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Matrix-Isolation and Electronic Structure of Vinyl-Substituted Silylenes and Their Complexes with Bases [1]

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ABSTRACT

*Vinyl-substituted silylenes, 2,5-bis(methylene)-1-silacyclopentane-1,1-diyl (**1**) and 2-methylene-1-silacyclopentane-1,1-diyl (**2**), generated photochemically from the corresponding trisilanes in 3-methylpentane (3-MP) at 77 K, showed broad bands at 505 and 475 nm, respectively, which were assigned to the n(Si)-3p(Si) transition. The origin of the red shift in the n(Si)-3p(Si) transition is ascribed to the significant lowering of the 3p(Si) orbital level caused by the vinyl substitution on the silylene; the relatively high-lying 3p(Si) orbital can interact more effectively with the antibonding π^* orbital than with the bonding π orbital of the vinyl group. The absorption spectra for **1** and **2** in the presence of several bases in 3-MP glass matrix shifted significantly to blue due to the formation of the corresponding base complexes. Analysis of the spectral change of the silylenes upon complexation with bases was very constructive for the understanding of the structural characteristics of substituted silylenes.*

INTRODUCTION

Generation, structure, and reactions of divalent silicon species, silylenes, have been extensively studied as important reactive intermediates both experimentally and theoretically [2]. The electronic structure of silylenes has been discussed more in-depth since the first matrix isolation of dimethylsilylene by Drahnak et al. in 1979 [3a]; they observed that dimethylsilylene produced by the irradiation of dodecamethylcyclohexasilane in an argon matrix at 10 K or in a 3-methylpentane (3-MP) glass matrix at 77 K showed a characteristic absorption maximum at ca. 450 nm [3a]. Although there was a controversy concerning the absorption spectra of dimethylsilylene [4], recent extensive spectroscopic studies by using matrix isolation [3,5], laser flash photolysis [6], and theoretical calculations [7,8] have confirmed that the 450 nm absorption is ascribed to the *n*(Si)-3*p*(Si) transition of singlet dimethylsilylene. Intriguing experimental targets in silylene chemistry involve (1) generation and characterization of silylenes having a triplet ground state and (2) synthesis and isolation of stable singlet silylenes as pure substances. Systematic studies of the electronic and steric effects of substituents on the structure and reactivity of silylene would be required in order to achieve these goals. There have been very limited studies of the substituent effects reported [9] because of difficulty in the generation and matrix isolation of desired silylenes.

We report herein the isolation of vinyl-substituted silylenes, **1** and **2**, in 3-MP and 2-methyltetrahydrofuran (2-MeTHF) matrices at 77 K [10]. In disagreement with a recent theoretical prediction [7], the n(Si)-3p(Si) absorption maxima for the vinylsilylenes in 3-MP is shifted to a significantly longer wavelength than that for dimethylsilylene. The origin of the red shift is discussed in terms of the substantial conjugation between the vacant vinyl π^* and 3*p*(Si) orbitals.

A number of experimental [11] and theoretical [12] studies have anticipated formation of silylene-

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Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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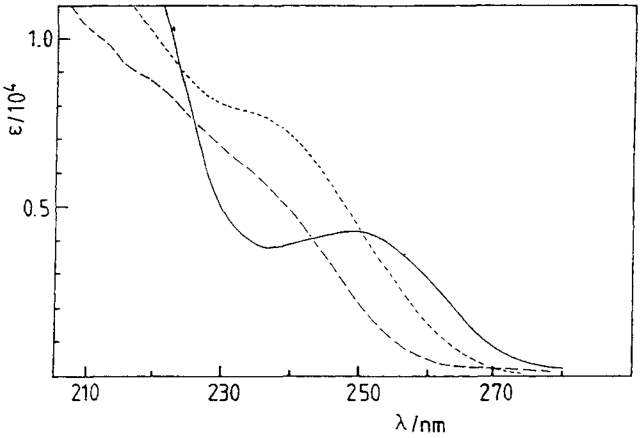
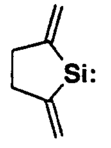


FIGURE 1. UV spectra of trisilanes **3** (———), **4** (– – –), and **5** (-----) in hexane.

base complexes during reactions of silylenes with oxygen-, sulfur-, nitrogen-, and phosphorus-containing compounds. Recent UV-vis spectroscopic studies [13,14] of the formation of acid-base complexes of silylenes showed that the absorption maximum of dimethylsilylene was shifted to 350 nm by complexation with 2-MeTHF [13a]. In this article, the absorption spectra for **1** and **2** in the presence of several bases in 3-MP glass matrices are reported and the structural features for the produced silylene-base complexes are discussed in detail. Analysis of the spectral change of the silylenes by complexation with bases was very constructive for the understanding of the structural characteristics of substituted silylenes.



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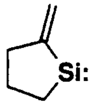

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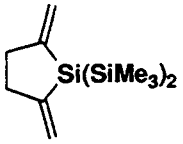
RESULTS AND DISCUSSION

Generation of Silylenes by Photolysis of Vinyl-Substituted Trisilanes and Their Absorption Spectra

As photochemical precursors for vinyl-substituted silylenes, 2,5-bis(methylene)-1,1-bis(trimethylsilyl)-1-silacyclopentane (**3**), 2-methylene-1,1-bis(trimethylsilyl)-1-silacyclopentane (**4**), 2,2-divinylheptamethyltrisilane (**5**), 1,1-dimethyl-4,4-bis(trimethylsilyl)-1,4-disila-2,5-cyclohexadiene (**6**), and 1,1-dimethyl-4,4-bis(phenyldimethylsilyl)-1,4-disila-2,5-cyclohexadiene (**7**) were investigated. Figure 1 shows the UV spectra of **3**–**5** in hexane. The absorption maximum for **3** (253 nm) appeared at a significantly longer wavelength than that for **4** (240 nm), being indicative of the effective π(vinyl)-σ(SiSi)-π(vinyl) through conjugation. On the other hand, a simple 2,2-divinyltrisilane **5** showed the absorption maximum at ca. 10 nm shorter wavelength than that for **3**, suggestive of the restrictive geometrical requirement for the through π-σ-π conjugation.



