Unusual Isomerization Reactions in 1,3-Diaza-2-silacyclopentanes

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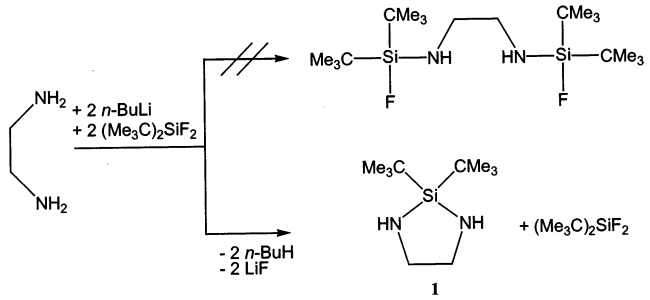
Summary: The preparation of a doubly NH functional 1,3-diaza-2-silacyclopentane is reported. A new rearrangement of N-silylated diazasilacyclopentanes is described, and density functional calculations are used to predict a two-step reaction mechanism correlated with the experimental data.

Focal points in chemical research on silicon- and nitrogen-containing compounds are pyrolytic reactions yielding binary and ternary ceramic powders and the stabilization of silicon with coordination numbers lower than four: e.g., in the form of silanimines or silylenes. In this context, five-membered rings synthesized by starting from ethylenediamine with elements of the main group IV of the periodic table have been the subject of intensive research over the last few years.[1−3] Their chemistry shows unprecedented reactions, where in particular 2-fold-coordinated compounds of elements of the main group IV (carbenes, silylenes) could be stabilized.[1−3]

Though N,N′-bis(silylated) 1,3-diaza-2-silacyclopentanes had already been synthesized in 1959,[4−6] attempts to isolate the corresponding NH-functional five-membered rings have not been successful so far.[7] Thus, their reactive behavior is completely unknown. We have found that the dilithium derivative of ethylenediamine reacts smoothly with di-*tert*-butyldifluorosilane to give the hitherto unknown ring species **1** (Scheme 1).[8] Neither by changing the conduction of the reaction nor by varying the molar ratios was the formation of the acyclic N,N′-bis(fluorosilyl)ethylenediamines observed.

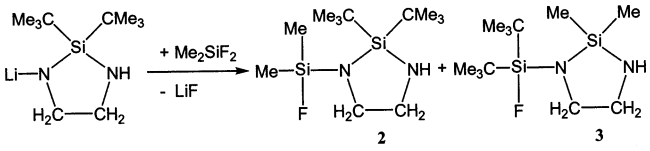
Having isolated the 2-fold NH-functional compound **1**, a five-membered heterocycle has been provided that allows a stepwise substitution as well as a coupling of ring systems. Already the first follow-up reactions have

Scheme 1



shown unusual results: in the reaction of the lithiated 1,3-diaza-2-silacyclopentane **1** with Me_2SiF_2 not only the expected compound 1-(fluorodimethylsilyl)-2,2-di-*tert*-butyl-1,3-diaza-2-silacyclopentane (**2**)[9] was obtained but also the structural isomer 1-(di-*tert*-butylfluorosilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane (**3**)[9] could be isolated, which is formed according to a hitherto unknown isomerization mechanism. A separation of the two isomers by distillation or chromatography was not possible.

Scheme 2



The product ratio **2**:**3** was determined to be 2:1 by means of NMR spectroscopy. The product ratio was established after a distillation with boiling point of 129 °C / 20 mbar. The heat in the distillation flask was measured as 160 °C. The experimental product ratio correlates with the fact that **2** is calculated to be more stable than **3** by ca. 3.3 kcal mol^{-1}.

