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Insertion of Silylenes into Si−H and Si−Cl Bonds. Comparison of Mechanism and Substituent Effects

Zheng Xu, Juan Jin, Haixia Zhang, Zhifang Li, Jianxiong Jiang, Guoqiao Lai,* and Mitsuo Kira*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, China

Ⓢ *Supporting Information*

ABSTRACT: Electronic and steric substituent effects on the insertion reactions of dimethylsilylene (**1**) and 2,2,5,5-tetrasilylsilacyclopentane-1,1-diyl (**2′**) into Si−H bonds are compared with those into Si−Cl bonds using DFT calculations at the B3LYP/6-31++G(d,p) level. For both **1** and **2′**, the $\Delta G^{\ddagger}$ value for the insertion into a Si−H bond of SiH_4 is close to and only ca. 1.5 kcal mol^{-1} lower than that into the Si−Cl bond of H_3SiCl. Effects of in-plane substituents on the $\Delta G^{\ddagger}$ values for both Si−H and Si−Cl insertion reactions are mainly electronic and electron-withdrawing substituents lower the $\Delta G^{\ddagger}$ values. Sensitivity of the Si−H insertion to the substituent effects is similar to that of the Si−Cl insertion. Effects of out-of-plane substituents are largely steric, and their sensitivity for the Si−H insertion is close to that for the Si−Cl insertion. The $\Delta G^{\ddagger}$ values for the insertion reactions of sterically bulky **2′** are significantly larger than those of **1**. The puzzling prior observation that a bulky isolable silylene inserts into the Si−Cl bond of H_2SiCl_2 and the Si−H bond of Me_2SiHCl is explained on the basis of the substituent effects on the insertion reactions.
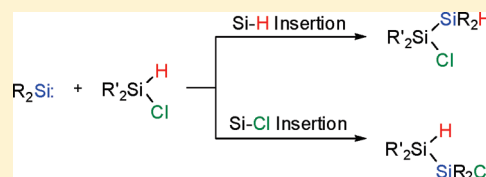
■ INTRODUCTION

A number of experimental and theoretical studies of insertion of dimethylsilylene (**1**) and other transient silylenes into a Si−X σ bond (X = H, Cl, etc.) have been reported so far because the insertion reactions provide not only a mechanistic proof for detecting the transient silylenes but also a useful synthetic method for the formation of Si−Si bonds.[1] As an interesting issue on the Si−X insertion, we have recently shown diverse selectivity between Si−H and Si−Cl insertion reactions.[2] The reaction of isolable dialkylsilylene **2**[3] with H_2SiCl_2 affords exclusively Si−Cl insertion product **3**, while silylene **2** inserts into a Si−H bond of Me_2SiHCl to give **4** quantitatively (Scheme 1).

To understand the rather unexpected selectivity of the insertion (Si−H/Si−Cl selectivity), comparison of the detailed mechanisms between the two insertion reactions is necessary. Although the mechanism of Si−H insertion has been extensively investigated both experimentally and theoretically[4−6] and its concerted nature has been established, substituent effects on the activation energy or the reaction rate have not been investigated systematically. On the other hand, we have recently studied in detail the transition-state structures of the insertion of dimethylsilylene **1** into a Si−Cl bond of various substituted chlorosilanes using DFT calculations.[7]

We wish herein to compare the electronic and steric substituent effects on the insertion reactions into Si−H bonds with those into Si−Cl bonds. For this purpose, detailed DFT calculations were performed at the B3LYP/6-31++G(d,p) level for the Si−H and Si−Cl insertion reactions of dimethylsilylene **1** and 2,2,5,5-tetrasilylsilacyclopentane-1,1-diyl as a model of sterically bulky dialkylsilylene **2** (**2′**, Chart 1). Although the geometries of
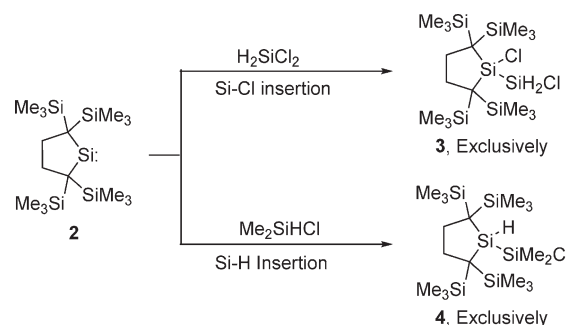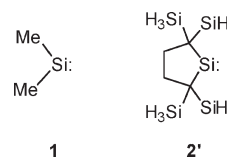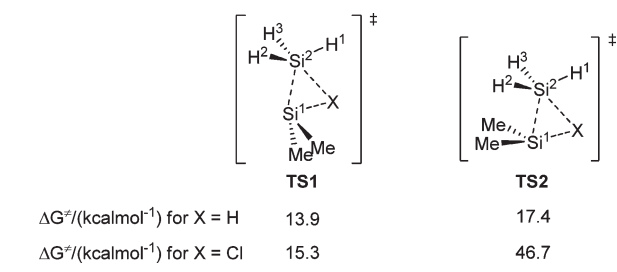
Scheme 1

Chart 1

the transition states (TS) are very different between Si−H and Si−Cl insertion reactions, the substituent effects on the activation energies were found to be rather similar, allowing us to predict qualitatively the Si−H/Si−Cl selectivity.

