Ab initio Study of Some Intramolecularly Donor-Stabilized Silenes

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Keywords: Silenes / Ab initio calculations / Donor-acceptor systems

Ab initio calculations were performed to predict geometric structures, stabilizing energies and rotational barriers of some intramolecularly donor-stabilized silenes. Calculations were performed using the HF, MP2, and B3LYP method with the 6-31G(d) and 6-31++G(d,p) basis set. Results were compared to experimentally available X-ray structures and energy barriers known from temperature dependent ^{1}H NMR measurements. Various approaches were applied to get an insight into the remarkable stability of these thermodynamically stabilized Si=C compounds. The results indicate a strong stabilizing effect of the intramolecular Si–N donor-acceptor bond.

1. Introduction

Silenes, silicon derivatives with an Si=C double bond, are extremely labile compounds. In absence of scavenger reagents they undergo rapid dimerizations or oligomerizations, if they are not stabilized. A kinetic stabilization can be achieved by means of bulky substituents attached to the Si=C group. Some highly congested silenes could be isolated and structurally characterized.[1,2] Coordination of donor molecules like amines, THF or fluoride anions to the electrophilic silene silicon atom leads to an effective thermodynamic stabilization of the compounds.[3–6] A particularly effective stabilization is expected, when substituents with donor groups are introduced to the silenes and intramolecular donor–acceptor interaction between this donor group and the electrophilic silicon center is possible. Such intramolecular N→Si coordination was concluded from theoretical calculations of Gusel′nikov et al.[7] for a 1-methylene-5-methyl-2,8-dioxa-5-aza-1-silacyclooctane, and a stable dibenzosilafulvene with an 8-dimethylaminomethyl-1-naphthyl group at the silicon atom was isolated by Chernyshev et al.[8,9] However, no X-ray crystal structure analysis of the compound could be performed to validate their results.

Recently we were able to obtain the following silenes (Figure 1):[10–12]

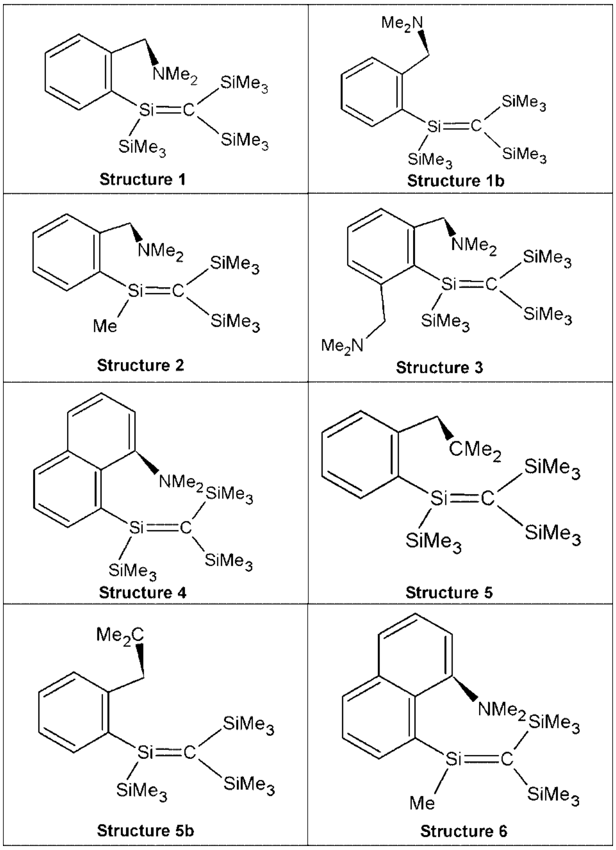

Figure 1. Selected structures of studied substances (schematically).

1-[2-(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**1**),

1-[2-(dimethylaminomethyl)phenyl]-1-methyl-2,2-bis(trimethylsilyl)silene (**2**),

1-[2,6-bis(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**3**), and

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Supporting information for this article is available on the WWW under http://www.eurjic.com or from the authors.

