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Formation of (SiN_2SiC) Five-Membered Rings by Intramolecular Insertion into the Si−N Bond: A Quantum Chemical Study

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The formation of the diazadisilacyclopentane **2** in a ring expansion reaction is the first example of an SiR_2-CH_2 insertion into the nitrogen−silicon single-bond accompanied by migration of a hydrogen atom from a carbon to a nitrogen atom [*J. Organomet. Chem.* **1994**, *482*, 285]. Density functional calculations support the experimental findings and suggest a reaction mechanism which includes two four-center transition states and an intermediate silahydrazone (**3b**). The reaction enthalpy $\Delta_R H°$ (298 K) of the isomerization reaction converting the three-membered ring $(Me_3SiN)_2SiH_2$ (**1b**) into the diazadisilacyclopentane $Me_2Si(NHNSiMe_3CH_2)SiH_2$ (**2b**) is calculated to be -23 kcal mol^{-1}. Another intermediate of the system shows an unexpected electronic structure with a lone electron pair at the SiH_2 silicon atom. The transition states and the unimolecular reaction mechanism are discussed in detail. The calculated geometry for the product **2b** is in very good agreement with X-ray structure data.

1. Introduction

It is well known that silyl groups in neutral and anionic molecules can undergo easy migrations.[1−4] This has been applied to the synthesis of isomeric compounds as well as to stabilizing elements in lower coordination.[5,6] The synthesis of the first cyclic and acyclic silylhydrazines was reported by Aylett[7] and Wannagat.[8,9] Klingebiel et al. have been studying the chemistry of silylhydrazines for several years and were able to synthesize a three-membered SiN_2 ring.[10] Attempts to dissolve and crystallize diazasilacyclopropanes led to diaminosilanes[10] or thermally to the formation of 1,2-diaza-3,5-disilacyclopentanes (Scheme 1).[11] A crystal structure of the five-membered 1,2-diaza-3,5-disilacyclopentane **2a** could be determined.[11] It was supposed that in a first step diazasilacyclopropane **1a** is formed, which subsequently undergoes isomerization into **2a**. However, it is not yet clear how the reaction **1a** → **2a** proceeds and whether a single transition state (TS) is involved or whether intermediate species play a role in the isomerization process.

A bimolecular reaction mechanism is unlikely because experimental investigations have shown that no crossover products were formed when differently substituted educt species were present in the reaction. For that reason, a possible bimolecular mechanism will not be studied in this work.

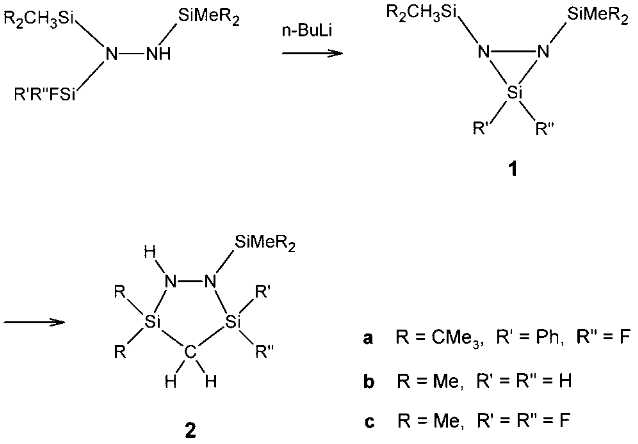
In a recent joint experimental−theoretical paper,[12] the synthesis of a four-membered cyclodisilazane via an intermediate diazasilacyclopropane was reported. A reaction mechanism was suggested, which is supported by density functional theory (DFT) calculations. The isomerization proceeds via a single transition state, and large amplitude motions play a crucial role in the unimolecular rearrangement process.

In this article we present a study of the potential energy hypersurface (PES) of the isomerizing system **1b** with particular emphasis on the mechanism of SiR_2CH_2 insertion into the Si−N bond of the ring.

2. Methodology

To reduce the computational expense, the calculations were performed for the derivatives of *N*,*N*′-bis(trimethylsilyl)hydrazine instead of those of *N*,*N*′-bis(di-tert-butylmethylsilyl)hydrazine. Because both exocyclic silicon atoms have three methyl groups as substituents, only one isomerization pathway is possible for symmetry reasons. From the corresponding lithium derivative the three-membered ring **1b** is formed which subsequently undergoes isomerization into the five-membered ring **2b**.