Since the exchange of endo- and exocyclic silicon atoms cannot be explained using a simple reaction mechanism, we have carried out quantum-chemical (density functional, DFT) calculations to shed more light on the isomerization process. Though the calculations

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(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.
(2) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, W.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem.* **1992**, *104*, 1489.
(3) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691.
(4) Henglein, F. A.; Lienhard, K. *Macromol. Chem.* **1959**, *32*, 218.
(5) Kummer, D.; Rochow, E. G. *Z. Anorg. Allg. Chem.* **1963**, *321*, 21.
(6) Diedrich, F.; Ebker, C.; Klingebiel, U.; Reiche, C.; Labahn, T.; Magull, J.; Noltemeyer, M. *Z. Naturforsch.* **2002**, *57b*, 99.
(7) Schlosser, T.; Sladek, A.; Hiller, W.; Schmidbaur, H. *Z. Naturforsch.* **1994**, *49b*, 1247.

(8) Synthesis of **1**: 0.02 mol of ethylendiamine in 100 mL of *n*-hexane was metalated with twice the molar amount of *n*-butyllithium. At 0 °C, 0.02 mol of $(Me_3C)_2SiF_2$ was added dropwise and the mixture was heated under reflux for 5 h. Thermal separation in vacuo (0.01 mbar) and distillation (95 °C/13 mbar) gave an 80% yield of **1**. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.73 (s, 2H, NH), 1.00 (s, 18H, CMe_3), 3.08 (s, 4H, CH_2). ^{13}C NMR (250 MHz, $CDCl_3$): δ 21.3 (s, CMe_3), 27.8 (s, CMe_3), 44.7 (s, CH_2). ^{15}N NMR (500 MHz, $CDCl_3$): δ −372.4 (d, NH, $^1J_{NH}$ = 75.9 Hz). ^{29}Si NMR (250 MHz, $CDCl_3$): δ 11.5 (s, Si). MS (EI; *m*/*z* (%) [u]): 143 (100) $[M - CMe_3]^+$. Anal. Calcd for $C_{10}H_{24}N_2Si$ (mol wt 200.45): C, 59.92; H, 12.07. Found: C, 60.05; H, 12.24.

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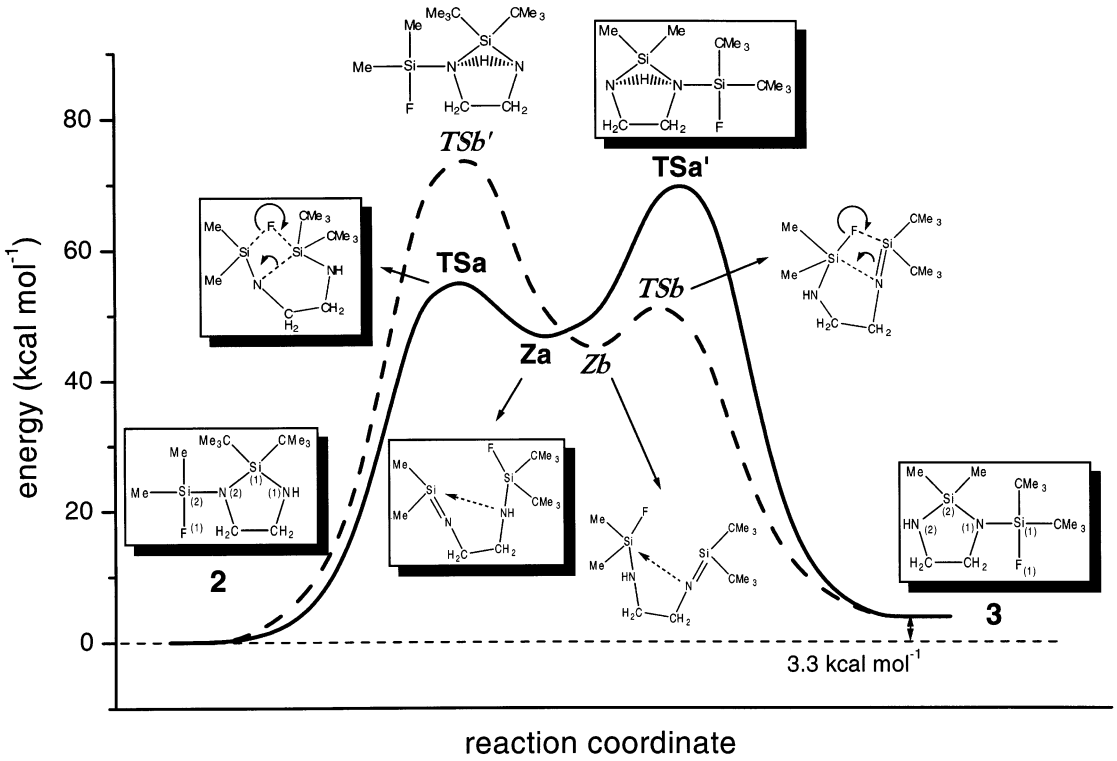

