

# Isomerization of Silyllallene

Hideaki Shimizu<sup>†</sup> and Mark S. Gordon\*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

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The isomerization of silyllallene to seven of its isomers has been studied using *ab initio* molecular orbital theory. The energetics were obtained using quadratically convergent configuration interaction (QCISD(T)) with the 6-311G(d,p) basis set, at geometries optimized by second-order perturbation theory (MP2) with the 6-31G(d) basis set. Test calculations using multiconfiguration wave functions show that the configurational mixing is small; therefore, the single-configuration-based methods are reliable. In comparison to the isomerization of the parent allene, the silyl group was found to migrate more easily than the hydrogen. In particular, the 1,3-migration that converts silyllallene to silylpropyne has barriers of 55.8 and 52.9 kcal mol<sup>-1</sup> for the forward and backward reactions, respectively. These are roughly half of the 1,3-hydrogen migration barrier in allene.

## Introduction

Thermal isomerization of allene has been well studied experimentally<sup>1</sup> and understood thoroughly by a recent theoretical study<sup>2</sup> using multiconfigurational (MC) self-consistent field (SCF) and multireference configuration interaction (CI) calculations. The main path for the isomerization of allene to propyne is predicted to be allene (CH<sub>2</sub>=C=CH<sub>2</sub>) → vinylmethylene (CH<sub>2</sub>=CH-C(H):) → cyclopropene (c-CH=CH-CH<sub>2</sub>) → propylidene (CH<sub>3</sub>CH=C:) → propyne (CH<sub>3</sub>≡CH).

Silyllallenes have received much less attention than allene. Slutsky and Kwart carried out a kinetic study of (trimethylsilyl)allene isomerization<sup>3</sup> and investigated its mechanism. Recently there has been increasing interest in silyllallenes and in the synthetic use of silyllallene isomerization.<sup>4</sup> Also, silacycloallenes have been prepared and their thermal ring contractions and photochemistry have been studied.<sup>5,6</sup>

The purpose of this study is to compare the potential energy surfaces of allene and silyllallene using *ab initio* molecular orbital theory and to determine how the silyl group modifies the potential energy surface. In particular, how does silyl migration differ from hydrogen migration? One may follow the analog of the established allene isomerization mechanism as illustrated in Scheme 1. In this diagram, minima on the potential energy surface are indicated by a number (underlined

and in bold) beneath the structure. Transition states are indicated by a capital letter adjacent to the appropriate double arrow.

## Computational Methods

Since Scheme 1 includes some molecules for which a single-reference wave function may not be adequate, test calculations were performed using complete active space (CAS) MCSCF calculations (referred to as CASSCF),<sup>7</sup> in which we include all electronic configurations that arise from distributing 10 electrons among 10 orbitals (all electrons and orbitals excluding those in CH or SiH bonds). This amounts to correlating all CC and SiC bonds in the system. Geometry optimizations were carried out with second-order perturbation theory (MP2<sup>8</sup>) using the orbitals obtained from the Hartree-Fock (HF) wave function. The 6-31G(d) basis set<sup>9</sup> was used for both calculations.

In order to determine whether a stationary point is a minimum or a transition state, the matrix of energy second derivatives (Hessian) was calculated for each optimized geometry. Diagonalization of this matrix determines whether the structure is a minimum (no negative eigenvalues) or a transition state (one negative eigenvalue). The intrinsic reaction coordinates (IRC),<sup>10</sup> minimum energy paths connecting reactants and products through transition states, were followed to verify that each transition state does indeed connect the appropriate minima.

In order to obtain reliable energetics, higher level methods were employed for single-point energy calculations at the optimized geometries. Both full fourth-order perturbation theory (MP4SDTQ)<sup>11</sup> and quadratically convergent configuration interaction (QCISD(T))<sup>12</sup> calculations were performed at the MP2 geometries using the 6-311G(d,p) basis set.<sup>13</sup> The CASSCF calculations were done using GAMESS<sup>14</sup> and the MP2, MP4, and QCISD(T) calculations using Gaussian92.<sup>15</sup>

<sup>†</sup> Present address: Shin-Etsu Chemical Co., Ltd., 1-10, Hitomi, Matsuida, Gunma 379-02, Japan.