SCHEME 1



The structures of the stationary points **1b**, **2b**, **3b**, **4b**, **TS1b**, **TS2b**, and **TS3b** were fully optimized using Becke's three-parameter hybrid method with Becke's exchange functional and the LYP correlation functional (B3LYP). The 6-31G* basis set was employed in the DFT calculations; it comprises 217 contracted Gaussian type orbitals (cGTOs) for $C_6H_{20}N_2Si_3$. To confirm that true minima on the PES were found, the Hessians at the stationary points were calculated. The energies were further corrected for zero-point vibrational effects which, however, are usually only of minor importance in isomerization reactions. The TS routine of GAUSSIAN98[13] and the intrinsic reaction coordinate (IRC) method were employed for the calculation of the transition state (first-order saddle point) geometries.

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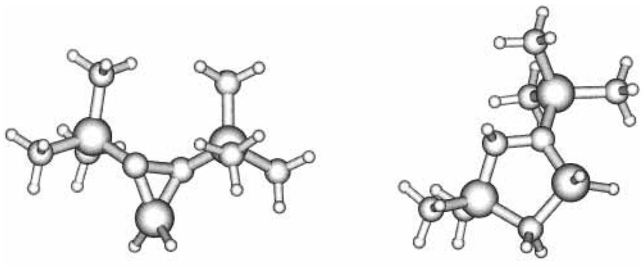

1b **2b**

Figure 1. Structures of the three-membered ring **1b** and the five-membered ring **2b**.

3. Results and Discussion

Diazasilacyclopropane. As for the corresponding species with R′ = R″ = F,[12] a structure with C_2 symmetry (Figure 1, left figure) was found as the energetic minimum of **1b**. The most important structural parameters are calculated as follows (geometrical data of **1c**[12] in parentheses): r(N−N) = 162.4 (173.6) pm, α(N−SiH$_2$−N) = 56.1 (62.1)°, r(H$_2$Si−N) = 172.8 (168.4) pm, r(Me$_3$Si−N) = 177.5 (177.9) pm, α(N−N−SiMe$_3$) = 114.5 (114.5)°. Due to the electron withdrawing effect of the fluorine atoms, the N−N single bond is longer in **1c**[12] compared to **1b**. As a consequence, the N−Si−N angle in **1b** is smaller by 6.0°. The SiMe$_3$ groups are tilt out of the SiN$_2$ ring plane with a dihedral angle θ(Me$_3$Si−N−N−SiMe$_3$) of 119.0 (115.8)°. The nitrogen atoms show sp^3 hybridization.

Diazadisilacyclopentane. The B3LYP/6-31G* structure of the five-membered ring **2b** is displayed graphically in Figure 1. A crystal structure could be determined for the diazadisilapentane **2a**;[11] in what follows, the corresponding data are given in parentheses for comparison with the structure of **2b**.

The N−N bond of the five-membered ring **2b** is contracted by 15.6 pm to r(N−N) = 146.8 (150.3) pm compared to **1b**. The remaining four bonds of the five-membered ring are calculated as follows: r(Me$_2$Si−NH) = 178.1 (176.8) pm, r(Me$_2$Si−CH$_2$) = 190.5 (187.5) pm, r(H$_2$C−SiH$_2$) = 189.3 (185.7) pm, and r(H$_2$Si−N) = 175.5 (173.4) pm. The exocyclic N−Si bond is calculated to be r(N−SiMe$_3$) = 176.0 (175.6) pm. The new N−H bond is determined to be r(N−H) = 102.9 pm. The five inner-ring angles are given by α(Me$_2$Si−N−N) = 109.7°, α(N−N−SiH$_2$) = 110.9 (110.9)°, α(N−SiH$_2$−CH$_2$) = 101.8 (103.8)°, α(H$_2$Si−CH$_2$−SiMe$_2$) = 101.5°, and α(H$_2$C−SiMe$_2$−NH) = 101.9 (101.6)°. The H−Si−H angle is calculated to be 107.7°. The angles involving the exocyclic trimethlsilyl group are α(HN−N−SiMe$_3$) = 113.9 (113.6)° and α(H$_2$Si−N−SiMe$_3$) = 136.1°. The ring is far from planarity as is obvious from the two dihedral angles θ(Me$_2$Si−N−N−SiH$_2$) = −41.5° and θ(Me$_2$Si−N−N−SiMe$_3$) = 136.7°.

Within the error bars of both theory and experiment, and taking into account that the substituents of **2a** and **2b** are different, the calculated geometry of the five-membered ring **2b** agrees nicely with the structure for **2a** obtained by X-ray diffraction.[11]

The energetic difference, ΔE_1, between **1b** and **2b** is calculated to be 24.0 kcal mol^{-1}. Taking the vibrational zero-point energy (harmonic level, unscaled) into account, ΔE_1 reduces to 22.3 kcal mol^{-1}. The reaction enthalpy for **1b** → **2b** is given by $\Delta_R H°(298\ K) = -23.1$ kcal mol^{-1}. Thus, under experimental conditions the reaction should be thermodynamically irreversible.

