Supporting Information

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

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Contents

1. A Full List of Authors for Ref. 8

Gaussian 03 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

2. Table S1

Table S1. Relative Energies of the Precursor Complexes and Activation Parameters for Possible TSs of Insertion of **2'** into Si–H and Si–Cl Bonds of H_2SiCl_2 and Me_2SiHCl Calculated at the B3LYP/6-31++G(d,p)+ZPE Level[a]

		E_{cplx}	E_a	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
H_2SiCl_2	**TS^H-18-1**	-0.9	9.7	22.8	9.4	-44.9
	TS^H-18-2		12.9	25.6	12.7	-43.3
	TS^{Cl}-18-1	-1.0	6.2	19.0	5.6	-44.9
	TS^{Cl}-18-2		11.6	24.7	11.0	-46.0
Me_2SiHCl	**TS^H-19-1**	-0.6	9.0	23.0	8.6	-48.3
	TS^H-19-2		13.1	26.7	12.8	-46.6
	TS^{Cl}-19-1	-0.4	14.5	28.8	14.1	-49.3
	TS^{Cl}-19-2		15.0	28.7	14.7	-47.0

a. E_{cplx}, E_a, $\Delta G^{\neq}$, and $\Delta H^{\neq}$ are all based on the starting reagent systems (**2'** + R_2SiHCl) and given in kcal mol^{-1}. $\Delta S^{\neq}$ values are in cal mol^{-1} K^{-1}.

3. Figure S1

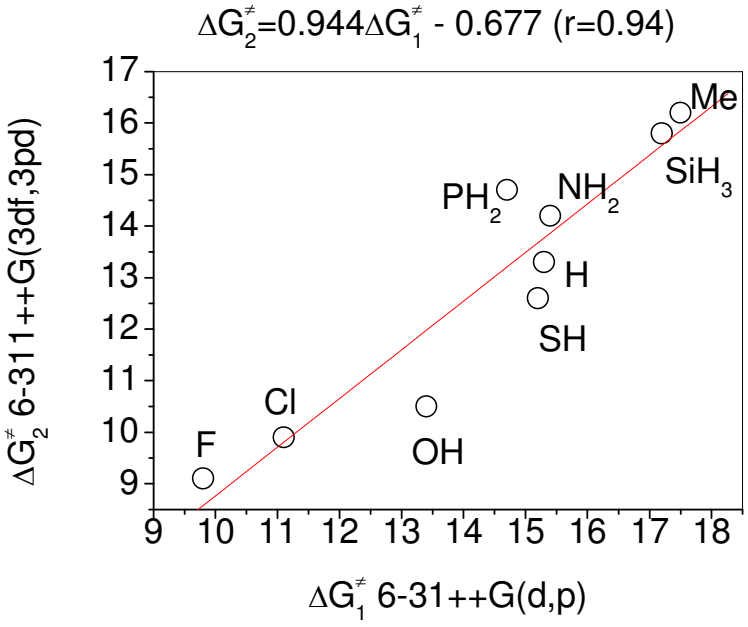

Figure S1. A plot of $\Delta G^{\neq}$ values for reaction 1 calculated at the B3LYP/6-311++(3df,3pd) level [$\Delta G_2^{\neq}$] vs. those at the B3LYP/6-31++G(d,p) level [$\Delta G_1^{\neq}$].

4. Table S2

Table S2. Activation Parameters for the Insertion of Silylene **1** into Si-Cl Bond of YH_2Si-Cl (Reaction 1) Calculated at B3LYP/6-311++G(3df,3pd) + ZPE Level[a]

Y	TS1A(in-plane Y)		
	E_a	$\Delta H^{\neq}$	$\Delta G^{\neq}$
H	2.6	2.1	13.3
Me	4.4	4.0	16.2
NH_2	2.4	2.0	14.2
OH	-1.0	-1.1	10.5
F	-2.0	-2.3	9.1
SiH_3	4.2	3.9	15.8
PH_2	2.9	2.7	14.7
SH	0.9	0.6	12.6
Cl	-1.2	-1.4	9.9

a. E_a, $\Delta G^{\neq}$, and $\Delta H^{\neq}$ are all based on the starting reagent systems (**1** + YH_2Si-Cl) and given in kcal mol^{-1}.