Chart 2

	TS1	**TS2**
$\Delta G^{\ddagger}/(\text{kcal mol}^{-1})$ for X = H	13.9	17.4
$\Delta G^{\ddagger}/(\text{kcal mol}^{-1})$ for X = Cl	15.3	46.7

■ COMPUTATIONAL METHODS

All calculations were performed on an SGI Altix 450 server using the Gaussian 03 package.[8] Geometries of all stationary points were optimized utilizing the DFT (B3LYP) method in conjunction with the 6-31++G(d,p) basis set. GaussView was used for visual inspection of the final geometries and vibrational frequencies and for drawing the optimized structures. All the structures obtained here were verified by examination of their Hessian matrix as minima (all frequencies real) or transition states (one imaginary frequency). Unscaled zero-point vibrational energies (ZPE) were incorporated into total energies. At every transition state, the transition-state vector was animated with the GaussView program, and if necessary, the intrinsic reaction coordinate (IRC) was computed to connect the corresponding minima.

■ RESULTS AND DISCUSSION

Insertion of Dimethylsilylene into a Si—X Bond of H₃Si—X (X = H, Cl). We have already compared the reaction of dimethyl-silylene **1** with SiH₄ and SiH₃Cl.[7b] A weak initial complex is formed between silylene **1** and SiH₄ or SiH₃Cl, and then a final insertion product is produced via a three-membered cyclic transition state. Although two different structures are possible for the TS (transition state) depending on the relative approach of **1** toward a Si—X bond (X = H or Cl) of SiH₃X (**TS1** and **TS2** in Chart 2) as first discussed by Becerra, Walsh, et al.,[4f] the activation free energy ($\Delta G^{\ddagger}$ at 298.15 K) for **TS1** is lower than that for **TS2**, while the $\Delta G^{\ddagger}$ difference between **TS1** and **TS2** for the Si—H insertion (3.5 kcal mol⁻¹) is much smaller than that for the Si—Cl insertion (31.4 kcal mol⁻¹). The natural bond orbital (NBO) analysis for the **TS1**s of the Si—H and Si—Cl insertion reactions indicated two important sets of interactions: first, a donor—acceptor interaction involving the silylene $n(\text{Si})$ as the donor and the in-plane $\sigma^*(\text{Si}^2-\text{H}^1)$ orbital as the acceptor; second, two donor—acceptor interactions involving the $p\pi(\text{Si})$ orbital as the acceptor and the $\sigma(\text{Si}^2-\text{X})$ and/or $n(\text{X})$ orbitals as donors. Apparently, **TS1** is preferred because these interactions are geometrically less effective in **TS2**.[4a,b,7]

Although the shapes of **TS1** for both Si—H and Si—Cl insertion reactions (Figure 1) are similar, the geometries are rather different because the standard Si—Cl bond distance (2.02 Å) is much longer than that of the Si—H bond (1.47 Å). However, the arrangement of substituents on the Si² atom (silane silicon) is similar, with one hydrogen substituent on Si² being located in the plane of the Si¹Si²X ring and the other two hydrogens being out of the plane. The geometry around the pentacoordinate Si² atom in **TS1** is regarded as a trigonal bipyramidal (TBP), which is popular in nucleophilic substitution reactions at silicon, while the geometry is largely distorted from the ideal TBP.
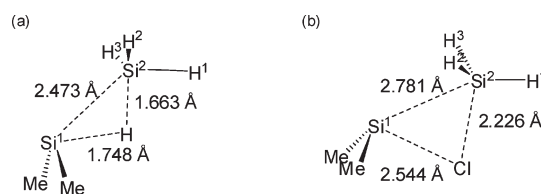

Figure 1. **TS1** structures for dimethylsilylene insertion reactions into the Si—X bond of H₃SiX: (a) X = H; (b) X = Cl.
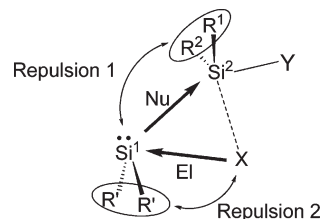
Figure 2. Schematic representation of important substituent effects on dialkylsilylene insertion into the Si—X bond of YR¹R²Si—X. Lone pair electrons of silylene Si¹ atom attack the Si² atom as a nucleophile, and a vacant $p\pi$ orbital on Si¹ atom approaches X lone-pair and/or Si—X σ electrons as an electrophile.

Chart 3
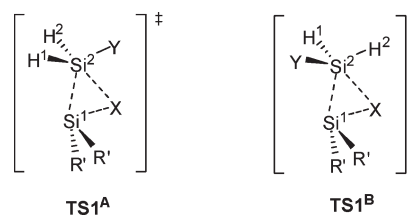
The activation free energy for the Si—H insertion reaction of **1** via **TS1** is lower than that for the corresponding Si—Cl insertion reaction, but the difference is only 1.4 kcal mol⁻¹, suggesting the Si—H/Si—Cl selectivity may be altered by the in-plane and out-of-plane substituents on silane.

