Silyl Group Insertion into the N−N Bond: Experimental and Quantum Chemical Results

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Abstract: The synthesis of the cyclodisilazane **1b** in a ring-expansion reaction is the first example of a reductive insertion into the nitrogen−nitrogen single bond accompanied by migration of a phenyl group from the silicon to a nitrogen atom. An analogous ring expansion is observed in the synthesis of the cyclodisilazane **2b**, which is the first reaction that involves migration of a hydrogen atom from a silicon to a nitrogen atom. A crystal structure is presented for compound **1b**. Quantum chemical calculations support the experimental findings. The reaction enthalpy $\Delta_R H°$(298 K) of the isomerization reaction converting the three-membered-ring $(Me_3SiN)_2SiF_2$ (**3a**) into the cyclodisilazane $Me_2Si(NSiMe_3NMe)SiF_2$ (**3b**) is calculated to be −72.1 kcal mol^{-1}. The transition state and the unimolecular reaction mechanism are discussed in detail.

1. Introduction

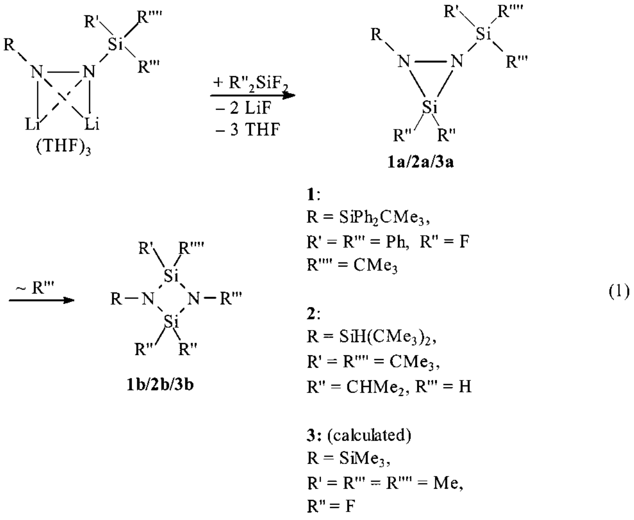
The discovery of the easy migration of silyl groups in anionic and neutral molecules has been a milestone in the chemistry of inorganic molecules.[1−4] Silyl group migration has been applied to the synthesis of isomeric compounds as well as to stabilizing elements in lower coordination.[5−6] The first example of an insertion of a silyl group into an N−O single bond was described by Boudjouk and West in 1971.[7] They observed that tris(alkylsilyl)hydroxylamines isomerize thermally to give silylaminosiloxanes. The isomerization includes the insertion into the N−O bond together with the migration of an alkyl group from a silicon atom to a nitrogen atom.[3,7−9]

We have been studying the chemistry of silylhydrazines for several years and we were able to synthesize three-membered BN_2 rings in the reaction of lithiated bis(silyl)hydrazides with difluoroboranes[10,11] and a three-membered SiN_2 ring with di-*tert*-butyldifluorosilane.[12] While an X-ray structure determination has been carried out for the cyclic BN_2 compound, this proved impossible in the case of the SiN_2 compound, which solidifies in a glasslike fashion. In the BN_2 ring the longest (SiN−NSi) single bond measures 168 pm.[10] This shows that N−N bonds in three-membered rings are very weak and explains that attempts to dissolve and crystallize diazasilacyclopropanes lead to diaminosilanes[12] or thermally to the formation of 1,2-diaza-3,5-disilacyclopentanes.[13] In four- and six-membered cyclic and acyclic silylhydrazines the N−N distances range from 142 to 156 pm.[14,15]

In this article we present the first example of a silyl group insertion into the N−N bond.

2. Results and Discussion

2.1. Experiment. The dilithium derivative of *N,N′*-bis(*tert*-butyldiphenylsily)hydrazine reacts with tetrafluorosilane in an autoclave above room temperature to form the cyclodisilazane **1b**. At lower temperatures (−70 to −20 °C) no reaction takes place. In an analogous reaction, the cyclodisilazane **2b** is formed by treating the dilithium derivative of *N,N′*-bis(di-*tert*-butylsilyl)hydrazine with difluorodiisopropylsilane.



