Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 197–204
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

From lithium ketazides to isomeric silylketazine-rings – imine-enamine tautomerism

Nina Armbruster [a], Martin Görth [a], Uwe Klingebiel [a,*], Stefan Schmatz [b]

[a] Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany
[b] Institut für Physikalische Chemie der Universität Goettingen, Tammannstrasse 6, D-37077 Göttingen, Germany

Received 12 March 2007; received in revised form 9 October 2007; accepted 16 October 2007
Available online 25 October 2007

Abstract

Di(*tert*-butylmethyl)ketazine (**I**) reacts with *n*-BuLi in a 1:1 molar ratio to give a monolithium salt (**II**). The reaction of **II** with $^{t}Bu_2SiF_2$ in *n*-hexane leads, even in a 1:1 molar ratio, to the formation of the isomeric five- and four-membered ring compounds **1** and **2**. Compound **1** has an endocyclic imine and an exocyclic enamine unit. The opposite is found for **2**. The acyclic monosubstitution product, $^{t}Bu_2SiFCH_2–C^{t}Bu{=}N–N{=}C^{t}BuCH_3$ (**III**) could not be isolated. It reacts with the lithium ketazide to give **1** or **2**. **I** is reformed. The reaction in THF yields only the four-membered ring **2**. In a comparable reaction of the lithium ketazide and $(H_3C)_2SiF_2$, the substitution product **3** could be isolated. A possible formation mechanism for **2** includes an intermediate silene **IV**. Both compounds **1** and **2** react with $H_3C–OH$ under cleavage of the endocyclic Si–N-bond to give the addition product **5**. The reaction mechanism includes a hydrogen shift from a nitrogen atom to a carbon atom via an imine-enamine tautomerism. In a 2:1 molar ratio, *n*-BuLi and the di(*tert*-butylmethyl)-ketazine (**I**) form the dilithium salt, **6**. Compound **6** crystallizes from THF as trimer with four imine and two enamine units. A seven-membered ring (**7**) isomeric to **1** and **2** is the result of the reaction of **6** with $^{t}Bu_2SiF_2$. Compound **7** contains one imine and one enamine unit in the ring skeleton.

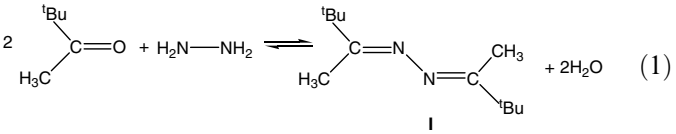
The comparable reaction of the $(CH_3)_3Si$-substituted dilithium-di(*tert*-butylmethyl)ketazide and $^{t}Bu_2SiF_2$ yields the five-membered ring compound **8** with one endocyclic imine and one exocyclic enamine unit.

Quantum chemical calculations of **1**, **2**, **7** and the intermediate silene **IV** have been carried out and show a low energy difference between the cyclic silyl-ketazine isomers.

Keywords: Silylketazine-rings; Dilithium ketazide; Structural isomers; Imine-enamine tautomerism; Quantum chemical calculations

1. Introduction

Ammonia or primary amines react with ketones or aldehydes to form imines. Enamines are obtained from aldehydes or ketones with secondary amines. Enamines of primary amines or even of ammonia also exist, but only in equilibrium with an imine isomer. The imine obtained from the reaction of an aldehyde or ketone with hydrazine in a 2:1 molar ratio is an azine, resp. ketazine,

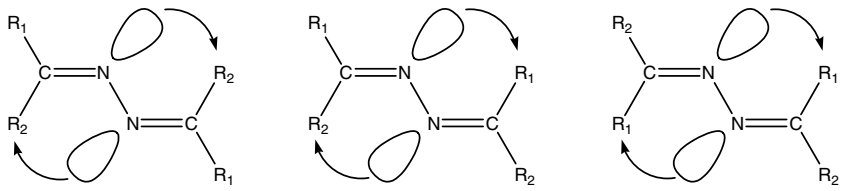


(1)

The isomerism of ketazines corresponds to the C=N-isomerism [1–3]. Differences of the chemical properties are based on the *syn*- and *anti*-configuration of the ketazines. Depending on the neighborhood of the lone electron pair of the nitrogen and the substituent R_1, these isomers are called *anti–anti*-, *anti–syn*-, and *syn–syn*-conformers [2,3] (see Scheme 1).

* Corresponding author. Tel.: +49 551 393 052; fax: +49 551 393 373.
E-mail address: uklinge@gwdg.de (U. Klingebiel).

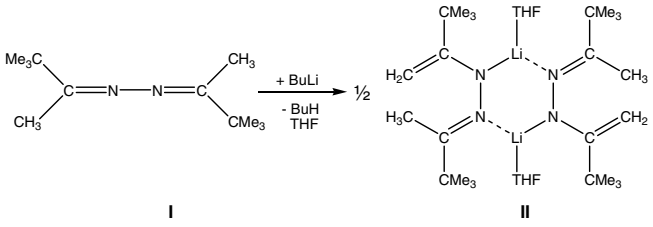
0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.10.033



Scheme 1. Conformers of azines.

Bulky substituents are able to prevent this isomerization [4]. Due to quantum chemical calculations [5], four stable structures of the monolithium salt and one structure of the dilithium salt of **I** exist and give an indication of an imine-enamine tautomerism in ketazides.