Comparison of Substituent Effects between Si—H and Si—Cl Insertion Reactions. In a previous paper,[7b] we have investigated the insertion reactions of silylene **1** into the Si—Cl bond of a series of YH₂SiCl [Y = H (**a**), Me (**b**), NH₂ (**c**), OH (**d**), F (**e**), SiH₃ (**f**), PH₂ (**g**), SH (**h**), and Cl (**i**)] and a series of YR¹R²SiCl [R¹, R² (out-of-plane substituents) = H, Me, Cl, i-Pr, t-Bu; Y = H, Cl]. This study revealed remarkable substituent effects, as schematically shown in Figure 2 (X = Cl). Because the nucleophilic approach of silylene to the chlorosilane silicon atom is largely affected by the in-plane substituent (Y), the $\Delta G^{\ddagger}$ value for the Si—Cl insertion is remarkably reduced when an electron-withdrawing Y substituent is located in the ring plane. The $\Delta G^{\ddagger}(Y)$ values correlate roughly linearly with Charlton $\sigma_I(Y)$ constants[9] as a scale of inductive effect of Y. Sterically bulky out-of-plane substituents (R¹ and R²) increase the $\Delta G^{\ddagger}$ value due to the steric repulsion between the out-of-plane substituents and the silylene Si¹ atom (repulsion 1 in Figure 2); $\Delta G^{\ddagger}(R^1, R^2)$ values show a linear correlation with Taft's steric substituent constants (E_s).[10] If bulky dialkylsilylene **2** were used instead of **1**, the $\Delta G^{\ddagger}$ value may increase by the enhanced steric repulsion between the substituents on silylene and X (repulsion 2 in Figure 2).

Table 1. Relative Energies of Precursor Complexes and Activation Parameters for the Insertion of Silylene 1 into the Si–H Bond of YH$_2$Si–H (Reaction 2) Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a,b]

Y	E_{cplx}	TS1^A (in-plane Y)				TS1^B (out-of plane Y)				$\Delta G^{\ddagger}_{A-B}{}^c$
		E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	
H	0.2 (−1.4)	4.70 (0.2)	13.9 (11.2)	3.6 (−1.0)	−34.5 (−40.9)	4.7	13.9	3.6	−34.5	0.0
Me	−0.3 (−3.1)	3.50 (−1.4)	14.3 (10.0)	2.8 (−2.4)	−38.6 (−41.7)	3.4 (−2.2)	14.7 (9.6)	2.6 (−3.1)	−40.6 (−42.6)	−0.4 (0.4)
NH$_2$	0.1	−0.60	10.8	−1.5	−41.3	_^{d}	_^{d}	_^{d}	_^{d}	_^{d}
OH^e	−0.5					−0.9	10.6	−1.9	−41.9	
F^e	−1.7					3.7	14.6	3.0	−38.9	
SiH$_3$	0.1	4.60	14.9	4.1	−36.2	2.8	14.2	2.1	−40.6	0.7
PH$_2$	0.0	3.00	14.6	2.4	−40.9	2.1	13.5	1.4	−40.6	1.1
SH	−0.5	0.20	11.6	−0.5	−40.6	1.2	12.6	0.5	−40.6	−1.0
Cl^e	−1.5					4.8	15.9	4.3	−38.9	

^{a} E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems (1 + YSiH$_3$) and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. ^{b} Values calculated at the G2(MP2, SVP)//B3LYP/6-31G(d) level (ref 4g) are shown in parentheses. See ref 11. ^{c} $\Delta G^{\ddagger}_A$ − $\Delta G^{\ddagger}_B$, kcal mol^{-1}. ^{d} Strong coordination of amine to silylene during the approach prevented the determination of the TS. ^{e} The transition states were not located. See ref 12.

The aim of the present study is to elucidate (1) whether the above analysis for the electronic and steric substituent effects is applicable for the corresponding Si–H insertion, (2) how the mode and sensitivity of the substituent effects are different between Si–H and Si–Cl insertion reactions, and (3) how the Si–H/Si–Cl selectivity observed experimentally is rationalized by the present theoretical analysis.

In-Plane Substituent Effects. To compare the electronic substituent effects between the Si–Cl and Si–H insertion reactions, the TSs and their activation parameters were investigated using DFT calculations at the B3LYP/6-31++G(d,p) level for the following four sets of insertion reactions. In addition to the reactions of 1 with the Si–Cl bond of 6a–6i (reaction 1) reported previously,[7b] those of 1 with the Si–H bond of 8a–8i reaction 2) and the corresponding reactions of 2′ (reactions 3 and 4) have also been computed.[11]

Me$_2$Si: + YH$_2$Si–Cl ⟶ YH$_2$Si-SiMe$_2$-Cl (1)
1   6   7

Me$_2$Si: + YH$_2$Si–H ⟶ YH$_2$Si-SiMe$_2$-H (2)
1   8   9

Y = H (a), Me (b), NH$_2$ (c), OH (d), F (e), SiH$_3$ (f), PH$_2$ (g), SH (h), Cl (i); R = SiH$_3$

Similarly to reaction 1, there are two possible arrangements of substituents at the **TS1** (**TS1^A** and **TS1^B** in Chart 3) for reactions 2–4; substituent Y is in-plane for **TS1^A**, while Y is out-of plane for **TS1^B**.