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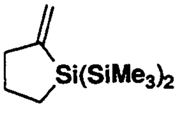

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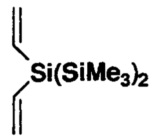

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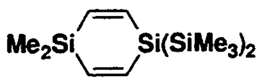

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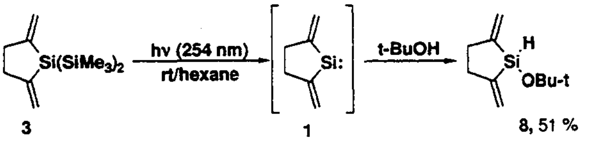
A purple color was induced by irradiation of **3** in a 3-MP matrix at 77 K with a 125 W low-pressure Hg arc lamp. The absorption spectrum showed a broad band at 505 nm and a relatively intense band at 290 nm (Table 1). The purple species is assigned as the corresponding cyclic divinylsilylene **1** on the basis of the following observations. (1) Upon annealing of the matrix, the two bands disappeared simultaneously, whereas no band due to the disilene which was expected to be formed by dimerization of **1** was observed; **1** may react favorably with the double bonds of the precursor **3**. (2) Similar photolysis of **3** in a 3-MP/2-MeTHF (95:5) matrix at 77 K afforded two bands at 290 and 505 nm; upon annealing of the matrix for several seconds, the two bands disappeared and a new band emerged at 375 nm. The 375 nm band was also observed when **3** was irradiated in a pure 2-MeTHF matrix, assignable to the complex of **1** with 2-MeTHF (vide infra). (3) Repeated irradiation of **3** in the presence of excess *t*-butyl alcohol in a 3-MP matrix at 77 K followed by warming to melt gave a *t*-butyl alcohol adduct to **1** (**8**), as shown by GC–MS analysis of the reaction mixture. (4) Irradiation of a mixture of **3** and *t*-butyl alcohol in hexane at ambient temperature afforded **8** as a sole volatile product in the isolated yield of 51%.

 (1)

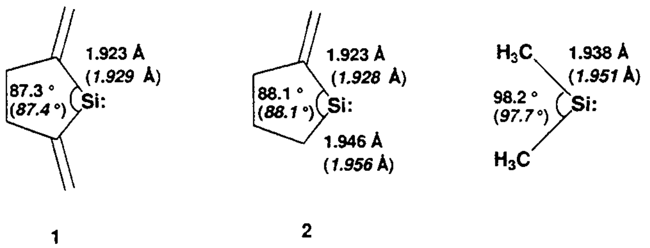
Similar irradiation of 2-methylene-1,1-bis(trimethylsilyl)-1-silacyclopentane (**4**) gave the corresponding cyclic vinylsilylene **2**, whose absorption maximum appeared at 475 nm in a 3-MP matrix and shifted to 345 nm in a 2-MeTHF matrix at 77 K.

TABLE 1 Experimental and Theoretical Transition Energies of **1**, **2**, and Dimethylsilylene

	Experimental[a]		*Calcd $\tilde{\nu}_{max}/cm^{-1}$*		
Compound	*λ_{max}/nm*[b]	*$\tilde{\nu}_{max}/cm^{-1}$*	*CNDO/S*[c, d]	*CIS/D95//D95*[c]	*Assignment*
1	505(1)	19,800	19,800(3 × 10^{-4})	23,900(0.0451)	n(Si) → $3p$(Si)
	290(7.4)	34,500	31,700(0.132)	44,300(0.515)	π → $3p$(Si)
2	475	21,000	19,700(4 × 10^{-5})	23,200(0.0451)	n(Si) → $3p$(Si)
			34,100(0.067)	47,900(0.283)	π → $3p$(Si)
Me_2Si:	453[e]	22,000	18,000(5.0 × 10^{-5})	21,700(0.0475)	n(Si) → $3p$(Si)

[a] In 3-methylpentane.
[b] Relative absorption coefficients are shown in parentheses.
[c] Oscillator strengths are shown in parentheses.
[d] Geometry optimized with the 3-21G basis sets was used for the calculations.
[e] Ref. [3a].

Photolysis of the related 2,2-divinyltrisilanes, **5**, **6**, and **7**, in 3-MP at 77 K gave no absorption bands due to the corresponding silylenes. Instead, photolysis of **5** in hexane at room temperature gave mainly products via 1,3-silyl migration (see the Experimental Section). These results indicate that the photoreaction pathways of 2,2-divinyltrisilanes vary severely, depending on the structures; the geometrical and electronic conditions for the selective generation of silylenes by the photolysis of 2,2-divinyltrisilanes have not been fully understood until now [15].



1 **2**

FIGURE 2. Structural parameters for **1**, **2**, and dimethylsilylene optimized by *ab initio* MO calculations with D95 and 3-21G (in parentheses) basis sets.

Vinyl-Substituent Effects on the Absorption Spectra of Silylene

The n(Si)-$3p$(Si) transition bands for **1** and **2**, which were found at 505 and 475 nm, respectively, red-shifted significantly relative to that for dimethylsilylene, in disagreement with a recent *ab initio* theoretical prediction by Apeloig and Karni [7]; they have predicted that a vinyl group serves as a π donor substituent on silylene to cause a substantial blue shift of the n(Si)-$3p$(Si) transition. Although the theory also predicted a red shift of the n(Si)-$3p$(Si) transition of silylenes when the apex angle increases, the apex angles for **1** and **2** estimated by the *ab initio* calculations were even smaller than the angle for dimethylsilylene [16]; geometrical parameters for **1**, **2**, and dimethylsilylene fully optimized with the D95, and 3-21G basis sets are shown in Figure 2.