Crystals, isolated from THF, of the lithiated di(*tert*-butylmethyl)ketazine (**I**) were characterized as the dimer **II** [5], which contains two imine- and two enamine units,



(2)

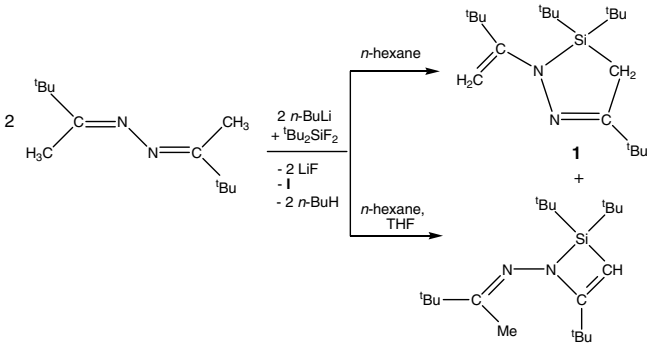
Recently represented reactions of lithiated ketazines with haloboranes [5,6], -silanes [7,8], and -phosphanes [6] yielded surprising results, e.g., the backbone of the ketimine structure is maintained in reactions with halotriorganylsilanes [7,8]. On the other hand, half an imine-enamine isomerization occurs in reactions with dihaloboranes, -silanes, and -phosphanes [4,8]. Five-membered rings with an endocyclic imine- and exocyclic enamine-bond are obtained. Reactions of the dilithiated ketazine with dihalosilanes gave only the five-membered ring isomer with the silyl group as part of the ring bonded to one nitrogen and one methylene group.

In this paper, we present results of our efforts to characterize the dilithium salt of **I** (**II**) and carry out reactions of the mono- and dilithiated ketazine, as well as its mono-trimethylsilyl-substituted derivative **7** with di-*tert*-butyldifluorosilane.

2. Results and discussion

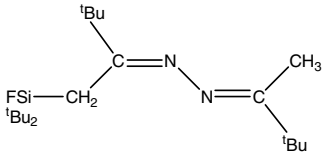
2.1. Isomeric four- and five-membered silylketazine-rings

The reaction of the lithium salt of di(*tert*-butylmethyl) ketazine **I** with $^{t}Bu_2SiF_2$ leads in *n*-hexane at 0 °C to the formation of a mixture of the isomeric four- and five-membered rings **1** and **2**. Using THF as solvent, the lithium ketazide **II** is formed and only the four-membered 1-aza-2-sila-cyclobutene **2** is obtained,



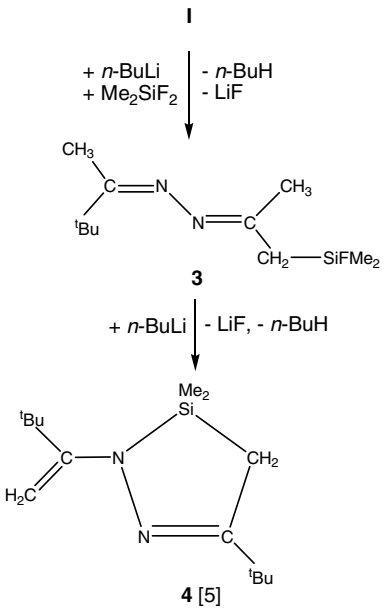
(3)

The reactions were carried out in a 1:1 molar ratio. The mono substitution product (**III**) could not be isolated.



III

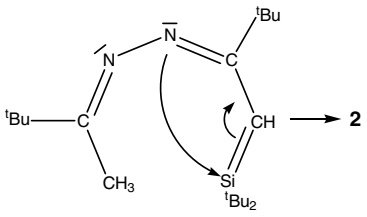
However, it is easily obtained in the comparable reaction of lithiated di(*tert*-butylmethyl)ketazine **I** with F_2SiMe_2. In this case the five-membered ring [5] is formed in a second step,



(4)

Complex **1** has an endocyclic imine and an exocyclic enamine unit, whereas the opposite is true for **2**. The substitution product **III**, primarily formed, has two types of acidic H-atoms, the CH_2Si- and the CH_3C-group. Depending on the reaction conditions and the solvent used, one of these groups is deprotonated by the lithium ketazide and the ketazine is reconverted. LiF-elimination in *n*-hexane leads to the formation of the five-membered 1,2-diaza-3-silacylopentene **1** and to the four-membered 1-aza-2-silacyclobutene **2**, whereas in THF only **2** is obtained (see Scheme 2).

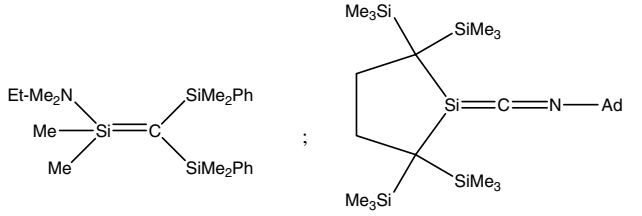
The formation of **2** probably occurs via an intermediate silene (**IV**).



IV

Unfortunately, we did not succeed in preparing single crystals of **1** or **2** suitable for a crystal structure analysis, but the isomers **1** and **2** are definitely identified. The NMR data of **1** are comparable with those of known 1,2-diaza-3-silacyclopentenes [5].

The ^1H NMR-spectrum of **1** shows the $SiCH_2$-protons at 1.46 ppm and two signals for the $=CH_2$ protons (2.46; 2.47 ppm). The $N{=}CCH_3$ protons of compound **2** are observed at 1.70 ppm and the =CH proton at 4.91 ppm with the couplings $^2J_{^1H^{29}Si} = 12.2$ Hz, and $^3J_{^1H^{15}N} = 8.2$ Hz. In the ^{13}C NMR spectrum of **2** the =CH-carbon is found at 92.0 ppm with a coupling constant $J_{^{13}C^{29}Si} = 62.3$ Hz. The ^{29}Si NMR spectrum of **2** shows the resonance signal at 33.3 ppm, which can also be consistent with the data of the silene **IV** and is in the range of signals of an imine adduct of a silene described by Wiberg [9] or a silaketimine synthesized by Kira [10].