Saddle Point I. To elucidate the unimolecular rearrangement process, a search of the transition structure (first-order saddle point) **TS1b** has been carried out. The energy of the C_1 saddle point (see Figure 2, right figure) is $\Delta E_2 = 69.1$ kcal mol^{-1} above the three-membered ring **1b**. Inclusion of zero-point effects decreases this value to 66.5 kcal mol^{-1}.

The most important structural parameters of **TS1b** are calculated as follows: The N−N bond length r(N−N) = 151.2 pm is remarkably shortened with respect to **1b** and is close to the value of **2b**. The distance r(Me$_2$Si−N) = 171.3 pm is shorter than in the product **2b** by 6.8 pm. The silicon−carbon distance r(Me$_2$Si−CH$_2$) = 229.0 pm is larger by 38.5 pm compared to **2b**. The methylene−silylene distance r(H$_2$C−SiH$_2$) = 190.3 pm is very close to the corresponding value in the product species **2b**. The same holds for the bond distance r(N−SiH$_2$) = 176.2 pm and the exocyclic bond r(N−SiMe$_3$) = 175.5 pm.

The reactive center is characterized as a four-center transition state involving a silicon, a carbon, a nitrogen, and a hydrogen atom. The latter is connected to the three other atoms. The corresponding distances are given as follows: r(Si−H) = 167.6 pm, r(C−H) = 135.2 pm, and r(N−H) = 150.6 pm.

The endocyclic angles are, in principle, very similar to those of the five-membered ring: α(Me$_2$Si−N−N) = 106.4°, α(N−N−SiH$_2$) = 112.1°, α(N−SiH$_2$−CH$_2$) = 95.4°, and α(H$_2$Si−CH$_2$−SiMe$_2$) = 101.5°. Compared to **2b**, however, the angle α(H$_2$C−SiMe$_2$−N) = 83.6° of the reactive center is shorter by 18.3°, whereas the silylene angle α(H−Si−H) = 108.0° is not changed compared to the product **2b**. The angles of the exocyclic trimethysilyl group with the ring may also be compared with the diazadisilacyclopentane: α(N−N−SiMe$_3$) = 110.7° and α(H$_2$Si−N−SiMe$_3$) = 131.8°. The dihedral angle θ(Me$_2$Si−N−N−SiH$_2$) = −70.1° is wider than in **1b**, whereas the angle θ(Me$_2$Si−N−N−SiMe$_3$) = 132.8° is almost unchanged.

The imaginary harmonic vibrational frequency of the reactive motion (passage through the transition state) amounts to $\omega = 1647\,i$ cm^{-1} with a reduced mass of 1.088 amu, which indicates that the motion can be described by the migration of a hydrogen

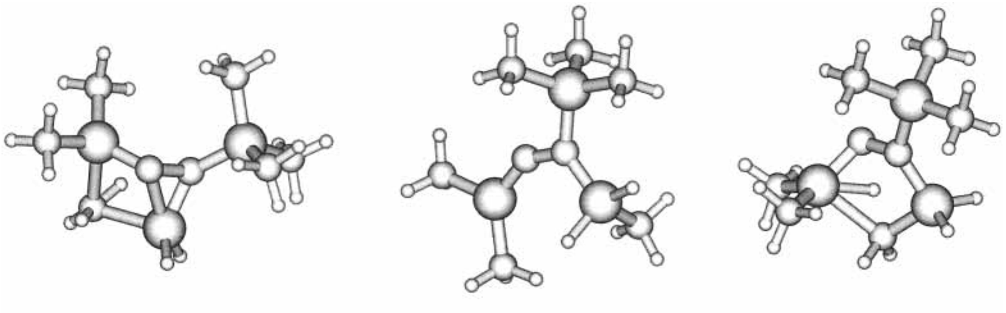

TS2b **3b** **TS1b**

Figure 2. Structures of saddle point II (**TS2b**), the stable intermediate I (**3b**), and saddle point I (**TS1b**).