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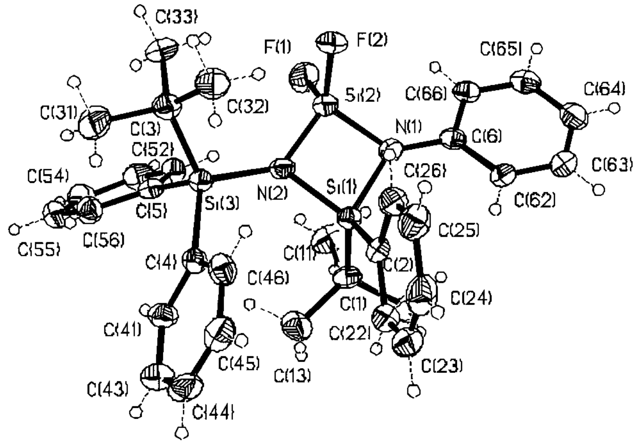

Figure 1. Crystal structure of **1b**. Selected bond lengths [pm] and angles [deg]: Si(1)−N(1) 176.1(4), Si(1)−N(2) 179.1(4), F(1)−Si(2) 157.9(4), N(1)−C(6) 141.1(6), N(1)−Si(2) 169.2(4), Si(2)−F(2) 157.6(3), Si(2)−N(2) 170.4(4), N(2)−Si(3) 174.4(4), N(1)−Si(1)−N(2) 86.1(2), C(6)−N(1)−Si(2) 134.2(3), C(6)−N(1)−Si(1) 133.7(3), Si(2)−N(1)−Si(1) 92.1(2), N(1)−Si(2)−N(2) 91.1(2), Si(2)−N(2)−Si(3) 136.8(3), Si(2)−N(2)−Si(1) 90.7(2), Si(3)−N(2)−Si(1) 132.5(2).

Besides polymers no other condensation products are found. Nor were crossover products detected when two different reaction mixtures of SiF_4 and dilithiated silylhydrazines were heated together. These observations and the intermolecular interactions (β-donor−acceptor interactions) between the silicon and the β-nitrogen atoms of silylhydrazines which have been demonstrated by X-ray crystallography and ab initio calculations (MP2/6-311G)[15] suggest an intramolecular mechanism as was described for the silyl group insertion into the N−O bond.[2,7]

We presume the following mechanism for the reactions: Initially, the 1,2-diazasilacyclopropanes **1a** and **2a** are formed. They stabilize in a second step which involves both the insertion of a Me_3CSiR unit into the N−N bond (**1**, R = Ph; **2**, R = CMe_3) and the migration of a phenyl group (**1b**) or an hydrogen atom (**2b**) from a silicon to a nitrogen atom. The reductive silyl group insertion appears to be unique in the chemistry of hydrazines. As far as we know, the migration of a hydrogen atom from a silicon to a nitrogen atom is also unknown.

2.2. X-ray Structure Analysis of 1b. 1b forms a planar, four-membered ring in the crystal [Figure 1], according to the results of the X-ray structure analysis. The nitrogen atoms show a sum of angles of 360°. The bonds from the Si(2) atom neighboring N atoms (Si(2)−N(1) = 169.2 pm, Si(2)−N(2) = 170.4 pm) are relatively short due to the electron-withdrawing effect of the fluorine substituents. With the exception of the N(1)−Si(1)−N(2) angle (86.1°), all the inner angles are larger than 90°.