$\delta^{29}Si = 35{,}4$ ppm [9] $\delta^{29}Si = 23{,}4$ ppm [10]

Comparable silenes of silyl-hydrazones were obtained and characterized as dimers via the Si=C-bond [11–13].

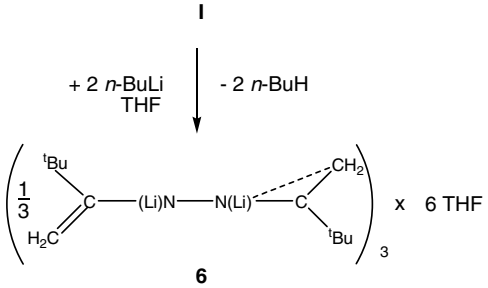
However, the very different chemical shifts of the N-atoms in the ^{15}N NMR experiment at −232.5 and −39.1 ppm can only be explained by means of a structure of the isomer **2**.

2.2. Addition reactions of CH_3OH and the isomeric silylketazine-rings *1* and *2*

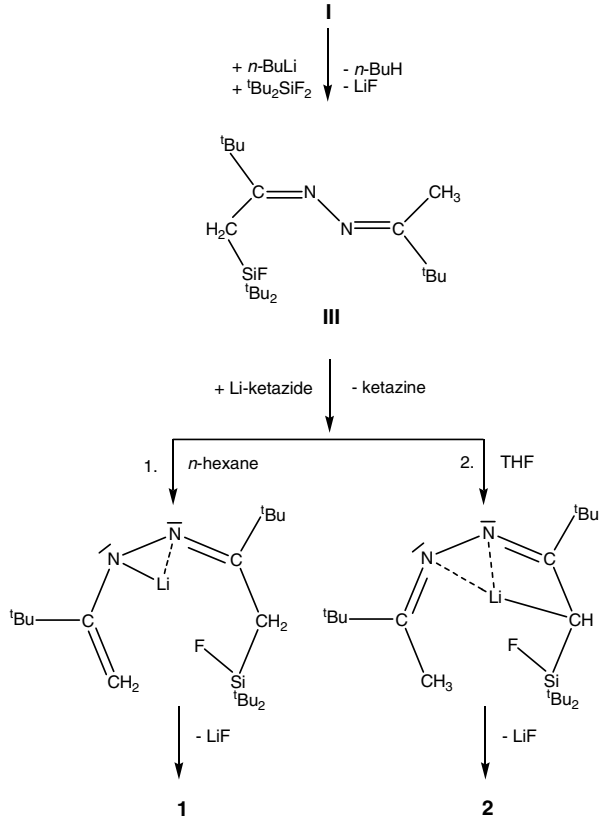
Control reactions did not help to clear up the structure because both, **2** and **1**, added H-acidic compounds, e.g. methanol under Si–N-cleavage and generated the same product, (Scheme 3).

2.3. Dilithium-di(tert-butylmethyl)-ketazide, *6*

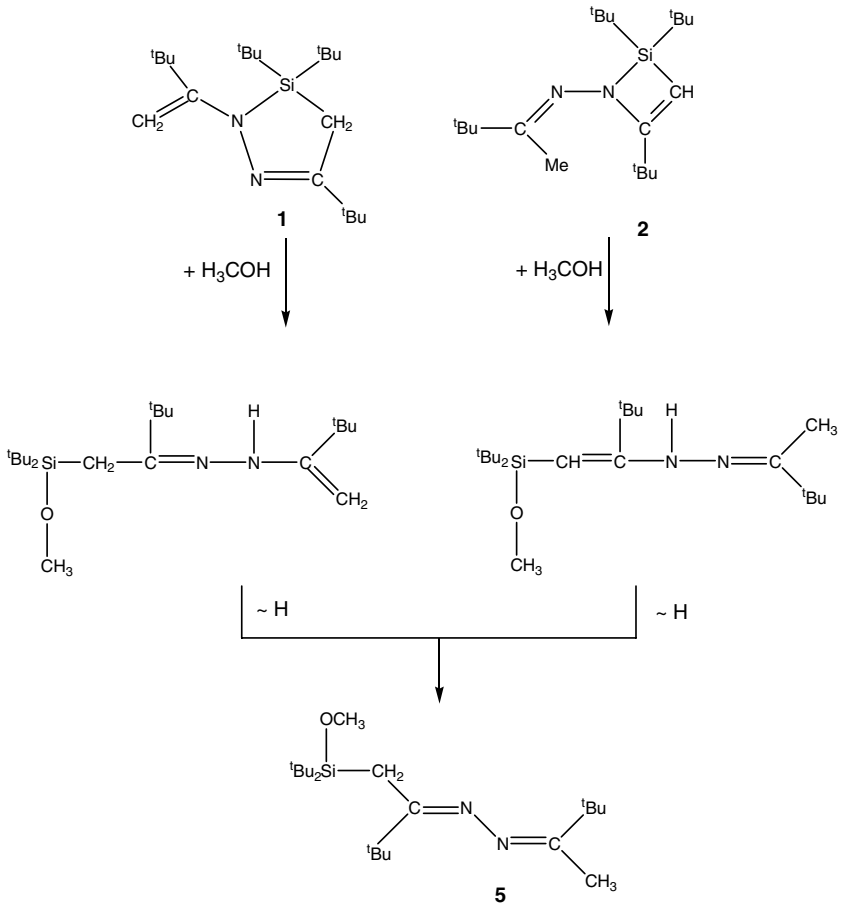
To increase the yields of **1** and **2**, di(*tert*-butylmethyl) ketazine **I** was dilithiated and a reaction of this dilithium salt with $^tBu_2SiF_2$ was carried out,



6 (5)



Scheme 2. Possible reaction mechanisms for the formation of **1** and **2**.



