

# Relation between the $\pi$ -Contribution to Reversed Si=C Bond Polarization and the Reaction Profile for the Thermolytic Formation of Silenes

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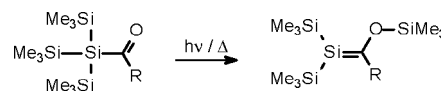
A quantum chemical investigation of the reaction profiles for the thermal formation of silenes  $Z_2\text{Si}=\text{C}(\text{XSiH}_3)\text{Y}$  from silanes  $Z_2(\text{H}_3\text{Si})\text{Si}-\text{C}(=\text{X})\text{Y}$  ( $\text{X} = \text{O}, \text{S}, \text{NMe}$ ;  $\text{Y} = \text{NMe}_2, \text{OMe}, \text{SMe}, \text{Me}$ ;  $\text{Z} = \text{SiH}_3, \text{Me}$ ) has been performed. Focus was put on the influence of the  $\pi$ -conjugative contribution to reversed Si=C bond polarization ( $\text{Si}^{\delta-}=\text{C}^{\delta+}$ ) as determined by natural resonance theory (NRT) at the B3LYP density functional theory level. Good linear correlations between the weights of  $\pi$ -conjugated reverse polarized resonance structures ( $\Sigma\Phi_{\text{RP}}(\pi)$ ) in the electronic structure and the Si=C bond lengths were found for the two classes of silenes with  $\text{Z} = \text{SiH}_3$  and  $\text{Me}$  ( $r^2 = 0.957$  and  $0.955$ , respectively). Silenes that are strongly influenced by the  $\pi$ -conjugative reverse polarization have low barriers for back-reaction to the silanes, making these silenes more difficult to isolate when formed through a [1,3]-silyl shift than those that are naturally polarized. Modest exponential dependencies of the activation barriers for the reverse reactions on  $\Sigma\Phi_{\text{RP}}(\pi)$  are found ( $r^2 = 0.685$  for  $\text{Z} = \text{SiH}_3$  and  $r^2 = 0.699$  for  $\text{Z} = \text{Me}$ ). Species with the silyl groups replaced by trimethylsilyl groups, e.g., the Brook-type silene  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)t\text{-Bu}$ , have lower contributions of  $\Sigma\Phi_{\text{RP}}(\pi)$  by 3–23% than the corresponding model silenes, a result of steric bulk. The weight  $\Sigma\Phi_{\text{RP}}(\pi)$  to the electronic structure of  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)t\text{-Bu}$  was calculated to be 7.4%. With  $\text{Z} = \text{Me}$ , the silenes are in general not equally influenced by  $\Sigma\Phi_{\text{RP}}(\pi)$  as with  $\text{Z} = \text{SiH}_3$ , their energies relative to the silanes are higher, and they have higher activation barriers for both forward and backward reactions.

## Introduction

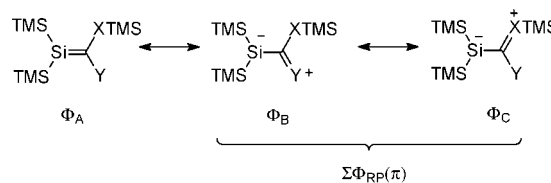
In the last decades considerable attention has been given to the synthesis of compounds with Si=C double bonds, so-called silenes.<sup>1</sup> This development was initiated by Gusev'nikov and Flowers' finding in 1967 on formation of transient silenes during the pyrolysis of a silacyclobutane.<sup>2</sup> In 1981, Brook and co-workers reported the photolytic generation of the first isolable silene, 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1-adamantyl)silene (Scheme 1,  $\text{R} = 1\text{-Ad}$ ), through a [1,3]-shift of a trimethylsilyl group from the Si to the O atom of an acylpolysilane.<sup>3</sup> Today, there are several additional synthetic methods developed to generate silenes.<sup>1</sup> Yet, the [1,3]-silyl shift of acylpolysilanes is one of the most widely used methods for synthesis of Si=C bonded compounds, and it can be carried out under thermolytic or photolytic conditions.

As C is more electronegative than Si, most silenes have a partial positive charge on Si and a partial negative charge on

## Scheme 1. Silene Formation from an Acylpolysilane



## Scheme 2. Resonance Structures of Silenes with $\pi$ -Donor Substituents at the Carbon Atom



C, referred to as the natural polarity of silenes ( $\text{Si}^{\delta+}=\text{C}^{\delta-}$ ). However, the Si=C bond polarity can be reduced, or even reversed ( $\text{Si}^{\delta-}=\text{C}^{\delta+}$ ), through  $\pi$ -conjugative electron delocalization from  $\pi$ -donor substituents at C (resonance structures  $\Phi_{\text{B}}$  and  $\Phi_{\text{C}}$ , Scheme 2), as well as through inductive  $\sigma$ -electron donation from substituents at Si, e.g.,  $\text{SiMe}_3$  (TMS) groups. The silenes formed through the [1,3]-silyl shift in acylpolysilanes are all influenced to some extent by reversed Si=C bond polarity, as they have a  $\pi$ -donating siloxy substituent at the C atom.<sup>4</sup> The 2-siloxysilenes that have been generated thermolytically have R in Scheme 1 as either  $\text{CH}=\text{CMe}_2$ , Me, 1-Ad, Ph, Mes, *t*-Bu, *i*-Pr,  $\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{Si}(\text{SiMe}_3)_3$ , or  $\text{NRR}'$  ( $\text{R}, \text{R}' = \text{Me}$  or Ph), and the temperatures required are in the range

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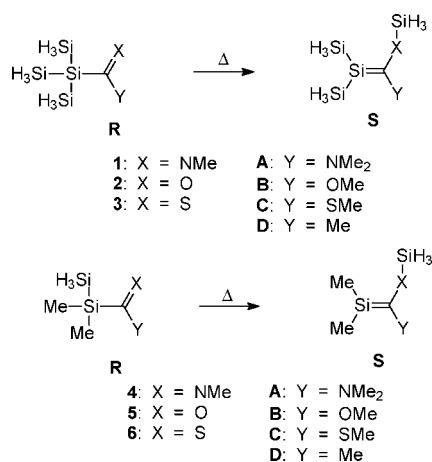
(1) For recent reviews on multiply bonded Si compounds see: (a) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *36*, 71. (b) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley Interscience: New York, 1998; p 857. (c) West, R. *J. Organomet. Chem.* **2001**, *21*, 467. (d) Gusev'nikov, L. E. *Coord. Chem. Rev.* **2003**, *244*, 149. (e) Ottosson, H.; Steel, P. G. *Chem.-Eur. J.* **2006**, *12*, 1576. (f) Ottosson, H.; Eklöf, A. M. *Coord. Chem. Rev.* **2008**, *252*, 1287.

(2) Gusev'nikov, L. E.; Flowers, M. C. *J. Chem. Soc., Chem. Commun.* **1967**, 864.