The activation parameters for the reactions together with the energies of the precursor complexes relative to those of the initial reagent systems are summarized in Tables 1–3. Unfortunately,
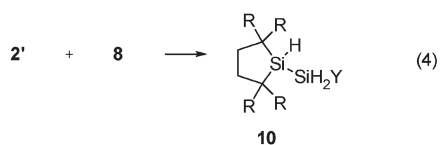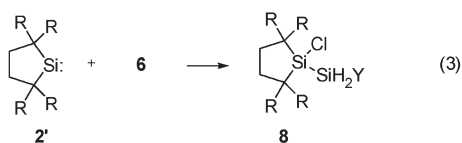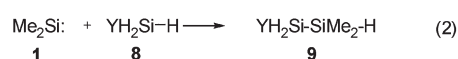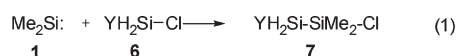
Table 2. Relative Energies of Precursor Complexes and Activation Parameters for the Insertion of Silylene 2′ into a Si–Cl Bond of YH$_2$Si–Cl (Reaction 3) Calculated at B3LYP/6-31++G(d,p)+ZPE Level[a]

Y	E_{cplx}	TS1^A (in-plane Y)				TS1^B (out-of-plane Y)				$\Delta G^{\ddagger}_{A-B}{}^b$
		$E^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$E^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	
H	−0.3	10.9	24.1	10.4	−46.0	10.9	24.1	10.4	−46.0	0
Me	−0.3	12.8	26.2	12.6	−45.6	12.5	26.1	12.2	−46.6	0.1
NH$_2$	−0.3	10.9	24.3	10.6	−46.0	9.1	22.7	8.7	−47.0	1.6
OH	−0.6	8.7	22.1	8.4	−46.0	10.1	23.4	9.7	−46.0	−1.3
F	−1.1	5.2	18.7	4.9	−46.3	9.9	23.1	9.7	−44.9	−4.4
SiH$_3$	−0.4	12.3	25.4	12.2	−44.3	9.7	23.4	9.5	−46.6	2.0
PH$_2$	−1.3	10.3	23.4	10.6	−42.9	8.4	21.6	8.5	−43.9	1.8
SH	1.0	10.7	24.2	10.6	−45.6	8.1	21.8	7.7	−47.3	2.4
Cl	−1.0	6.9	20.1	6.7	−44.9	10.5	23.3	10.4	−43.3	−3.2

^{a} E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems (2′ + YSiH$_2$Cl) and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. ^{b} $\Delta G^{\ddagger}_A$ − $\Delta G^{\ddagger}_B$, kcal mol^{-1}.

the TSs for **TS1^A** with Y = OH, F, and Cl for reaction 2 could not be located probably due to the very low activation energies at the theoretical levels.[12] Strong coordination of amine to silylene during the approach prevented the determination of the TS for **TS1^B** with Y = NH$_2$ (Table 1).

As shown in Tables 1–3, the $\Delta G^{\ddagger}$ values for **TS1^A** are substantially lower than those for **TS1^B** when Y is an electron-withdrawing group such as F and Cl, while for other substituents, the difference ($\Delta G^{\ddagger}_{A-B}$) is small but either positive or negative. Similarly to the substituent effects on the insertion of 1 into the Si–Cl bond,[7b] an approximate linear relationship between $\Delta G^{\ddagger}(Y)$ and $\sigma_I(Y)$ is observed for the three Si–X insertion reactions (reactions 2–4) via **TS1^A** with in-plane Y substituents (Figures 3 and 4; correlation coefficient $r > 0.77$), indicating the importance of the nucleophilic mechanism involving the silylene lone-pair electrons and their approach of the silane silicon atom in both Si–H and Si–Cl insertion reactions. No linear correlation was observed between the $\Delta G^{\ddagger}$ values for **TS1^B** and σ_I ($r < 0.6$).

The parameters (slope, intercept, and correlation coefficient, r) for the linear relationship between $\Delta G^{\ddagger}(Y)$ and $\sigma_I(Y)$ for **TS1^A**

Table 3. Relative Energies of Precursor Complexes and Activation Parameters for the Insertion of Silylene $2'$ into the Si−H Bond of YH_2Si−H (Reaction 4) Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a]

		TS1[A] (in-plane Y)			TS1[B] (out-of-plane Y)				
Y	E_{cplx}	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}{}_{A-B}{}^{b}$
H	0.1	11.9	22.6	10.8	−39.4	11.9	22.6	10.8	−39.4	0
Me	−0.2	10.4	23.1	9.7	−45.1	10.1	23.3	9.4	−46.6	−0.2
NH_2	0.0	6.0	18.9	5.1	−46.5	5.5	18.6	4.6	−47.0	0.3
OH	−0.6	5.2	18.4	4.3	−47.2	5.9	19.0	5	−47.0	−0.6
F	−1.3	4.3	17.3	3.5	−46.4	9.7	22.4	9.1	−44.6	−5.1
SiH_3	0.1	12.0	25.1	11.4	−46.0	10.0	23.4	9.3	−47.3	1.7
PH_2	−0.1	10.4	23.5	9.8	−46.0	10.0	23.1	9.4	−46.0	0.4
SH	−0.5	7.6	20.9	6.9	−46.9	8.5	21.7	7.8	−46.6	−0.8
Cl	−1.3	6.2	19.0	5.6	−44.9	11.6	24.7	11.1	−45.6	−5.7

[a] E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems ($2'$ + $YSiH_3$) and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. [b] $\Delta G^{\ddagger}{}_{A}$ − $\Delta G^{\ddagger}{}_{B}$, kcal mol^{-1}.