Scheme 3. Formation of **5** by methanolysis of **1** and **2**.

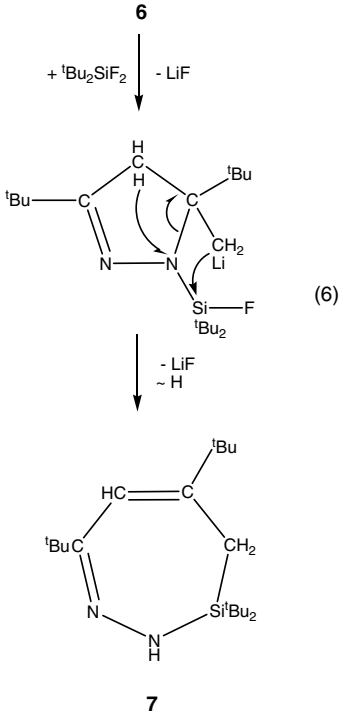
In the first step of the reaction, we succeeded in isolating single crystals of the dilithium salt **6**, recrystallized from *n*-hexane/thf. It crystallizes as trimer in the triclinic crystal system, space group $P\bar{1}$.

Because of the low quality of the crystals no bond length and angles are reported. The quantum-chemical calculated dilithium ketazide has a c_i-symmetry [5].

2.4. Synthesis of a 1,2-diaza-3-sila-hepta-5,7-diene (7) and -5-pentene (8)

The reaction of the dilithium salt **6** and ^{t}Bu$_2$SiF$_2$ leads to the formation of the seven-membered diazasilacycloheptadiene (**7**), which contains endocyclicly one imine and one enamine unit. The following reaction mechanism is possible (Scheme 4). Starting in a stepwise reaction, the dilithium salt **6** will be substituted by an FSi^{t}Bu$_2$ group at one nitrogen atom. After this LiF-elimination, a hydrogen shift to this nitrogen atom, and the formation of a C═C– and a Si–C bond occurs (Eq. (6)).

Compound **7** is a yellow liquid which could be distilled without decomposition in vacuo and could be completely characterized by NMR-spectroscopy. In the

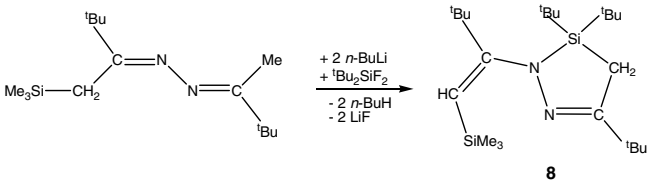


(6)

Scheme 4. Formation of **7**.

^{1}H NMR experiment the NH proton was found at 4.88 ppm and the =CH proton at 5.83 ppm. In the ^{13}C NMR spectrum the unsaturated carbon atom had the following chemical shifts: CH = 116.6, HC = *C* = 153.2, C=N = 160.6 ppm.

In order to prepare comparable four-, five-, and seven-membered ring isomers, we carried out the reaction of a dilithiated Me_3Si-substituted ketazine [7] with $^tBu_2SiF_2$ and could isolate only the five-membered ring **8**,



8

2.5. Quantum chemical calculations

To obtain a better understanding of the key species involved in the presented interconversion processes, quantum-chemical calculations of **1**, **2**, **7** and **IV** have been carried out. As in our previous work on related compounds, we made use of density functional theory in its B3LYP variant. The B3LYP hybrid method [14] combines the Becke 3-parameter exchange functional [15] and the Lee, Yang and Parr [16] correlation functional. The 6-31G(d) basis set was used throughout the calculations which were performed using GAUSSIAN03 [17].

The structures were fully optimized covering the full configuration space of the system. The minima were confirmed by analysis on the Hessian matrices, and zero-point vibrational energy effects were included within the harmonic oscillator-rigid rotor model. The structures we calculated are shown in Fig. 2, while relative energies are reported in Table 1. The first optimizations were performed for all *tert*-butyl groups substituted by methyl groups. Since the corresponding results indicate a different behaviour, the data are also given in Table 1.

Species **2** is less stable than **1** by 5.7 kcal mol^{-1} (including zero-point energy effects). The heptacyclic system **7** is the most stable one with a difference of −4.3 kcal mol^{-1} with respect to **1**. Thus, we have a clear trend towards larger rings with increasing stability. The non-cyclic structure **IV**, however, is very high in energy, 36.2 kcal mol^{-1} above **1**. The bond distances between the two nitrogen atoms may shed additional light on the stability of the four structures: It is calculated to be 141.9, 139.3, 137.4 and 138.0 pm in **1**, **2**, **7** and **IV**. The N–Si distance in **1**, **2** and **7** amounts to 181.3, 185.4 and 177.3 pm. None of the structures contains an exactly planar backbone with more than three atoms. There are only approximately planar units: Si–N–N–C in **1**, the four-membered ring in **2** and C–C(CH$_3$)=N–N in **IV**. The heptacyclus shows boat-conformation with the methylene group and the C–N unit moved out of the plane (see Fig. 2).

As already mentioned above, substitution of *tert*-butyl by methyl has remarkable consequences: **1** is slightly more stable than the heptacyclus **7** (by 0.9 kcal mol^{-1}), while the structure with the four-membered ring is considerably increased in energy. Definitely, the bulky *tert*-butyl groups stabilize the seven-membered ring. The energetic position of the non-cyclic species **IV** is almost unchanged.

