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New bicyclic sila-heterocycles: syntheses and crystal structure analyses of *rac*-7-ethoxy-2,2-diorganyl-2,3,5,7a-tetrahydro-1*H*-3a,6-diaza-2-sila-inden-4-ones

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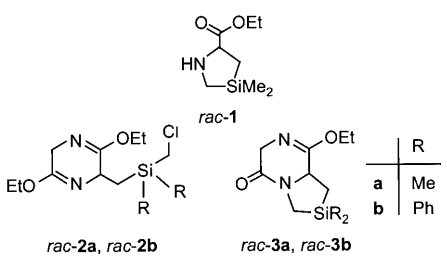
Abstract

Metalation of 3,6-diethoxy-2,5-dihydropyrazine with one molar equivalent of *n*-BuLi and subsequent treatment with one molar equivalent of $R_2Si(CH_2Cl)_2$ (R = Me, Ph) yielded the racemic 2-$R_2Si(CH_2Cl)CH_2$-substituted 3,6-diethoxy-2,5-dihydropyrazines *rac*-**2a** (R = Me) and *rac*-**2b** (R = Ph). Heating of *rac*-**2a** and *rac*-**2b** led almost quantitatively (along with the formation of EtCl) to the new bicyclic sila-heterocycles *rac*-7-ethoxy-2,2-dimethyl-2,3,5,7a-tetrahydro-1*H*-3a,6-diaza-2-sila-inden-4-one (*rac*-**3a**) and *rac*-7-ethoxy-2,2-diphenyl-2,3,5,7a-tetrahydro-1*H*-3a,6-diaza-2-sila-inden-4-one (*rac*-**3b**), respectively. Compounds *rac*-**2b**, *rac*-**3a**, and *rac*-**3b** were structurally characterized by NMR studies and crystal structure analyses. In addition, the kinetics of the cyclization reaction *rac*-**2a** → *rac*-**3a** were investigated.

Keywords: Bicyclic sila-heterocycles; Kinetics; Syntheses; Crystal structures; NMR spectroscopy

1. Introduction

Recently, we have reported on the synthesis of *rac*-2-{[(chloromethyl)dimethylsilyl]methyl}-3,6-diethoxy-2,5-dihydropyrazine (*rac*-**2a**) which served as a precursor for the preparation of *rac*-4,4-dimethyl-4-sila-proline ethyl ester (*rac*-**1**) [1]. The sila-proline derivative *rac*-**1** was synthesized in context with our studies on silicon-containing α-amino acids and peptides [1–4]. As already reported briefly (without any experimental details), compound *rac*-**2a** undergoes a thermally induced cyclization reaction to give *rac*-7-ethoxy-2,2-dimethyl-2,3,5,7a-tetrahydro-1*H*-3a,6-diaza-2-sila-inden-4-one (*rac*-**3a**) [1]. We now could demonstrate that the derivative *rac*-**3b** can be obtained analogously, starting from *rac*-**2b**. We report here on the syntheses of the bicyclic sila-heterocycles *rac*-**3a** and *rac*-**3b** on a preparative scale, including kinetic studies of the cyclization reaction *rac*-**2a** → *rac*-**3a**. In addition, the crystal structures of *rac*-**2b**, *rac*-**3a**, and *rac*-**3b** are described. Compounds *rac*-**3a** and *rac*-**3b** represent derivatives of a new type of sila-heterocycle (for recent reviews on sila-heterocycles, see refs. [5–7]). The studies presented here were carried out in the context of our systematic investigations on biologically active organosilicon compounds. In general, sila-heterocycles are promising compounds for the development of silicon-based drugs and agrochemicals.