The transition energies for **1**, **2**, and dimethylsilylene, calculated by using the semiempirical CNDO/S [18] as well as *ab initio* CIS/D95//D95 [19] calculations, are shown in Table 1 together with the experimental values. A fairly good agreement was observed between the calculated and experimental values for dimethylsilylene, suggesting that a weak band at the longest wavelength is assigned to the n(Si)-$3p$(Si) transition. The calculations allow us also to assign the relatively intense band at 290 nm for **1** to the π-$3p$(Si) transition. Disappearance of the 290 nm band in the silylene-2-MeTHF complex may be compatible with the assignment, because the lift of the vacant $3p$(Si) orbital level by the partial bonding with the oxygen base should cause blue shifts of both the n(Si)-$3p$(Si) and π-$3p$(Si) transitions (vide infra). Neither CNDO/S nor CIS/D95 calculations reproduced the red shift of the n(Si)-$3p$(Si) transition by the introduction of vinyl substituents. A more sophisticated level of calculations would be needed to reproduce the vinyl-substituent effects on the transition energy of silylene; very recently, it has been announced that the red shift of the absorption band of silylene by ethynyl- and vinyl-group substitution has been reproduced by using the UMP4STDQ/6-31G* method with spin projection annihilation [20]. The origin of the red shift is ascribed to the significant lowering of the $3p$(Si) orbital level caused by the vinyl substitution on silylene; a relatively high-lying $3p$(Si) orbital can interact more effectively with the antibonding π^* orbital than with the bonding π orbital of vinyl groups.

Lewis Base Adducts to Vinylsilylenes

According to the procedure of Gillette et al. [13a], the absorption spectra of various base complexes of **1** and **2** were observed in a 3-MP glass matrix at 77 K. Thus, silylene precursors **3** and **4** were dis-

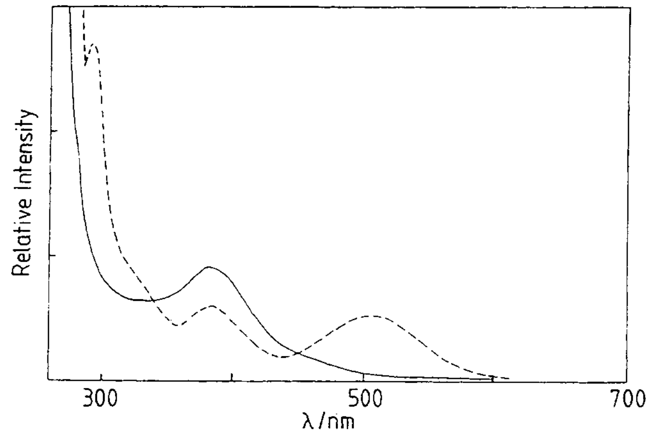


FIGURE 3. UV spectra observed during photolysis of **3** in 3-MP/Et_2O (95:5) matrix: (a) after 15 minutes of irradiation at 77 K (– – –); (b) after annealing of the matrix (———).

solved in a mixture of 95:5 3-MP/base (base = 2-MeTHF, Et_2O, Et_3N, and Bu_2S), degassed, and frozen at 77 K. Irradiation of the resulting glass with 254 nm light produced a colored matrix, the electronic spectrum of which corresponded to that of the free silylene. As the matrix was warmed, the band for the silylene diminished and a new band grew in at a shorter wavelength, which we assigned to the silylene-base complex. The new band disappeared upon further warming, whereas bands due to the disilene were never observed in our system. The UV spectra for the complex between **1** and diethyl ether are shown in Figure 3, as a typical example.

The absorption maxima of these complexes varied little over the series of the bases employed (Table 2). A similar trend was also observed for various base complexes of mesityl-substituted silylenes by Gillette et al. [13a]. However, the average change in the transition energies upon complexation with bases from that in free silylene ($\Delta(\tilde{\nu})$) depended significantly on the structure of the silylene. Thus, the $\Delta\tilde{\nu}$ value decreased with an increase in the number of vinyl substituents. It is interesting to note that the vinylsilylenes having longer wavelength absorption maxima showed a smaller blue shift in the observed absorption maximum.

TABLE 2 Absorption Maxima for Silylene Complexes with Several Bases in 3-MP

	λ_{max}/nm			$\Delta\tilde{\nu}^a$/cm^{-1}		
Base	***1***	***2***	*Me_2Si:*	***1***	***2***	*Me_2Si:*
	505	475	450^b	—	—	—
Et_3N	389	352	287^b	5910	7360	12,620
2-MeTHF	375	345	294^b	6870	7940	11,790
Et_2O	381	347	299^b	6450	7770	11,220
n-Bu_2S	353	342	309^b	8530	8190	10,140
Average^c				6940	7820	11,600

$^a\Delta\tilde{\nu} = \tilde{\nu}$ (complex) − $\tilde{\nu}$ (free silylene).
^{b}Data were taken from Ref. [13b].
^{c}Averaged $\Delta\tilde{\nu}$ for all the base complexes observed here.

$$\Delta\tilde{\nu}(\mathbf{1}) < \Delta\tilde{\nu}(\mathbf{2}) < \Delta\tilde{\nu}(Me_2Si:) \qquad (2)$$