DOI: 10.1002/ejic.200500126

1-(8-dimethylamino-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**4**).

They were clearly characterized by X-ray structural analyses as intramolecularly donor-stabilized silenes. They proved to be thermally stable up to 140 °C and have a dramatically reduced reactivity compared with uncomplexed silenes.

In this paper we report some ab initio calculations of the geometric structures and energies of **1**, as well as some related compounds. The aim of these calculations was to estimate the impact of the intramolecular Si–N donor bond on the Si=C double bond. Additionally, the temperature dependent ^{1}H NMR spectra of **1**, **2** and **3** were interpreted in form of a hindered rotation about the Si=C bond and evaluated quantitatively by comparison of experimental data for the Gibbs activation energy $\Delta G^{\neq}$ with values calculated by ab initio methods.

2. Results and Discussions

The experimentally available X-ray structures of **1**, **2** and **3**[10–12] can be compared to the quantum mechanically fully optimized geometric structures of the isolated species. Obviously, some deviations between the isolated species and the species in the solid phase are to be expected, since packaging effects in the solid phase could not be accounted for in the ab initio calculations. Nevertheless, the geometric structure obtained by using the HF/6-31++G(d,p) method agrees favorably with the X-ray structure, as the results in Table 1 show for **1**. Worth mentioning is the short interatomic Si···N distance of about 2.0 Å, which is much shorter than the sum of the van der Waals radii (3.5 Å) and longer than a covalent Si–N bond (about 1.8 Å), supporting the idea of an Si···N donor–acceptor stabilized interaction. Therefore a distinct pyramidalization at the silene silicon center (sum of angles < 350°) is observed, whereas the configuration at the silene carbon atom is trignonal planar (sum of angles > 359°). The Si=C bond length is about 1.76 Å. This is distinctly longer than in the similarly substituted stable silene $Me_2Si{=}C(SiMe_3)(SiMe\textit{t}Bu_2)_2$ (1.702 Å),[4] where no donor stabilization takes place. The Si=C distance is in good agreement with the corresponding distance in the intermolecular adduct of the silene $Me_2Si{=}C(SiMe_2Ph)_2$ with ethyldimethylamine (1.761 Å).[5] This supports the idea that the interaction of silenes with donor groups leads to an elongation of the Si=C bond[3–6] caused by a weakening of the Si–C π interaction. The Si=C distances of the kinetically stabilized silenes $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (1.764 Å, Ad = 1-adamantyl)[13] and $(Me_3Si)(\textit{t}BuMe_2Si){=}Ad'$ (1.741 Å, Ad′ = 2-adamantylidene)[14] are almost the same as those of the thermodynamically stabilized silenes, but these elongations were accounted for by the electronic effects of the substituents.[14,15]

For compound **3** the situation is quite comparable to compound **1**, as the results in Table 2 show. Only one of the two dimethylamino groups interacts with the tetra-coordinated silene silicon atom. This leads again to a pyramidalization at the silene silicon atom and one short interatomic Si···N distance. The configuration at the silene carbon atom is perfectly trigonal planar and the Si=C bond length is only slightly longer than in compound **1**.

There are several possibilities to calculate the stabilizing effect of the Si–N donor-acceptor interaction on the stability of the silenes and in particular of the Si=C double bond. For intermolecularly donor-stabilized silenes this energy can easily be calculated from the difference between the total energy of the complex and of the isolated molecules, using the so-called supermolecule approximation.

Table 1. Selected structural parameters of compound **1**.

