228; found, 533.1224.

10. Reaction of Silaneselone 5 with Isoprene. After a mixture of silaneselone **5** (98 mg, 0.22 mmol), isoprene (579 mg, 8.50 mmol), and degassed toluene (3 mL) in a sealed glass tube was heated at 100 °C for 1 week, the volatile materials were pumped out. Isoprene adduct **13** (46 mg, 0.089 mmol) was purified using HPLC (ODS column; eluent, methanol/THF = 7:3) in 41% yield. **13**: colorless crystals; mp 114 °C; ^{1}H NMR (C_6D_6, δ) 0.23 (s, 18H, $SiMe_3$), 0.33 (s, 18H, $SiMe_3$), 1.71 (d, $J = 1.2$ Hz, 3H, CH_3), 1.82−1.95 (m, 4H, CH_2), 1.97 (d, $J = 7.2$ Hz, 2H, CH_2), 2.78 (s, 2H, CH_2), 5.45 (dt, $J = 1.2$ Hz, 7.2 Hz, 1H); ^{13}C NMR (C_6D_6, δ) 4.8 (Me_3Si), 4.9 (Me_3Si), 13.3 (C), 21.5 (CH_2), 21.8 (CH_2), 23.4 (CH_3), 33.9 (CH_2), 122.3 ($CH{=}$), 136.3 ($C{=}$); ^{29}Si NMR (C_6D_6, δ) 3.6, 4.5, 40.5; MS (EI, 70 eV) *m/z* (%) 520 (M^+, 18), 452 ($M^+ - C_5H_8$), 437 (86), 373 (26). Anal. Calcd for $C_{21}H_{48}SeSi_5$: C, 48.51; H, 9.30. Found: C, 48.53; H, 9.15.

11. Reaction of Silanetellone 6 with Isoprene. A mixture of silanetellone **6** (126 mg, 0.252 mmol) and isoprene (617 mg, 9.01 mmol) in toluene (2 mL) was heated at 100 °C for 4 days to give adduct **14** (94 mg, 0.17 mmol) in 66% yield. **14**: colorless crystals; mp 105 °C (decomp); ^{1}H NMR (C_6D_6, δ) 0.24 (s, 18H, $SiMe_3$), 0.32 (s, 18H, $SiMe_3$), 1.73 (s, 3H, CH_3), 1.87 (brs, 4H, CH_2), 2.13 (d, $J = 8.0$ Hz, 2H, CH_2), 2.78 (s, 2H, CH_2), 5.31 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (C_6D_6, δ) 1.1 (CH_2), 4.8 (Me_3Si), 14.1 (C), 22.8 (CH_3), 23.4 (CH_2), 34.6 (CH_2), 121.7 ($CH{=}$), 136.4 ($C{=}$); ^{29}Si NMR (C_6D_6, δ) 3.8, 4.9, 42.2; MS (EI, 70 eV) *m/z* (%) 570 (M^+, 17), 502 ($M^+ - C_5H_8$, 100), 373 (38), 300 (38). Anal. Calcd for $C_{21}H_{48}Si_5Te$: C, 44.36; H, 8.51. Found: C, 43.77; H, 8.32.

12. X-ray Crystallographic Analysis. Single crystals of **4**−**6** suitable for X-ray diffraction study were obtained by recrystallization from hexane at −20 °C. Tetrathiasilolane **7** was recrystallized from ethanol at room temperature. X-ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXL-97 program.[24]

12.a. Crystal Data of Silanethione 4. $C_{16}H_{40}Si_5S$, $M = 404.98$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 10.317(2)$ Å, $b = 14.994(3)$ Å, $c = 15.823(3)$ Å, $V = 2447.8(8)$ Å^3, $T = 150$ K, $Z = 4$, μ(Mo Kα) = 0.374 mm^{-1}, 26 121 reflections measured, 5567 unique ($R_{int} = 0.032$). The final $R1$ and $wR2$ were 0.0289 ($I > 2\sigma(I)$) and 0.0802 (for all data), respectively.

12.b. Crystal Data of Silaneselone 5. $C_{16}H_{40}Si_5Se$, $M = 451.88$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.416(3)$ Å, $b = 15.906(4)$ Å, $c = 14.489(4)$ Å, $\beta = 108.730(3)°$, $V = 2491(1)$ Å^3, $T = 150$ K, $Z = 4$, μ(Mo Kα) = 1.745 mm^{-1}, 27 165 reflections measured, 5687 unique ($R_{int} = 0.037$). The final $R1$ and $wR2$ were 0.0323 ($I > 2\sigma(I)$) and 0.0769 (for all data), respectively.

12.c. Crystal Data of Silanetellone 6. $C_{16}H_{40}Si_5Te$, $M = 500.52$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.528(3)$ Å, $b = 15.578(4)$ Å, $c = 16.128(5)$ Å, $\beta = 106.003(4)°$, $V = 2542.6(13)$ Å^3, $T = 150$ K, $Z = 4$, μ(Mo Kα) = 1.403 mm^{-1}, 53 749 reflections measured, 5783 unique ($R_{int} = 0.029$). The final $R1$ and $wR2$ were 0.0263 ($I > 2\sigma(I)$) and 0.0736 (for all data), respectively.

12.d. Crystal Data of Tetrathiasilolane 7. $C_{16}H_{40}Si_5S_4$, $M = 501.16$, monoclinic, space group $P2_1/n$ (no. 14), $a = 16.320(3)$ Å, $b = 16.719(3)$ Å, $c = 20.453(4)$ Å, $\beta = 104.144(3)°$, $V = 5411.5(18)$ Å^3, $T = 150$ K, $Z = 8$, μ(Mo Kα) = 0.574 mm^{-1}, 50 607 reflections measured, 12 359 unique ($R_{int} = 0.038$). The final $R1$ and $wR2$ were 0.0363 ($I > 2\sigma(I)$) and 0.0738 (for all data), respectively. In the single crystal of **7** used for X-ray analysis, two crystallographically independent molecules A and B existed in an asymmetric unit. The SiS_4 ring of both molecules A and B adopted a half-chair conformation as observed for Tbt(Mes)-SiS_4 (Tbt = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$, Mes = 2,4,6-trimethylphenyl).[25] The molecular structure of **7** is given in the Supporting Information.

13. Theoretical Calculations. All DFT calculations were carried out using the Gaussian 98 program.[14] Geometries of **4′**−**6′** were optimized using Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP)[27] and B1 basis set (6-31G+(d) for C and H atoms and Lanl2dzpd[15] for Si, S, Se, and Te atoms). The ^{29}Si chemical shifts were calculated using the GIAO (gauge independent atomic orbitals)[28]-B3LYP method using the 6-311+G(2df,p) basis set. The absorption band energies and oscillator strengths of **4′**−**6′** were calculated using the time-dependent hybrid DFT method (TDDFT)[22] with the B1 basis set.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan [Grant-in-Aids for Scientific Research on Priority Areas (No. 14078203, "Reaction Control of Dynamic Complexes") and Specially Promoted Research (No. 17002005)].

Supporting Information Available: Details of theoretical calculations of **4′**, **5′**, and **6′**, X-ray analysis of compound **7**, complete ref 14, and the X-ray crystallographic data of compounds **4**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065774F

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