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(1) (a) Sakakibara, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1268. (b) Levush, S. S.; Abadzhev, S. S.; Shevchuk, V. U. *Neftekhimiia* **1969**, *9*, 215. (c) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680. (d) Bradley, J. N.; West, K. O. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 967. (e) Lifshitz, A.; Frenklach, M.; Burcat, A. *J. Phys. Chem.* **1975**, *79*, 1148. (f) Lifshitz, A.; Frenklach, M.; Burcat, A. *J. Phys. Chem.* **1976**, *80*, 2437. (g) Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2137. (h) Bailey, I. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1146. (i) Hopf, H.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

(2) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 4198–4209.

(3) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678–8685.

(4) Robinson, L. R. Dissertation, DA8721925, 1987.

(5) Pang, Y.; Petrich, S. A.; Young, V. G., Jr.; Gordon, M. S.; Barton, T. *J. Am. Chem. Soc.* **1993**, *115*, 2534–2536.

(6) (a) Shimizu, T.; Hojo, F.; Ando, W. *J. Am. Chem. Soc.* **1993**, *115*, 3111. (b) Hojo, F.; Shimizu, T.; Ando, W. *Organometallics* **1994**, *13*, 3402.

(7) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

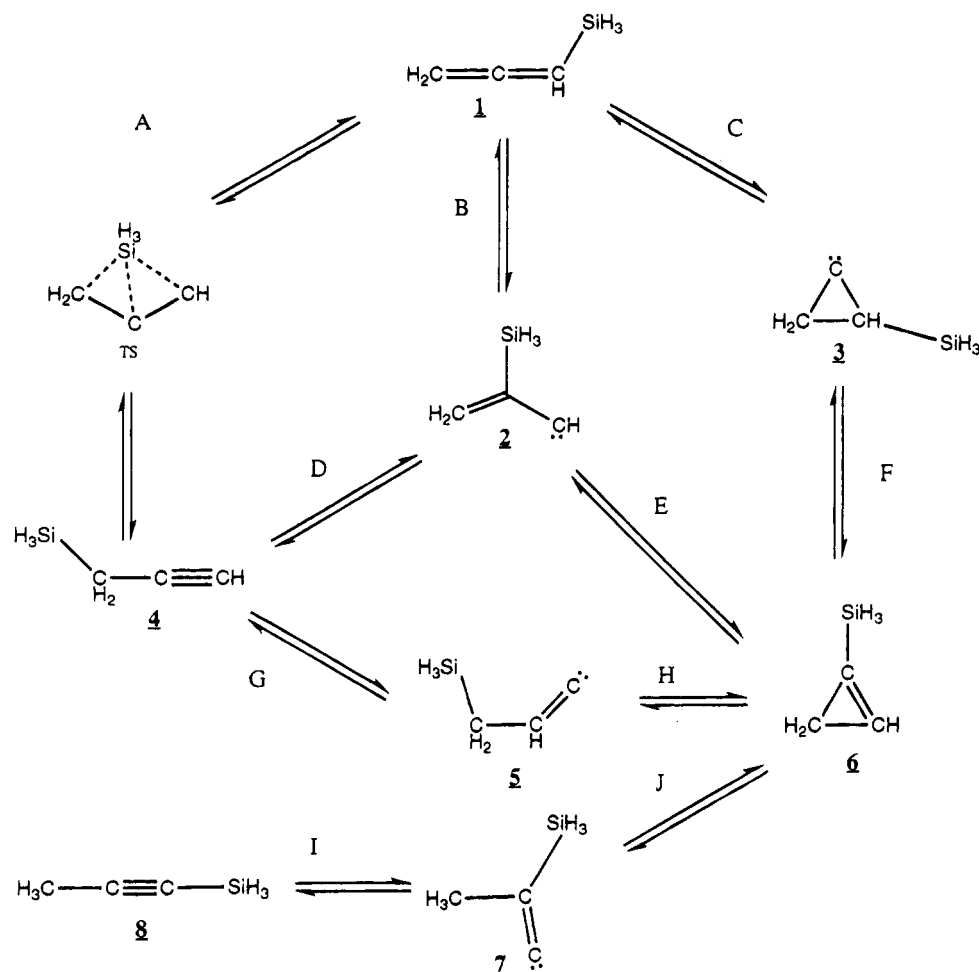
(8) (a) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41, 51, 65. (b) Lam, B.; Schmidt, M. W.; Ruedenberg, K. *J. Phys. Chem.* **1985**, *89*, 2221.