	HF/6-31++G(d,p)	B3LYP/6-31++G(d,p)	X-ray results
Distance (Si=C) [Å]	1.755	1.761	1.748
Distance (Si···N) [Å]	2.096	2.175	2.004
Distance (C–SiMe$_3$) [Å]	1.854	1.858	1.824
Distance (C–SiMe$_3$) [Å]	1.865	1.869	1.832
Distance (Si–Ph) [Å]	1.907	1.910	1.890
Distance (Si–SiMe$_3$) [Å]	2.431	2.422	2.381
Angle (Ph–Si=C–SiMe$_3$) [°]	0.671	–0.071	–3.405
Sum of angles (silene Si) [°]	346.94	348.44	343.60
Sum of angles (silene C) [°]	359.83	359.81	359.35

Table 2. Selected structural parameters of compound **3**.

	HF/6-31++G(d,p)	B3LYP/6-31++G(d,p)	X-ray results
Distance (Si=C) [Å]	1.760	1.765	1.758
Distance (Si···N) [Å]	2.119	2.199	2.035
Distance (Si···N) [Å]	3.812	3.818	3.441
Distance (C–SiMe$_3$) [Å]	1.862	1.865	1.837
Distance (C–SiMe$_3$) [Å]	1.867	1.870	1.839
Distance (Si–Ph) [Å]	1.919	1.919	1.892
Distance (Si–SiMe$_3$) [Å]	2.444	2.422	2.402
Angle (Ph–Si=C–SiMe$_3$) [°]	19.40	18.13	20.66
Sum of angles (silene Si) [°]	350.00	350.71	348.48
Sum of angles (silene C) [°]	359.99	359.97	360.00

Unfortunately, since donor and acceptor are subunits in the same molecule in **1**, **2** and **3**, this strategy does not work. There is no direct way to calculate this stabilizing contribution since it is superimposed by other effects like steric repulsion. Nevertheless, several approaches were undertaken and will be described in the following sections.

2.1. Calculations with the NBO Model

The stabilizing influence of the N→Si donor–acceptor interaction and the resulting elongation of the Si=C double bond in the intramolecularly donor-stabilized silenes can easily be rationalized by a mesomeric interpretation which predicts an ylide-like nature of the donor stabilized silenes (see Figure 2).

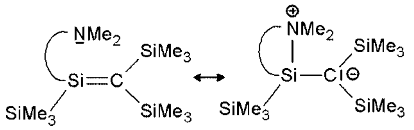

Figure 2. Mesomeric structures of compounds **1**, **3**, and **4**.

A similar conclusion is reached by using the Natural Bond Orbital (NBO) analysis.[16–18] This method transforms the delocalized Hartree–Fock orbitals into localized electron orbitals ("natural bond orbitals") that are closely tied to chemical bonding concepts and resembles the well known Lewis structure. Deviations from "normal" Lewis structures are represented as antibonding orbitals. The orbitals can interact very strongly. The energetic importance of the possible interaction between "filled" (donor) and "empty" (acceptor) NBO's can be estimated by using the NBODel keyword. In this method, the interactions between user defined orbitals are switched off to calculate their influence on the molecular stability. For compound **1** as well as for the conformer **1b**, where the CH_2–NMe_2 group is turned away from the electrophilic silicon atom, calculations were performed using the HF/6-31G(d) method. For compound **1**, the energy attributed to hyperconjugation between the lone pair at N and the empty orbital at the silene silicon atom is calculated as 277 kJ/mol and the Si–C π interaction is calculated as 87 kJ/mol. For compound **1b**, no N–Si interaction is possible, and the hyperconjugative Si–C π interaction is calculated as 168 kJ/mol. When the Si–N donor acceptor interaction takes place, the Si–C π interaction is strongly diminished and a reduction of the rotational barrier about the Si=C double bond in comparison to uncomplexed silenes in the order of 80 kJ/mol is conceivable. Since the occupation of the antibonding Si–C orbital is increased, an elongation of the Si=C bond has to be expected in comparison to silenes without a donor stabilization.