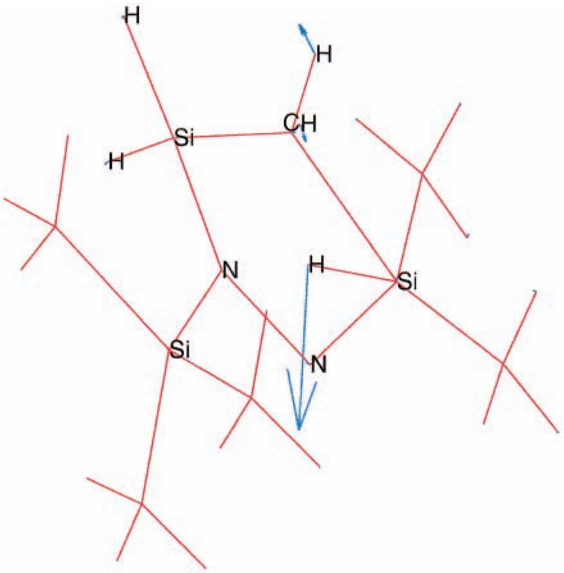


Figure 3. Reaction coordinate at saddle point I (**TS1b**), i.e., the normal coordinate with the imaginary harmonic vibrational frequency (see the text).

atom. The corresponding normal coordinate is displayed graphically in Figure 3. The hydrogen atom migrates from carbon via silicon to nitrogen. It should be noted that the hydrogen atom may tunnel through the barrier and that a remarkable isotope effect should be observable for the deuterated species.

Starting from the saddle point, the reaction path (RP) was followed in both directions using the IRC method as implemented in GAUSSIAN98.[13] Here, the geometry is optimized at each point along the RP such that the segment of the RP between any two adjacent points is described by an arc of a circle and so that the gradient vectors at the end points of the arc are tangents to the path.[14,15] The obtained product-like structure was identified as the diazadisilacyclopentane **2b**. However, the educt structure obtained from the RP following was not **1b** but rather an acyclic structure **3b** which is described in the following section.

Intermediate I (Silahydrazone). The stable structure **3b** found using the IRC method shows a double bond between one nitrogen atom and the attached exocyclic silicon atom (see Figure 2, middle figure). With respect to **TS1b**, the bond between the inserted silicon atom and the attached methylene group is broken and the hydrogen atom is connected to the methylene group. The species can be transformed into a C_s structure by a 120° clockwise or counterclockwise rotation of the SiH_2Me group around the $N-SiH_2Me$ single bond.

The most important B3LYP/6-31G* structural parameters are as follows: The N−N bond $r(N-N) = 138.7$ pm is shortened by 23.7 pm with respect to **1b**, indicating pronounced double bond character. The lengths of the exocyclic N−Si bond of $r(N-SiMe_3) = 178.2$ pm are very close to the value of **1b**. This also holds for the distance $r(N-SiH_2Me) = 175.4$ pm. The Si−N double bond distance is $r(N-SiMe_2) = 161.1$ pm. The angle $\alpha(N-N-SiH_2Me) = 119.0°$ is widened by 6.9° with respect to the transition state **TS1b**. The sum of angles at the $N-SiH_2Me$ nitrogen atom is 360.0°, indicating sp^2 hybridization. The angle $\alpha(Me_2Si-N-N) = 144.1°$ indicates sp^2 hybridization of the silicon atom. The $C_2Si-N-NSi_2$ skeleton is nearly planar with dihedral angles of 4.1° ($Me_2Si-N-N-SiMe_3$) and 5.0° ($Me_2Si-N-N-SiH_2Me$).

The energetic difference, ΔE_3, between the energy minima **3b** and **1b** is calculated to be 12.5 kcal mol^{-1}. Taking the vibrational zero point energy (harmonic level, unscaled) into account, the difference is slightly increased to 12.7 kcal mol^{-1}. The calculated reaction enthalpy is $\Delta_R H°(298\ K) = +13.0$ kcal mol^{-1}. In principle, the structure **3b** should be experimentally observable. It should be possible to intercept the intermediate silahydrazone by an addition reaction involving the Si−N double bond. A dimeric silahydrazone has already been isolated.[16,17]

Saddle Point II. Having identified the structure **3b**, it remains to establish a connection between this species and the educt diazacyclopropane **1b**. Making use of the IRC method, a first-order saddle point **TS2b** was shown to connect the three-membered ring **1b** with **3b**. It is located $\Delta E_4 = 66.7$ kcal mol^{-1} above **1b** (66.1 kcal mol^{-1} including zero-point energy).

The transition state **TS2b** is characterized as follows (see Figure 2, left figure): A four- and a three-membered ring have the N−Si bond with $r(N-SiH_2) = 200.0$ pm in common. $r(N-N) = 155.6$ pm is contracted by 5.8 pm compared to **1b**, whereas $r(H_2Si-N) = 172.3$ pm is almost identical with the corresponding distance in the educt ring.

The remaining three bond lengths of the four-membered ring are calculated to be $r(Me_2Si-N) = 171.2$ pm, $r(Me_2Si-CH_3) = 219.6$ pm, and $r(H_3C-SiH_2) = 217.0$ pm. The angles of the four-membered ring are $\alpha(N\text{-}Me_2Si-CH_3) = 83.4°$, $\alpha(Me_2Si-CH_3-SiH_2) = 88.1°$, $\alpha(H_3C-SiH_2-N) = 77.9°$, and $\alpha(Me_2Si-N-SiH_2) = 109.6°$; the sum of angles is 361.8°, indicating planarity.