(3) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(4) Apeloig, Y.; Kami, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

## Scheme 3. Model Systems and Reactions Investigated



**Table 1. Relative Energies of S1A–S3D, FS1A–FS3A, and FS1D–FS3D at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) Level<sup>a</sup>**

silene	$\Delta E$ [silene – silane]	$\Delta E^+$ [silene → silene]	$\Delta E^+$ [silene → silane]
<b>S1A</b>	11.0	11.8	0.8
<b>S1B</b>	8.1	11.3	3.2
<b>S1C</b>	14.9	21.4	6.5
<b>S1D</b>	20.0	23.5	3.5
<b>S2A</b>	25.0	25.7	0.7
<b>S2B</b>	24.0	35.0	11.0
<b>S2C</b>	21.8	32.0	10.2
<b>S2D</b>	13.8	31.0	17.2
<b>S3A</b>	21.9	26.3	4.4
<b>S3B</b>	11.6	26.5	14.9
<b>S3C</b>	16.1	28.8	12.7
<b>S3D</b>	6.8	28.2	21.4
<b>FS1A</b>	10.0, 7.8	20.7, 15.5	10.7, 7.7
<b>FS2A</b>	17.5, 21.1	26.6, 27.4	9.1, 6.3
<b>FS3A</b>	14.7, 17.4	28.1, 27.0	13.4, 9.6
<b>FS1D</b>	13.9, 14.0	28.2, 27.4	14.3, 13.3
<b>FS2D</b>	4.8, 6.6	34.2, 36.1	29.5, 29.5
<b>FS3D</b>	1.4, 1.5	36.3, 35.3	33.0, 33.8

<sup>a</sup>Energies in kcal/mol. Values in italics are from IEF-PCM calculations with the dielectric constant set to that of acetonitrile.

65–200 °C.<sup>5–13</sup> The extent of reverse polarity can be varied through the R group, and it is the largest in the 2-amino-2-siloxysilenes.<sup>13,14</sup>

Apeloig and co-workers recently calculated that the activation energy for addition of water to a silene with the O atom added to Si increases significantly as the extent of reverse Si=C bond polarization increases.<sup>15</sup> Thus, if the temperature for the thermolysis reaction to a reverse polarized silene can be lowered and if the silene formed is not air and moisture sensitive, one

**Table 2. Correlation Coefficients for Correlation between the Extent of  $\pi$ -Conjugative Reverse Polarization ( $\Sigma\Phi_{RP}(\pi)$ ) as Determined by NRT and a Series of Different Properties**

property	S1A–S3D	FS1A–FS3A, FS1D–FS3D
$r_{SiC}$	0.957	0.944
$n_{SiC}^a$	0.946	0.791
$\Delta q(\text{Si}-\text{C})$	0.625	0.720
$q(\text{Si})$	0.760	0.925
$\Sigma(\text{Si})^b$	0.546	0.782
$\Delta E(\text{silane} \rightarrow \text{silene})$	0.097	0.347, 0.299 <sup>c</sup>
$\Delta E^+(\text{silane} \rightarrow \text{silene})$	0.214	0.560, 0.441 <sup>c</sup>
$\Delta E^+(\text{silene} \rightarrow \text{silane})$	0.623	0.539, 0.565 <sup>c</sup>

<sup>a</sup>Natural bond order of SiC bond. <sup>b</sup>Sum of valence angles at Si. <sup>c</sup>Correlation coefficients in italics from IEF-PCM calculations with dielectric constant set to that of acetonitrile.

**Table 3. Atomic Charges and Charge Differences, Bond Orders of  $\Sigma\Phi_{RP}(\pi)$ , and SiC Bond Lengths and Bond Orders of Silenes S1A–S3D, FS1A–FS3A, FS1D–FS3D, H<sub>2</sub>Si=CH<sub>2</sub>, Me<sub>2</sub>Si=C(SiH<sub>3</sub>)<sub>2</sub>, and (H<sub>3</sub>Si)<sub>2</sub>Si=CMe<sub>2</sub> at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) Level**

silene	$q(\text{Si})$	$q(\text{C})$	$\Delta q(\text{Si}-\text{C})^a$	$\Sigma\Phi_{RP}(\pi)^b$ [%]	$r_{Si=C}$ (Å)	$n_{Si=C}$
<b>S1A</b>	0.08	0.03	0.05	25.2	1.852	1.46
<b>S1B</b>	0.03	0.20	-0.18	36.7	1.870	1.39
<b>S1C</b>	0.30	-0.48	0.79	17.2	1.796	1.67
<b>S1D</b>	0.18	-0.20	0.38	21.7	1.820	1.58
<b>S2A</b>	-0.04	0.25	-0.29	46.9	1.920	1.23
<b>S2B</b>	0.08	0.30	-0.22	22.0	1.838	1.66
<b>S2C</b>	0.29	-0.36	0.65	14.6	1.782	1.77
<b>S2D</b>	0.27	-0.11	0.38	11.0	1.774	1.84
<b>S3A</b>	0.19	-0.41	0.61	22.1	1.819	1.57
<b>S3B</b>	0.21	-0.26	0.47	17.5	1.801	1.74
<b>S3C</b>	0.53	-1.01	1.54	10.4	1.757	1.84
<b>S3D</b>	0.53	-0.75	1.28	6.3	1.746	1.89
<b>FS1A</b>	0.05	-0.02	0.08	20.4	1.836	1.69
<b>FS2A</b>	-0.04	0.18	-0.23	23.4	1.869	1.44
<b>FS3A</b>	0.28	-0.49	0.77	13.1	1.787	1.82
<b>FS1D</b>	0.39	-0.35	0.74	3.5	1.764	1.86
<b>FS2D</b>	0.28	-0.14	0.42	6.4	1.772	1.84
<b>FS3D</b>	0.46	-0.74	1.20	3.7	1.758	1.88
H <sub>2</sub> Si=CH <sub>2</sub>	0.91	-1.08	1.20		1.711	2.00
Me <sub>2</sub> Si=C(SiH <sub>3</sub> ) <sub>2</sub>	1.72	-1.77	3.49		1.721	1.88
(H <sub>3</sub> Si) <sub>2</sub> Si=CMe <sub>2</sub>	0.46	-0.53	0.99		1.749	1.89

<sup>a</sup>The charge on the Si atom minus the charge on the C atom of the Si=C double bond. <sup>b</sup>Combined contribution of resonance structures  $\Phi_B$  and  $\Phi_C$  to the total electronic structure.

could carry out the thermolysis reaction under standard conditions, rendering it a wide applicability. Indeed, we previously found that some of the transient 2-amino-2-siloxysilenes can be formed and further reacted with dienes when refluxed open to the ambient atmosphere in nondistilled THF, and high yields were found similar to those resulting when the reaction was performed under inert conditions.<sup>13,16</sup>

An apparent problem with the formation of silenes strongly influenced by the  $\pi$ -conjugative contribution to reversed Si=C bond polarization through a thermolytic or photolytic [1,3]-silyl shift is the low barrier for back-transfer of a TMS group, leading to regeneration of the starting silane.<sup>13</sup> This is exemplified by the formation of 2-amino-2-siloxysilenes. Some years ago, Lickiss and Brook attempted formation of 1,1-bis(trimethylsilyl)-2-(*N,N*-dimethylamino)-2-(trimethylsilyloxy)silene through photolysis of tris(trimethylsilyl)-*N,N*-dimethylsilaacetamide, however, without success.<sup>17</sup> We later found that the 2-amino-2-siloxysilene is 17.5 kcal/mol less stable than the corresponding silane, and a barrier of only 10.7 kcal/mol for the back-reaction (B3LYP/6-31G(d)) makes

(16) Guliashevili, T., Ph.D. thesis, Uppsala University (Sweden), Interfaculty Units, Acta Universitatis Upsaliensis, 2004.

(17) Al-Juaid, S. S.; Deriouishe, Y.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1991**, *403*, 293.

(5) Brook, A. G.; Ionkin, A.; Lough, A. J. *Organometallics* **1996**, *15*, 1275.