The very high value for the N–Si hyperconjugation interaction as predicted in the framework of the NBO model does not represent the net stabilization energy of the Si–N donor acceptor interaction. Other effects like Pauli exchange repulsion and to a lesser extent electrostatic interactions drastically diminish the stabilizing effect of the hyperconjugation, as was pointed out in the discussions concerning the internal rotational barrier of ethane.[19–22] This net stabilization energy has to be computed by other methods.

2.2. Influence of the Si–N Distance

If the CH_2–NMe_2 group is pointed towards the Si atom in the Si=C bond as in compound **1**, a Si–N donor-acceptor interaction is possible [*d*(Si–N) ≈ 2.0–2.1 Å]. If the direction of the CH_2–NMe_2 group is changed to point away from the Si atom as in conformer **1b**, no such interaction is possible [*d*(N–Si) ≈ 4.5 Å]. Both geometric structures were optimized using the HF/6-31++G(d,p) method. The structures show some distinctive deviations. In the conformer with the long Si–N distance, the Si=C double bond is shortened to 1.722 Å in comparison to 1.755 Å in the conformer with short Si–N distance. In the same way, the conformer **1b** shows no longer a pyramidalization at the silene silicon atom (sum of angles at the silene Si atom = 359.16°). Both results agree with our interpretation of the influence of the Si–N interaction on the Si=C double bond as a donor-acceptor interaction between the lone pair at N and the π* orbital of the silene double bond. This picture is also qualitatively supported by the contour plots of the HOMO and LUMO of conformer **1**, which are shown in Figures 3 and 4. A recognizable overlap between the n(N)- and the π(Si=C)-orbital is observed for the conformer with the short Si–N distance, whereas the HOMO and LUMO of the other conformer do not indicate any interaction between the N and Si atom.

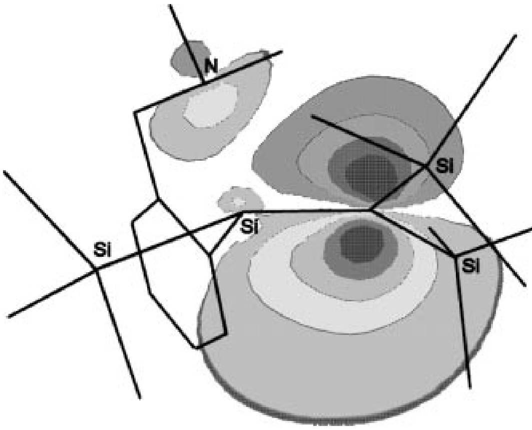

Figure 3. Contour plot of the HOMO orbital of compound **1**. The Figure shows the HOMO in the plane containing the N atom and the Si=C double bond.

Energy calculations of the conformers **1** and **1b** were performed using the MP2/6-31++G(d,p) method. These calculations showed that the structure with the short Si–N distance is energetically favored by 77 (37) kJ/mol at the MP2 (HF) level. This energy consists of the Si–N donor-acceptor stabilization energy and the steric repulsion effects in both conformers and is in reasonable accordance with the value of 82 (92) kJ/mol found by Gusel′nikov et al.[7] for the intramolecularly N-donor-stabilized 1-methylene-5-methyl-2,8-

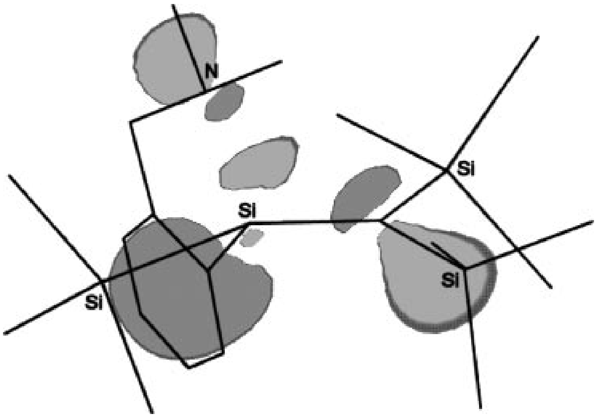

Figure 4. Contour plot of the LUMO orbital of compound **1**. The Figure shows the LUMO in the plane containing the N atom and the Si=C double bond.

dioxa-5-aza-1-silacyclooctane (MADS), calculated by the same method but using the smaller 6-31G(d) basis set. In contrast to the calculations of Gusel′nikov, a strong deviation between the results obtained with the MP2 and the HF method was observed for compound **1**, showing that electron correlation can not be neglected in this case.