2.3. Quantum Chemical Study. To understand the formation of the four-membered ring **1b** from the three-membered ring **1a** in a unimolecular isomerization process, quantum chemical calculations were carried out. To reduce the computational expense, these calculations were performed for the derivatives of *N*,*N*′-bis(trimethylsilyl)hydrazine instead of those of *N*,*N*′-bis(*tert*-butyldiphenylsilyl)hydrazine. Since both exocyclic silicon atoms have three methyl groups as substituents, only one isomerization pathway is possible. The corresponding dilithium derivative reacts with SiF_4 to form the three-membered ring **3a**, which subsequently undergoes isomerization into the four-membered ring **3b**.

The structures of **3a** and **3b** were initially fully optimized at the SCF level of theory in conjunction with the standard 6-31G* basis set which comprises 243 contracted Gaussian-type orbitals (cGTOs). The obtained equilibrium geometries were refined by 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 density functional theory (DFT) calculations. To confirm that true minima on the potential energy surface (PES) were found, the Hessians at the stationary points were calculated. The energies were further corrected for zero-point vibrational effects which, however, are only of minor importance in isomerization reactions. The geometry of the transition state was calculated by using the TS routine of GAUSSIAN94[16] and the intrinsic reaction coordinate (IRC) method. The search of the saddle point turned out to be difficult due to the high dimensionality of the problem and the large number of large-amplitude motions involved.

Under the assumption that the Si−N−Si−N−Si skeleton of the three-membered ring **3a** is planar,[17] a structure with C_{2v} symmetry is obtained. However, after having calculated all harmonic vibrational frequencies it turned out that this structure is not a true minimum on the PES. Rather, a geometry with C_2 symmetry (Figure 2, left figure) was found as the energy minimum of **3a**, lying 19.3 kcal mol^{-1} lower in energy compared to the C_{2v} structure. Here, the $SiMe_3$ groups are tilted out of the SiN_2 plane with a dihedral angle of 115.8°. The nitrogen atoms show sp^3 hybridization. The most important structural parameters are calculated as follows (data for C_{2v} structure in parentheses): r(N−N) = 173.6 (168.8) pm, α(N−Si−N) = 62.1 (60.9)°, $r(F_2Si{-}N)$ = 168.4 (166.5) pm, $r(Me_3Si{-}N)$ = 177.9 (175.4) pm, $\alpha(N{-}N{-}SiMe_3)$ = 114.5 (145.1)°.

For the same reasons as with **3a**, planarity was expected for the four-membered ring **3b**. However, the corresponding structure with C_s symmetry is not a true minimum as is indicated by the existence of an imaginary vibrational frequency. This is due to the $N{-}CH_3$ internal rotation that breaks the C_s symmetry resulting in a symmetry-less C_1 structure (Figure 2, right figure). Compared to the optimum C_s geometry, this structure is 1.9 kcal mol^{-1} lower in energy, a value that is on the order of magnitude of typical barriers for internal rotation around single bonds. Nevertheless, the ring is planar with a sum of angles of 360°. The most important structural parameters are calculated as follows (data for the C_s structure in parentheses): $\alpha(N{-}SiMe_2{-}N)$ = 86.9 (86.9)°, $\alpha(N{-}SiF_2{-}N)$ = 90.7 (90.7)°, r(N−N) = 244.0 (244.0) pm, $r(N{-}CH_3)$ = 145.4 (145.5) pm, $r(Me_2Si{-}NCH_3)$ = 177.7 (177.8) pm, $r(Me_3SiN{-}SiMe_2)$ = 177.0 (177.1) pm, $r(F_2Si{-}NCH_3)$ = 171.0 (170.9) pm, $r(Me_3SiN{-}SiF_2)$ = 172.1 (171.9) pm, $r(Me_3Si{-}N)$ = 175.4 (175.6) pm. Since the energetic difference is almost exclusively due to the hindered rotation of the methyl group connected to the nitrogen atom, it should be a reasonable assumption to use C_s symmetry in more extensive electronic structure calculations.

Within the error bars of both theory and experiment and taking into account that the substituents of **1b** and **3b** are different, the calculated geometry of the four-membered ring **3b** agrees nicely with the structure for **1b** obtained by X-ray diffraction.