(9) (a) H. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728. (b) C. O. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (c) Si: Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163–168. (d) Standard polarizations were used: H (*p* = 1.1), C (*d* = 0.8), O (*d* = 0.8), Si (*d* = 0.395).

(10) (a) Garrett, B. C.; Redmon, M. J.; Steckler, R.; Truhlar, D. G.; Baldrige, K. K.; Bartol, D.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem.* **1988**, *92*, 1476–1488. (b) Gonzales, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527. (c) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853–5860.

(11) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244–4245.

## Scheme 1. Silyllallene Isomerization Diagram

Table 1. Calculated Barriers for Allene and Silyllallene (kcal mol<sup>-1</sup>)<sup>a</sup>

path	direction	silyllallene QCISD(T) <sup>b</sup>	allene <sup>c</sup> MRCI <sup>d</sup>
A	1-TS	55.8	94.9 <sup>e</sup>
	4-TS	52.9	95.6 <sup>e</sup>
B	1-TS	64.8	65.8
	2-TS	12.1	12.1
E	2-TS	4.5	4.5
	6-TS	43.8	35.8
D	2-TS		18.9
	4-TS		72.9
C	1-TS	76.5	72.2
	3-TS	11.4	10.2
F	3-TS	4.2	14.9
	6-TS	49.1	54.5
G	4-TS	49.8	38.1
	5-TS		18.6
H	5-TS		-2.4
	6-TS	32.0	39.8
I	8-TS	66.5	38.1
	7-TS		18.6
J	7-TS		-2.4
	6-TS	37.5	39.8

<sup>a</sup> Labels and paths correspond to those in Scheme 1. <sup>b</sup> QCISD(T)/6-311G(d)//MP2/6-31G(d). <sup>c</sup> Reference 2. <sup>d</sup> MRCI/6-31G(d)/CASSCF(6,6)/6-31G(d). <sup>e</sup> All but path A for allene include ZPE correction.

## Results and Discussion

**Preliminary Considerations.** The geometries of the stationary points found on the silyllallene potential energy surface are shown in Figure 1. The relative

energies are summarized in Table 1, together with results for the allene isomerization for comparison. Note that several of the pathways (B-E, C-F, G-H, I-J) predicted in the earlier study<sup>2</sup> on the parent allene correspond to two-step processes. In the current work on silyllallene, only the G-H path is found to be a two-step process. All of the others merge into a single, concerted path.

One can assess the importance of performing a multiconfigurational (CASSCF) calculation by defining a simple index  $N_v$ , calculated as the sum of natural orbital occupation numbers in the restricted Hartree-Fock (RHF) virtual space. If the single-configuration RHF calculation is correct,  $N_v$  should be zero. Thus,  $N_v$  is an indicator of the importance of the additional configurations. The values calculated for  $N_v$ , using the CASSCF(10,10) wave function discussed in the previous section, on the MP2 potential energy surface are sum-

(12) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968-5975.

(13) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-654.

(14) GAMESS (General Atomic and Molecular Electronic Structure System): Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347-1363.

(15) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92; Gaussian Inc., Pittsburgh, PA, 1992.