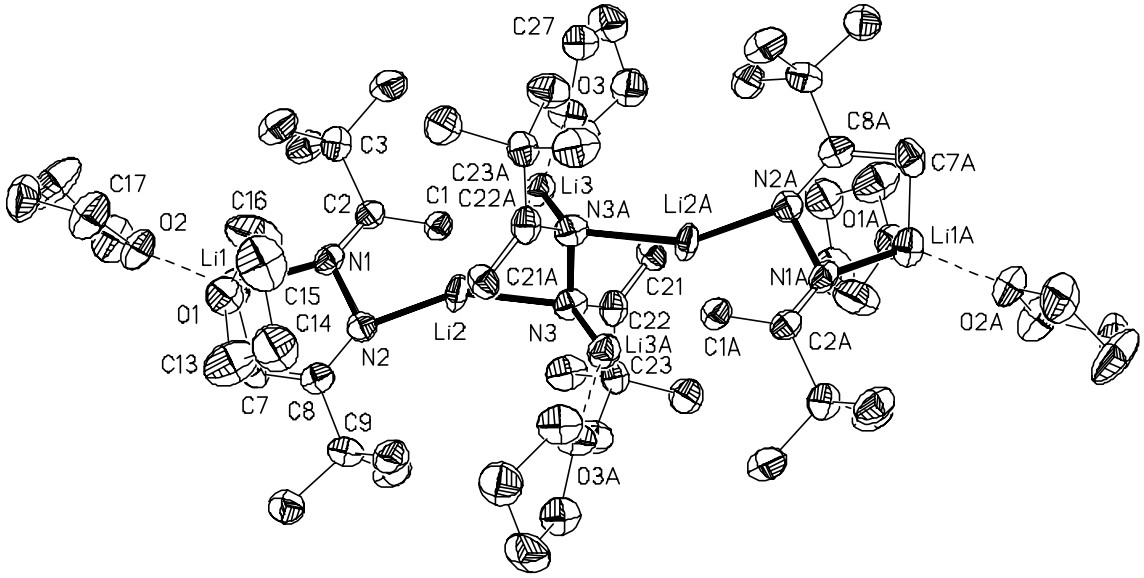
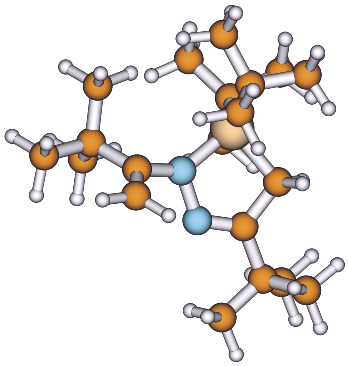
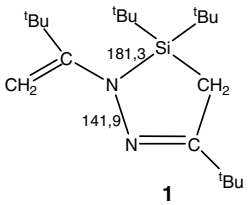


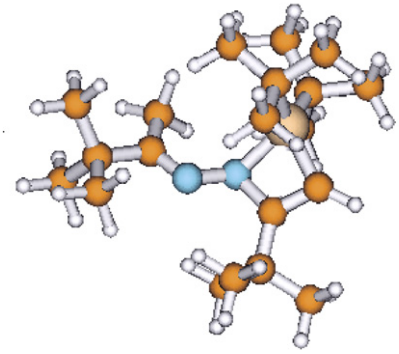
Fig. 1. Crystal structure of **6**. The hydrogen atoms have been omitted for clarity.



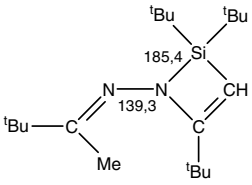
1



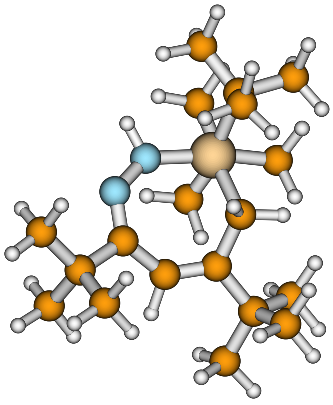
1



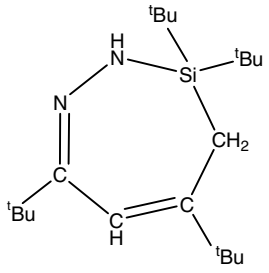
2



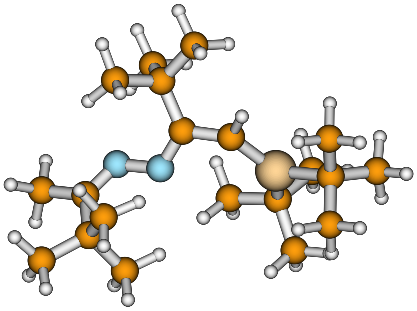
2



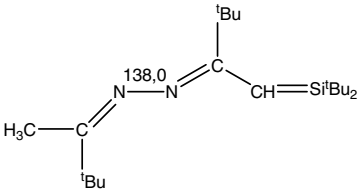
7



7



IV



IV

Fig. 2. Calculated structures of **1**, **2**, **7**, and **IV** (for details see text).

Table 1
B3LYP/6-31G(d) energies (in kcal mol^{-1}) for **1**, **2**, **7** and **IV**

	Including E_{zp}		All *tert*-butyl substituted by methyl	
			Including E_{zp}	
1	0	0	0	0
2	6.3	5.7	17.9	17.3
7	−5.5	−4.3	−0.01	0.87
IV	36.9	36.2	38.4	37.5

Results for the species with all *tert*-butyl groups substituted by methyl are also reported.