2. Results and discussion

2.1. Syntheses

The title compounds *rac*-**3a** and *rac*-**3b** were synthesized according to Scheme 1, starting from 3,6-di-

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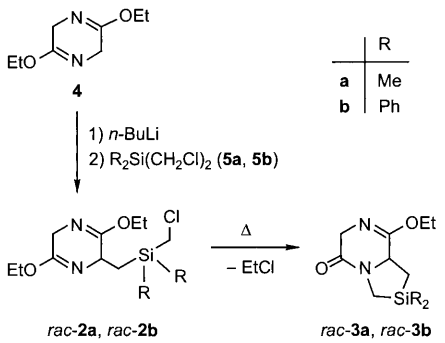
ethoxy-2,5-dihydropyrazine (**4**). Metalation of **4** with one molar equivalent of *n*-butyllithium and subsequent treatment with one molar equivalent of the bis-(chloromethyl)silane $Me_2Si(CH_2Cl)_2$ (**5a**) and Ph_2Si-$(CH_2Cl)_2$ (**5b**), respectively, gave compounds *rac*-**2a** (yield 50%) and *rac*-**2b** (yield 53%). The products were isolated as a colorless liquid (*rac*-**2a**) or crystalline solid (*rac*-**2b**). Heating of neat *rac*-**2a** and *rac*-**2b** at 120°C gave the crystalline title compounds *rac*-**3a** and *rac*-**3b** in almost quantitative yield. Their identities were estab-



Scheme 1.

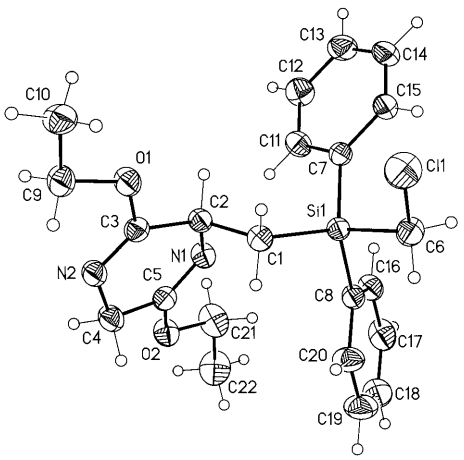


Fig. 1. Molecular structure of one of the two enantiomers of molecule A in the crystal of *rac*-**2b** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. The structure of molecule B (not depicted) is very similar.

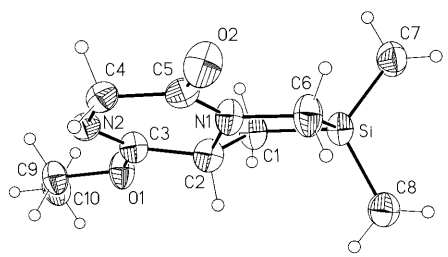


Fig. 2. Molecular structure of one of the two enantiomers in the crystal of *rac*-**3a** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

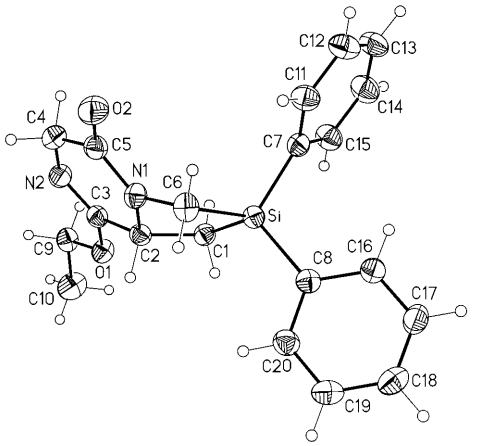


Fig. 3. Molecular structure of one of the two enantiomers in the crystal of *rac*-**3b** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

lished by elemental analyses (C, H, N), NMR-spectroscopic investigations (^1H, ^{13}C, ^{29}Si), and crystal structure analyses.

2.2. Crystal structure analyses

Compounds *rac*-**2b**, *rac*-**3a**, and *rac*-**3b** were structurally characterized by single-crystal X-ray diffraction. They crystallize in the space group $P\bar{1}$ (*rac*-**2b**), *Pbca* (*rac*-**3a**), and $P2_1/c$ (*rac*-**3b**). The molecular structures are depicted in Figs. 1–3. The crystal data and the experimental parameters used for the crystal structure analyses are summarized in Table 1. Selected interatomic distances and angles are listed in Tables 2 and 3.

Compound *rac*-**2b** crystallizes with two molecules (A and B) in the asymmetric unit. As can be seen from Table 2, the interatomic distances and angles of molecules A and B are quite similar. The respective six-membered ring systems (C2, C3, N2, C4, C5, N1; C32, C33, N32, C34, C35, N31) are almost planar with mean deviations of 0.08 Å (molecule A) and 0.10 Å (molecule B) from the best plane.