Figure 1. Two possible reaction pathways for the intramolecular isomerization **2** → **3** (B3LYP/6-31+G(d,p) results): solid line, mechanism **a**; dotted line, mechanism **b**. The structures pertinent to the most likely mechanism (**a**) are displayed in frames.

were performed for isolated molecules in the gas phase, the results can easily be compared with the experiment that was conducted in the aprotic, nonpolar solvent *n*-hexane.

The structures of the eight stationary points **2**, **3**, **TSa, Za, TSa′, TSb′, Zb**, and **TSb** (see Figure 1 and Table 1; **a** and **b** denote the different isomerization pathways) on the potential energy surface (PES) were fully optimized employing the three-parameter hybrid method of Becke, B3LYP,[10,11] first in conjunction with the 6-31G(d) basis set. The optimized geometry was further refined using the 6-31+G(d,p) basis, which contains diffuse functions and additional polarization functions at the hydrogens to guarantee an appropriate description of the loose bonding situation in the saddle point structures. Hessian matrices at all stationary points on the PES were calculated to verify their nature. The energies were further corrected with respect to zero-point vibrational effects, which however have only a small influence on the relative energies in isomerization reactions. The geometries of the first-order saddle points ("transition states") were identified using the intrinsic reaction coordinate (IRC) method.[12,13] All computations were carried out using the program package Gaussian 98.[14]

Table 1. Relative Energies (in kcal mol^{-1}) of the Species Involved in the Isomerization[a]

mechanism a		mechanism b	
2	0.0 (0.0)		
TSa	55.7 (55.0)	**TSb′**	74.3 (71.6)
Za	46.1 (44.6)	**Zb**	44.3 (42.8)
TSa′	70.5 (67.4)	**TSb**	52.2 (51.0)
3	3.3 (3.6)		

[a] From B3LYP/6-31+G(d,p) calculations. Data in parentheses include the zero-point vibrational energy (at the harmonic level; transitional modes not included). Note that E(**TSa**) > E(**TSb**) and E(**TSa′**) < E(**TSb′**).