3. Conclusion

^{t}Bu$_2$SiF$_2$ reacts with lithium salt of di(*tert*-butylmethyl) ketazine to give isomeric four-, five-, and seven-membered rings. To understand the mechanisms of the reactions in the ketazine system, quantum chemical calculations were carried out and show that there is only a low energy difference between di-*tert*-butyl(silyl)-groups containing cyclic ketazine isomers. Depending on the reaction conditions the lithiated di(*tert*-butylmethyl)ketazine reacts with F$_2$Si^{t}Bu$_2$ to give a four-, five-, or seven-membered ring isomer.

4. Experimental

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert-atmosphere and vacuo-line techniques. All NMR spectra were obtained on a Bruker AM-250, MSL-400, or Avance 500 spectrometer with $SiMe_4$ as internal reference or $MeNO_2$ as external reference. The mass spectra are reported in mass to charge units (*m*/*z*) with their relative intensities in parentheses. The NMR spectra confirmed the purity of **1**, **2**, **3**, **5**, **7**, and **8**.

4.1. Compounds *1* and *2*

To a solution of 14.7 g (0.075 mol) of di(*tert*-butylmethyl)ketazine in hexane was added drop wise 32 g (0.075 mol) *n*-butyllithium in hexane (15%). The mixture was heated to reflux for 3 h. 0.075 mol (13.5 g) di-*tert*-butyl-difluorosilane was added drop wise to the suspension obtained at 0 °C. The mixture was warmed to ambient temperature and refluxed for 5 h. After the mixture was cooled to room temperature, the products were separated from LiF in vacuo. The clear liquid obtained was fractionally distilled under reduced pressure to yield 4.3 g (18%) of **1** and 3.6 (15%) of **2**. Using THF as solvent only **2** is obtained, 9.2 g (38%).

4.2. 1,2-Diaza-3-sila-cyclo-4-pentene (*1*)

B.p. 88 °C/0.01 mbar. ^{1}H NMR ($CDCl_3$): δ 1.07 ($SiC(CH_3)_3$, s, 18H), 1.15 ($C(CH_3)_3$, s, 9H), 1.46 (CH_2, s, 2H), 1.51 ($C(CH_3)_3$, s, 9H), 4.26 (=CH_2, d, $^2J_{HAHB}$ = 0.8 Hz, 1H), 4.27 (=CH_2, d, $^2J_{HAHB}$ = 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.0 (CH_2), 21.8 ($SiC(CH_3)_3$), 28.8 ($C(CH_3)_3$), 28.8 ($SiC(CH_3)_3$), $C(CH_3)_3$, 30.5 ($C(CH_3)_3$), 36.7 ($C(CH_3)_3$), 37.3 ($C(CH_3)_3$), 85.3 (=CH_2), 155.7 (*C*N), 161.1 (*C*N). ^{15}N NMR ($CDCl_3$): δ = −232.0 (d, $^3J_{NH}$ = 11.6 Hz, *N*–C), −35.0 (C=N, d, $^3J_{NH}$ = 4.7 Hz). ^{29}Si NMR ($CDCl_3$) δ 27.6. MS (E.I.) *m*/*z* [%]: 336 (100) [M$^+$].

4.3. 1-Aza-2-sila-cyclo-3-butene (*2*)

B.p. 71 °C/0.02 mbar. ^{1}H-NMR ($CDCl_3$): δ 1.11 ($C(CH_3)_3$, s. 9H), 1.12 ($SiC(CH_3)_3$, s, 18H), 1.36 ($C(CH_3)_3$, s, 9H), 1.70 (CH_3, s, 3H), 4.91 (=CH, s, $^2J_{^1H^{29}Si}$ 12.2 Hz, $^3J_{^1H^{15}N}$ = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 12.5 (CH_3), 4.91 (=CH, s, $^2J_{^1H^{29}Si}$ 12.2 Hz, $^3J_{^1H^{15}N}$ =8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 12.5 (CH_3), 21.4 ($SiC(CH_3)_3$), 28.2 ($SiC(CH_3)_3$), 28.4 ($C(CH_3)_3$), 28.6 ($C(CH_3)_3$), 37.1 ($C(CH_3)_3$), 38.4 ($C(CH_3)_3$), 92.0 (=CH, $^1J_{^{13}C^{29}Si}$ = 62.3 Hz), 156.5 *C*N, 182.2 *C*N. ^{15}N NMR ($CDCl_3$): δ −233.5 (N–C, d, $^3J_{NH}$ = 8.5 Hz,), −39.1 (C=N, d, $^4J_{NH}$ = 3.7 Hz). ^{29}Si NMR ($CDCl_3$): δ33.3 (s, $^1J_{^{29}Si^{13}C}$ 62.3 Hz, $^1J_{^{29}Si^{13}C_2}$ = 63.2 Hz). MS (E.I.) *m*/*z* [%]: 336 (100) [M$^+$]. Anal. Calc. for $C_{20}H_{40}N_2Si_2$ (336.63); C, 71.36; H, 11.97. Found: C, 71.82, H, 12.26%.

4.4. 1,4-Di-tert-butyl-1-methyl-4-fluorodimethylsilyl-ketazine (*3*)

B.p. 52 °C/0.03 mbar. Yield: 20.4 g (75%). A suspension of 19.6 g (0.1 mol) lithium-di(*tert*-butylmethyl)ketazide in 200 ml *n*-hexane was added drop wise to 10.6 g (0.11 mol) F_2SiMe_2 in 50 ml *n*-hexane at −40 °C. After stirring the mixture for 5 h the raw product was warmed up to room temperature, separated from LiF in vacuo, and cleaned by distillation.