In order to elucidate the origin of the blue shift of the $n(Si) \rightarrow 3p(Si)$ transition of silylenes caused by complexation with bases, it may be useful first to discuss the structure of silylene-base complexes. Theoretical calculations for the insertion reaction of silylene to an O–H bond have revealed the intermediate formation of a silylene-water complex preceding the insertion reaction [12]. Interestingly, the interaction complex between SiH_2 and H_2O has the C_1 structure as shown, with an oxygen lone-pair orbital directed along the empty 3*p* orbital on silicon. The *ab initio* HF/6-31G* calculations by our hands showed also that, even if starting from a more symmetric C_s structure, the final geometry reached the same C_1 structure. The silicon lone-pair orbital is nearly orthogonal to the second lone-pair orbital of oxygen at the optimized geometry. The H–O–H plane makes an angle of about 50° with the plane formed by Si–O and the H–Si–H bisector. The calculated stabilization energy by complexation was reported to be 13 kcal/mol [12b]. The long Si–O bond (212.9 pm) for the calculated structure of the intermediate complex, which may be caused by the lone-pair repulsion present in this geometry, suggests that the complex should not be described as a silaylide but as a weak donor-acceptor complex.

Rotational Conformations of the Complex of H_2Si: with H_2O

Transition energies and oscillator strengths for silylene and its water complex calculated at the CIS/6-31G*//6-31G* level are shown in Table 3. Whereas the calculated maximum for silylene (485 nm) is not quite in agreement with the experimental value (480–650 nm) [21], the significant blue shift (485 → 295 nm) and increase of the oscillator strength (0.046 → 0.10) by complexation with water is reproduced well. By complexation, both the HOMO and the LUMO are shifted to higher ener-

TABLE 3 Transition Energies and Oscillator Strengths for Silylene and Its Water Complex Calculated with the CIS/6-31G*//6-31G* Method

Compound	λ_{max}/nm	$\tilde{\nu}_{max}$/cm^{-1}	f^a	*Assignment*
SiH_2	485	20,600	0.046	n(Si) → 3p(Si)
	225	44,400	0.000	
	159	62,900	0.480	
SiH_2–H_2O	295	33,900	0.100	n(Si) → σ^*(SiO)
	171	58,500	0.166	
	163	61,300	0.283	

[a]Oscillator strength.

gies, while the extent was found to be much larger for the LUMO than for the HOMO.

The MO study suggests that the electronic structure of a free silylene is only weakly perturbed by complexation with a base. In this situation, energy levels of n(Si) (E_n) and 3p(Si) (E_p) orbitals for a silylene and the energy level (E_b) of the orbital occupied by lone-pair electrons of the base (n(base)) will be modified, as shown in Figure 4. Thus, a bonding interaction between the 3p(Si) orbital (LUMO) and the n(base) orbital causes the lift of the LUMO whose extent (ΔE_p) would be represented by Equation 3 according to the perturbation theory; H'_{bp} is the perturbation term represented by Equation 4, where Ψ_b and Ψ_p are the wave functions for the pertinent orbitals. Furthermore, the anionic character of the n(Si) orbital may increase to cause the lift of the energy level.

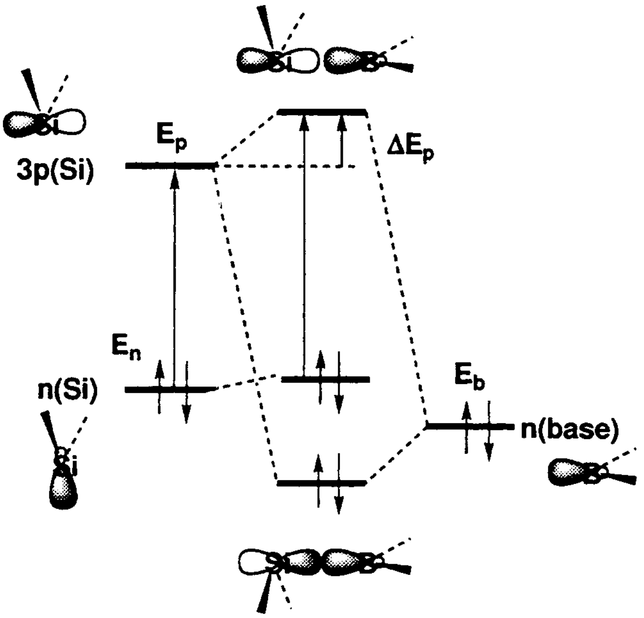


FIGURE 4. Schematic MO diagram for the interaction between a silylene and a base.

$$\Delta E_p = \frac{|H'_{bp}|^2}{E_p - E_b} \qquad (3)$$

$$H'_{bp} = \int \Psi_b H' \Psi_p \, d\tau \qquad (4)$$

If we assume here that raising the 3p(Si) level is of primary importance for the blue shift due to complexation, as suggested by the *ab initio* MO study, ΔE_p is expected to be parallel with the blue shift ($\Delta\nu$). The following effects on the electronic transition of the base complexes will be brought about on the basis of the second-order perturbation theory. Thus, a base having a lower ionization potential will give a larger ΔE_p, and therefore a larger blue shift, because of the smaller ($E_p - E_b$) value. Therefore, the blue shift caused by complexation with triethylamine (IP_1 = 7.50 eV) [19] should be larger than that with diethyl ether (IP_1 = 9.53 eV) [19]. However, the $\Delta\tilde{\nu}$ values for triethylamine complexes were similar or even smaller than those for ether complexes. This tendency may be derived from the delicate balance between the ($E_p - E_b$) term and the $|H'_{bp}|^2$ term in Equation 3, since the latter may be smaller for the amine complexes due to the larger steric hindrance.