The angle $\alpha(N-SiH_2-N) = 48.7°$ is smaller than in **1b**. $\alpha(H-Si-H)$ amounts to 105.2° The exocyclic Si−N bond $r(N-SiMe_3) = 175.9$ pm is insignificantly changed with respect to **1b**. The angles made up of the NN unit and the $SiMe_2$ group of the four-membered ring and the exocyclic $SiMe_3$ group, respectively, are $\alpha(Me_2Si-N-N) = 112.4°$ and $\alpha(N-N-SiMe_3) = 114.9°$.

The inner H−C−H angle of the CH_3 group at the reaction center amounts to $\alpha_{in}(H-C-H) = 136.7°$, whereas the corresponding outer angles $\alpha_{out}(H-C-H) = 113.0°$ and 110.3° are much smaller. The sum of angles of the CH_3 unit amounts to 360°.

The transition state is very close to the reactant (early TS). The three-membered ring is still intact. The two Si−C bond lengths at the reaction center are nearly equal in length. Apart from linearity, the reactive center shows a similarity with the transition state in nucleophilic bimolecular substitution (S_N2) reactions. The SiH_2 silicon atom is 5-fold coordinated. The saddle point structure can be described as a four-center transition state ($Me_2Si-CH_3-SiH_2-N$).

The normal mode corresponding to the imaginary harmonic vibrational frequency $\omega = 777.1\ i$ cm^{-1} is displayed graphically in Figure 4. Mainly the two outer hydrogen atoms are involved, and the corresponding reduced mass amounts to $\mu = 1.780$ amu. The reactive mode is similar to the umbrella bending mode at the transition state of S_N2 reactions.

Intermediate II. During the search for saddle point **TS1b**, a further stable intermediate **4b** was found, which will be characterized in what follows (see Figure 5, right figure). The structure has an almost planar $Si-N-N-Si_2$ skeleton with an unusual electronic structure. The short N−N bond distance $r(N-N) = 128.9$ pm indicates high double bond character (33.5 pm shorter than in **1b**). The trimethylsilyl-nitrogen distance $r(Me_3Si-N) = 180.0$ pm is longer by 2.5 pm compared to the diazacyclopropane **1b**. The nitrogen−silicon distance $r(N-SiH_2) = 182.6$ pm is elongated by as much as 9.8 pm. The trimethylsilyl group connected to the same nitrogen atom has a bond length of $r(N-SiMe_3) = 187.4$ pm, which is considerably

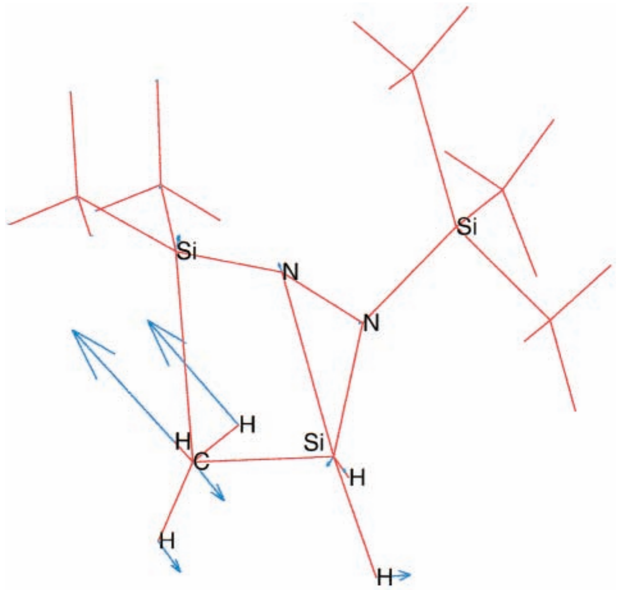
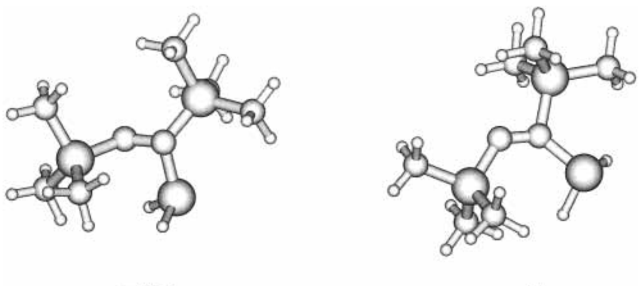


Figure 4. Reaction coordinate at saddle point II (**TS2b**), i.e., the normal coordinate with the imaginary harmonic vibrational frequency (see the text).