The hypothetical intermolecular stabilization of dimethylsilene with NH_3 was calculated by Gusel′nikov et al.[7] as 31 kJ/mol using the MP2/6-31G(d) method in the supermolecular approximation. This value is smaller than the value obtained for silene **1**, showing that the electronic and steric effect of the different substituents can not be neglected.

To understand the influence of the steric repulsion on our results, some calculations were performed with model compound **5** (see Figure 1). In this compound, the dimethylamino group of **1** is replaced with the sterically similar isopropyl group. Again, configurations with a short (2.4 Å) and a long (4.7 Å) distance between this group and the silene silicon atom were calculated, representing the structures **5** and **5b**, respectively. In contrast to the NMe_2 group, no donor–acceptor interaction with the electrophilic silicon atom is expected for the isopropyl group. The energy difference between both conformers of **5** should thus be determined solely by steric repulsions. This leads to a strong stabilization of the configuration with the long isopropyl-silene silicon atom distance of 75 (122) kJ/mol calculated at the MP2/6-31++G(d,p) [HF/6-31++G(d,p)] level.

Under the assumptions made above, the Si···N interaction energy without steric repulsion effects can now be calculated as the difference between the two stabilization energies of the different conformers of compounds **1** and **5**. As a result, the Si···N interaction energy without the influence of steric repulsion is calculated as 152 (159) kJ/mol using the MP2/6-31++G(d,p) [HF/6-31++G(d,p)] method. This energy shows only a small dependence on electron correlation, since the errors in the HF calculations, which are mainly due to incorrect interorbital pair correlations, cancel out each other favorably.

2.3. Comparison of Stabilization Effect of NMe_2 Group on Silenes and Silanes

The results obtained above indicate a strong donor–acceptor interaction of the free electron pair of the N atom with the Si=C bond. Without the Si–C antibonding orbital of the Si=C bond, no strong donor-acceptor interaction should be possible. If the dimethylamino group is exchanged for an isopropyl group, again no strong donor–acceptor interaction is possible, regardless whether there exists a Si=C double bond or not. In the hydrogenation reactions of **1** and **5b** with H_2 leading to the saturated compounds **1c** and **5c** these effects determine the difference in the following two standard reaction energies:

1 + $H_2 \rightarrow$ **1c**; $\Delta E_{H(1)}$
5b + $H_2 \rightarrow$ **5c**; $\Delta E_{H(5)}$

The stabilizing effect of the NMe_2 group on the Si=C bond can be calculated from the difference between the hydrogenation reactions:

$\Delta E_{stab} = \Delta E_{H(1)} - \Delta E_{H(5)}$

As a result, a stabilizing effect ΔE_{stab} of 74 kJ/mol (41 kJ/mol) was obtained at the MP2/6-31++G(d,p) [HF/6-31++G(d,p)] level. These stabilization energies agree nearly quantitatively with the energies obtained from the investigation in section 2.2. A strong influence of electron correlation is also observed in these results.

Again it has to be assumed that other factors like higher steric repulsions in compound **1** in comparison to compound **5b** have a major impact on these stabilization energies. Using the results from the study of model compounds **5** and **5b** in section 2.2., a stabilization energy without the influence of steric repulsion of 149 (163) kJ/mol can be attributed to the Si···N interaction using the MP2/6-31++G(d,p) [HF/6-31++G(d,p)] method.