The energetic difference, ΔE, between **3a** and **3b** is calculated to be 74.7 kcal mol^{-1}. Taking the vibrational zero-point energy

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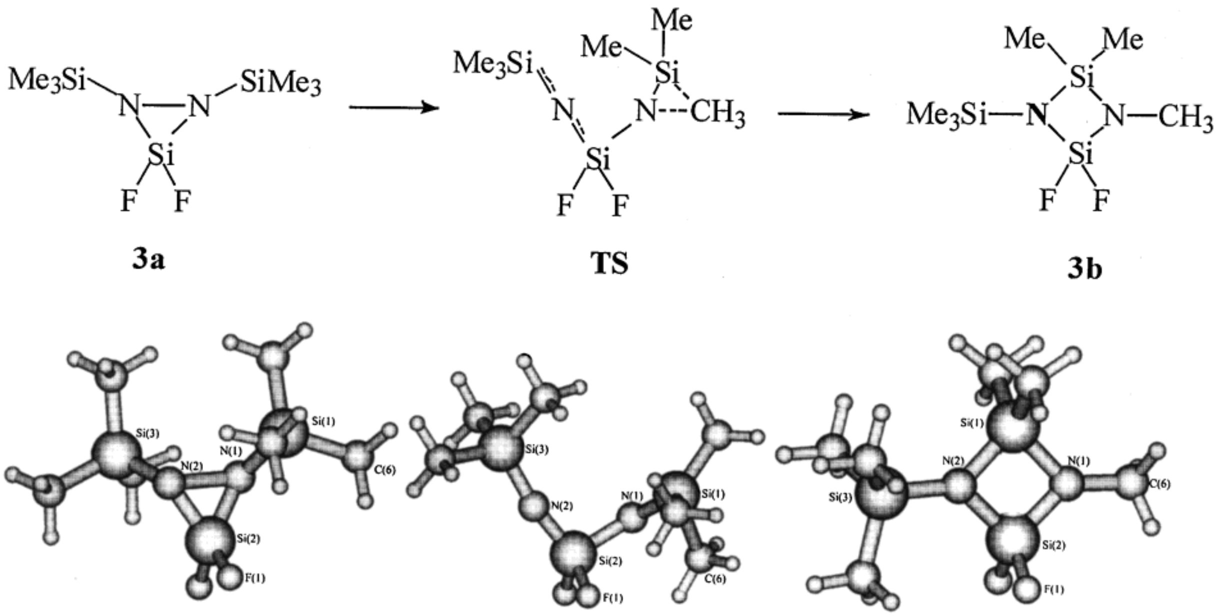

Figure 2. Structures of the three-membered ring, the transition state, and the four-membered ring.

(harmonic level, unscaled) into account, ΔE reduces to 72.4 kcal mol^{-1}. The reaction enthalpy is given by $\Delta_R H°$ (298 K) = −72.1 kcal mol^{-1}. Thus, under the experimental conditions the reaction should be thermodynamically irreversible.