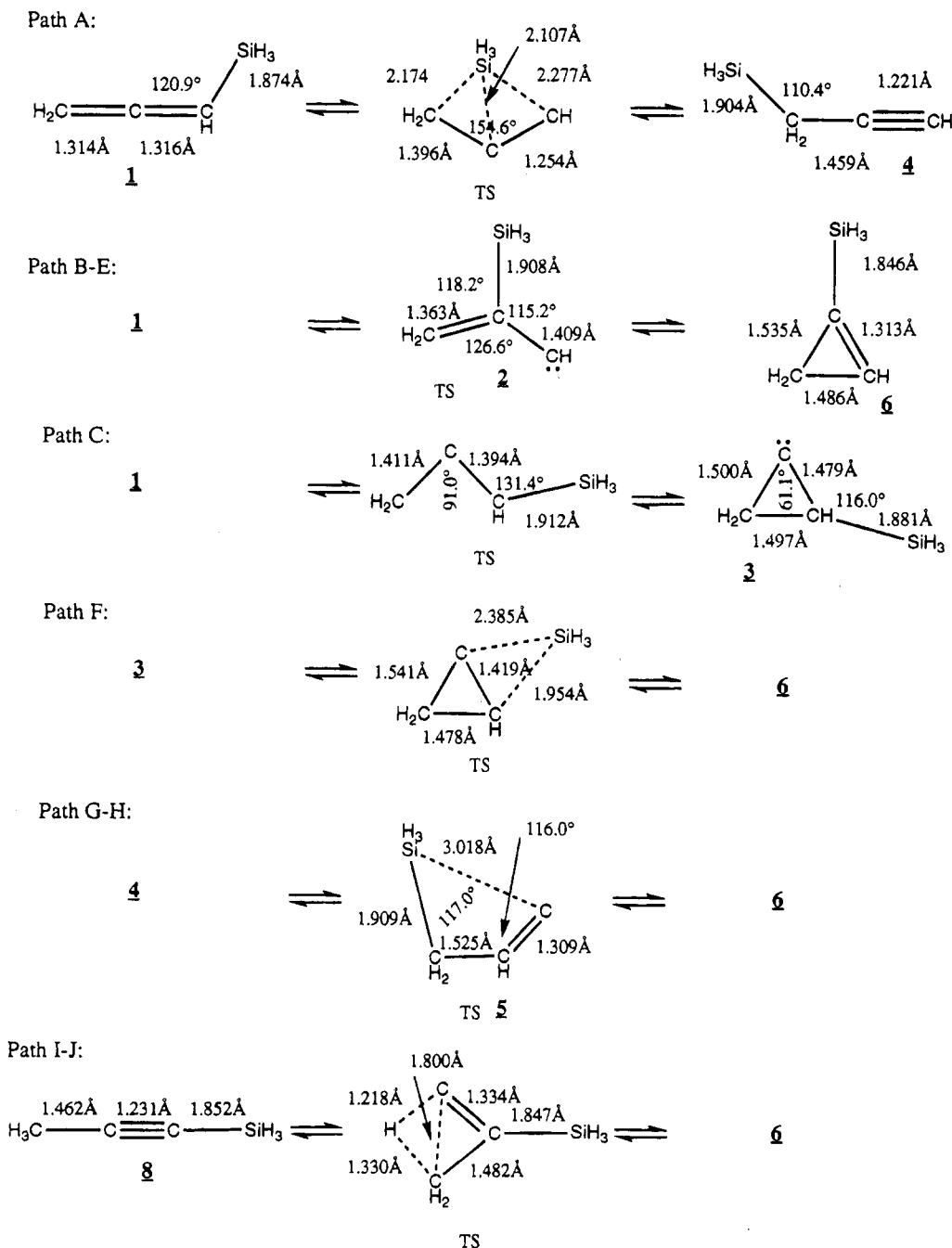


Figure 1. MP2/6-31G(d) geometries.

Table 2.  $N_v$  Values from CASSCF(10,10) for MP2-Optimized Geometries of Transition States