TS3b **4b**

Figure 5. Structures of saddle point III (**TS3b**) and the stable intermediate II (**4b**).

longer than in **1b**. The angle $\alpha(\mathrm{Me_3Si{-}N{-}N}) = 127.5°$ indicates sp^2 hybridization of the nitrogen atom. The three angles around the other nitrogen atom are $\alpha(\mathrm{N{-}N{-}SiH_2}) = 132.5°$, $\alpha(\mathrm{H_2Si{-}N{-}SiMe_3}) = 119.3°$, and $\alpha(\mathrm{N{-}N{-}SiMe_3}) = 107.3°$. The sum of angles amounts to 359.1°, indicating almost exact planarity. This is in keeping with the small dihedral angle $\theta(\mathrm{Me_3Si{-}N{-}N{-}SiMe_3}) = 1.1°$.

The SiH$_2$ silicon atom, however, is not sp^2 hybridized. It is almost tetrahedrically surrounded by the two hydrogen atoms and a lone electron pair, which is displayed graphically in Figure 6. The bond angle and dihedral angles characterizing the SiH$_2$ group are $\alpha(\mathrm{N{-}Si{-}H'}) = 101.8°$, $\alpha(\mathrm{N{-}Si{-}H''}) = 97.8°$, $\alpha(\mathrm{H'\text{-}Si\text{-}H''}) = 103.9°$, $\theta(\mathrm{N{-}N{-}Si{-}H'}) = 37.9°$, and $\theta(\mathrm{N{-}N{-}Si{-}H''}) = 36.0°$, where H′ (H″) denotes the inner (outer) SiH$_2$ hydrogen atom.

The canonical orbitals of **4b** were obtained from an SCF/6-31+G* (261 cGTOs) calculation at the B3LYP/6-31G* geometry. As can be seen from Figure 6, the HOMO of **4b** is essentially the lone pair at the SiH$_2$ silicon atom. Mulliken charges have been employed to rationalize this structure. The data for the silicon and nitrogen atoms are given in Table 1. The charges at the two nitrogen atoms are roughly the same, but less negative in **4b** compared to **1b**. The charge of the exocyclic SiMe$_3$ silicon atom does not shown any significant change. The Mulliken charge of the SiH$_2$ silicon atom becomes more negative in keeping with the lone pair at this site. In the Lewis formula picture, the species **4b** should thus be given as a zwitterionic structure (Scheme 2). Due to the high electron density at the SiH$_2$ group, the species should act as a strong nucleophile. The structure should be stabilized in polar solvents.

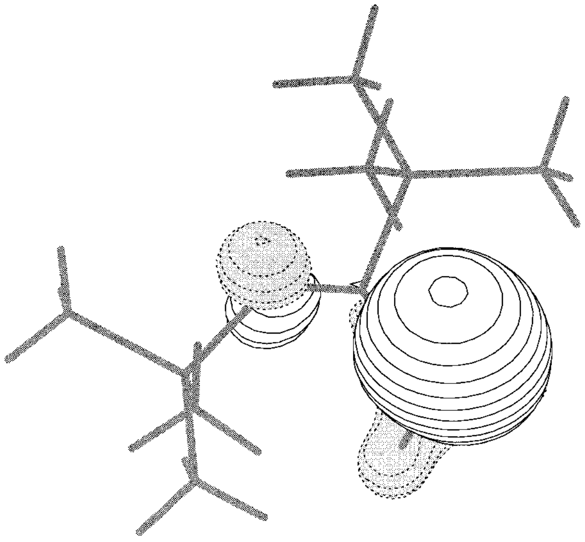
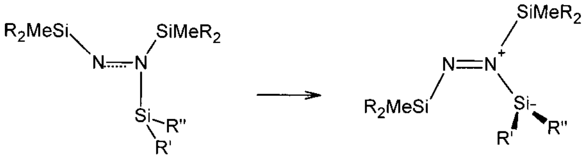


Figure 6. HOMO of **4b** (lone electron pair at the SiH$_2$ silicon atom).

TABLE 1: Mulliken Charges of the Silicon and Nitrogen Atoms in 1b, TS3b, and 4b

atom	1b	TS3b	4b
Me$_3$***Si***−N−N−SiH$_2$	0.874	0.822	0.814
Me$_3$Si−***N***−N−SiH$_2$	−0.536	−0.386	−0.352
Me$_3$Si−N−N−***Si***H$_2$	0.583	0.277	0.152
Me$_3$Si−N−***N***−SiH$_2$	−0.536	−0.469	−0.382
H$_2$Si−N−***Si***Me$_3$	0.874	0.878	0.874

SCHEME 2



TS3 **4**

The structure **4b** is energetically localized $\Delta E_5 = 27.8$ kcal mol^{-1} above the three-membered ring **1b**. Zero-point vibrational effects reduce this value to 24.2 kcal mol^{-1}. The reaction enthalpy **1b** → **4b** is given by $\Delta_R H°(298\ \mathrm{K}) = +24.5$ kcal mol^{-1}.