B.p. 52°C/0.03 mbar. ^{1}H NMR ($CDCl_3$): δ 0.23 ($Si(CH_3)_2$, d, $^3J_{HF}$ = 7.56, 6H), 1.12 ($C(CH_3)_3$, s, 9H), 1.16 ($C(CH_3)_3$, s, 9H), 1.79 (CH_3, s, 3H), 2.04 (CH_2, d, $^3J_{HF}$ = 8.12, 2H). ^{13}C NMR ($CDCl_3$): δ −0.2 (($CH_3)_2$SiF, d, $^2J_{CF}$ = 15.27), 19.89 (CH_2SiF, d, $^2J_{CF}$ = 14.26), 27.84 ($C(CH_3)_3$, s), 28, 2 ($C(CH_3)_3$, d, $^5J_{CF}$ = 0.65), 38, 36 (CH_3, s), 38, 46 ($C(CH_3)_3$, s), 38, 62 ($C(CH_3)_3$, s), 164, 42 ($NC(CH_3)_3$, s), 168.56 ($NC(CH_3)_3$, s). ^{19}F NMR ($CDCl_3$): δ 9.25 (SiF, t, sept, $^3J_{HF}$ = 7.7). ^{29}Si NMR ($CDCl_3$): δ 29, 17 (C*Si*F, d, J_{SiF} = 284.24). $C_{14}H_{29}FN_2Si$, 272 g/mol, MS (E.I.) *m*/*z* 272 (100%) [M]$^+$.

4.5. 1-Siloxi-ketazine (*5*)

To a solution of 0.01 mol (3.4 g) of **1** resp. **2** in 40 ml hexane 0.015 mol (0.4 g) methanol was added drop wise. The mixture was refluxed for 1 h. Then the reaction was complete and quantitative.

B.p.: 74 °C/0.01 mbar. Yield: 98%. ^{1}H NMR ($CDCl_3$): δ 1.09 ($SiC(CH_3)_3$, 18H), 1.16 ($C(CH_3)_3$, 9H), 1.41 ($C(CH_3)_3$, 9H), 1.91 (CCH_3, 3H), 2.39 (CH_2, 2H), 3.45 (OCH_3, 3H). ^{13}C NMR($CDCl_3$): δ13.6 (CCH_3), 14.4 (CH_2), 22.4

(Si(C(CH$_3$)$_3$)$_2$), 28.0 (C(CH$_3$)$_3$), 28.9 (Si(C(CH$_3$)$_3$)$_2$), 29.8 (C(CH$_3$)$_3$), 38.9 (C(CH$_3$)$_3$), 39.5 (C(CH$_3$)$_3$), 52.6 (OCH$_3$), 169.4 (CN), 173.2 (CN). ^{29}Si NMR (CDCl$_3$) δ 9.5 (OSi(C(CH$_3$)$_3$)$_2$). MS (E.I.) m/z [%]: 338 (3) [M]$^+$. Anal. Calc. for $C_{21}H_{44}N_2Osi$ (368.67): C, 68.42; H, 5.74. Found: C, 68.69, H, 5.87%.

4.6. 1,2-Diaza-3-sila-cyclo-hepta-5,7-diene (7)

To a solution of 0.13 mol (25.5 g) di(*tert*-butylmethyl)ketazine in 250 ml hexane were added 0.26 mol (16.6 g) *n*-Buli (15% in *n*-hexane). The mixture was heated to reflux for 4 h. After this, 0.13 mol (23.4 g) ^{t}Bu$_2$SiF$_2$ were added drop wise, and the solvent was removed by distillation. The raw product was warmed to 130 °C for 3 h and separated from LiF by centrifuging. The liquid obtained was fractionally distilled under reduced pressure to yield 5.7 g (13%), b.p. 97 °C/0.01 mbar. ^{1}H NMR (CDCl$_3$): δ 1.01 (SiC(CH_3)$_3$, 18 H,), 1.11 (C(CH_3)$_3$, 9H), 1.22 (C(CH_3)$_3$, 9 H,), 1.60 (CH_2,2H), 4.88 (NH, 1 H,), 5.83 (=CH, 1H). ^{13}C NMR (CDCl$_3$): δ 10.6 (CH$_2$, $^1J_{^{13}C^{13}C}$ = 38.6 Hz, $^1J_{^{13}Si^{29}Si}$ = 52.1 Hz), 22.1 (Si(C(CH$_3$)$_3$)$_2$, $^1J_{^{13}C^{29}Si}$ = 55.6 Hz), 29.1 (Si(C(CH$_3$)$_3$)$_2$), 29.3 (C(CH$_3$)$_3$), 30.5 (C(CH$_3$)$_3$, $^1J_{^{13}C^{13}C}$ = 35.6 Hz), 38.5 (C(CH$_3$)$_3$, $^1J_{^{13}C^{13}C}$ = 41.2 Hz, $^1J_{^{13}C^{13}C}$ = 35.6 Hz), 39, 0 (C(CH$_3$)$_3$, $^1J_{^{13}C^{13}C}$ = 49.7 Hz), 116.6 (=CH, $^1J_{^{13}C^{13}C}$ = 74.5 Hz, $^1J_{^{13}C^{13}C}$ = 52.4 Hz), 153, 2 (C=C, $^1J_{^{13}C^{13}C}$ = 74.5 Hz, $^1J_{^{13}C^{13}C}$ = 41.2 Hz, $^1J_{^{13}C^{13}C}$ = 38.6 Hz), 160, 6 (C=N, $^1J_{^{13}C^{13}C}$ = 52.4 Hz, $^1J_{^{13}C^{13}C}$ = 49.7 Hz). ^{15}N NMR (CDCl$_3$): δ −276.1 (NH, d, $^1J_{NH}$ = 73.3 Hz), −49.9 (C=N). ^{29}Si NMR (CDCl$_3$) δ 34.5 (Si((CH$_3$)$_3$)$_2$, $^1J_{^{29}Si^{13}C}$ = 55.6 Hz, $^1J_{^{29}Si^{13}C}$ = 52.1 Hz). MS (EI): m/z [%]: 336 (12) [M$^+$]. Anal. Calc. for $C_{20}H_{40}N_2Si$ (336.63): C, 71.36; H, 11.98. Found: C, 71.01; H, 11.72%.