As can be seen from Figs. 2–4 and Table 3, the six-membered rings of the bicyclic heterocycles *rac*-**3a** and *rac*-**3b** are almost planar, whereas the five-membered rings adopt envelope conformations. These envelope conformations differ from one another, the carbon atom C2 (*rac*-**3a**) and the nitrogen atom N1 (*rac*-**3b**), respectively, deviating from the plane generated by the other four atoms of the five-membered rings (deviations from the plane: 0.60 Å, C2; 0.55 Å, N1). The atoms of the bicyclic skeletons of *rac*-**3a** and *rac*-**3b** form two planes [plane A, with the atoms C6, N1, C2, C3, N2, C4, and C5; plane B, with the atoms N1, C6, Si, and C1 (*rac*-**3a**) and with the atoms C6, Si, C1, and C2 (*rac*-**3b**)], the mean deviations from these planes amounting to 0.05 Å (*rac*-**3a**, plane A), 0.01 Å (*rac*-**3a**,

plane B), 0.03 Å (*rac*-**3b**, plane A), and 0.01 Å (*rac*-**3b**, plane B). The respective dihedral angles formed by these planes amount to −160.8° (*rac*-**3a**) and 132.4° (*rac*-**3b**), indicating significant differences between the conformations of the bicyclic skeletons of *rac*-**3a** and *rac*-**3b** in the crystal.

2.3. Kinetic studies

The 2-{[(chloromethyl)diorganylsilyl]methyl}-3,6-diethoxy-2,5-dihydropyrazines *rac*-**2a** and *rac*-**2b** (neat compounds or solutions in diethyl ether) were found to be thermally stable at −20°C. No significant changes could be observed over a period of 2 weeks (^{1}H-NMR studies). However, upon heating both compounds undergo a cyclization reaction to yield the bicyclic products *rac*-**3a** and *rac*-**3b**, respectively, along with ethyl chloride (isolated by condensation and identified by ^{1}H-NMR spectroscopy).

As monitored by ^{1}H-NMR spectroscopy (Fig. 5), the transformation *rac*-**2a** → *rac*-**3a** is characterized by first-order kinetics, with a rate constant $k = 1.3 \times 10^{-5}$ s^{-1} at 80°C (solvent C_6D_6; Fig. 6). This result is in accordance with an intramolecular cyclization process.

3. Experimental

3.1. Syntheses

3.1.1. General procedures

The syntheses of *rac*-**2a**, *rac*-**2b**, and **5b** were carried out under dry nitrogen. Tetrahydrofuran (THF) was dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point apparatus. The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded at 22°C on a Bruker

Table 1
Crystal data and experimental parameters for the crystal structure analyses of *rac*-**2b**, *rac*-**3a**, and *rac*-**3b**

	rac-**2b**	*rac*-**3a**	*rac*-**3b**
Empirical formula	$C_{22}H_{27}ClN_2O_2Si$	$C_{10}H_{18}N_2O_2Si$	$C_{20}H_{22}N_2O_2Si$
Formula mass (g mol^{-1})	415.00	226.35	350.49
Collection T (K)	173(2)	173(2)	173(2)
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group (no.)	$P\bar{1}$ (2)	*Pbca* (61)	$P2_1/c$ (14)
Unit cell parameters			
a (Å)	9.0176(12)	15.8531(12)	8.0321(16)
b (Å)	13.762(2)	6.9484(6)	31.250(6)
c (Å)	18.149(3)	22.044(2)	7.1882(14)
α (°)	84.184(17)	90	90
β (°)	82.431(16)	90	96.03(3)
γ (°)	79.866(16)	90	90
V (Å^3)	2190.7(5)	2428.3(4)	1794.3(6)
Z	4	8	4
D_{calc} (g cm^{-3})	1.258	1.238	1.297
μ (mm^{-1})	0.249	0.178	0.147
F(000)	880	976	744
Crystal dimensions (mm)	0.5 × 0.4 × 0.3	0.6 × 0.3 × 0.3	0.7 × 0.5 × 0.4
2θ Range (°)	4.54–54.10	4.50–51.82	5.10–54.10
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-23 \le l \le 23$	$-19 \le h \le 18$, $-8 \le k \le 8$, $-26 \le l \le 27$	$-10 \le h \le 10$, $-39 \le k \le 39$, $-9 \le l \le 9$
Collected reflections	32039	12731	23502
Independent reflections	8888	2360	3855
R_{int}	0.0338	0.0769	0.0507
Reflections used	8888	2360	3855
Parameters	509	139	230
S [a]	1.055	0.897	1.051
Weight parameters a/b [b]	0.0526/0.4712	0.0705/0.0000	0.0491/0.6323
R_1 [c] [$I > 2\sigma(I)$]	0.0352	0.0420	0.0377
wR_2 [d] (all data)	0.0978	0.1146	0.0981
Maximum/minimum residual electron density (e Å^{-3})	+0.261/−0.330	+0.591/−0.338	+0.281/−0.313