To elucidate the unimolecular rearrangement process, a search of the transition structure (first-order saddle point) has been carried out. In the first search, C_s symmetry was imposed with a planar Si−N−Si−N−Si skeleton. Since the calculation of harmonic vibrational frequencies revealed the existence of more than one imaginary frequency, the symmetry was lowered to C_1. The energy of the C_1 saddle point (see Figure 2, middle structure) is 5.0 kcal mol^{-1} lower than that in C_s symmetry. The most important structural parameters are calculated as follows (data for the C_s structure in parentheses): The nitrogen−nitrogen distance r(N−N) = 259.2 (258.4) pm is stretched by 85.6 (89.6) pm compared to that of **3a**. Thus, the corresponding bond is broken and a diradical is formed. The angle α(N−Si−N) =100.4 (100.7)° is widened by 38.3 (39.8)° compared to that of **3a**. The Si−N−Si angle on the nonreactive (nr) side, α^{nr}($Me_3Si-N-SiF_2$) = 162.4 (174.2)°, indicates that the unpaired electron is delocalized along the Si−N−Si chain. The Si−N−Si angle on the reactive (r) side, α^{r}($F_2Si-N-SiMe_3$) = 127.6 (166.2)°, has changed very little in comparison with **3a** (128.9°). The reactive center C−Si−N forms a nearly equilateral triangle with r(C−Si) = 209.5 (210.4) pm, r(N−C) = 197.6 (195.1) pm, and α(C−Si−N) = 62.2 (61.4)°. The four Si−N distances are given as follows: r^{nr}($N-SiF_2$) = 159.8 (159.6) pm, r^{r}(F_2Si-N) = 177.3 (175.6) pm, r^{nr}(Me_3Si-N) = 169.8 (169.0) pm, and r^{r}($N-SiMe_3$) = 166.5 (163.2) pm. Compared to the bonds in the three-membered ring the two Si−N bonds on the nonreactive side are shortened by 8.1 (Me_3Si-N) and 8.6 pm ($N-SiF_2$) pm, respectively. The Si−N bond of the reactive center is shortened by 11.4 pm, whereas the neighboring Si−N bond is stretched by 8.9 pm. The complete structural data set is available from one of the authors (sschmat@gwdg.de).

The imaginary frequency of the reactive motion (passage through the transition state) amounts to 447i cm^{-1} with a reduced mass of 6.8 amu. The corresponding normal coordinate is graphically displayed in Figure 3. The carbon atom C(6) and the nitrogen atom N(1) approach each other and form a new bond. The reduced mass for the relative motion of a nitrogen atom and a methyl group is 7.2 amu.

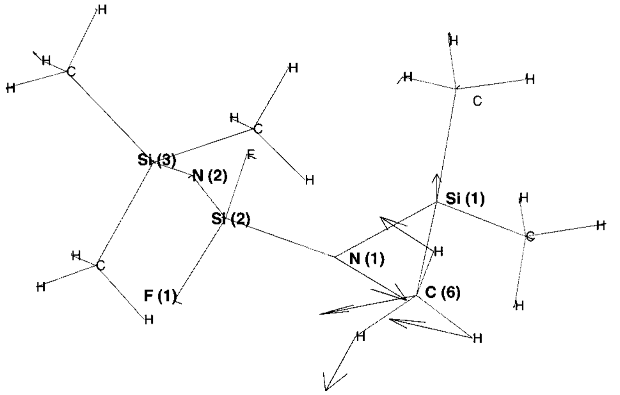

Figure 3. The reaction coordinate at the saddle point, i.e., the normal coordinate of the mode with the imaginary vibrational frequency. The nitrogen atom N(1) and the methyl group C(6)H_3 move toward each other (see the text).

Starting from the saddle point the reaction path (RP) was followed in both directions by using the IRC method as implemeted in GAUSSIAN94.[16] 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 gradients at the end points of the arc are tangent to the path.[18,19] The result obtained with mass-weighted internal coordinates and the standard step size 0.1 amu$^{1/2}$ a_0 (= 5.3 amu$^{1/2}$ pm) is given in Figure 4. The calculation terminated at point A (B) in the reactant (product) valley. Starting from these geometries (points A and B in Figure 4) which are very similar to those of the species **3a** and **3b**, it was possible to reach straightway the reactant and product minimum structures **3a** and **3b**. Only the path within the interval [A,B] in Figure 4 is an approximation to the true minimum energy path (MEP).[20] Beyond these points the abscissa in Figure 4 scales with the number of iterations in the geometry optimization and is not proportional to any well-defined geometrical parameter. Nev-

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(20) To assess the validity of this approximation, we repeated the IRC calculation with step sizes of 0.05 amu$^{1/2}$ a_0 and 0.2 amu$^{1/2}$ a_0. Particularly in the vicinity of the transition state, the resulting curves are indistinguishable from the curve given in Figure 4.