5. Figure S2

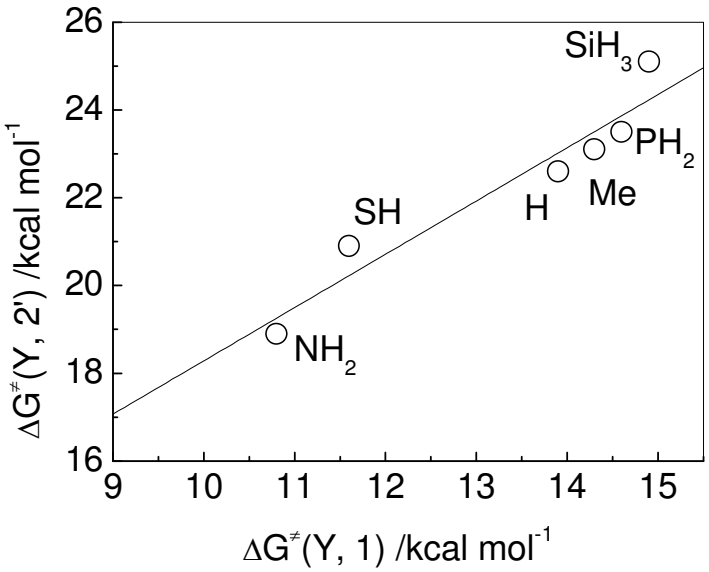

Figure S2. A plot of $\Delta G^{\neq}$(Y, **1**) versus $\Delta G^{\neq}$(Y, **2'**) for the reactions with YH_2Si–H (Y=H, Me, NH_2, SiH_3, PH_2, SH, Cl). The linear equation is $\Delta G^{\neq}$(Y, **1**) =0.826$\Delta G^{\neq}$(Y, **2'**) -5.08 and the correlation coefficient r = 0.96. The $\Delta G^{\neq}$(Y, **1**) for Y=F, OH, and Cl are evaluated to be 9.2, 10.1 and 10.6 kcal mol^{-1} by the linear equation.

6. Figure S3

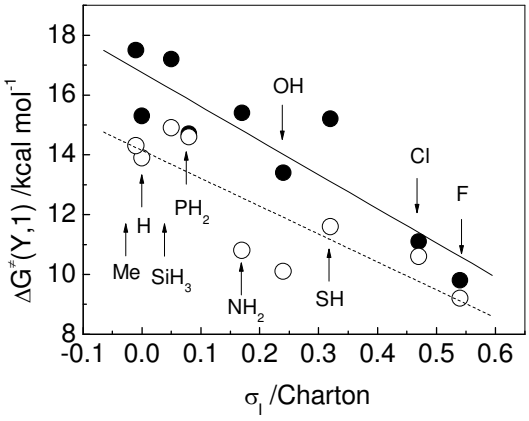

Figure S3. Plots of $\Delta G^{\neq}$ values for insertion reactions of silylene **1** into an Si–X bond of YH_2Si–X versus Charton σ_I constants; X = H (○), X = Cl (●). For the plot for X = H, three points for Y = F, OH, and Cl whose $\Delta G^{\neq}$ values were estimated using the plot shown in Figure S2 are included. See ref. 12 in text.

7. Table 3

Table S3. Charton σ_I Constants and Taft's Steric Substituent Constants (Es) for Related Substituents

substituent	Charton σ_I
H	0
Me	–0.01
NH_2	0.17
OH	0.24
F	0.54
SiH_3	0.05
PH_2	0.08
SH	0.32
Cl	0.47

substituent	Es
H	1.24
Me	0
Cl	0.18
i-Pr	–0.47
t-Bu	–1.54