2.4. Rotational Barrier About the Si=C Double Bond

For compound **1**, **3** and the structurally quite similar compound **6**, temperature-dependent ^1H NMR studies were performed.[23] As expected, at room temperature two separate signals were found for the two nonequivalent trimethylsilyl groups at the carbon atom of the above-mentioned compounds. For compound **1** and **6** the dynamic ^1H NMR studies revealed that at elevated temperatures a coalescence of the signals of the $CSiMe_3$ groups occurred. For compound **3**, at temperatures of up to 80 °C no coalescence of these two signals could be observed. The data were used to determine the rotational barrier $\Delta G^{\neq}$ about the Si=C bond. The following approximate equation derived from the Eyring equation was used:[24]

$$\Delta G^{\neq} = T_c \cdot 19.13 \cdot (9.97 + \lg\frac{T_c}{\Delta \nu_c})$$

$\Delta G^{\neq}$ is the free energy barrier, T_c the coalescence temperature and $\Delta \nu_c$ is the signal separation of the $CSiMe_3$ groups extrapolated to the coalescence temperature.

These results can be compared to some data obtained from ab initio calculations. The rotational barrier of the Si=C bond was determined by performing a relaxed potential energy surface scan involving the dihedral angle Ph–Si=C–SiMe$_3$ of compounds **1**, **2**, and **3** using the HF/6-31G(d) method. The resulting energy vs. dihedral angle diagram is show in Figure 5. The geometries belonging to the maximal values of these curves were then recalculated using the higher 6-31++G(d,p) basis set at the HF and the MP2 level. The difference between these absolute energies corresponds approximately to the rotational barrier of the Si=C double bond. Since the rotational barrier is strictly speaking a difference of Gibbs energies, the following corrections were applied to the calculated energies $\Delta E^{\neq}_{\text{elec}}$ using the HF/6-31G(d) method:

$$\Delta G^{\neq} = \Delta E^{\neq}_{\text{elec}} + \Delta ZPE^{\neq} + \Delta E^{\neq}_{\text{vib}} + \Delta E^{\neq}_{\text{rot}} - T\Delta S^{\neq}$$

$\Delta ZPE^{\neq}$ is the correction due to zero point energy, $\Delta E^{\neq}_{\text{vib}}$ + $\Delta E^{\neq}_{\text{rot}}$ are the contributions due to vibration and rotation and $\Delta S^{\neq}$ is the entropy difference.

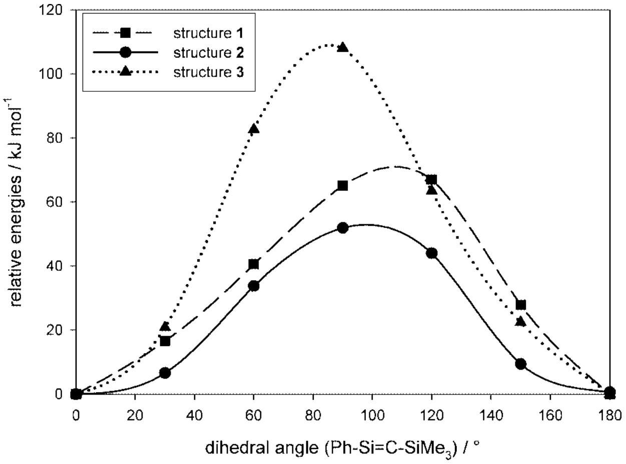

Figure 5. Rotational barrier of the Si=C double bond calculated at the HF/6-31G(d) level.

The resulting free energies as well as the energies obtained at the HF/6-31++G(d,p), the MP2/6-31++G(d,p) level and the experimental ^{1}H NMR results are shown in Table 3. Our best estimates for the rotational barrier in Table 3 (column 6) are obtained by using the results from the MP2 single point energy calculation (column 5) and applying the corrections according to the equation above by using the HF/6-31G(d) method (difference between column 3 and column 2). The rotational barriers determined by this quantum mechanical approach agree surprisingly well with the spectroscopically determined rotational barriers, supporting our interpretation of the experimental data.