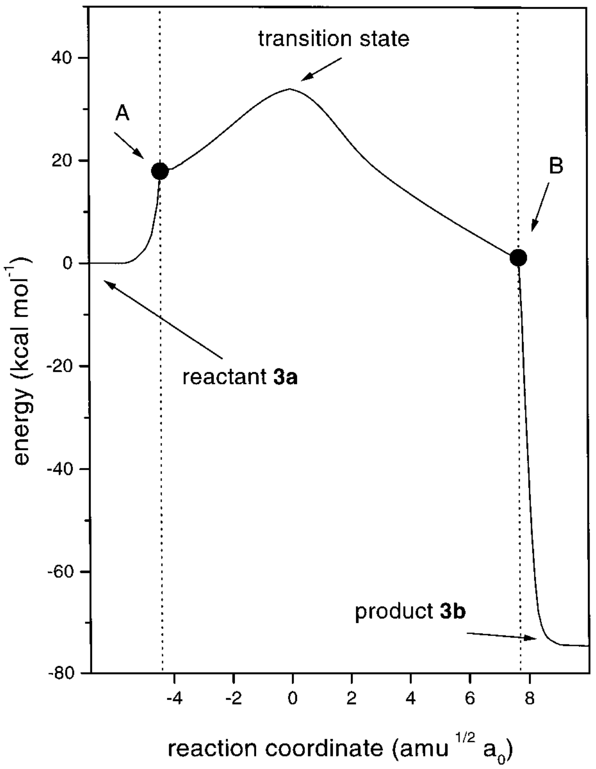

Figure 4. Minimum energy path for the isomerisation reaction **3a** → **3b** calculated by using the intrinsic reaction coordinate method (see the text). Beyond the dashed lines through points A and B the curve shows that a direct connection exists between reactants and products; however, the abscissa has no physical significance for these parts of the reaction path (see the text).

ertheless, this investigation sufficiently demonstrates that the rearrangement process proceeds through a single transition structure without further reaction intermediates.

In summary, the unimolecular rearrangement process can be described as follows: The reaction starts with the stretching and eventually breaking of the strained N−N single bond. Measured from the reactant side, the barrier height amounts to 34.0 kcal mol^{-1} (inclusion of zero-point vibrational energy contribution yields 33.0 kcal mol^{-1}). Thus, the energy needed for the N−N bond cleavage is relatively small. The process is compensated by the energy gain through the delocalization of one of the two N−N bond electrons along the $Me_3Si-N-SiF_2$ structure on the nonreactive side. This explanation is supported by the small deviation from linearity for this structure and the fact that both Si−N bonds are shortened by more than 8 pm.

The nonreactive $SiMe_3$ group takes a coplanar configuration with respect to the NSiN three-membered structure. At the transition state a triangle is formed of Si(1), C(6), and N(1) (see Figure 2). Thus, the rate determining simultaneous motion is the fission of the Si−C bond and the formation of the C−N bond, in summary a methyl group transfer. After formation of the C−N bond, the $SiMe_2$ moiety swings inward and recombines with the unsaturated nitrogen atom. As usual for radical pair recombinations no activation energy is required.

The saddle point is characterized as an early TS that is closer to **3a** than to **3b**. Under the experimental conditions, the activation energy of 34 kcal mol^{-1} is provided by heating and additionally through the exothermicity of the reaction.

Making use of the structural parameters and harmonic vibrational frequencies of the reactant species **3a** and the transition state the rate constant for the isomerization process can be estimated within the framework of transition state theory.[20] All free and hindered rotational modes were treated as torsional vibrations. A symmetry number $\sigma = 2$ was used in the rotational partition function of **3a**. An Arrhenius plot for the rate constant in the temperature interval from 300 to 500 K is shown in Figure 5. The rate constant is given by $k(T) = (3.49 \times 10^{14})\ \exp(-33.7\ \text{kcal mol}^{-1}/RT)\ s^{-1}$.