are summarized in Table 4 together with those for reaction 1.[7b] Although the r value of the linear relationship for reaction 2 is less satisfactory because points for important electron-withdrawing substituents (Y = OH, F, and Cl) are missing in the plot,[12] it should be noted that the slope (−10.5) is close to the other three series of reactions (Table 4). In other words, the sensitivity of the in-plane substituent effects is similar in both the Si−H and Si−Cl insertion reactions, despite the different migrating group on the Si[2] atom. No remarkable difference is found in the intercept between the Si−H and Si−Cl insertion reactions of **1**, which is true of $2'$, while the intercept is strongly dependent on the bulkiness of silylene. The intercept for the insertion reactions of $2'$ is roughly 9 kcal mol^{-1} higher than that of **1** due to the larger steric repulsion between $2'$ and X (repulsion 2 in Figure 2).

Out-of-Plane Substituent Effects. To elucidate the features of the out-of-plane substituent effects on the Si−H and Si−Cl insertion reactions, the following four series of insertion reactions (reactions 5−8) were investigated.

$$\textbf{1} + HR^1R^2Si-Cl \longrightarrow HR^1R^2Si-SiMe_2-Cl \quad (5)$$
$$\qquad\qquad \textbf{11} \qquad\qquad\qquad \textbf{12}$$

$$\textbf{1} + HR^1R^2Si-H \longrightarrow HR^1R^2Si-SiMe_2-H \quad (6)$$
$$\qquad\qquad \textbf{13} \qquad\qquad\qquad \textbf{14}$$

$$\textbf{2'} + \textbf{11} \longrightarrow \quad (7)$$
15

$$\textbf{2'} + \textbf{13} \longrightarrow \quad (8)$$
16

R_1R_2 = H$_2$ (**j**), HCl (**k**), HMe (**l**), Cl$_2$ (**m**), Me$_2$ (**n**), i-Pr$_2$ (**o**), t-Bu$_2$ (**p**); R = SiH$_3$

The results for reactions 6−8 are summarized in Tables 5−7; those for reaction 5 have been reported previously.[7b] Similarly to the insertion reactions of **1** into a Si−Cl bond (reaction5),[7b] the $\Delta G^{\ddagger}$ values of the other three insertion reactions increase with

Figure 3. Plots of $\Delta G^{\ddagger}$ values for insertion reactions of silylene **1** into the Si−X bond of YH_2Si−X versus Charton σ_I constants; X = H (○), X = Cl (●).

Figure 4. Plots of $\Delta G^{\ddagger}$ values for insertion reactions of silylene $2'$ into the Si−X bond of YH_2Si−X versus Charton σ_I constants; X = H (□), X = Cl (■).

Table 4. Linear Correlation of $\Delta G^{\ddagger}$ vs Charton σ_I for the Insertion Reactions of Silylenes 1 and $2'$ into the Si−X Bond of YH_2Si−X (X = Cl, H) via TS1[A,a,b]

silylene	Si−X insertion	linear relationship[c]
1	reaction 1, X = Cl[d]	$\Delta G^{\ddagger} = -11.4\sigma_I + 16.8$ (0.89)
	reaction 2, X = H[e]	$\Delta G^{\ddagger} = -10.5\sigma_I + 14.4$ (0.77)
2'	reaction 3, X = Cl	$\Delta G^{\ddagger} = -10.7\sigma_I + 25.4$ (0.88)
	reaction 4, X = H	$\Delta G^{\ddagger} = -10.8\sigma_I + 23.2$ (0.81)

[a] Each plot includes nine points for nine Y substituents (**a**−**i**) unless otherwise noted. See ref 9 and Supporting Information for the σ_I values of Y substituents. [b] $\Delta G^{\ddagger}$, kcal mol^{-1}. [c] Correlation coefficient (r) is shown in parentheses. [d] Ref 7b. [e] The plot includes only 6 points for Y substituents **a**−**c** and **f**−**h**. See ref 12.

the increasing steric bulkiness of the out-of-plane substituents. As shown in Figure 5 and Table 8, the plots of $\Delta G^{\ddagger}$ values against the sum of Taft's steric substituent constants (ΣE_s)[10] show a roughly linear correlation with a slope of ca. 1.0 for both the Si−H and Si−Cl insertion reactions of **1**. Similar linear correlations are found for the insertion reactions of $2'$ (reactions 7 and 8) but with the slope of ca. 2.4. The larger slope observed for $2'$ when compared to the case of **1** suggests that the bulkiness of $2'$ indirectly enhances the sensitivity of the steric effects caused by the out-of-plane substituents. The larger intercept for $2'$ than that for **1** would be the reflection of the difference of the steric bulkiness between silylene **1** and $2'$ (repulsion 2 in Figure 2).