Saddle Point III. The saddle point **TS3b** (see Figure 5, left figure), which connects **1b** and **4b**, is $\Delta E_6 = 41.2$ kcal mol^{-1} higher in energy than the reactant **1b**. Zero-point effects reduce this value to 39.8 kcal mol^{-1}. The structure is relatively close to the educt species (see Figure 5, right figure). The ring Si−N bond is already broken, and the N−N−Si angle amounts to 99.3°.

The structure, however, is far from being planar. The B3LYP/6-31G* structural parameters of **TS3b** are given as follows: $r(\mathrm{N{-}N}) = 134.3$ pm, $r(\mathrm{Me_3Si{-}N}) = 179.1$, $r(\mathrm{N{-}SiMe_3}) = 182.0$ pm, $r(\mathrm{N{-}SiH_2}) = 181.7$ pm, $\alpha(\mathrm{Me_3Si{-}N{-}N}) = 125.1°$, $\alpha(\mathrm{N{-}N{-}SiMe_3}) = 114.7°$, $\alpha(\mathrm{H_2Si{-}N{-}SiMe_3}) = 121.5°$, and $\theta(\mathrm{Me_3Si{-}N{-}N{-}SiMe_3}) = 31.3°$.

The SiH$_2$ group is almost tetrahedral as is indicated from the three bond angles [$\alpha(\mathrm{N{-}Si{-}H'}) = 109.0°$, $\alpha(\mathrm{N{-}Si{-}H''}) = 105.6°$ and $\alpha(\mathrm{H'\text{-}Si\text{-}H''}) = 108.2°$]. The dihedral angles amount to $\theta(\mathrm{N{-}N{-}Si{-}H'}) = -93.9°$ and $\theta(\mathrm{N{-}N{-}Si{-}H''}) = 22.7°$.

The normal coordinate corresponding to the imaginary harmonic vibrational frequency $\omega = 312.9\,i$ cm^{-1} is displayed

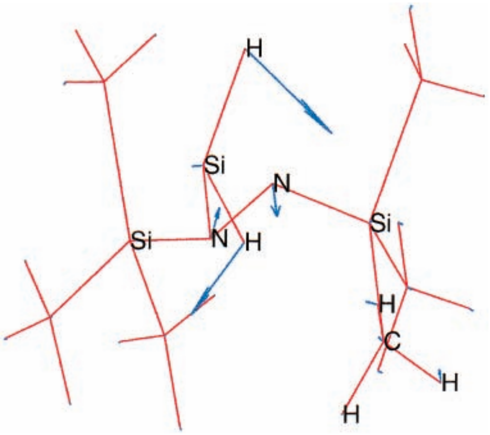


Figure 7. Reaction coordinate at saddle point III (**TS3b**), i.e., the normal coordinate with the imaginary harmonic vibrational frequency (see the text).

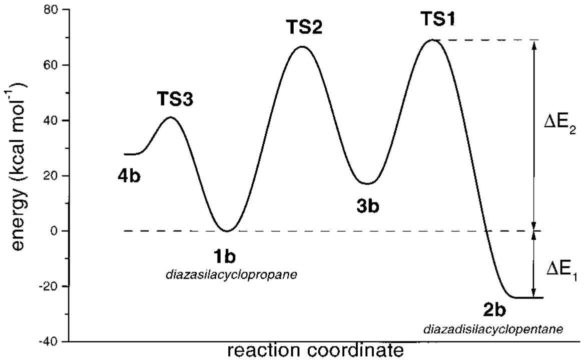


Figure 8. Schematic reaction profile (B3LYP/6-31G* results; zero-point energy contribution not taken into account); $\Delta E_1 = 24.0$ kcal mol^{-1}, $\Delta E_2 = 69.1$ kcal mol^{-1}.