path	$N_v$	path	$N_v$
A	0.181	F	0.160
B-E	0.264	G-H	0.186
C	0.220	I-J	0.193

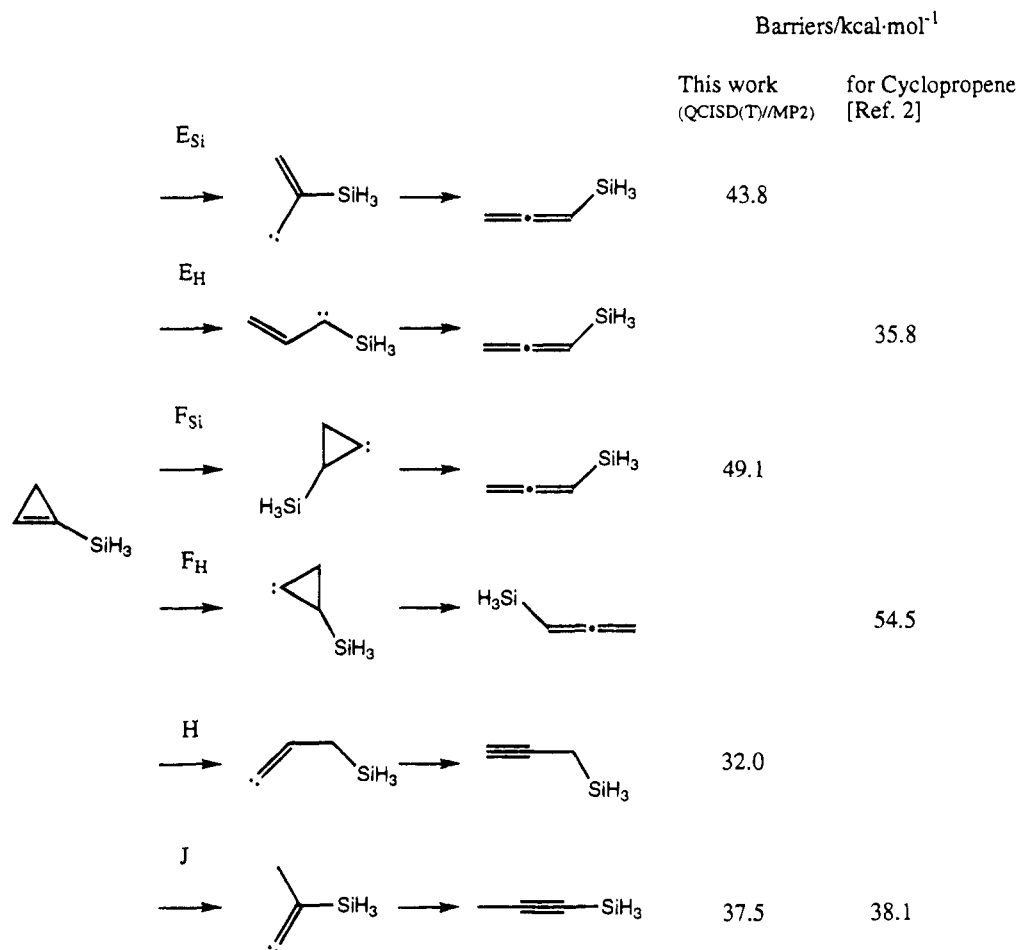
marized in Table 2. It is clear from the small values for  $N_v$ , that MP2-optimized geometries are likely to be reliable and that quantitative differences between the MP2 and CASSCF potential energy surfaces are likely to be due to the importance of dynamic correlation that is included to some extent in the MP2 energies, but not in the CASSCF results. Hence, the following discussion is based on QCISD(T) energies obtained at MP2-optimized geometries.

**Reaction Energetics.** Table 1 contains the reaction energetics calculated at the QCISD(T) level of theory,

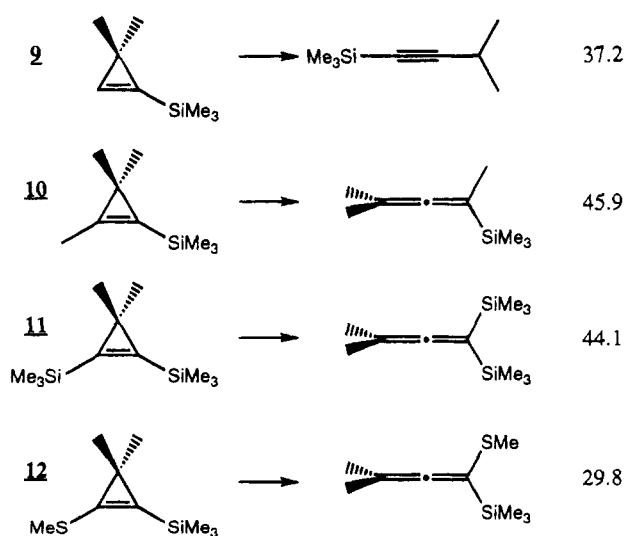
using the MP2 geometries. A negative entry in this table means that although a transition state was identified at the level of theory used to determine stationary points, higher level single-point calculations reversed the relative energies of the minimum and apparent transition states. This may be taken as evidence that the transition state may disappear at the higher levels of theory.

Note that a transition state corresponding to process D on the allene reaction path was not found for silyllallene. This is not surprising, since structure 2 is itself predicted to be a transition state at the MP2 level of theory. Thus, it is likely that the competing lower energy 1,3-silyl shift (path A) is preferred.

The 1,3-silyl migration (path A) of silyllallene has a quite low (56 kcal mol<sup>-1</sup>) barrier (Table 1) compared to the 95 kcal mol<sup>-1</sup> barrier for hydrogen migration in the parent allene.<sup>2</sup> This activation energy of 56 kcal



**Figure 2.** Possible reaction paths from silylcyclopropene and theoretical activation energies. The relevant path is indicated over the arrow.