(6) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Organometallics* **1996**, *15*, 3836.

(7) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Main Group Chem.* **1996**, *1*, 219.

(8) Naka, A.; Ohnishi, H.; Ohshita, J.; Ikadai, J.; Kunai, A.; Ishikawa, M. *Organometallics* **2005**, *24*, 5356.

(9) Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **2003**, *685*, 162.

(10) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 83.

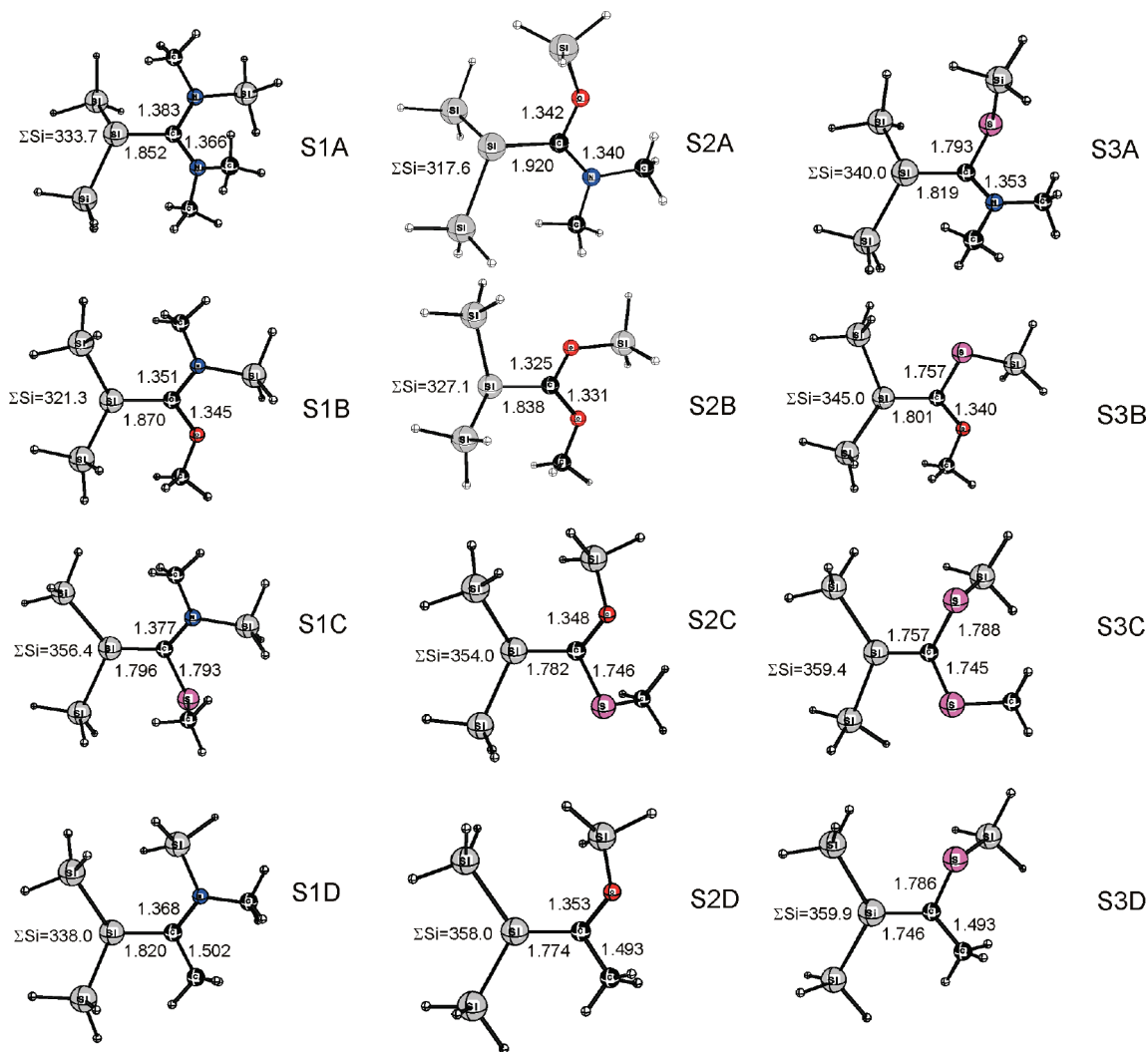
(11) Naka, A.; Ishikawa, M.; Matsui, S.; Ohshita, J.; Kunai, A. *Organometallics* **1996**, *15*, 5759.

(12) Ohshita, J.; Yoshimoto, K.; Iida, T.; Kunai, A. *J. Am. Chem. Soc.* **2001**, *123*, 8400.

(13) El-Sayed, I.; Guliashevili, T.; Hazell, R.; Gogoll, A.; Ottosson, H. *Org. Lett.* **2002**, *4*, 1915.

(14) Ottosson, H. *Chem.–Eur. J.* **2003**, *9*, 4144.

(15) Bendikov, M.; Quadt, S. R.; Rabin, O.; Apeloig, Y. *Organometallics* **2002**, *21*, 3930.



**Figure 1.** Optimal geometries of silenes **S1A**–**S3D** at the B3LYP/6-31G(d) level. Distances in Å and angles in deg.

it difficult to directly observe silene formation with standard spectroscopic techniques.<sup>13</sup> It was only when the thermolysis was carried out in the presence of 2,3-dimethyl-1,3-butadiene as trapping reagent, leading to formation of a [4 + 2] cycloadduct in high yields, that evidence for 2-amino-2-siloxysilenes formation was obtained.<sup>13</sup> Recently, Ohshita and co-workers also carried out kinetic studies and experimentally determined the activation barriers for the thermolytic [1,3]-TMS shift of the silanes (Me<sub>3</sub>Si)<sub>3</sub>SiC(=O)R to the corresponding Brook-type silenes.<sup>18</sup> A small yet noticeable reduction of ~1 kcal/mol in the isomerization barrier was found when R was changed from adamantyl to isopropyl, indicating that the donicity of the R group is important for the reaction profile.

With this background, it should now be interesting to explore which features of the silanes (**R**) and silenes (**S**) affect the activation barrier and the relative energy of silenes formed thermolytically through [1,3]-silyl shift. We reason that novel target silenes influenced by reverse Si=C bond polarity could be identified through quantum chemical calculations. Primarily, we examined the model systems shown in Scheme 3; however, for some systems we also replaced the SiH<sub>3</sub> groups by SiMe<sub>3</sub> groups, leading to systems that could be probed experimentally. At the end, we probed how dialkyl substitution at Si affects the reaction profile.

(18) Ohshita, J.; Takahashi, H.; Kunai, A.; Komaguchi, K.; Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **2006**, *691*, 541.