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters.
[b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (\text{Max } F_o^2, 0 + 2F_c^2)/3$.
[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

Table 2
Selected interatomic distances (Å) and angles (°) for *rac*-**2b**

Molecule A		Molecule B	
Si1–C1	1.8875(15)	Si2–C31	1.8892(14)
Si1–C6	1.8938(17)	Si2–C36	1.8895(16)
Si1–C7	1.8767(15)	Si2–C38	1.8738(15)
Si1–C8	1.8659(16)	Si2–C37	1.8670(16)
C1–C2	1.538(2)	C31–C32	1.538(2)
C2–C3	1.5084(19)	C32–C33	1.5148(19)
C4–C5	1.498(2)	C34–C35	1.502(2)
N1–C2	1.458(2)	N31–C32	1.460(2)
N1–C5	1.2666(19)	N31–C35	1.2681(19)
N2–C3	1.267(2)	N32–C33	1.2656(19)
N2–C4	1.449(2)	N32–C34	1.450(2)
O1–C3	1.348(2)	O31–C33	1.345(2)
O2–C5	1.347(2)	O32–C35	1.344(2)
C1–Si1–C6	106.63(7)	C31–Si2–C36	106.45(7)
C1–Si1–C7	112.18(7)	C31–Si2–C38	112.84(7)
C1–Si1–C8	112.51(7)	C31–Si2–C37	112.76(7)
C6–Si1–C7	109.92(7)	C36–Si2–C38	109.61(7)
C6–Si1–C8	103.91(7)	C36–Si2–C37	106.58(7)
C7–Si1–C8	111.24(7)	C37–Si2–C38	108.37(7)
Si1–C1–C2	114.32(10)	Si2–C31–C32	115.66(10)
C1–C2–C3	111.61(12)	C31–C32–C33	111.15(12)
N1–C2–C1	109.23(12)	N31–C32–C31	109.92(12)
N1–C2–C3	113.55(12)	N31–C32–C33	112.95(12)
N2–C3–C2	127.42(15)	N32–C33–C32	126.87(14)
N2–C3–O1	121.85(13)	N32–C33–O31	121.89(13)
O1–C3–C2	110.73(12)	O31–C33–C32	111.24(12)
N2–C4–C5	115.05(13)	N32–C34–C35	114.61(13)
N1–C5–C4	126.76(15)	N31–C35–C34	126.35(15)
N1–C5–O2	122.14(13)	N31–C35–O32	122.45(13)
O2–C5–C4	111.11(13)	O32–C35–C34	111.20(13)
C2–N1–C5	117.10(12)	C32–N31–C35	116.74(12)
C3–N2–C4	116.41(13)	C33–N32–C34	116.27(13)

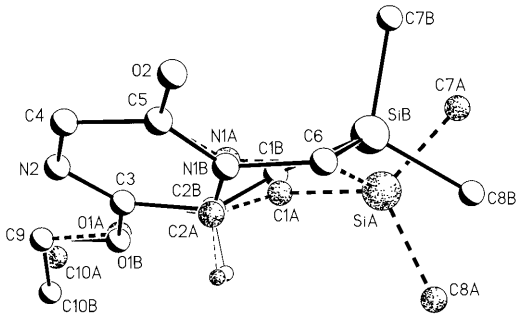


Fig. 4. Superposition of the bicyclic skeletons of one of the two enantiomers each of *rac*-**3a** and *rac*-**3b**, indicating their different conformations in the crystal. The hydrogen atoms (except for C2–*H*) are omitted for clarity.

DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) or Bruker DMX-600 NMR spectrometer (^{1}H, 600.1 MHz). $CDCl_3$ was used as solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, $\delta = 7.24$), $CDCl_3$ (^{13}C, $\delta = 77.0$), and external TMS (^{29}Si, $\delta = 0$). Assignment of the ^{1}H-NMR data of *rac*-**2b**, *rac*-**3a,** and *rac*-**3b** was supported by ^{1}H,^{1}H COSY experiments, and for *rac*-**3a** and *rac*-**3b** additionally by ^{1}H,^{1}H NOESY experiments. The ^{1}H spin systems of *rac*-**2a**, *rac*-**2b**, *rac*-**3a**, and *rac*-**3b** were analyzed by simulations using the Bruker software program WIN-DAISY 4.0 [8]. Assignment of the ^{13}C-NMR data was supported by DEPT 135 experiments, and for *rac*-**3a** and *rac*-**3b** additionally by ^{13}C,^{1}H HMBC experiments.

Table 3
Selected interatomic distances (Å) and angles (°) for *rac*-**3a** and *rac*-**3b**

	rac-**3a**	*rac*-**3b**		*rac*-**3a**	*rac*-**3b**
Si–C1	1.883(2)	1.8831(13)	C6–Si–C8	111.86(12)	111.90(6)
Si–C6	1.890(2)	1.8903(15)	C7–Si–C8	111.80(12)	108.76(6)
Si–C7	1.852(3)	1.8696(14)	Si–C1–C2	102.83(15)	104.15(9)
Si–C8	1.853(3)	1.8691(14)	C1–C2–C3	116.4(2)	114.13(11)
C1–C2	1.512(3)	1.5480(18)	N1–C2–C1	107.24(19)	109.12(10)
C2–C3	1.502(3)	1.5017(18)	N1–C2–C3	109.72(18)	110.91(11)
C4–C5	1.498(3)	1.506(2)	N2–C3–C2	128.5(2)	128.64(12)
N1–C2	1.479(3)	1.4683(17)	N2–C3–O1	121.8(2)	121.95(12)
N1–C5	1.339(3)	1.3460(19)	O1–C3–C2	109.50(18)	109.39(11)
N1–C6	1.469(3)	1.4650(17)	N2–C4–C5	118.99(18)	119.30(12)
N2–C3	1.250(3)	1.2612(18)	N1–C5–C4	117.78(18)	117.44(12)
N2–C4	1.450(3)	1.4562(19)	O2–C5–C4	120.2(2)	119.94(13)
O1–C3	1.359(3)	1.3520(16)	N1–C5–O2	122.0(2)	122.62(13)
O2–C5	1.227(3)	1.2303(18)	Si–C6–N1	104.96(15)	102.03(8)
C1–Si–C6	92.87(10)	94.48(6)	C2–N1–C5	124.41(18)	125.34(11)
C1–Si–C7	115.30(12)	113.81(6)	C2–N1–C6	113.11(18)	112.59(11)
C1–Si–C8	111.25(12)	115.14(6)	C5–N1–C6	121.74(18)	121.54(12)
C6–Si–C7	112.46(13)	112.24(7)	C3–N2–C4	118.59(18)	118.35(12)

3.1.2. rac-2-{[(Chloromethyl)dimethylsilyl]methyl}-3,6-diethoxy-2,5-dihydropyrazine (rac-**2a**)

This compound was synthesized according to ref. [1].