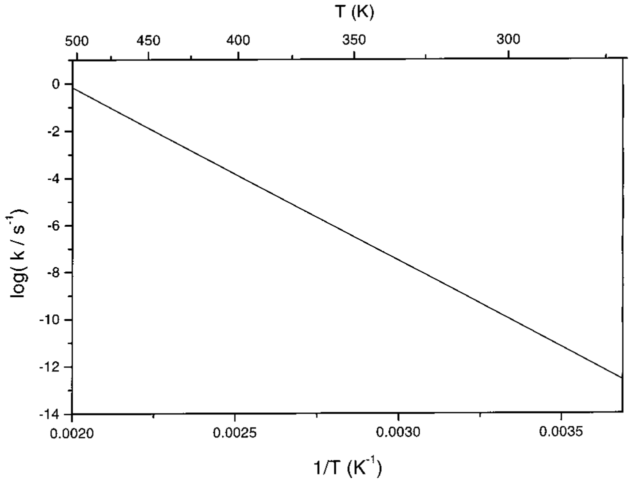

Figure 5. Arrhenius plot for the isomerization reaction **3a** → **3b** in the temperature range from $T = 270$ to 500 K.

It should be noted that a bimolecular reaction mechanism is in principle possible. However, experimental investigations have shown that no crossover products were formed when different reactant species were present. For that reason, a possible bimolecular mechanism was not studied in this work.

For comparison with the DFT results, MP2 calculations were performed at the B3LYP/6-31G* geometries of **3a**, **3b**, and the transition state. The (s,p) parts of Dunning's cc-pVTZ basis set[22] were employed for carbon, nitrogen, fluorine, and silicon. Functions of d-type were taken from the cc-pVDZ basis set[22] which was also used for the s and p functions at hydrogen; in total, the chosen basis set comprises 336 cGTOs. The calculations were carried out with MOLPRO 2000.1[23] on the Compaq DS 20 workstation of the Abteilung für Theoretische Chemie at Göttingen. The energetic difference between reactants and products was calculated to be 73.3 kcal mol^{-1}. This value agrees nicely with the DFT/6-31G* result. Making use of the DFT/6-31G* vibrational frequencies, we obtain $\Delta_R H°(298\ K) = -70.7$ kcal mol^{-1}. The height of the barrier to isomerization is calculated to be 46.0 kcal mol^{-1}, which is 35% larger than the DFT result.

Mixing polarization functions from one basis set with the valence functions from another can in some cases lead to an unbalanced treatment of electron correlation. For that reason we repeated the above single-point calculations with the cc-pVDZ basis set for all atoms (284 cGTOs).[22] Although somewhat smaller and less flexible than the hybrid basis, it avoids the potential pitfalls of an uneven treatment of correlation. In good agreement with the above results we obtain 74.3 kcal mol^{-1} for the energetic difference between **3a** and **3b** and 47.1 kcal mol^{-1} for the barrier height.

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Quantitatively better results can only be achieved by methods which include the major fraction of the electron correlation energy in a systematic way (e.g. MP4 or CCSD(T)). However, a resonable 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.

Experimental Section

All reactions were conducted under an argon or nitrogen atmosphere.

Mass spectra were taken on either a Varian CH5-spectrometer, a Finnigan MAT 8200-spectrometer, or a Finnigan MAT 95-spectrometer. NMR spectra were recorded in $CDCl_3$ (TMS) on either a Bruker AM 250-, a MSL-400-, or an AVANCE 500 DRX-spectrometer.