On the basis of the perturbation theory, vinyl-substituent effects on the absorption maximum for silylene-base complexes may be explained as follows: The n(Si) → 3p(Si) transition energies of a silylene are decreased by vinyl-substitution because of lowering the 3p(Si) level by the interaction with the π^* (vinyl) orbital, as discussed in the previous section. Thus, the energy difference ($E_p - E_b$) should increase according to Equation 5. It should be noted, however, that the maximum difference of the transition energies among **1**, **2**, and Me_2Si: amounts merely to 2300 cm^{-1}, which is far smaller than the transition energy of 22,300 cm^{-1} for Me_2Si:. Since the ($E_p - E_b$) values are expected to be much larger than the transition energies, the ($E_p - E_b$) values may be taken to have no significant differences among **1**, **2**, and Me_2Si:

$$E_p(\mathbf{1}) < E_p(\mathbf{2}) < E_p(Me_2Si{:}) \qquad (5)$$

On the other hand, the contribution of the 3p(Si) atomic orbital in the LUMO of silylene should decrease by delocalization to the vinyl-carbon $p\pi$ orbitals due to 3p(Si)-π^* (vinyl) interaction. Therefore, the value of the $|H'_{bp}|^2$ term should increase in the following order (Equation 6).

$$|H'_{bp}(\mathbf{1})|^2 < |H'_{bp}(\mathbf{2})|^2 < |H'_{bp}(Me_2Si{:})|^2 \qquad (6)$$

The observed order of $\Delta\tilde{\nu}$ (Equation 2) is in accord with the idea that the H'_{bp} term is a predominant factor to determine the relative order of the ΔE_p.

There are many factors influencing the electronic structures of silylene-base complexes. The following are important among them: (1) nucleophilicity of the bases; (2) steric hindrance on the complexes (a distance between Si and the central atom of base); (3) conformational changes between free silylenes and complexed silylenes; (4) intramolecular stabilization of the silylene by π- and n-donor substituents, which should cause the lift of the silylene LUMO to render the electrophilicity smaller; and (5) conjugative interactions between the silylene LUMO and π and/or π^* orbitals of the substituents, which reduce the coefficient of the 3p(Si) atomic orbital in the delocalized LUMO and therefore the electrophilicity of the central silicon. Since factors (2) and (3) can be leveled in a series of **1**, **2**, and Me_2Si:, the electrophilicity of silylene serves as the primary factor to influence the electronic structure of the silylene-base complexes. Gillette et al. [13b] have previously observed the significant substituent effects on the electronic structure of various mesityl-substituted silylene-base complexes; the smallest blue shift upon complexation has been found for mesityl(2,6-diisopropylphenoxy)silylene, which is stabilized intramolecularly by the lone-pair electrons of the oxy substituents, reducing the electrophilicity of the silylene. However, steric factors should play important roles in the series of silylene-base complexes to make it difficult to abstract the essential factors in the substituent effects.

EXPERIMENTAL

General Methods

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker AC300P NMR spectrometer. Mass spectra were recorded on a JEOL JMS D-300 mass spectrometer. Absorption spectra were obtained on a Shimadzu UV-2000 spectrometer. GLC analysis was conducted by using Shimadzu 8A and 15A gas chromatographs.

Materials

2,2-Dichloro-1,1,1,3,3,3-hexamethyltrisilane [22a] was prepared by dephenyl-chlorination of 2,2-diphenylhexamethyltrisilane [22b] with HCl and a catalytic amount of $AlCl_3$ in benzene. 2,5-Dibromohexadiene was prepared according to the reported method [23]. Tetrahydrofuran and diethyl ether were dried over sodium benzophenone ketyl and distilled prior to use. 3-Methylpentane and 2-methyltetrahydrofuran were dried over $LiAlH_4$ and distilled prior to use.

2,5-Dimethylene-1,1-bis(trimethylsilyl)-1-silacyclopentane (**3**)

To an ether (40 mL) suspension of lithium powder (0.361 g, 52.0 mmol) was added 2,5-dibromo-1,5-hexadiene (2.69 g, 11.2 mmol), and then the mixture was stirred for 5 hours at 0°C. After filtration, the filtrate was added to an ether (100 mL) solution of 2,2-dichlorohexamethyltrisilane (2.80 g, 11.4 mmol). Stirring overnight at room temperature and then usual workup gave the title compound in 63% yield.

White crystals: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 18H), 2.36 (s, 4H), 5.19 (d, J = 2.7 Hz, 2H), 5.71 (d, J = 2.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 153.9, 121.0, 40.7, −1.3; ^{29}Si NMR ($CDCl_3$) δ −15.5, −52.2; MS m/z (rel intensity) 254 (M^+, 13), 239 (44), 73 (100); UV (hexane) λ_{max}/nm (ϵ) 249 (4230); HRMS m/z: found, 254.1346; calcd for $C_{12}H_{26}Si_3$, 254.1344.

2-Methylene-1,1-bis(trimethylsilyl)-1-silacyclopentane (**4**)

To an ether (40 mL) suspension of lithium powder (127 mg, 18.3 mmol) was added 2-bromo-5-chloro-1-pentene [24] (657 mg, 3.58 mmol) at 0°C. After the mixture had been stirred for 2 hours at room temperature, 2,2-dichlorohexamethyltrisilane (885 mg, 3.61 mmol) was added to this solution. Stirring for 2 hours and then usual workup gave the title compound in 44% yield.

A colorless oil: bp 115°C/15 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18), 0.95 (t, J = 7.0 Hz, 2), 1.68 (tt, J = 6.7 and 7.0 Hz, 2), 2.21 (tt, J = 6.7 and 2.0 Hz, 2), 5.17 (q, J = 2.0 Hz, 1), 5.70 (q, J = 2.0 Hz, 1); ^{13}C NMR ($CDCl_3$) δ −1.0, 9.5, 28.1, 41.2, 120.1, 153.9; ^{29}Si NMR ($CDCl_3$) δ −15.9, −44.2; MS m/z (rel intensity) 242 (M^+, 23), 227 (16), 141 (62), 73 (100); HRMS m/z: found, 242.1341; calcd for $C_{11}H_{26}Si_3$, 242.1342.