TABLE 2: B3LYP/6-31G* and MP2/cc-pVDZ Energies (in kcal mol^{-1}) of the Seven Stationary Points (calculated at B3LYP/6-31G* equilibrium geometries)[a]

stationary point	B3LYP/6-31G*	MP2/cc-pVDZ
4b	27.8	28.8
TS3b	41.2	37.3
1b	0.0	0.0
TS2b	66.7	64.2
3b	17.2	15.3
TS1b	69.1	63.9
2b	−24.0	−24.8

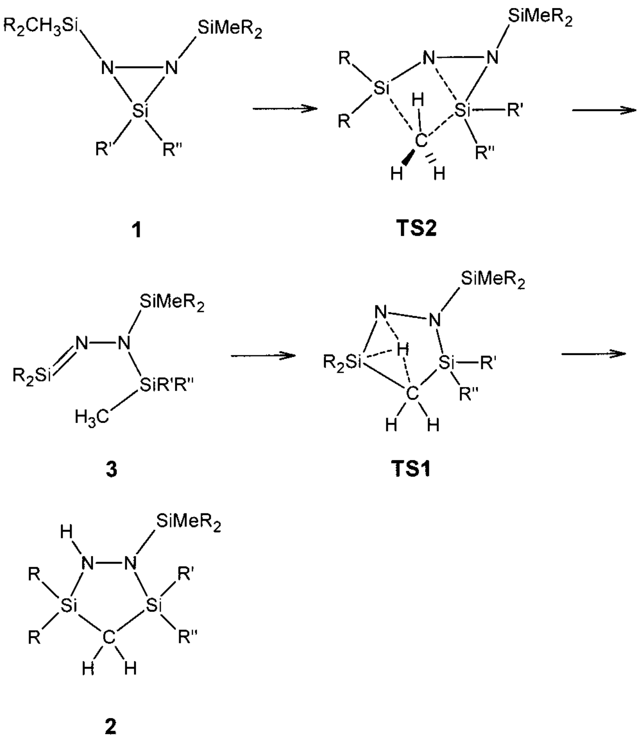
[a] The energy of **1b** is set to zero for both methods.

graphically in Figure 7. The corresponding reduced mass is $\mu = 3.06$ amu. The reaction coordinate is roughly described as follows: First, one of the N−Si single bonds is stretched and eventually breaks up. After passage of the transition state **TS3b**, the molecular skeleton is transformed into a planar conformation.

MP2 Calculations. For comparison with the DFT results, second-order perturbation calculations according to Møller and Plesset (MP2) were performed at the B3LYP/6-31G* geometries of the seven stationary points. The chosen basis set cc-pVDZ[18] comprises 266 cGTOs for $C_6H_{20}N_2Si_3$. The calculations were carried out with MOLPRO 2000.1[19] on workstations of the Abteilung für Theoretische Chemie at Göttingen.

The MP2 relative energies with respect to **1b** are given in Table 2. The data agree nicely with the DFT/6-31G* results. The deviation is less than 2 kcal mol^{-1} for the stable species and at most 5.2 kcal mol^{-1} for the transition states. Making use of the DFT/6-31G* vibrational frequencies, we obtain $\Delta_R H°$ (298 K) = −23.9 kcal mol^{-1} for reaction **1b** → **2b** at the MP2 level of theory.

SCHEME 3



Quantitatively better results can be achieved only by methods that include the major fraction of the electron correlation energy in a systematic way (e.g., MP4 or CCSD(T)). However, a reasonable result from these methods requires a well-balanced basis set, which results in high memory and CPU time demands so that such calculations are out of reach for us at present.

4. Conclusions

The complex unimolecular rearrangement process can be described as follows: The reaction starts with one of the two $SiMe_3$ moieties swinging inward. A bond between the carbon atom of one methyl group and the SiH_2 silicon atom is formed, resulting in a structure with the three-membered ring and a new four-membered ring sharing an Si−N single bond (**TS2b**). The shared Si−N bond stretches, and the N−N−SiH_2 angle becomes larger. The methyl group is transferred, and a stable intermediate silahydrazone **3b** is formed, which in principle should be experimentally observable. It is characterized by a $Me_2Si{=}N$ double bond. Now, the $SiMeH_2$ methyl group attacks the $SiMe_2$ silicon atom and forms a loose Si−C bond. Simultaneously, one of the hydrogen atoms of the CH_3 group forms a bond with the sp^2 hybridized $SiMe_2$ silicon atom. The hydrogen atom approaches the silicon and forms a relatively stable bond. In the transition state **TS1b**, the silicon atom at the reactive center is 5-fold coordinated. Finally, the hydrogen moves toward the nitrogen atom and forms a polar N−H bond, which stabilizes the five-membered ring. **TS1b** is relatively close to **2b** (late transition state), whereas **TS2b** is close to **1b** (early transition state). The isomerization process **1b** → **TS2b** → **3b** → **TS1b** → **2b** is shown schematically in Scheme 3 (R = Me, R′ = R″ = H). The reaction profile (B3LYP/6-31G*) is displayed in Figure 8. The calculated structure of the product **2b** is in good agreement with the geometry of a similar species obtained by X-ray diffraction.

Under the experimental conditions, the activation energy of 67 kcal mol^{-1} may be overcome by heating and additionally through the exothermicity of the reaction.

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