(9) Synthesis of **2**/**3** (yields a product mixture): 0.01 mol of **1** in 50 mL of *n*-hexane was lithiated with 0.01 mol of *n*-butyllithium (15% in *n*-hexane) and added dropwise to 0.01 mol of Me_2SiF_2 in 50 mL of *n*-hexane at −30 °C. Distillation (20 mbar/129 °C) gave a product mixture of **2** and **3** in 54% and 27% yields, respectively. Data for **2** are as follows. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.28 (d, 6H, $SiMe_2F$, $^3J_{HF}$ = 6.45 Hz), 1.02 (d, 18H, $SiCMe_3$, $^6J_{HF}$ = 0.26 Hz), 3.10 (m, 4H, CH_2). ^{13}C NMR (250 MHz, $CDCl_3$): δ −0.8 (d, $SiMe_2F$, $^2J_{CF}$ = 18.7 Hz), 22.0 (s, $SiCMe_3$), 28.2 (d, $SiCMe_3$, $^5J_{CF}$ = 1.2 Hz), 44.4 (s, CH_2NH), 46.1 (d, CH_2, $^3J_{CF}$ = 3.4 Hz). ^{19}F NMR (200 MHz, $CDCl_3$): δ 21.3 (sep, SiF, $^3J_{FH}$ = 6.5 Hz). ^{29}Si NMR (250 MHz, $CDCl_3$): δ 7.3 (d, SiF, $^1J_{SiF}$ = 269.1 Hz), 15.4 (d, $SiCMe_3$, $^3J_{SiF}$ = 0.4 Hz). MS (EI; *m*/*z* (%) [u]): 276 (5) $[M]^+$, 219 (100) $[M - CMe_3]^+$. The MS data of **2** and **3** are equal and could not be separated by GC/MS. Anal. Calcd for $C_{12}H_{29}FN_2Si$ (mol wt 276.54): C, 52.12; H, 10.57. Found: C, 52.31; H, 10.74. Data for **3** are as follows. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.18 (d, 6H, $SiMe_2$, $^5J_{HF}$ = 1.32 Hz), 1.06 (d, 18H, $SiFCMe_3$, $^4J_{HF}$ = 1.11 Hz), 3.10 (m, 4H, CH_2). ^{13}C NMR (250 MHz, $CDCl_3$): δ 2.0 (d, $SiMe_2$, $^4J_{CF}$ = 2.8 Hz), 21.4 (d, $FSiCMe_3$, $^2J_{CF}$ = 13.6 Hz), 28.7 (d, $FSiCMe_3$, $^3J_{CF}$ = 1.0 Hz), 44.8 (s, CH_2NH), 47.0 (d, CH_2, $^3J_{CF}$ = 1.6 Hz). ^{19}F NMR (200 MHz, $CDCl_3$): δ 7.5 (s, $SiFCMe_3$, $^1J_{FSi}$ = 282.2 Hz). ^{29}Si NMR (250 MHz, $CDCl_3$): δ 4.3 (d, $SiFCMe_3$, $^1J_{SiF}$ = 282.3 Hz), 15.0 (d, $SiMe_2$, $^3J_{SiF}$ = 3.0 Hz).

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(12) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(13) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.: Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN98. Revision A.7; Gaussian, Inc., Pittsburgh, PA, 1998. *Gaussian 98*, Revision A.7; Gaussian, Inc., Pittsburgh, PA, 1998.