Origin of the Experimental Si−H/Si−Cl Selectivity. The substituent effects between the Si−H and Si−Cl insertion reactions of dimethylsilylene (**1**) may be summarized as follows: (1) The $\Delta G^{\ddagger}$ value for the insertion into a Si−H bond of SiH_4

Table 5. Relative Energies of Precursor Complexes and Activation Parameters for the Insertion of 1 into the Si−H Bond of HR^1R^2Si−H (Reaction 6) Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a]

silane R^1, R^2	E_{cplx}	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H, H (13j)[b]	0.6	4.7	13.9	3.6	−34.5
H, Cl (13k)	−1.5	4.8	15.9	4.3	−38.9
H. Me (13l)	−0.2	3.4	14.7	2.6	−40.6
Cl, Cl (13m)	−1.1	6.1	17.1	5.8	−37.9
Me, Me (13n)	−1.1	2.6	13.8	2.0	−39.6
i-Pr, i-Pr (13o)	−1.3	3.8	16.4	3.2	−44.3
t-Bu, t-Bu (13p)	−1.2	5.8	19.1	5.1	−47.0

[a] E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems $(1 + HR^1R^2SiH)$ and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. [b] 13j = 8a.

Table 6. Relative Energies of Precursor Complexes and Activation Parameters for Insertion of 2′ into the Si−Cl Bond of HR^1R^2SiCl (Reaction 7) Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a]

chlorosilane R^1, R^2	E_{cplx}	$E^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H, H (11j)[b]	−1.3	10.9	24.1	10.4	−46.0
H, Cl (11k)	−1.0	10.5	23.3	10.4	−43.3
H, Me (11l)	−0.3	12.5	26.2	12.2	−47.0
Cl, Cl (11m)	−0.7	11.4	23.6	11.5	−40.6
Me, Me (11n)	−0.6	14.5	28.8	14.1	−49.3
i-Pr, i-Pr (11o)	0.3	14.7	29.6	14.4	−51.0
t-Bu, t-Bu (11p)	−0.2	20.5	36.4	20.2	−54.3

[a] E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems $(2′ + HR^1R^2SiCl)$ and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. [b] 11j = 6a.

Table 7. Relative Energies of Precursor Complexes and Activation Parameters for Insertion of 2′ into the Si−H Bond of HR^1R^2SiH (Reaction 8) Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a]

silane R^1, R^2	E_{cplx}	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H, H (13j)[b]	0.1	11.9	22.6	10.8	−39.6
H, Cl (13k)	−1.3	11.6	24.7	11.1	−38.9
H. Me (13l)	−0.2	10.1	23.3	9.4	−46.6
Cl, Cl (13m)	−1.0	12.9	25.6	12.7	−43.3
Me, Me (13n)	−0.1	10.0	23.2	9.4	−46.3
i-Pr, i-Pr (13o)	0.1	12.6	27.7	12.1	−52.3
t-Bu, t-Bu (13p)	0.0	20.9	36.8	20.2	−55.7

[a] E_{cplx}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ are all based on the starting reagent systems $(2′ + HR^1R^2SiH)$ and given in kcal mol^{-1}. $\Delta S^{\ddagger}$ values are in cal mol^{-1} K^{-1}. [b] 13j = 8a.

(8a) is close to and only ca. 1.4 kcal mol^{-1} lower than that into the Si−Cl bond of H_3SiCl (6a). (2) Effects of in-plane substituents on the $\Delta G^{\ddagger}$ value for both Si−H and Si−Cl insertion reactions are mainly electronic, and electron-accepting substituents lower the $\Delta G^{\ddagger}$ value. Sensitivity of the Si−H insertion to the substituent effects is similar to that of the Si−Cl insertion. (3) Effects of out-of-plane substituents are largely steric, and their
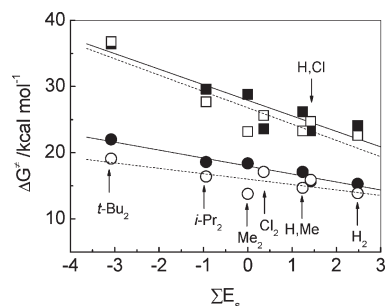

Figure 5. Plots of $\Delta G^{\ddagger}$ vs Taft's steric substituent constants of R^1 and R^2 in the Si−H and Si−Cl insertion reactions: (●) 1 + HR^1R^2 Si−Cl (reaction 5), (○) 1 + HR^1R^2Si−H (reaction 6), (■) 2′ + HR^1R^2Si−Cl (reaction 7), and (□) 2′ + HR^1R^2Si−H (reaction 8). See Supporting Information and ref 10 for Taft's steric substituent constants.
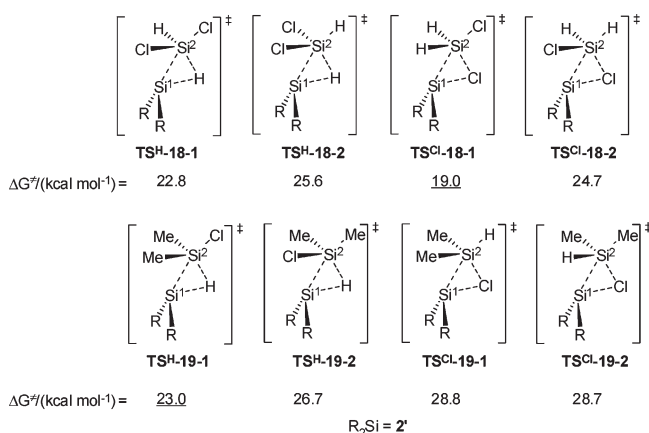

Figure 6. Possible TSs for the Si−H and Si−Cl insertion reactions of 2′ with H_2SiCl_2 (18) and Me_2SiHCl (19). The $\Delta G^{\ddagger}$ values shown are those calculated for the corresponding reactions of 2′ at the B3LYP/6-31++G(d,p) level. Underline indicates the lowest $\Delta G^{\ddagger}$ value among the four possible TSs. See Supporting Information for the detailed activation parameters for the reactions.