These values are also very close to values found for intermolecular silene adducts THF·Me$_2$Si=C(SiMe$_3$)SiMe*t*Bu$_2$ and NMe$_3$·Me$_2$Si=C(SiMe$_3$)SiMe*t*Bu$_2$, where values of 50 kJ/mol and 65 kJ/mol, respectively, were reported.[25]

The calculated rotational barriers of isomer interconversion are smaller than in uncomplexed silenes, which were found to be about 160 kJ/mol.[1] This shows that the interaction of donor groups with the Si=C bond leads to a weakening of the Si–C π interaction in the order of 60–100 kJ/mol, in qualitative agreement with our results from the NBO calculation. The value for the cis/trans isomerization in alkenes, which amounts to approximately 250 kJ/mol,[26] is considerably higher than the value for the silenes, as expected.

3. Conclusions

The ab initio calculations on the silene compounds **1**, **2**, and **3** in the gas phase are in good agreement with data from X-ray structural analysis. Both methods show an Si–N distance that is shorter than in saturated counterparts. A strong interaction between the free N orbital and the antibonding orbital at the electrophilic silicon atom was observed. This is accompanied by a weakening of the Si=C double bond, which results in the elongation of the Si=C bond and the reduction of the rotational barrier about the Si=C bond. The stabilization energy gained of the donor-stabilized silenes in comparison to unstabilized silenes by coordination with the dimethylamino group is in the order of about 75 kJ/mol. This energy consists of a stabilizing donor-acceptor interaction (app. 150 kJ/mol) and a weakening steric repulsion effect (app. 75 kJ/mol).

The spectroscopically determined rotational barriers about the Si=C double bond of compounds **1**, **3** and **6** could be quantitatively reproduced by our ab initio calculations.

4. Computational Details

All calculations were performed for isolated species using the GAUSSIAN98 and GAUSSIAN03 program package.[27] At first, a full geometry optimization was performed using the 6-31G(d) basis set on the RHF level. All calculated structures represent minima on the potential energy surface; this means no negative frequencies were observed. The calculated frequencies were used to obtain the zero point energies and other thermodynamic properties of those structures. Some further geometry optimizations using the 6-

Table 3. Rotational barriers from ab initio calculation (kJ/mol).

Structure	$\Delta E^{\neq}$ (HF/6-31G(d))	$\Delta G^{\neq}$ (HF/6-31G(d))	$\Delta E^{\neq}$ (HF/6-31++G(d,p))	$\Delta E^{\neq}$ (MP2/6-31++G(d,p))	$\Delta G^{\neq}$ (best estimate)	Experiment[20] (^{1}H NMR)
1	70.9	73.4	64.5	64.3	66.8	71.5
2	52.6	52.7	57.4	56.2	56.3	63.3[a]
3	108.0	114.9	107.6	93.8	100.7	> 100[b]

[a] Similar compound **6**. [b] Up to 80 °C no coalescence could be observed.

31++G(d,p) basis set on the HF and the B3LYP level were performed for the most important structures. All main structural elements from the X-ray structures could be reproduced qualitatively with both of the applied ab initio methods. The results from the B3LYP/6-31++G(d,p) geometry optimization show larger deviations from the X-ray structure (see Tables 1 and 2). This may be due to problems of B3LYP in describing steric interactions correctly. Therefore, we decided to use the geometric structures obtained from the HF calculations as the foundation for any further calculations like frequency calculations or single point energy calculations using the more sophisticated but also very time consuming MP2 method. Due to the high computational cost of the MP2 method for these large molecules, only single point energy calculations were performed using the MP2/6-31++G(d,p) method on the geometric structures obtained at the HF level. No geometry optimization was attempted at the MP2 theoretical level.

All NBO calculations were performed with NBO version 3.1[28] as incorporated in Gaussian03.