### Computational Methods

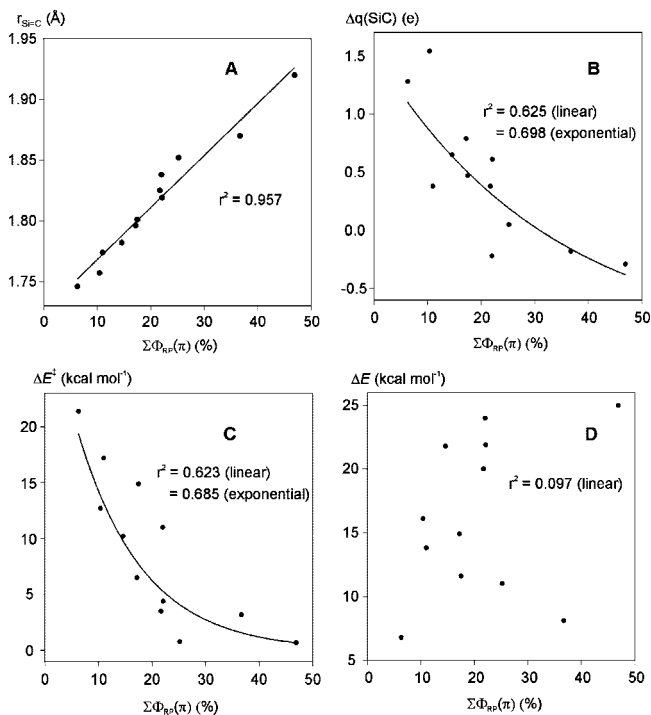
Geometry optimizations of reactants (silanes **R**), products (silenes **S**), and transition states (**TS**) were performed using the B3LYP hybrid density functional theory (DFT) method.<sup>19</sup> The possible conformers of the various silanes and silenes were located, and the analysis herein is based on the lowest energy ones. For a selected number of model silanes, silenes, and transition states, geometries were also optimized at the MP2 and CCSD levels. For the B3LYP and MP2 optimizations we used the 6-31G(d) valence double- $\zeta$  basis set of Pople and Hariharan,<sup>20</sup> whereas for the CCSD optimizations the 6-311G(d) valence triple- $\zeta$  basis set of Pople and co-workers was selected.<sup>21</sup> Frequency calculations were performed at the B3LYP and MP2 levels to probe the character of the stationary points located. Studies by Truhlar and co-workers have shown that the inclusion of diffuse basis functions is more important for DFT calculations than increasing the size of the basis set from double- $\zeta$  to triple- $\zeta$  quality.<sup>22</sup> Therefore, we carried out single-point energy calculations at the B3LYP/6-31+G(d) level of computation on all optimized geometries. Calculations based on

(19) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(20) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213.

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

(22) Lynch, B. J.; Zhao, Y.; Truhlar, D. J. *J. Phys. Chem. A* **2003**, *107*, 1384.



**Figure 2.** Dependencies of (A)  $r_{\text{SiC}}$ , (B)  $\Delta q(\text{SiC})$  charge differences, (C) transition state energy for silene (product) to silene (reactant) route, and (D) relative energy of silene as compared to the energy of the corresponding silane, on the weight of  $\pi$ -conjugated reverse polarized resonance structures  $\Sigma\Phi_{\text{RP}}(\pi)$  as determined by NRT. Note that the exponential fit of  $\Delta q(\text{SiC})$  against  $\Sigma\Phi_{\text{RP}}(\pi)$  has been done for  $\Delta q(\text{SiC})$  values shifted  $+1e$ .

the CCSD/6-311G(d) geometries were also performed at the CCSD(T) level using the cc-pVTZ basis set of Woon and Dunning.<sup>23</sup>

Natural population analysis (NPA)<sup>24</sup> and natural resonance theory (NRT)<sup>25–27</sup> calculations were performed at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level of theory to determine the atomic charges and the influence of  $\pi$ -conjugated reverse polarized resonance structures, respectively. The total weight of the reverse polarized resonance structures  $\Phi_{\text{B}}$  and  $\Phi_{\text{C}}$  ( $\Sigma\Phi_{\text{RP}}(\pi)$ , Scheme 2) for the electronic structure of a silene as determined by NRT is taken as a measure of the influence of  $\pi$ -conjugative reverse polarization of that silene.

For the fully substituted silenes, we also made single-point energy calculations employing the polarizable continuum model in the integral-equation formalism (IEF-PCM) of Tomasi and co-workers and with acetonitrile as a polar solvent ( $\epsilon = 37$ ) to simulate solvation effects.<sup>28</sup> The calculations were performed with Jaguar 5.5, Gaussian03, and Weinhold's NBO program in a version that runs together with Jaguar.<sup>29–31</sup>

## Results and Discussion

First, we discuss model silenes with silyl substituents at Si since these resemble Brook-type silenes and the transient 2-amino-2-siloxysilenes produced thermally from acylsilanes and carbamylsilanes, respectively. It has also been shown that silyl substituents at Si help reduce the  $\text{Si}^{\delta+}=\text{C}^{\delta-}$  bond polarity.<sup>32</sup> Thus, there is both a  $\pi$ - and a  $\sigma$ -component to reverse SiC polarization. Using the NRT method, we analyze the reaction profile, charge distribution, and geometry effects depending on the  $\pi$ -contribution to the reverse polarization effect ( $\Sigma\Phi_{\text{RP}}(\pi)$ ). On the basis of the results from the calculations on these model systems, we probe a selection of more realistic target systems with the silyl groups exchanged for trimethylsilyl groups. To justify the usage of B3LYP for the bulk of the calculations, we compared geometries, relative energies of silenes, and activation energies for a small set of minimal model compounds against CCSD and CCSD(T) results (see Supporting Information). Calculations were also performed at the MP2 level. From this comparison we conclude that B3LYP is a significantly better choice as an inexpensive method to describe the energies. However, MP2 geometries for the small selection of systems agree slightly better with those from CCSD. It should furthermore be noted that in cases where several conformers exist for a silene or silene we discuss the results for the most stable conformer.

**Structures and Charge Distributions of Silenes (Z = SiH<sub>3</sub>).** The set of silenes **S1–S3** contain species with SiC bond lengths typical of a true Si=C double bond (1.7039 Å in H<sub>2</sub>Si=CH<sub>2</sub> according to millimeter wave spectroscopy),<sup>33</sup> as well as silenes with SiC bond lengths typical of Si–C single bonds (1.87–1.89 Å)<sup>34</sup> (Table 1). Since the influence of  $\pi$ -conjugative reverse polarization should be reflected in the SiC (double) bond length and bond order, we argue that a silene that is strongly influenced by  $\Sigma\Phi_{\text{RP}}(\pi)$  more easily rotates around the SiC (double) bond. A weakened  $\pi$ -bond should allow the molecule to more easily adopt the conformation from which 1,3-silyl shift occurs, leading to a lowered barrier for the back-reaction.

To examine the extent of reverse polarization, we performed natural resonance theory (NRT) calculations at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level, and the correlation between the weight  $\Sigma\Phi_{\text{RP}}(\pi)$  and various properties for silenes **S1–S3** is listed in Table 2. From these calculations one sees that  $\Sigma\Phi_{\text{RP}}(\pi)$  roughly follows the intuitively expected order based on the electron-donating ability of the substituents at the C atom (Table 3), and  $\Sigma\Phi_{\text{RP}}(\pi)$  also correlates well with the SiC bond lengths as well as with the SiC bond order (Table 2 and Figure 2A). For silenes **S3A–S3D**, the SiC bond length decreases when going from **S3A** to **S3D** (Figure 3), and the same trend is seen for silenes **S2A–S2D** but not for **S1A–S1D**. Since the N atom of an amino group generally is a better  $\pi$ -electron donor than the O atom of an alkoxy group, one could expect the SiC bond

(23) Woon, D. E., Jr *J. Chem. Phys.* **1993**, *98*, 1358.

(24) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(25) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593.

(26) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610.

(27) Glendening, E. D.; Badenhop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

(28) (a) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (b) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151. (c) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *J. Chem. Phys. Lett.* **1998**, *286*, 253. (d) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.

(29) *Jaguar 5.5*, Schrodinger; LLC: Portland, OR, 2003.