4.7. 1,2-Diaza-3-sila-cyclopent-5-ene (8)

To a solution of 0.1 mol (26.8 g) of the silyl substituted ketazine, ^{t}BuMeC=N–N=C(^{t}Bu)CH$_2$SiMe$_3$ [7] in 250 ml *n*-hexane were added 0.2 mol (12.8 g) *n*-BuLi (15%) in *n*-hexane. The mixture was heated to reflux for 3 h, then cooled to room temperature and added drop wise to 0.1 mol (18.0 g) ^{t}Bu$_2$SiF$_2$ in 50 ml THF. After this the mixture was heated to reflux for 1 h, separated from LiF, and fractionally distilled. Yield: 40.9 g (80%), b.p. 130 °C/0.5 mbar. ^{1}H NMR (CDCl$_3$): δ 0, 35 (=CSi(CH_3)$_3$, 9H), 1.08 (Si(C(CH_3)$_3$)$_2$, 18H), 1.14 (C(CH_3)$_3$, 9H), 1.42 (CH_2, 2H), 1.55 (C(CH_3)$_3$, 9H), 4.58 (=CH, 1H). ^{13}C NMR (CDCl$_3$): δ 3.8 (=CSi(CH$_3$)$_3$), 12.8 (CH$_2$), 21.8 (Si-(C(CH$_3$)$_3$)$_2$), 28.7 (C(CH$_3$)$_3$), 29.1 (Si(C(CH$_3$)$_3$)$_2$), 31.3 (C(CH$_3$)$_3$), 36.8 (C(CH$_3$)$_3$), 38.8 (C(CH$_3$)$_3$), 96.8 (=CH), 156, 3 (CN), 169.1 (CN). ^{29}Si NMR (CDCl$_3$): δ −11.9 (=CSi(CH$_3$)$_3$), 27, 3 (Si(C(CH$_3$)$_3$)$_2$). MS (EI): m/z [%]: 408 (14) [M$^+$]. Anal. Calc. for $C_{23}H_{48}N_2Si_2$ (408.81): C, 67.58; H, 11.83. Found: C, 67.43; H, 11.69%.

4.8. X-ray structure determination of 6

Low resolution data of **6** were collected on a STOE IPDS2 diffractometer with Mo Kα radiation at 133 K. The structures were solved using the SHELX program suite [18,19]. Despite the low quality an overall structure can be seen in Fig. 1.

The space group of **6** is triclinic, $P\bar{1}$, with unit-cell dimensions $a = 1012.21(12)$, $b = 1250.28(18)$, $c = 1316.78(18)$ pm, $\alpha = 77°(11)$, $\beta = 89.85°(10)$, $\gamma = 88.79°(11)$, $u = 1.626(4)$ nm^3, $Z = 1$.

References

[1] E. Lederer, Bull. Soc. Chim. Fr (1946) 172.
[2] E. Arnal, J. Elguero, R. Jacquier, C. Marzin, J. Wylde, Bull. Soc. Chim. Fr. (1965) 877.
[3] K. Appenroth, M. Reichenbaecher, R. Paetzold, Tetrahedron 37 (1981) 569.
[4] T. Groh, G. Elter, M. Noltemeyer, H.-G. Schmidt, A. Meller, Organometallics 19 (2000) 2477.
[5] F. Armbruster, N. Armbruster, U. Klingebiel, S. Schmatz, M. Noltemeyer, Z. Naturforsch 61b (2006) 1261.
[6] F. Armbruster, U. Klingebiel, M. Noltemeyer, Z. Naturforsch 61b (2006) 225.
[7] N. Armbruster, U. Klingebiel, M. Noltemeyer, Z. Naturforsch. 60b (2005) 1123.
[8] N. Armbruster, U. Klingebiel, M. Noltemeyer, Z. Anorg. Allg. Chem. 632 (2006) 1097.
[9] N. Wiberg, G. Wagner, G. Reber, J. Riede, G. Müller, Organometallics 6 (1987) 35.
[10] T. Abe, T. Iwamoto, C. Kabuto, M. Kira, J. Am. Chem. Soc. 128 (2006) 4228.
[11] W. Clegg, U. Klingebiel, G.M. Sheldrick, P. Werner, Angew. Chem. 93 (1981) 391;
W. Clegg, U. Klingebiel, G.M. Sheldrick, P. Werner, Angew. Chem., Int. Ed. Engl. 20 (1981) 384.
[12] W. Clegg, U. Klingebiel, S. Pohlmann, G.M. Sheldrick, P. Werner, Angew. Chem 93 (1981) 390;
W. Clegg, U. Klingebiel, S. Pohlmann, G.M. Sheldrick, P. Werner, Angew. Chem., Int. Ed. Engl 20 (1981) 383.
[13] W. Clegg, O. Graalmann, M. Haase, U. Klingebiel, G.M. Sheldrick, P. Werner, G. Henkel, B. Krebs, Chem. Ber. 116 (1983) 282.
[14] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M. Frisch, J. Phys. Chem. 98 (1994) 11623.
[15] A.D. Becke, J. Chem Phys. 98 (2003) 5648.
[16] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, GAUSSIAN03, Gaussian Inc., Pittsburg, PA, 2003.
[18] G.M. Sheldrick, SHELX-97, Universität Göttingen, 1997.
[19] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.