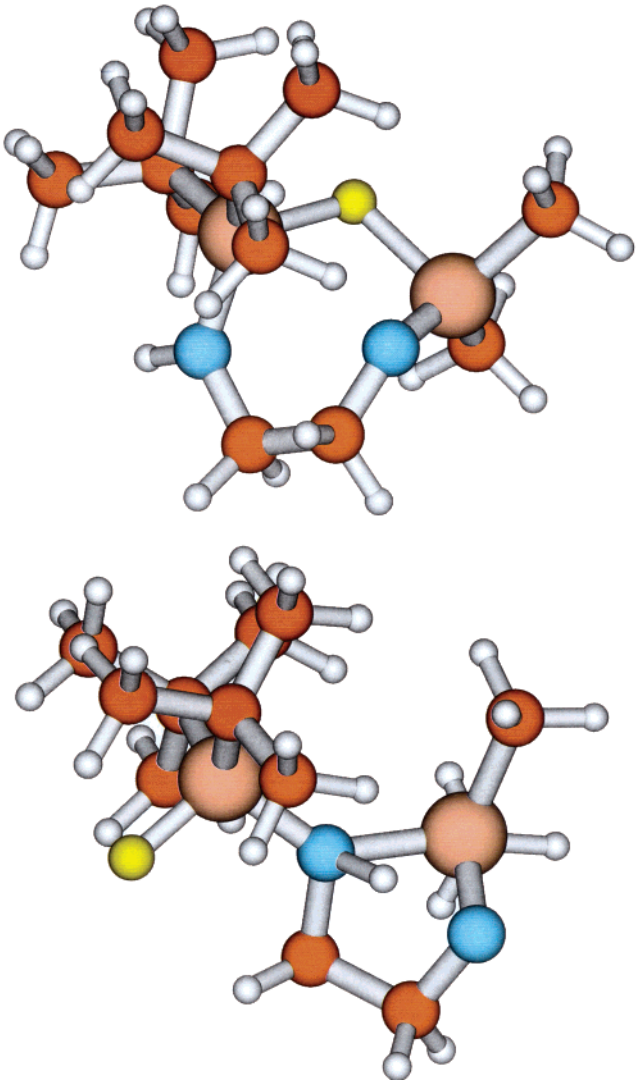

Figure 2. Calculated structures for the transition states **TSa** (top) and **TSa′** (bottom): nitrogen, blue; fluorine, yellow. Important geometrical parameters are as follows. **TSa**: $r((Me_3C)_2Si-F) = 181.3$ pm; $r(F-SiMe_2) = 194.5$ pm; $\alpha(Si-F-Si) = 110.6°$; $r((Me_3C)_2Si-NSi) = 274.5$ pm. **TSa′**: $r(FSiN-H) = 122.5$ pm; $r(H-N) = 153.4$ pm ; $\alpha(N-H-N) = 120.6°$. Note that **TSa** is characterized as a "late" transition state, while **TSa′** is an "early" transition state. The harmonic vibrational wavenumbers of the transitional modes are calculated to be ω_{TS}(**TSa**) = 147.0 i cm^{-1} and ω_{TS}(**TSa′**) = 1403.6 i cm^{-1}.

According to our calculations, the reaction mechanism comprises two steps and can be summarized as follows. In the first step, the $(Me_3C)_2Si-NSiMe_2F$ bond in **2** is broken after thermal excitation (during the distillation process), yielding the iminosilane **Za** with an $N=SiMe_2$ double bond. The pertinent transititon state **TSa** is described by a loose four-center structure with two intramolecular Si···F and one Si···N interactions (see Figure 2, top). The bridge formation between the fluorine atom and the endocyclic silicon leads to an F transfer to this atom.

The free electron pairs of the nitrogen atoms in the intermediate structure **Za** are in close contact with the respective silicon atom that they are not bonded to directly. **Za** has only a slightly lower energy than the first saddle point **TSa**, while the second transition state **TSa′** lies considerably higher in energy. Now, the $SiMe_2$ group attacks the HN nitrogen atom, re-forming the five-membered-ring species **3**. During ring closure, the hydrogen migrates to the other nitrogen atom. The corresponding transition state structure (see Figure 2, bottom) suffers substantial intramolecular steric repulsion and rationalizes the high classical barrier for this reaction. A similar two-step mechanism including a 1,3-H shift in the second step has been found in the formation of five-membered SiN_2SiC rings.[15]

Since the structures of reactant **2** and product **3** are identical, apart from the substituents at the endo- and exocyclic silicon atoms that change position, also a reverse mechanism should be possible to explain the reaction. Thus, starting from **2**, first the sterically demanding transition state **TSb′** is passed (see Figure 1) that includes the 1,3-H shift between the two silicon atoms and the ring opening yielding the intermediate **Zb**, which is characterized by an $N=Si(CMe_3)_2$ double bond. In the second step (**TSb**), the fluorine atom attacks the other silicon atom, reconstructing the five-membered-ring species **3**, while simultaneously an intramolecular bond between the Me_2Si silicon atom and the nitrogen is formed.

While on the basis of quantum-chemical calculations both mechanisms are possible, a clear statement which pathway is in fact taken can only be obtained from dynamic calculations. Quantum-dynamic investigations of such relatively complex systems are not possible at present and classical studies ("molecular mechanics") do not account for quantum effects (in particular tunneling), which play an important role in the H shift. However, simple arguments support mechanism **a** (**2** → **TSa** → **Za** → **TSa′** → **3**) under thermal conditions: Here, the activation energy that is needed to overcome the highest point in the reaction profile is divided into two steps. In mechanism **b** (**2** → **TSb′** → **Zb** → **TSb** → **3**), on the other hand, the whole activation energy has to be provided in the first step. Thus, mechanism **a** is the favored reaction pathway for this unexpected intramolecular rearrangement. A bimolecular mechanism can be excluded, because the result of the reaction does not depend on concentration effects. The isomerization presented in this article provides a preparative approach to 1,3-diaza-2-silacyclopentanes with *any* substituents at the endocyclic silicon atom. These species cannot be synthesized directly so far.

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(15) Schmatz, S. *J. Phys. Chem. A* **2001**, *105*, 3875.