(30) Frisch, M. J. et al. *Gaussian 03, Revision D.01*; Gaussian, Inc.: Pittsburgh, PA, 2001.

(31) Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 50*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

(32) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovski, D. *J. Am. Chem. Soc.* **1996**, *118*, 12228.

(33) (a) Bailleux, S.; Bogey, M.; Breidung, J.; Burger, H.; Fajgar, R.; Liu, Y.; Pola, J.; Senzlober, M.; Thiel, W. *Angew. Chem. Int. Ed., Engl.* **1996**, *35*, 2513. (b) Bailleux, S.; Bogey, M.; Breidung, J.; Burger, H.; Fajgar, R.; Liu, Y.; Pola, J.; Senzlober, M.; Thiel, W. *J. Chem. Phys.* **1997**, *106*, 10016.

(34) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Vol. 1, pp 227–303.



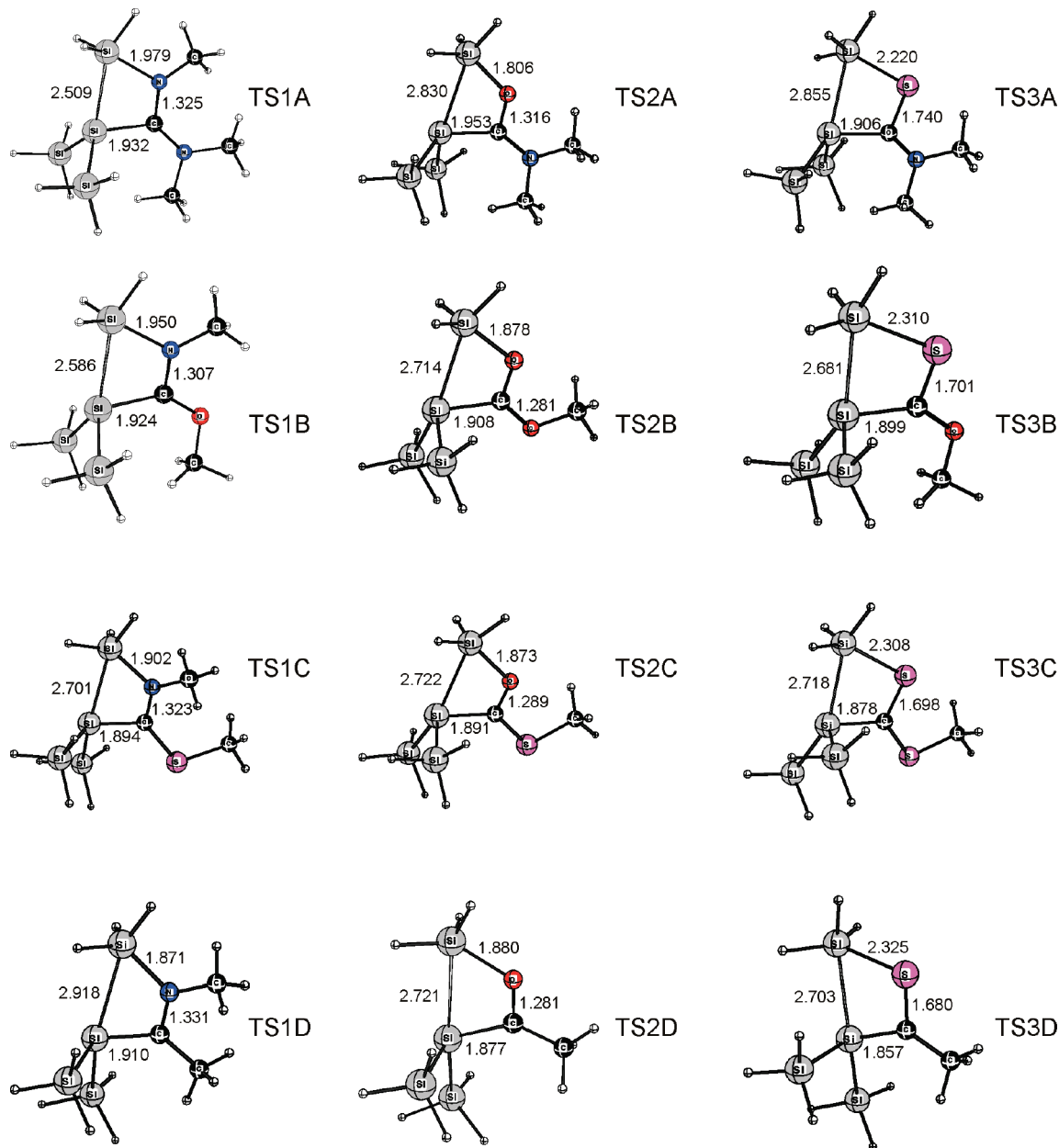


Figure 3. Optimal geometries of TS1A–TS3D. Distances in Å.

Table 4. Geometric Data of the Transition States of the Me<sub>3</sub>Si-Substituted Systems<sup>a</sup>

silene	Si–X	Si–Si	Si–C	C–X
FS1A	1.990	2.677	1.939	1.335
FS2A	1.931	2.747	1.946	1.297
FS3A	2.344	2.846	1.941	1.738
FS1D	2.031	2.719	1.916	1.309
FS2D	1.954	2.829	1.898	1.279
FS3D	2.435	2.844	1.870	1.694

<sup>a</sup> Distances in Å and angles in deg.

length to be a little shorter in silenes **S2A**–**S2D** than in silenes **S1A**–**S1D**. This is also observed for all species except the **S1A**/**S2A** pair, presumably a result of larger steric congestion in **S1A** than in **S2A**. When the lp(N) of the amino group cannot conjugate with the Si=C bond, its  $\pi$ -donor ability is insignificant, an effect that was exploited earlier by Müller and Apeloig for design of a tetraaminodisilene with a Si=Si double bond.<sup>35</sup>