Table 8. Linear Relationship between $\Delta G^{\ddagger}$ vs ΣE_s for Si−H and Si−Cl Insertion Reactions[a,b]

silylene	Si−X insertion X	linear relationship[c]
1	X = H	$\Delta G^{\ddagger} = -0.8\Sigma E_s + 16.0$ (0.78)
	X = Cl[d]	$\Delta G^{\ddagger} = -1.2\Sigma E_s + 18.0$ (0.97)
2′	X = H	$\Delta G^{\ddagger} = -2.5\Sigma E_s + 26.8$ (0.91)
	X = Cl	$\Delta G^{\ddagger} = -2.3\Sigma E_s + 27.9$ (0.91)

[a] $\Delta G^{\ddagger}$, kcal mol^{-1}. [b] Sum of Taft's steric substituent constants (ref 10). See Supporting Information. [c] Correlation coefficient (r) is given in parentheses. [d] Ref 7b.

sensitivity for the Si−H insertion is close to that for the Si−Cl insertion. The above features 1−3 are applicable also to the corresponding insertion reactions of 2′, while the $\Delta G^{\ddagger}$ values for the insertions of 2′ are systematically larger than that of 1.

To discuss the experimentally observed difference in the intramolecular Si−H/Si−Cl selectivity between H_2SiCl_2 (18) and Me_2SiHCl (19) for silylene 2 (Scheme 1),[2] the reactions of 2′ with 18 and 19 were investigated theoretically. As shown in Figure 6, four TSs should be considered for each of the reactions

of **18** and **19** with **2′**; **TS^H-18-1** and **2** and **TS^{Cl}-18-1** and **2** for **18** and **TS^H-19-1** and **2** and **TS^{Cl}-19-1** and **2** for **19**. The lowest $\Delta G^{\ddagger}$ values are found at **TS^{Cl}-18-1** for **18** and at **TS^H-19-1** for **19**, and hence, the Si—Cl and Si—H insertions are preferred for **18** and **19**, respectively, being in accord with the experimental selectivity shown in Scheme 1. The selectivity difference is explained on the basis of the strong directing effect of the Cl substituent; an in-plane Cl accelerates but an out-of-plane Cl retards significantly a Si—X insertion reaction, as shown in the previous sections. Thus, the $\Delta G^{\ddagger}$ value for **TS^H-18-1** should be lower than that for **TS^H-18-2**, because the former TS has an in-plane Cl and the number of bulky out-of-plane Cl's is less. Similarly, for the Si—Cl insertion of **18**, the $\Delta G^{\ddagger}$ value for **TS^{Cl}-18-1** is lower than that for **TS^{Cl}-18-2**, because the former TS has an in-plane Cl and the number of bulky out-of-plane Cl's is smaller. Between **TS^H-18-1** and **TS^{Cl}-18-1**, the latter has a lower $\Delta G^{\ddagger}$ value, because the former has a bulky out-of-plane Cl, though they have an in-plane Cl. A similar discussion is extended to the Si—H/Si—Cl selectivity for **19**. Obviously, **TS^H-19-1** is more favorable than the other three TSs because **TS^H-19-1** has Cl as an in-plane substituent; although **TS^{Cl}-19-2** has less bulky out-of-plane substituents, it is less favorable than **TS^H-19-1** because the latter has an in-plane electron-donating methyl substituent in addition to the intrinsic lower reactivity of the Si—Cl insertion.

In conclusion, we have shown theoretically that substituent effects on the activation free energy of the insertion of a dialkylsilylene into Si—X bonds (X = H, Cl) are separated into three roughly independent factors: electronic in-plane and steric out-of-plane substituent effects of Si—X compounds and the steric effects of the dialkylsilylene. Electron-withdrawing in-plane substituents accelerate the insertion, and sterically bulky out-of-plane substituents retard the reaction. Because the activation energies for the prototype insertions of **1** and **2′** into a Si—H bond of SiH$_4$ is only 1.5 kcal mol^{-1} lower than that for the insertion into a Si—Cl bond of SiH$_3$Cl, the Si—H/Si—Cl selectivity for R$_2$SiHCl-type compounds may be altered by the substituents on Si—X compounds. The difference in the Si—H/Si—Cl selectivity observed between the reactions of silylene **2** with H$_2$SiCl$_2$ and Me$_2$SiHCl is explained by strong directing effects of chlorine substituent, which lowers the $\Delta G^{\ddagger}$ value as an in-plane substituent but increases it as an out-of-plane substituent. Because the insertion reactivity of a silylene is known to be remarkably dependent on the substituents on silylene,[4,13] the electronic effects of substituents on silylene may also be important to determine the Si—H/Si—Cl selectivity, although they have not been discussed in this paper.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. A full list of authors for ref 8, relative energies of precursor complexes and activation parameters for the reactions of silylene **2′** with H$_2$SiCl$_2$ and Me$_2$SiHCl, a plot of $\Delta G^{\ddagger}$ values for reaction 1 calculated at the B3LYP/6-311++(3df,3pd) level vs those at the B3LYP/6-31++G(d,p) level, activation parameters for insertion of silylene **1** into the Si—Cl bond of YH$_2$Si—Cl calculated at the B3LYP/6-311++G(3df,3pd)+ZPE level, a plot of $\Delta G^{\ddagger}$(Y, **1**) vs $\Delta G^{\ddagger}$(Y, **2′**) for the Si—H insertion of YH$_2$Si—H, and Charton σ_I and Taft's steric substituent constants (E_s) for related substituents. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: mkira@m.tohoku.ac.jp (M.K.); gqlai@hznu.edu.cn (G.L.).