3.1.3. rac-2-{[(Chloromethyl)diphenylsilyl]methyl}-3,6-diethoxy-2,5-dihydropyrazine (rac-**2b**)

A 1.6 M solution of *n*-butyllithium in *n*-hexane (500 μl, 800 μmol *n*-BuLi) was added dropwise at −10°C within 5 min to a stirred solution of **4** (605 mg, 3.55 mmol) in THF (20 ml). After cooling the reaction mixture to −70°C, again a 1.6 M solution of *n*-butyllithium in *n*-hexane (1.70 ml, 2.72 mmol *n*-BuLi) was added dropwise over a period of 20 min. The mixture was stirred at −70°C for 15 min, warmed up to −40°C, and then added dropwise at −5°C within 4 h to a stirred solution of **5b** (1.00 g, 3.56 mmol) in THF (20 ml). The resulting mixture was allowed to warm up to room temperature within 2 h, followed by addition of diethyl ether (100 ml) and water (100 ml). The organic phase was separated and the aqueous layer extracted with diethyl ether (3 × 100 ml), and the combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the oily residue purified by column chromatography on silica gel 60 (particle size 0.015–0.040 mm) using *n*-hexane–diethyl ether (2:1, v/v) as eluent. Compound *rac*-**2b** was isolated in 53% yield (767 mg, 1.85 mmol) as a crystalline solid; m.p. 49–52°C. ^{1}H-NMR (600.1 MHz): δ 1.14 (δ_X), 3.61 (δ_A), and 3.92 (δ_B) [^2J(AB) = 10.5 Hz, ^3J(AX) = 7.1 Hz, ^3J(BX) = 7.1 Hz, 5H; O–CH_AH_B–CH_{X3}], 1.21 (δ_X), 3.94 (δ_A), and 4.02 (δ_B) [^2J(AB) = 10.5 Hz, ^3J(AX) = 7.1 Hz, ^3J(BX) = 7.1 Hz, 5H; O–CH_AH_B–CH_{X3}], 1.55 (δ_A), 1.90 (δ_B), 3.92 (δ_K), 3.95 (δ_L), and 4.12 (δ_X) [^2J(AB) = 14.8 Hz, $^3J_{trans}$(AX) = 11.1 Hz, $^3J_{cis}$(BX) = 4.7 Hz, ^2J(KL) = 20.2 Hz, ^5J(KX) = 4.3 Hz, ^5J(LX) = 3.5 Hz, 5H; Si–CH_AH_B–CH_X–N=C–CH_KH_L] [9], 3.42 (s, 2H; $SiCH_2Cl$), 7.32–7.44 and 7.55–7.64 (m, 10H; SiC_6H_5). ^{13}C-NMR: δ 14.2 (2C, OCH_2CH_3), 18.0 ($SiCH_2CH$), 28.9 ($SiCH_2Cl$), 46.5 (CCH_2N), 52.5 ($SiCH_2CH$), 60.7 (OCH_2CH_3), 61.0 (OCH_2CH_3), 127.9 (C-2/C-6 or C-3/C-5, SiC_6H_5), 129.8 (2C, C-4, SiC_6H_5), 133.3 (C-1, SiC_6H_5), 133.5 (C-1, SiC_6H_5), 135.1 (C-2/C-6 or C-3/C-5, SiC_6H_5), 161.6 (C=N), 165.4 (C=N). ^{29}Si-NMR: δ −9.5. Anal. Calc. for $C_{22}H_{27}ClN_2O_2Si$ (415.0): C, 63.67; H, 6.56; N, 6.75. Found: C, 63.4; H, 6.4; N, 6.7%.

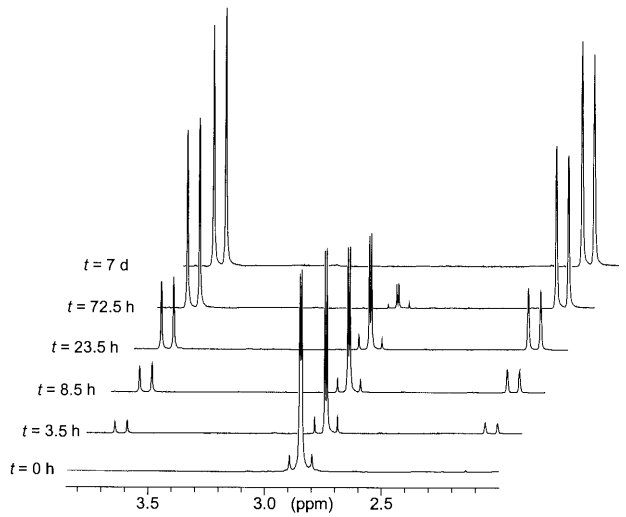


Fig. 5. Selected ^{1}H-NMR partial spectra showing the kinetics of the transformation *rac*-**2a** → *rac*-**3a** at 80°C in C_6D_6 ($SiCH_2Cl$ protons of *rac*-**2a** and $SiCH_2N$ protons of *rac*-**3a**; 300.1 MHz, 10°C, C_6D_6; for details, see Section 3).