The calculation of the rotational barrier about the Si=C double bond was accomplished at the HF/6-31G(d) level by using the Opt = ModRedundant keyword of GAUSSIAN03. We changed the dihedral angle Ph–Si=C–SiMe$_3$ in 5 steps of 30°, starting with the value of approximately 0° corresponding to the fully optimized geometry.

Supporting Information: The supporting information (see also the footnote on the first page of this article) includes the coordinates and total energies of the above mentioned structures as well as the thermodynamic corrections.

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[1] A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71–258.

[2] T. Müller, W. Ziche, N. Auner, in: *The Chemistry of organic silicon compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, vol. 2, p. 857–1062.

[3] N. Wiberg, H. Köpf, *J. Organomet. Chem.* **1986**, *315*, 9–18.

[4] N. Wiberg, G. Wagner, G. Reber, J. Riede, G. Müller, *Organometallics* **1987**, *6*, 35–41.

[5] N. Wiberg, K.-S. Joo, K. Polborn, *Chem. Ber.* **1993**, *126*, 67–69.

[6] N. Wiberg, G. Wagner, G. Müller, J. Riede, *J. Organomet. Chem.* **1984**, *271*, 381–386.

[7] V. G. Avakyan, L. E. Gusel′nikov, V. A. Pestunovich, A. A. Bagaturyants, N. Auner, *Organometallics* **1999**, *18*, 4692–4699.

[8] N. N. Zemljanskii, I. V. Borisova, A. K. Shestakova, Y. A. Ustynyuk, E. A. Chernyshev, *Izv. Akad. Nauk Ser. Khim.* **1998**, *47*, 486–491.

[9] N. N. Zemljanskii, I. V. Borisova, A. K. Shestakova, Y. A. Ustynyuk, E. A. Chernyshev, *Russ. Chem. Bull.* **1998**, *47*, 469–474.

[10] M. Mickoleit, K. Schmohl, R. Kempe, H. Oehme, *Angew. Chem.* **2000**, *112*, 1679–1681; *Angew. Chem. Int. Ed.* **2000**, *39*, 1610–1612.

[11] M. Mickoleit, R. Kempe, H. Oehme, *Chem. Eur. J.* **2001**, *7*, 987–992.

[12] M. Pötter, U. Bäumer, M. Mickoleit, R. Kempe, H. Oehme, *J. Organomet. Chem.* **2001**, *621*, 261–266.

[13] A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. M. R. Kallury, Y. C. Poon, Y.-M. Chang, W. Wong-Ng, *J. Am. Chem. Soc.* **1982**, *104*, 5667–5672.

[14] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228–12229.

[15] Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **1984**, *106*, 6676–6682.

[16] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

[17] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066–4073.

[18] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[19] L. Goodman, H. Gu, V. Pophristic, *J. Chem. Phys.* **1999**, *110*, 4268–4275.

[20] L. Goodman, V. Pophristic, F. Weinhold, *Acc. Chem. Res.* **1999**, *32*, 983–993.

[21] F. M. Bickelhaupt, E. J. Baerends, *Angew. Chem.* **2003**, *115*, 4315–4320.

[22] F. Weinhold, *Angew. Chem.* **2003**, *115*, 4315–4320.

[23] M. Mickoleit, K. Schmohl, M. Michalik, H. Oehme, *Eur. J. Inorg. Chem.* **2004**, *7*, 1538–1544.

[24] H. Kessler, *Angew. Chem.* **1970**, *82*, 237–253; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 219–235.

[25] N. Wiberg, H.-S. Hwang-Park, H.-W. Lerner, S. Dick, *Chem. Ber.* **1996**, *129*, 471–478.

[26] H. Beyer, W. Walter, *Lehrbuch der Organischen Chemie*, Hirzel, Leipzig, **1998**.

[27] 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, 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, J. A. Pople, *Gaussian 03 Revision B.04*, Gaussian, Inc., Pittsburgh PA, **2003**.

[28] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*.

Received: February 11, 2005