Synthesis of 1-*tert*-Butyldiphenylsilyl-2-*tert*-butyl-4,4-difluoro-2,3-diphenylcyclodisilazane (1b). *N*,*N′*-Bis(*tert*-butyldiphenylsilyl)hydrazine[24] (0.02 mol) in 100 mL of *n*-hexane was treated with 0.04 mol of *n*-butyllithium (23% in *n*-hexane). After the solution was boiled for 2 h, 50 mL of THF was added to dissolve the formed lithium derivative.[24] At a temperature of −180 °C, 0.02 mol of tetrafluorosilane was condensed to the solution of the lithium salt in an autoclave. The reaction solution was heated to 80 °C within 1 h and stirred for another 2 h. THF and *n*-hexane were removed in vacuo, and the residue was solved in *n*-hexane. Lithium fluoride was removed by centrifugation. **1b** crystallized at room temperature. $C_{32}H_{38}F_2N_2Si_3$: molecular weight = 572.9 g/mol, yield = 30%, mp 180 °C; MS (70 eV) *m*/*z* (%) 572 (5) [M^+]; NMR measurement in $CDCl_3$, TMS bzw. C_6F_6 int; ^{1}H NMR δ 0.87 $SiCMe_3$, 1.00 $SiCMe_3$, 6.6−7.7 C_6H_5; ^{13}C NMR δ 19.25 Si*C*Me_3-Ph_2, 21.80 Si*C*Me_3Ph (d, ^4J(CF) = 4.0 Hz), 27.18 SiC*C*$_3$ (d, ^5J(CF) = 1.8 Hz), 29.09 SiC*C*$_3$, 120.9−136.5 NC_6, SiC_6; ^{19}F NMR (AB Typ) δ 31.0 F_A, 33.3 F_B (d, $^2J(F_AF_B)$ = 89.24 Hz); ^{29}Si NMR −77.15 SiF_2 (t, *J*(SiF) = 263.57 Hz), −11.25 $SiCMe_3$, −8.79 $SiCMe_3$.

Synthesis of 1-Di(*tert*-butyl)silyl-2,2-di(*tert*-butyl)-4,4-di(isopropyl)cyclodisilazane (2b). A solution of 0.01 mol of *N*,*N′*-bis(di-*tert*-butylsilyl)hydrazine[25] in 20 mL of *n*-hexane was treated with 0.02 mol of *n*-butyllithium (23% in *n*-hexane) and the solution was boiled for 2 h. After the lithium salt[25] was disolved in THF, 0.01 mol of difluorodiisopropylsilane was added and the solution was boiled for 2 h. Lithiumfluoride was removed by centrifugation. **2b** crystallized at room temperature. $C_{22}H_{52}N_2Si_3$: molecular weight = 428.9 g/mol, yield = 30%, mp 153 °C; MS (70 eV) *m*/*z* (%) 371 (100) [$M^+ - CMe_3$]; NMR measurement in C_6D_6, ^{1}H NMR δ 0.65 NH, 1.19 $SiCMe_3$, 1.22 $SiCMe_3$, 1.25−1.42 $CHMe_2$, 4.33 SiH; ^{13}C NMR δ 19.28 *C*H, 19.78 $CHMe_2$, 19.82 $CHMe_2$, 21.76 *C*Me_3, 23.75 *C*Me_3, 29.41 C*C*$_3$, 30.23 C*C*$_3$; ^{29}Si NMR δ 2.73 $Si(CHMe_2)_2$, 6.77 $Si(CMe_3)_2$, 8.84 $Si(CMe_3)_2$.

Crystal Structure Determination. 1b: $C_{32}H_{38}F_2N_2Si_3$, monoklinic, $P2_1$, a = 848.17(11) Å, b = 1119.25(15) Å, c = 1634.20(3) pm, β = 98.482(12)°, V = 1.5344(4) nm^3, Z = 2, $\rho_{ber.}$ = 1.24 Mg/m^3, μ(Mo Kα) = 0.191 mm^{-1}, structure solution and refinement with SHELX-TL,[26] Stoe-Siemens-AED-diffractometer at 150 K, 2882 reflections measured, 2877 independent and 2875 used in refinement at F^2: wR_2 = 0.1288 [$I > 2\sigma(I)$], R_1 = 0.0497.

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Supporting Information Available: Tables of crystal data and structure refinement**,** atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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