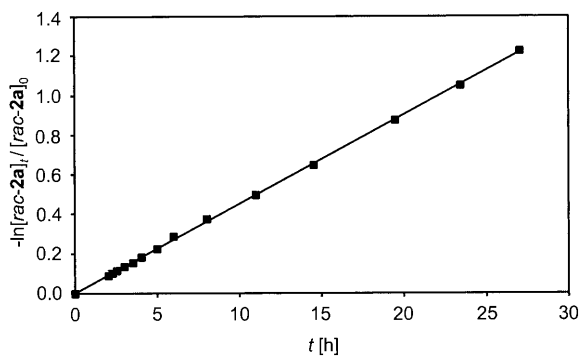


Fig. 6. First-order kinetics of the transformation *rac*-**2a** → *rac*-**3a** in C_6D_6 at 80°C as monitored by ^{1}H-NMR spectroscopy ([*rac*-**2a**]$_t$, concentration of *rac*-**2a** at the time *t*; [*rac*-**2a**]$_0$, concentration at the time *t* = 0; for details, see Section 3).

3.1.4. rac-7-Ethoxy-2,2-dimethyl-2,3,5,7a-tetrahydro-1H-3a,6-diaza-2-sila-inden-4-one (rac-**3a**)

Compound *rac*-**2a** (1.50 g, 5.16 mmol) was heated at 120°C in vacuo (300 Torr) for 6 h and the resulting product was then distilled in a Kugelrohr apparatus (oven temperature 130°C, 0.01 Torr). After crystallization from *n*-hexane at −20°C, compound *rac*-**3a** was isolated in quantitative yield (1.17 g, 5.16 mmol) as a crystalline solid; m.p. 45°C. ^{1}H-NMR (600.1 MHz): δ 0.24 (s, 3H; $SiCH_3$), 0.26 (s, 3H; $SiCH_3$), 0.92 (δ_A), 1.48 (δ_B), 2.32 (δ_K), 3.54 (δ_L), 3.96 (δ_X), 4.08 (δ_Y), and 4.17 (δ_Z) [^2J(AB) = 14.5 Hz, $^3J_{trans}$(AX) = 12.7 Hz, $^3J_{cis}$(BX) = 5.5 Hz, ^2J(KL) = 15.6 Hz, ^5J(KY) = 1.0 Hz, ^5J(KZ) = 0.6 Hz, ^5J(LY) = 0.6 Hz, ^5J(XY) = 4.0 Hz, ^5J(XZ) = 2.6 Hz, ^2J(YZ) = 20.9 Hz, 7H; Si–CH_AH_B–CH_X–C=N–CH_YH_Z–(C=O)–N–CH_KH_L] [10], 1.26 (δ_X), 4.08 (δ_A), and 4.10 (δ_B) [^2J(AB) = 10.6 Hz, ^3J(AX) = 7.1 Hz, ^3J(BX) = 7.1 Hz, 5H; O–CH_AH_B–CH_{X3}]. ^{13}C-NMR: δ −3.1 ($SiCH_3$), −3.0 ($SiCH_3$), 14.2 (OCH_2CH_3), 19.5 ($SiCH_2CH$), 33.1 ($SiCH_2N$), 51.0 (CCH_2N), 56.9 ($SiCH_2CH$), 61.3 (OCH_2CH_3), 160.5 (C=N), 166.6 (C=O). ^{29}Si-NMR: δ 11.5. Anal. Calc. for $C_{10}H_{18}N_2O_2Si$ (226.4): C, 53.06; H, 8.02; N, 12.38. Found: C, 53.0; H, 8.0; N, 12.6%.