2,2-Divinylhexamethyltrisilane (**5**)

To vinylmagnesium bromide in THF (60 mL), prepared by the reaction of magnesium turnings (2.51 g, 0.103 mol) with excess vinyl bromide, was added 2,2-dichlorohexamethyltrisilane (0.0425 mol). After the mixture had been stirred overnight, usual workup gave the title compound in the yield of 89%.

A colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 18), 5.70 (dd, J = 19.5 and 4.1 Hz, 2), 5.99 (dd, J = 14.3 and 4.1 Hz, 2), 6.16 (dd, J = 19.5 and 14.3 Hz, 2); ^{13}C NMR ($CDCl_3$) δ 133.9, 132.6, −0.9; ^{29}Si NMR (CDCl3) δ −16.2, −50.8; MS m/z (rel intensity) 228 (M^+, 4.3), 213 (31), 155 (37), 73 (100); UV (hexane) λ_{max}/nm (ϵ) 235 (9000); HRMS m/z: found, 228.1166; calcd for $C_{10}H_{24}Si_3$, 228.1186.

1,1-Dimethyl-4,4-bis(trimethylsilyl)-1,4-disila-2,5-cyclohexadiene (**6**)

To an ether (6 mL) solution of 4,4-dibutyl-1,1-dimethyl-1-sila-4-stanna-2,5-cyclohexadiene [25] (1.97

g, 5.72 mmol), *n*-butyllithium in hexane (1.58 N, 7.23 mL, 11.4 mmol) was added at −78°C and then warmed to 0°C to allow the formation of the precipitates of the corresponding dilithio compound. After the mixture had been cooled to −78°C, 2,2-dichlorohexamethyltrisilane (1.45 g, 5.91 mmol) in THF (30 mL) was added. Warming to room temperature and usual workup gave a mixture of **6** and tetrabutylstannane. Pure **6** was obtained by preparative GLC.

A colorless oil: ^{1}H NMR (CDCl$_3$) δ 0.08 (s, 6), 0.11 (s, 18), 6.86 (s, 4); ^{13}C NMR (CDCl$_3$) δ −1.05, −0.66, 145.72, 148.50; ^{29}Si NMR (CDCl$_3$) δ −62.05, −28.33, −16.31; MS *m/z* (rel intensity) 284 (M$^+$, 35), 269 (70), 211 (51), 73 (100); UV (hexane) λ_{max} (ϵ) 248.5 (13,400); HRMS *m/z*: found, 284.1268; calcd for $C_{12}H_{28}Si_4$, 284.1268.

1,1-Dimethyl-4,4-bis(dimethylphenylsilyl)-1,4-disila-2,5-cyclohexadiene (**7**)

The title compound was prepared in 37% yield by using 4,4-dibutyl-1,1-dimethyl-1-sila-4-stanna-2,5-cyclohexadiene (1.02 g, 2.97 mmol), *n*-butyllithium in hexane (1.55 N, 3.84 mL, 5.95 mmol), and dichlorobis[dimethyl(phenyl)silyl]silane (1.05 g, 2.86 mmol) with almost the same procedure as described above.

A colorless oil: bp 100–120°C/0.07 mmHg; ^{1}H NMR (CDCl$_3$) δ 0.03 (s, 6), 0.29 (s, 12), 6.89 (s, 4) 7.25–7.31 (m, 6), 7.35–7.40 (m, 4), ^{13}C NMR (CDCl$_3$) δ −2.92, −1.78, −0.87, 127.64, 128.52, 133.90, 139.00, 145.04, 149.32; ^{29}Si NMR (CDCl$_3$) δ −63.26, −27.97, −19.22; MS *m/z* (rel intensity) 408 (M$^+$, 19), 394 (17), 273 (39), 135 (100); UV (hexane) λ_{max} (ϵ) 253.8 (20,500); HRMS *m/z*: found, 408.1584; calcd for $C_{22}H_{32}Si_4$, 408.1581.

Photolysis at 77 K in 3-MP

A similar method to that described in an article by Gillette *et al.* [13a] was applied.

Preparative Photoreaction of **3** *in the Presence of t-BuOH*

A mixture of **3** (66.5 mg, 0.759 mmol), *t*-butyl alcohol (433 mg, 5.86 mmol), and hexane (2.5 mL) in a quartz tube (7 mmϕ) was irradiated under argon with a spiral low-pressure Hg arc lamp (125 W) for 1 hour. An insertion product of the corresponding silylene to the alcohol (**8**) was obtained in 51% yield, determined by GLC. Preparative GLC gave **8** in a yield of 9.2 mg (0.051 mmol). **8**: a colorless oil; ^{1}H NMR (CDCl$_3$) δ 1.30 (s, 9), 2.31–2.53 (m, 4), 4.95 (s, 1), 5.58 (s, 2), 5.80 (s, 2); ^{13}C NMR (CDCl$_3$) δ 151.2, 125.2, 73.7, 36.8, 31.6; ^{29}Si NMR (CDCl$_3$) δ −29.6; MS *m/z* (rel intensity) 182 (M$^+$, 3.1), 167 (13), 126 (100), 98 (71); HRMS *m/z*: found, 182.1124; calcd for $C_{10}H_{18}OSi$, 182.1127.

Preparative Photoreaction of **5** *in the Presence of t-BuOH*

A mixture of **5** (173.0 mg, 0.759 mmol), *t*-butyl alcohol (1.83 g, 24.8 mmol), and hexane (1 mL) in a quartz tube (7 mmϕ) was irradiated under argon with a spiral low-pressure Hg arc lamp (125 W) overnight. No silylene insertion product to *t*-butyl alcohol was detected by GLC. From the reaction mixture, the following products, formed via 1,3-silyl migration, were isolated by preparative GLC.