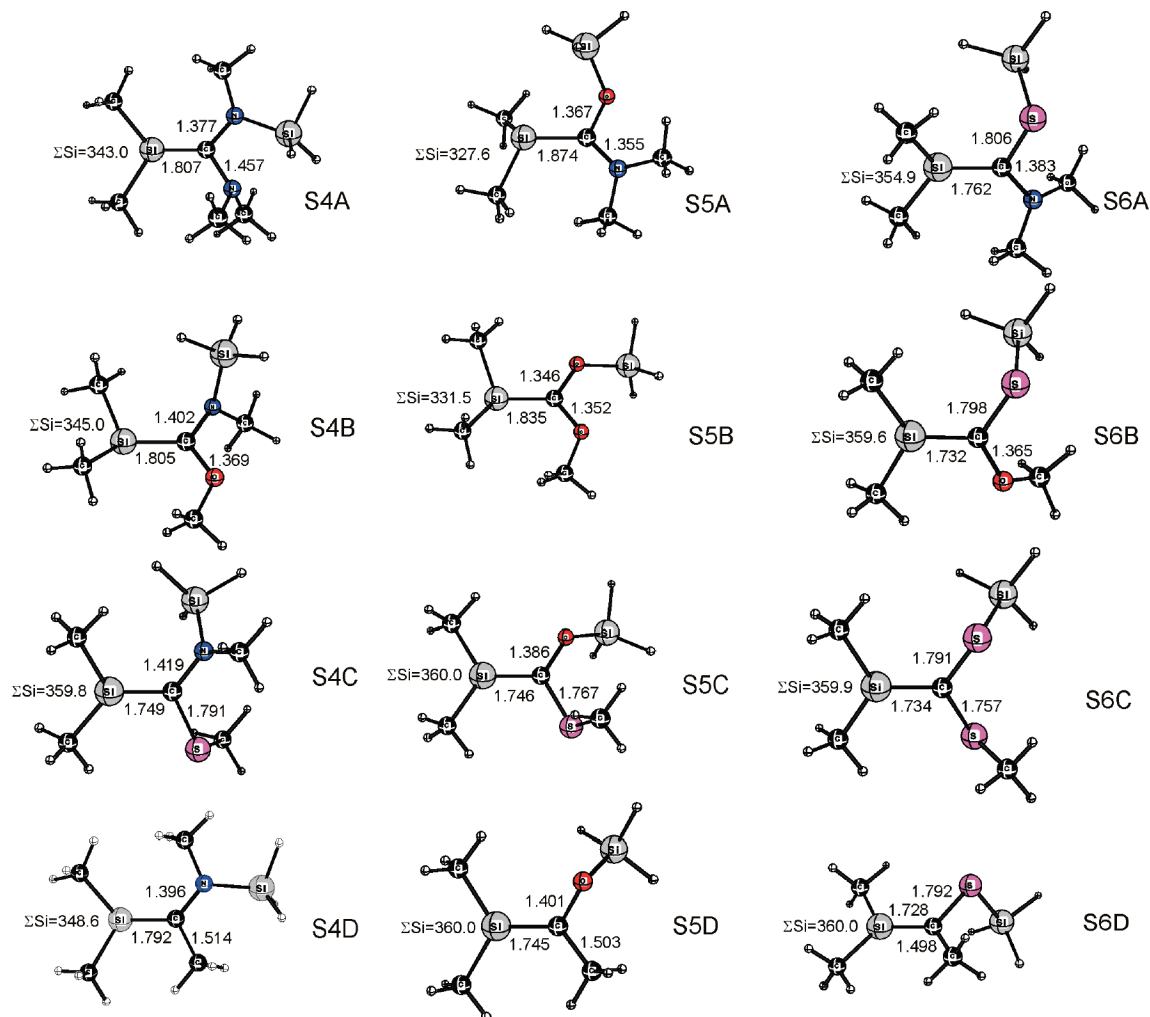
Table 5. Reaction Energies and Activation Energies for the Formation of the Methylated Silenes S4A–S6D<sup>a</sup>

silene	$\Delta E$ [silene – silane]	$\Delta E^\ddagger$ [silene → silene]	$\Delta E^\ddagger$ [silene → silane]
<b>S4A</b>	22.0	24.7	2.7
<b>S4B</b>	27.8	32.4	4.6
<b>S4C</b>	20.1	32.3	12.2
<b>S4D</b>	24.3	35.2	10.9
<b>S5A</b>	36.1	37.4	1.3
<b>S5B</b>	28.0	41.6	13.6
<b>S5C</b>	20.3	40.5	20.2
<b>S5D</b>	20.4	44.1	23.7
<b>S6A</b>	28.5	33.4	4.9
<b>S6B</b>	26.4	41.2	14.8
<b>S6C</b>	17.9	39.2	21.3
<b>S6D</b>	9.1	35.6	26.5

<sup>a</sup> Energies in kcal/mol.

A note should be given for silene **S2A**, which is the silene that is most strongly influenced by reverse polarization among those analyzed herein. The geometry of **S2A** as seen in Figure 1 clearly reveals a weakened  $\pi$ -bond, as the dihedral angles

(35) Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3457.



**Figure 4.** Optimal geometries of the silenes **S4A–S6D**. Distances in Å and angles in deg.

$Z\text{--Si--C--Y}$  and  $Z\text{--Si--C--X}$  deviate very much from the ideal  $0^\circ$  and  $180^\circ$  of a planar silene ( $\text{Si--Si--C--N} = 107.9^\circ$ ,  $\text{Si}'\text{--Si--C--N} = -2.9^\circ$ ,  $\text{Si--Si--C--O} = -82.4^\circ$ , and  $\text{Si}'\text{--Si--C--O} = 166.9^\circ$ ). A  $\pi$ -orbital axis vector analysis (POAV)<sup>36</sup> gives a dihedral angle between the two  $p/sp^n$  atomic/hybrid orbitals ( $3 \leq n$ ) of the  $\text{SiC}$  (double) bond of  $37.7^\circ$ , in line with a markedly distorted and weakened double bond, effected through strong contribution of  $\Sigma\Phi_{\text{RP}}(\pi)$  that places negative charge at Si, leading to a strong pyramidalization at this atom.

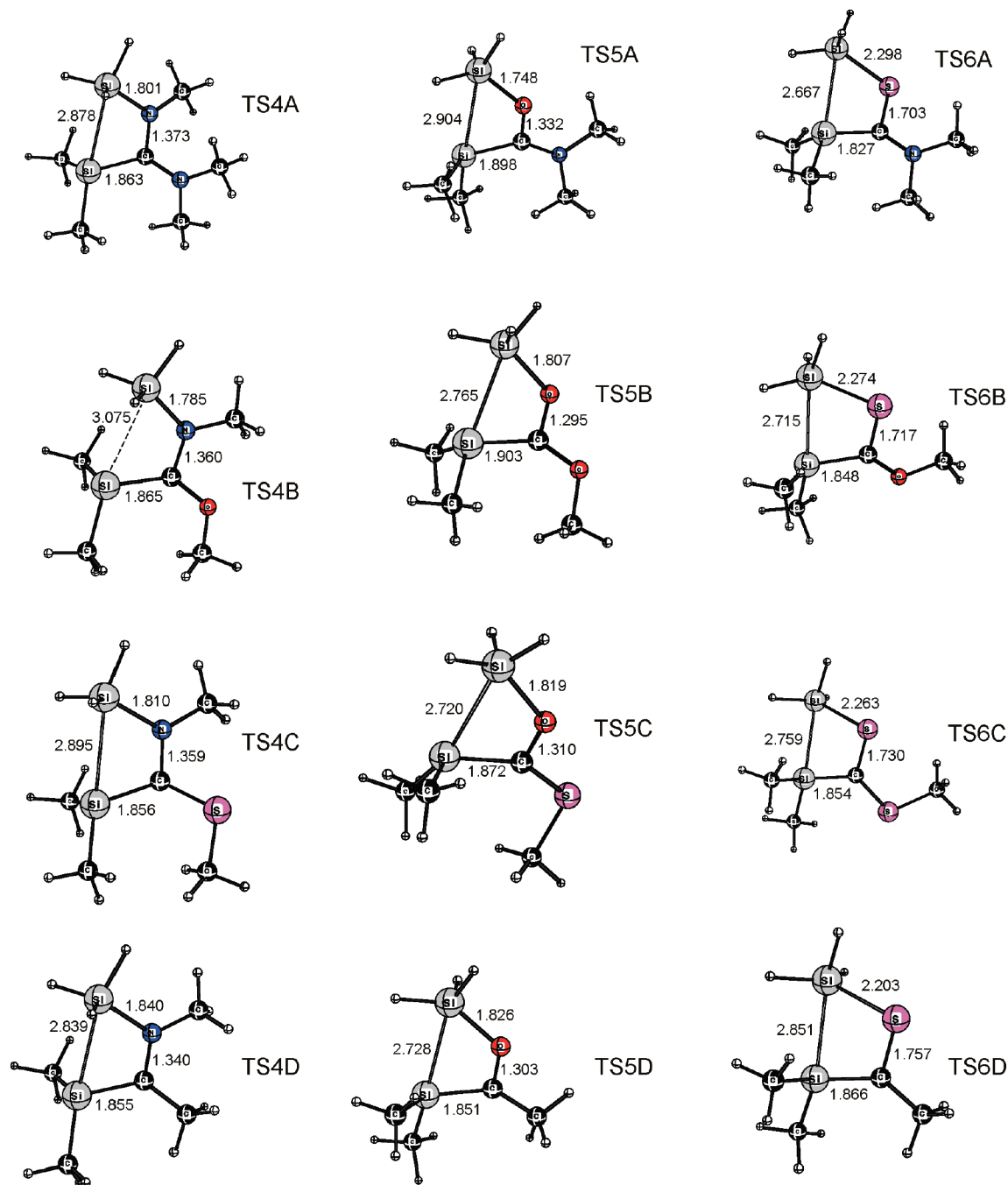
The pyramidalization at Si, as measured by the sum of valence angles at this atom ( $\Sigma\text{Si}$ ), is larger in silenes with longer SiC bonds (Figure 1),<sup>14</sup> and silene **S2A** has the longest SiC bond and the smallest  $\Sigma\text{Si}$  angle sum. As expected, the  $\Sigma\text{Si}$  angle sum shows a trend to become smaller as the  $\pi$ -conjugative influence of reverse polarization is increased (Table 3), consistent with a higher negative charge on Si. The charge difference between C and Si ( $\Delta q(\text{SiC})$ ) is a measure of the degree of reverse SiC bond polarization, i.e., the combined  $\sigma$ - and  $\pi$ -contributions. The correlation between  $\Sigma\Phi_{\text{RP}}(\pi)$  and  $\Delta q(\text{SiC})$  is modest (Table 2 and Figure 2B), but the charges on Si and C are also influenced by the inductive withdrawing/donating ability of the groups bonded to these atoms. The modest correlation thus demonstrates that the reverse polarization effect has both a  $\sigma$ - and a  $\pi$ -component. It is noteworthy that the charge difference, for a given group X, tends to increase