**Figure 3.** Experimental activation energies (kcal mol<sup>-1</sup>) of various silylcyclopropene derivatives.

mol<sup>-1</sup> is similar to the experimental value<sup>3</sup> of 49.9 kcal mol<sup>-1</sup> and is close to the 1,3-sigmatropic rearrangement activation energy of 50.2 kcal mol<sup>-1</sup> for allylsilane.<sup>16</sup>

Next, consider the pathways connecting **1** and **6** in Scheme 1. Paths B and E merge into a concerted reaction according to the MP2 calculations. The net QCISD(T) barrier height based on MP2 geometries (64.8 kcal mol<sup>-1</sup>) is very similar to that found for the parent

allene (65.8 kcal mol<sup>-1</sup>). The alternative pathway connecting **1** and **6**, via **3**, is predicted to have a net energy requirement of 76.5 kcal mol<sup>-1</sup>. This is slightly greater than the corresponding barrier (72.2 kcal mol<sup>-1</sup>) in allene.<sup>2</sup> Note that for the 1,2-migrations (paths F, B, and H), silyl migration tends to have a few kcal mol<sup>-1</sup> lower reaction barrier than that for hydrogen migration. This trend is consistent with the experimental evidence that silyl migrations are more facile than hydrogen migrations. This is reasonable, since C–Si bonds tend to be weaker (76 vs 100 kcal mol<sup>-1</sup>) and more polarizable than C–H bonds.

As noted earlier (see Table 1), MP2 predicts that structures **5** and **7** are transition states for concerted processes connecting **4** with **6** and **8** with **6**, respectively. The net energetic requirement for **4** → **6** is predicted to be somewhat higher (49.8 kcal mol<sup>-1</sup>) than that for the corresponding pathway in the parent allene (38.1 kcal mol<sup>-1</sup>). For the path (I–J) connecting **6** with **8**, the net barrier height is predicted to be 66.5 kcal mol<sup>-1</sup> at the QCISD(T)/MP2 level of theory. This is rather larger than the corresponding barrier in allene.<sup>2</sup>

Overall, the lowest energy path from silylallene (**1**) to 3-silylpropyne (**4**) occurs via a direct 1,3-silyl migration (A), with a barrier estimated to be about 56 kcal mol<sup>-1</sup>. The lowest energy path from silylallene to silylcyclopropene (**6**) occurs via transition state **2**, with an estimated barrier of about 65 kcal mol<sup>-1</sup>. To access

silylacetylene (**8**) from silylcyclopropene requires 37.5 kcal mol<sup>-1</sup>.

**Comparison with Cyclopropene Isomerization Experiments.** There have been extensive studies of isomerizations of silylcyclopropenes.<sup>17</sup> This enables us to compare part of this study with experimental values for the reaction barriers of isomerization reactions. The various reactions starting from silylcyclopropene and the calculated barriers are shown in Figure 2, and the experimental activation energies for methylated analogs are shown in Figure 3. For **9**, the observed activation energy of 37.2 kcal mol<sup>-1</sup> is close to the calculated value for path J. Steric hindrance due to the methyl groups, as well as the intrinsic energy difference between Me<sub>3</sub>-SiCH<sub>2</sub>C≡CH and Me<sub>3</sub>SiC≡CCH<sub>3</sub>, may explain why path H, predicted to be the lowest energy path, is not found

(17) (a) Walsh, R.; Untiedt, S.; Stohlmeier, M.; de Meijere, A. *Chem. Ber.* **1989**, *122*, 637-642. (b) Walsh, R.; Untiedt, S.; de Meijere, A. *Chem. Ber.* **1994**, *127*, 237-245.

experimentally. For compounds **10** and **11** path J is impossible, and the barrier for path H is again likely to be increased due to steric hindrance. Thus, the ring opening (path E) becomes the lowest energy path, and the observed activation energy (44.1 kcal mol<sup>-1</sup>) is again in good agreement with calculated value of 43.8 kcal mol<sup>-1</sup>. Although this reaction includes a 1,2-silyl migration in the latter stage, the transition state lies close to **2**, so that it is not affected by steric hindrance.

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