1 - *t*-Butoxy - 1-(2-trimethylsilylethyl) - 1-vinyltrimethyldisilane (14.6 mg, 0.0483 mmol, 6.4%): a colorless oil; ^{1}H NMR (CDCl$_3$) δ −0.04 (s, 9), 0.08 (s, 9), 0.39–0.46 (m, 2), 0.61–0.67 (m, 2), 5.70 (dd, *J* = 20 and 4.1 Hz, 1), 5.95 (dd, *J* = 15 and 4.1 Hz, 1), 6.22 (dd, *J* = 20 and 15 Hz, 1); ^{13}C NMR (CDCl$_3$) δ 139.5, 131.5, 72.1, 32.1, 9.2, 8.5, −1.3, −2.2; ^{29}Si NMR (CDCl$_3$) δ 3.1, −5.4, −22.3; MS *m/z* (rel intensity) 287 (M$^+$ −15, 0.9), 145 (100), 73 (66), 57 (68); HRMS *m/z*: found, 287.1693; calcd for $C_{13}H_{31}OSi_3$, 287.1683.

Di-*t*-butoxy-bis(2-trimethylsilylethyl)silane (7.9 mg, 0.0210 mmol, 2.8%): a colorless oil; ^{1}H NMR (CDCl$_3$) δ −0.05 (s, 18), 0.42 (s, 8), 1.26 (s, 18); ^{13}C NMR δ 71.8, 32.0, 8.38, 8.36, −2.2; ^{29}Si NMR (CDCl$_3$) δ 3.0, −18.4; MS *m/z* (rel intensity) 376 (M$^+$, 0.6), 361 (1.8), 163 (100), 73 (16), 57 (96); HRMS *m/z*: found, 376.2621; calcd for $C_{18}H_{44}O_2Si_3$, 376.2649.

CNDO/S Calculations

CNDO/S calculations were performed by an ACOS 2000 System at the Computer Center of Tohoku University [18]. Parameters for H and C for the calculations were taken from an article by Bene and Jaffe [26]. Following parameters for Si, which were determined so as to reproduce the experimental $\pi \rightarrow \pi^*$ transition energies of trimethylphenylsilane, were used; $-\beta^\circ_A = 8.50$, $(I_S + A_S)/2 = 12.12$, $(I_P + A_P)/2 = 6.00$.

Ab Initio MO Calculations

Structures of silylenes, **1**, **2**, and dimethylsilylene, have been optimized by using restricted Hartree–Fock (RHF) self-consistent field (SCF) analytical gradient techniques. The basis sets used were of standard double-ζ quality (including 3-21G, 6-31G*, and D95). For CIS [19] calculations of the transition energies, all single excitations from the SCF reference configuration were included. These ab initio MO calculations were performed with the GAMESS [27] program at the Computer Center of Tohoku University and with the Gaussian 90 [28] program at RIKEN Photodynamics Research Center.

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REFERENCES

[1] *Chemistry of Organosilicon Compounds*, 308.

[2] For reviews, see: (a) P. P. Gaspar: in M. Jones, Jr., R. T. Moss (eds): *Reactive Intermediates*, John Wiley, New York, vol. 1, ch. 7 (1978); (b) vol. 2, ch. 9 (1981); (c) vol. 3, ch. 9 (1985); (d) Tang, Y.-N.: in R. A. Abramovitch (ed): *Reactive Intermediates*, Plenum Press, New York, vol. 2, ch. 4 (1982); (e) K. K. Baldridge, J. A. Boatz, S. Koseki, M. S. Gordon, *Ann. Rev. Phys. Chem.*, *38*, 1987, 211; (f) Y. Apeloig: in S. Patai, Z. Rappoport (eds): *The Chemistry of Organic Silicon Compounds*, John Wiley, New York, Part 1, ch. 2 (1989).

[3] (a) T. J. Drahnak, J. Michl, R. West, *J. Am. Chem. Soc.*, *101*, 1979, 5427; (b) *J. Am. Chem. Soc.*, *103*, 1981, 1845; (c) C. A. Arrington, R. West, J. Michl, *J. Am. Chem. Soc.*, *105*, 1983, 6176; (d) C. A. Arrington, K. A. Klingensmith, R. West, J. Michl, *J. Am. Chem. Soc.*, *106*, 1984, 525; (e) H. Vancik, G. Raabe, M. J. Michalczyk, R. West, J. Michl, *J. Am. Chem. Soc.*, *107*, 1985, 4097; (f) G. Raabe, H. Vancik, R. West, J. Michl, *J. Am. Chem. Soc.*, *108*, 1986, 671; (g) G. R. Gillette, G. Noren, R. West, *Organometallics*, *9*, 1990, 2925.

[4] (a) A. S. Nazran, J. A. Hawari, D. Griller, I. S. Alnaimi, W. P. Weber, *J. Am. Chem. Soc.*, *106*, 1984, 7267; (b) J. A. Hawari, D. Griller, *Organometallics*, *3*, 1984, 1123; (c) A. S. Nazran, J. A. Hawari, D. Griller, I. S. Alnaimi, W. P. Weber, *J. Am. Chem. Soc.*, *108*, 1986, 5041.

[5] (a) G. Maier, G. Mihm, H. P. Reisenauer, D. Littmann, *Chem. Ber.*, *117*, 1984, 2369; (b) G. Maier, H. P. Reisenauer, K. Schottler, U. Wessolek-Kraus, *J. Organomet. Chem.*, *366*, 1989, 25.