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■ REFERENCES

(1) For recent reviews on silylenes, see: (a) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (b) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969. (c) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251.(d) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley &Sons: Chichester, 1998; Vol. 2, p 2463. (e) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (f) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. (g) Hill, N. J.; West, R. *J. Organomet. Chem.* **2004**, *689*, 4165.

(2) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Silicon Chem.* **2003**, *2*, 137.

(3) (a) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722. For recent accounts on the silylene, see:(b) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475. (c) Kira, M.; Ishida, S.; Iwamoto, T. *Chem. Rec.* **2004**, *4*, 243. (d) Kira, M.; Iwamoto, T.; Ishida, S. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 258. (e) Kira, M. *Chem. Commun.* **2010**, *46*, 2893.

(4) (a) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Walsh, R. *J. Am. Chem. Soc.* **1990**, *112*, 8337. (b) Jasinski, J. M.; Becerra, R.; Walsh, R. *Chem. Rev.* **1995**, *95*, 1203. (c) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 184. (d) Becerra, R.; Carpenter, I. W.; Roskop, M. S.; Walsh, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2121. (e) Becerra, R.; Walsh, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2817. (f) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Krylova, I. V.; Nefedov, O. M.; Promyslov, V. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4395. (g) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Krylova, I. V.; Nefedov, O. M.; Promyslov, V. M.; Walsh, R. *J. Phys. Chem. A* **2008**, *112*, 849.

(5) (a) Sakai, S.; Nakamura, M. *J. Phys. Chem.* **1993**, *97*, 4960. (b) Su, M.-D; Chu, S.-Y. *J. Phys. Chem. A* **1999**, *103*, 11011.

(6) For a recent discussion on the Si—H bond insertion of metallylenes, see: Karni, M.; Kapp, J.; Schleyer, P. v. R.; Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, 2001; Vol. 3, p 1, and references therein.

(7) (a) Lai, G.; Xu, Z.; Li, Z.; Jiang, J.; Kira, M.; Qiu, H. *Organometallics* **2009**, *28*, 3591–3593. (b) Xu, Z.; Jin, J.; Li, Z.; Qiu, H.; Jiang, J.; Lai, G.; Kira, M. *Chem.—Eur. J.* **2009**, *15*, 8605.

(8) Frisch, M. J. et al. *Gaussian 03*, revision D.01; Gaussian, Inc.: Pittsburgh, PA, 2003. See Supporting Information for a full list of the authors.

(9) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *92*, 165.

(10) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 3120.

(11) The activation parameters for the insertion reactions of dimethylsilylene into the Si—H bonds of SiH$_4$ and MeSiH$_3$ (reaction 2, Y = H and Me) at the G2(MP2,SVP)//B3LYP level have been reported by Walsh et al. (Table 1).[4g] The reported $\Delta G^{\ddagger}$ values are 2.7—5.1 kcal mol^{-1} lower than our values, but the very close $\Delta G^{\ddagger}$ values among the three insertion reactions (**TS1$^{A(B)}$** for Y = H and **TS1^A** and **TS1^B** for Y = Me) are compatible with the substituent effects discussed here. To test the basis set dependence of the substituent effects on the activation free energy, the calculations for reaction 1 were performed at the B3LYP/6-311++G(3df, 3pd) level. The substituent effects at the

B3LYP/6-311++G(3df, 3pd) level are parallel to those found at the B3LYP/6-31++G(d,p) level with the relationship $\Delta G^{\ddagger}$ (Y, 6-311G) = $0.944\Delta G^{\ddagger}$(Y, 6-31G) $-$ 0.677 (r = 0.94); see Supporting Information.

(12) A good linear relationship was observed between $\Delta G^{\ddagger}$ values for reaction 2 $[\Delta G^{\ddagger}(Y, \mathbf{1})]$ and those for reaction 4 $[\Delta G^{\ddagger}(Y, \mathbf{2}')]$; $\Delta G^{\ddagger}(Y, \mathbf{1}) = 0.826\Delta G^{\ddagger}(Y, \mathbf{2}') - 5.08$ (r = 0.96). From the equation, the $\Delta G^{\ddagger}$ values for Y = F, OH, and Cl, of reaction 2 are extrapolated to be 9.2, 10.1, and 10.6 kcal mol^{-1}, respectively. If these values are considered in the $\Delta G^{\ddagger}(Y, \mathbf{1})$ vs $\sigma_I(Y)$ plot for reaction 1, a linear equation, $\Delta G^{\ddagger} = -9.3\sigma_I + 14.2$ (r = 0.866), is obtained. For the plot, see Supporting Information.

(13) Gaspar, P. P. In *Reactive Intermediates*, Vol. 1; Jones, M., Moss, R. A., Eds.; John Wiley & Sons: New York, 1978; p 229.