in the order  $Y = \text{OMe}, \text{NMe}_2, \text{Me}, \text{SMe}$ . The unusual order between the OMe and  $\text{NMe}_2$  groups is likely a result of the larger steric bulk of the  $\text{NMe}_2$  group than of the OMe group.

**Silane to Silene Rearrangement Aptitude ( $Z = \text{SiH}_3$ ).** The  $\pi$ -contribution to reverse polarization has a dramatic effect on geometry, and its effect on reactivity should also be significant. Indeed, silenes with the longest SiC bond lengths have the lowest barriers for the reverse reaction, and the activation energies correlate weakly with both the contribution of  $\Sigma\Phi_{\text{RP}}(\pi)$  ( $r^2 = 0.685$  for exponential fit) and the SiC bond length ( $r^2 = 0.728$  for exponential fit) (Table 2 and Figure 2C). The correlation between  $\Sigma\Phi_{\text{RP}}(\pi)$  and activation energies is presumably weakened by factors such as bulk and differences in the strengths of the bonds formed and broken during the reaction. On the other hand, the activation energies for the back-reaction seem to depend on  $\Delta q(\text{SiC})$  to a much lower degree ( $r^2 = 0.334$  for linear fit and 0.364 for exponential fit). Here it should be noted that the most appropriate relationships between the various properties (linear, exponential, or another dependence) are unknown, and we have therefore applied both linear and exponential fits. A reduction in the transition state energy by 2 kcal/mol was also observed by Ohshita et al. for the  $\text{H}_3\text{SiH}_2\text{SiC(=O)R}$  to  $\text{H}_2\text{Si=C(OSiH}_3\text{)R}$  rearrangement when going from  $\text{R} = \text{H}$  to  $\text{R} = \text{Me}$ .<sup>18</sup>

In general, the longer the SiC bond length of the silene, the longer the corresponding bond length in the transition state for its formation (Figure 3). Thus, the SiC bond lengths tend to

(36) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243.



**Figure 5.** Optimal geometries of TS4A–TS6D. Distances in Å.

decrease when going from TS1A to TS1D, from TS2A to TS2D, and from TS3A to TS3D. On the other hand, the Si–X bond length in the transition state shows a tendency to increase when going from TS2A to TS2D and from TS3A to TS3D (Figure 3), but decrease when going from TS1A to TS1D.

The silenes are always higher in energy than the corresponding silane reactants, ranging from 6.8 kcal/mol for S3D to 25.0 kcal/mol for S2A. However, there is no correlation between  $\Sigma\Phi_{\text{RP}}(\pi)$  of a silene and its energy relative to that of the silane ( $r^2 = 0.097$ , Figure 2D and Table 3). It is noteworthy that S2D and S3D, which have Y = Me, have the highest barriers for the back-reaction within the groups they belong to. However, only silene S3D has a barrier that is above 20 kcal/mol, which is consistent with Brook's silene with X = O and Y = 1-Ad being a particularly stable and isolable silene. The thermolytic [1,3]-silyl shift will therefore most likely not be a successful

means for formation of isolable silenes that are strongly influenced by  $\Sigma\Phi_{\text{RP}}(\pi)$ , as the barriers for the back-reactions are generally very low, in accordance with our initial hypothesis. Instead, silenes of this type could be trapped with dienes, as these reactions seem to proceed with high [4 + 2] selectivity. Isolable species with formal Si=C bonds that are strongly influenced by reverse polarization need to be formed by other means, e.g., through treatment of acylpolysilanes with *t*BuOK, giving potassium silenolates.<sup>37</sup>

**Trimethylsilyl-Substituted Species.** Having established a connection between  $\Sigma\Phi_{\text{RP}}(\pi)$  and the reaction profile of the model compounds, we calculated a few systems with the silyl groups exchanged with trimethylsilyl (TMS) groups. These

(37) Guliashvili, T.; El-Sayed, I.; Fischer, A.; Ottosson, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1640.

systems could be investigated experimentally and include silenes **FS1A**, **FS2A**, **FS3A**, **FS1D**, **FS2D**, and **FS3D**, which correspond to the model silenes **S1A**, **S2A**, **S3A**, **S1D**, **S2D**, and **S3D**, respectively. The TMS-substituted silenes are less influenced by reverse polarization by 3–23% than the model silenes, as the steric bulk of the TMS group prevents good alignment of the lone-pair orbital of the heteroatom X with the Si=C  $\pi$ - and  $\pi^*$ -orbitals (Table 3). However, similar to the model systems, the full systems **FS1A**, **FS2A**, and **FS3A** are more influenced by reverse polarization than **FS1D**, **FS2D**, and **FS3D**.

The SiC bond lengths are shorter in the TMS-substituted silenes than in the corresponding model silenes (Table 3), a result of the lower weight of  $\Sigma\Phi_{\text{RP}}(\pi)$  in the full systems. The SiC bond lengths of the full systems also correlate well with the weight  $\Sigma\Phi_{\text{RP}}(\pi)$  ( $r^2 = 0.944$ ), as well as with the bond orders ( $r^2 = 0.929$ ). However, there is a very poor correlation between  $\Sigma\Phi_{\text{RP}}(\pi)$  and the barrier height separating the silene from the silane for the full systems ( $r^2 = 0.483$  for exponential fit). Interestingly, the correlation between  $\Delta q(\text{SiC})$  and  $\Sigma\Phi_{\text{RP}}(\pi)$  is slightly better than for the model systems ( $r^2 = 0.759$  vs 0.698 for exponential fits), but this improved correlation could be due to a too small number of TMS-substituted systems contained in the study rather than to a truly improved correlation.