[6] (a) G. Levin, P. K. Das, C. L. Lee, *Organometallics*, *7*, 1988, 1231; (b) G. Levin, P. K. Das, C. Bilgrien, C. L. Lee, *Organometallics*, *8*, 1989, 1206.

[7] Y. Apeloig, M. Karni, *J. Chem. Soc., Chem. Commun.*, 1985, 1048.

[8] R. S. Grev, H. F. Schaefer, III, *J. Am. Chem. Soc.*, *108*, 1986, 5804.

[9] (a) M. J. Michalczyk, M. J. Fink, D. J. De Young, C. W. Carlson, K. W. Welsh, R. West, J. Michl, *Silicon, Germanium, Tin Lead Compounds*, *9*, 1986, 75; (b) R. West, *Pure Appl. Chem.*, *56*, 1984, 163; (c) R. West, M. J. Fink, J. Michl, *Science*, *214*, 1981, 1343.

[10] M. Kira, T. Maruyama, H. Sakurai, *Tetrahedron Lett.*, *33*, 1992, 243.

[11] (a) D. Seyferth, T. F. O. Lim, *J. Am. Chem. Soc.*, *100*, 1978, 7074; (b) K. P. Steele, W. P. Weber, *J. Am. Chem. Soc.*, *102*, 1980, 6095; (c) T.-Y. Gu, W. P. Weber, *J. Am. Chem. Soc.*, *102*, 1980, 1641; (d) D. Tzeng, W. P. Weber, *J. Am. Chem. Soc.*, *102*, 1980, 1451; (e) A. Chihi, W. P. Weber, *Inorg. Chem.*, *20*, 1981, 2822.

[12] (a) K. Raghavachari, J. Chandrasekhar, M. S. Gordon, K. J. Dykema, *J. Am. Chem. Soc.*, *106*, 1984, 5853; (b) K. Raghavachari, J. Chandrasekhar, M. J. Frisch, *J. Am. Chem. Soc.*, *104*, 1982, 3779.

[13] (a) G. R. Gillette, G. H. Noren, R. West, *Organometallics*, *6*, 1987, 2617; (b) *Organometallics*, *8*, 1989, 487; (c) M.-A. Pearsall, R. West, *J. Am. Chem. Soc.*, *110*, 1988, 7228.

[14] (a) W. Ando, A. Sekiguchi, A. K. Hagiwara, A. Sakakibara, H. Yoshida, *Organometallics*, *7*, 1988, 558; (b) W. Ando, K. Hagiwara, A. Sekiguchi, *Organometallics*, *6*, 1987, 2270.

[15] In this relation, it should also be noted that the products derived from 1,3-migration of a trimethylsilyl group were not detected during the photoreactions of **3** and **4**, whereas the 1,3-silyl migration occurred efficiently in the photoreaction of a closely related vinyldisilane, 2,5-dimethylene-1-methyl-1-trimethylsilyl-1-silacyclopentane: M. Kira, T. Maruyama, H. Sakurai, *J. Am. Chem. Soc.*, *113*, 1991, 3986.

[16] Several authors have reported similar apex angles for dimethylsilylene estimated by *ab initio* MO calculations [8, 17].

[17] (a) K. Krogh-Jespersen, *J. Am. Chem. Soc.*, *107*, 1985, 537; (b) M. S. Gordon, M. W. Schmidt, *Chem. Phys. Lett.*, *132*, 1986, 294.

[18] We thank Prof. A. Tajiri (Hirosaki University) for the availability of the CNDO/S program.

[19] CIS denotes configuration interaction with single excitation.

[20] (a) R. West, K. Welsh, Y. Apeloig, R. Pauncz, M. Karni: Presented at the XXV Silicon Symposium, Los Angeles, April 1992, paper no. 1; (b) Y. Apeloig, private communication.

[21] (a) I. Dubois, G. Herzberg, K. D. Verma, *J. Chem. Phys.*, *47*, 1967, 4262; (b) I. Dubois, *Can. J. Phys.*, *46*, 1968, 2485; (c) I. Dubois, G. Duxbury, R. N. Dixon, *J. Chem. Soc., Faraday Trans. 2*, *71*, 1975, 799.

[22] (a) H. Gilman, R. L. Harrell, *J. Organomet. Chem.*, *5*, 1966, 199; (b) V. J. Tortorelli, M. Jones, Jr., S.-H., Wu, Z.-H. Li, *Organometallics*, *2*, 1983, 759.

[23] (a) A. J. Ashe, III; C. M. Kausch, O. Eisenstein, *Organometallics*, *6*, 1987, 1185; (b) D. Shehan: Ph.D. Dissertation, Yale University, 1964. See also, M. Kira, T. Hino, Y. Kubota, N. Matsuyama, H. Sakurai, *Tetrahedron Lett.*, *29*, 1988, 6939.

[24] (a) L. A. Brooks, H. R. Snyder, *Org. Syn. Col. Vol.*, *3*, 1955, 698; (b) L. Shi, C. K. Narula, K. T. Mak, L. Kao, Y. Xu, R. F. Heck, *J. Org. Chem.*, *48*, 1983, 3894.

[25] (a) H. Sakurai, T. Koyama, M. Kira, A. Hosomi, Y. Nakadaira, *Tetrahedron Lett.*, *23*, 1982, 543; (b) G. Märkl, H. B. Baier, R. Lieble, *Synthesis*, 1977, 842.

[26] J. D. Bene, H. H. Jaffe, *J. Chem. Phys.*, *48*, 1968, 1807.

[27] M. W. Schmidt, J. A. Boatz, K. K. Baldridge, S. Koseki, M. S. Gordon, S. T. Elbert, B. Lam, *QCPE Bull.*, *7*, 1987, 115.

[28] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople: Gaussian Inc., Pittsburgh, PA, 1990.