The activation energies for formation of the TMS-substituted silenes are generally higher than for the silyl substituents, which should stem from larger steric congestion in the transition state. This is reflected in the Si–X and C–X distances, which tend to be longer in the transition states for the formation of the TMS-substituted silenes than for the formation of the corresponding model silenes (Figure 3 and Table 4). Furthermore, the energies of the silenes relative to the silane reactants are lower than for the model systems by up to 9 kcal/mol, and consequently, the barriers for the back-reaction are higher for the TMS-substituted silenes.

For the TMS-substituted systems we also performed calculations using Tomasi's polarized continuum model in the integral-equation formalism (IEF-PCM) to simulate the action of a polar solvent (Table 1). It is noteworthy that these calculations treat only the nonspecific solvent interaction, and this represents an approximation, as the specific interaction between a nucleophilic solvent molecule and an electrophilic silene is not treated. We selected acetonitrile to represent the polar solvent ( $\epsilon = 37$ ). No general trend in the effect of a polar solvent on the relative energy of the silenes was found. For **FS2A**, **FS3A**, and **FS2D** it increases, for **FS1D** and **FS3D** it is similar, while for **FS1A** it is lower than in the gas phase. With regard to the activation energies for the back-reaction from the silene to silane they are similar or slightly lower than in the gas phase. The trend between the various silenes, however, does not change.

With increases in the barriers for back-reaction by approximately 10 kcal/mol when going from the silyl to the TMS-substituted silenes, we postulate that **FS2B**, **FS2C**, **FS3B**, and **FS3C** will have activation energies in the range 20–25 kcal/mol, respectively, which should give them lifetimes sufficiently long for experimental investigations. However, their influence by  $\pi$ -conjugative reverse polarization will most likely be only modest (10–15%). With high barriers of 29–34 kcal/mol, **FS2D** and **FS3D** are templates for isolable silenes, and **FS2D** is indeed a small Brook-type silene. The additional steric bulk caused by the 1-Ad group at the 2-position then provides hindrance for dimerization.

**Brook-Type Silenes.** We also performed calculations on the silene with three TMS groups and one *t*-Bu group,  $\text{TMS}_2\text{Si}=\text{C}(\text{OTMS})t\text{Bu}$  (**BS2D**). The reaction from the acylpolysilane to

the silene is shown to be endothermic by 12.0 kcal/mol, and the activation energy is 33.9 kcal/mol. The activation enthalpy determined experimentally for the same reaction is 26.8 kcal/mol,<sup>18</sup> and at the B3LYP/6-31G(d) level the  $\Delta H^\ddagger$  at 298 K is 21.1 kcal/mol. B3LYP may thus underestimate the reaction barriers for these reactions.

The transition state for the back-reaction lies 22 kcal/mol above **BS2D**, which is similar to the case for **S2D**, however, smaller than for **FS2D**. Primarily, it is the silene **BS2D** that has a higher relative energy when compared to that of **FS2D**, a result of larger steric congestion in **BS2D** caused by the *t*-Bu group. Steric factors are important in hindering the dimerization reaction; however, they prevent the silene from adopting a conformation in which the  $\pi$ -conjugative contribution to reverse polarization is maximal. Also, if the internal congestion is excessive, it will raise the relative energy of the silene and make it more prone for reacting back to the acylsilane. The calculated SiC bond length is 1.784 Å, a slight elongation when compared to the measured value for the corresponding silene with R = 1-Ad (1.764 Å).<sup>3</sup> The  $\pi$ -conjugated reverse polarized resonance structure contributes 7.4% to the total electronic structure of **BS2D**.

**Alkyl Substitution at Si.** Two methyl groups modeled the effect of alkyl substituents at Si. The dimethylated silenes **S4–S6** are nearly always higher in relative energy than the corresponding silylated silenes **S1–S3**, the exception being **S5C**, which is 1.5 kcal/mol below **S2C** (Tables 1 and 5). The SiC bond lengths in **S4–S6** are also shorter than in the analogous **S1–S3** (Figure 4), in line with our previous findings.<sup>14</sup> The weights  $\Sigma\Phi_{\text{RP}}(\pi)$  are in general lower (Table S3, Supporting Information), but there are still very good linear correlations of  $\Sigma\Phi_{\text{RP}}(\pi)$  with the SiC bond lengths and bond orders (0.955 and 0.948, respectively, Table S4). It is also known from comparison of Wiberg's and Apeloig's isolable silenes that alkyl substituents at the Si of an SiC bond cause bond shortenings when compared to silyl groups.<sup>32,38</sup> Because of the short SiC bonds of **S4–S6**, rotations about these bonds are thus more restricted and more energy will be required for the molecule to adopt the preferred conformation for the [1,3]-silyl shift. Consequently, the activation energies for this migration go up. As a result of the higher relative energy of the silenes, the transition states for the methylated species also tend to be more silene-like with longer Si–Si and shorter Si–C distances than for the corresponding transition states with Z = SiH<sub>3</sub> (Figures 3 and 5). Still, there is a weak correlation between the activation energy for silene to silane transformation and the weight  $\Sigma\Phi_{\text{RP}}(\pi)$  ( $r^2 = 0.699$  for an exponential fit).

Consequently, even though the two methyl substituents at Si destabilize the silene relative to the reactant, the barrier separating the silene from the silane reactant is higher when compared to the silylated silenes, suggesting that the methylated silenes will be more stable with regard to the back-reaction. On the other hand, they have larger Si<sup>δ+</sup>=C<sup>δ-</sup> bond dipoles, which will lead to more rapid dimerization as well as attack by nucleophilic reagents at the Si atom.

## Conclusions

Natural resonance theory (NRT) calculations on substituted silenes reveal good linear correlation between the weights of  $\pi$ -conjugative reverse polarized resonance structures ( $\Sigma\Phi_{\text{RP}}(\pi)$ ) and SiC bond lengths ( $r^2 = 0.957$ ). The correlation between

(38) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229.



the barrier height for back-reaction from silene to silane reactant and the extent of reverse polarization is only modest ( $r^2 = 0.685$  for exponential fit), whereas for the forward reaction there is no correlation ( $r^2 = 0.214$  for linear fit). The silenes most strongly influenced by the  $\pi$ -conjugative reverse polarization effect, **S1A–S1D**, have lower barriers for back-reaction to the corresponding silanes than naturally polarized silenes. The thermolysis reaction is therefore not suitable for formation of isolable silenes strongly influenced by the  $\pi$ -conjugative reverse polarization effect. Such silenes, which are formed thermolytically through [1,3]-silyl shifts, instead need to be trapped with, for example, dienes.

To expand the applicability of our investigation, we also calculated the TMS-substituted silenes **FS1A**, **FS2A**, **FS3A**, **FS1D**, **FS2D**, and **FS3D**. The activation energies for both their formation and back-reaction to the corresponding silanes are generally higher due to steric congestion at the transition state. They are also less influenced by the  $\pi$ -conjugative reverse

polarization effect than the model silenes, which translates to higher barriers for the silene to silane reaction.

Calculations were also performed on the systems with two of the silyl groups on Si replaced by methyl groups. The activation energies for formation of these silenes are in general larger. The same applies for the back-reaction, a result of the fact that these silenes are less influenced by reverse polarization.

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**Supporting Information Available:** Listings of Cartesian coordinates and absolute electronic energies of all investigated compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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