*3.1.5. rac-7-Ethoxy-2,2-diphenyl-2,3,5,7a-tetrahydro-1H-3a,6-diaza-2-sila-inden-4-one (rac-**3b**)*

Compound *rac*-**2b** (500 mg, 1.20 mmol) was heated at 120°C in vacuo (300 Torr) for 6 h and the resulting product was then distilled in a Kugelrohr apparatus (oven temperature 230°C, 0.01 Torr). After crystallization from *n*-hexane at −20°C, compound *rac*-**3b** was isolated in quantitative yield (420 mg, 1.20 mmol) as a crystalline solid; m.p. 107–109°C. ^{1}H-NMR (600.1 MHz): δ 1.27 (δ_X), 4.11 (δ_A), and 4.14 (δ_B) [^2J(AB) = 10.7 Hz, ^3J(AX) = 7.0 Hz, ^3J(BX) = 7.1 Hz, 5H; O–CH_AH_B–CH_{X3}], 1.46 (δ_A), 2.02 (δ_B), 2.90 (δ_K), 4.06 (δ_L), 4.13 (δ_Y), 4.19 (δ_X), and 4.23 (δ_Z) [^2J(AB) = 14.8 Hz, $^3J_{trans}$(AX) = 12.6 Hz, $^3J_{cis}$(BX) = 5.5 Hz, ^2J(KL) = 16.0 Hz, ^5J(XY) = 4.1 Hz, ^5J(XZ) = 2.5 Hz, ^2J(YZ) = 21.0 Hz, 7H; Si–CH_AH_B–CH_X–C=N–CH_YH_Z–(C=O)–N–CH_KH_L] [10], 7.33–7.53 and 7.57–7.61 (m, 10H; SiC_6H_5). ^{13}C-NMR: δ 14.2 (OCH_2CH_3), 18.8 ($SiCH_2CH$), 32.2 ($SiCH_2N$), 51.1 (CCH_2N), 57.2 ($SiCH_2CH$), 61.5 (OCH_2CH_3), 128.3 (C-2/C-6 or C-3/C-5, SiC_6H_5), 128.4 (C-2/C-6 or C-3/C-5, SiC_6H_5), 130.5 (C-4, SiC_6H_5), 130.6 (C-4, SiC_6H_5), 131.6 (C-1, SiC_6H_5), 131.8 (C-1, SiC_6H_5), 134.8 (C-2/C-6 or C-3/C-5, SiC_6H_5), 134.9 (C-2/C-6 or C-3/C-5, SiC_6H_5), 160.3 (C=N), 166.8 (C=O). ^{29}Si-NMR: δ 0.0. Anal. Calc. for $C_{20}H_{22}N_2O_2Si$ (350.5): C, 68.54; H, 6.33; N, 7.99. Found: C, 68.2; H, 6.3; N, 8.0%.

*3.1.6. 3,6-Diethoxy-2,5-dihydropyrazine (**4**)*

This compound was synthesized according to ref. [11].

*3.1.7. Bis(chloromethyl)dimethylsilane (**5a**)*

This compound was purchased from Aldrich.

*3.1.8. Bis(chloromethyl)diphenylsilane (**5b**)*

A 1.6 M solution of *n*-butyllithium in *n*-hexane (24.7 ml, 39.5 mmol *n*-BuLi; temperature of the solution −75°C) was added dropwise at −75°C within 30 min to a stirred solution of dichlorodiphenylsilane (5.00 g, 19.7 mmol) and bromochloromethane (10.2 g, 78.8 mmol) in THF (100 ml). The resulting mixture was stirred at −70°C for 15 min and was then allowed to warm up to room temperature within 12 h. The solvent of the reaction mixture was removed under reduced pressure and the residue extracted with *n*-pentane (3 × 100 ml). The solvent of the combined organic extracts was removed under reduced pressure and the residue purified by column chromatography on silica gel 60 (particle size 0.015–0.040 mm) using *n*-hexane as eluent. Compound **5b** was isolated after distillation in a Kugelrohr apparatus (oven temperature 140°C, 0.01 Torr) in 76% yield (4.23 g, 15.0 mmol) as a colorless liquid. ^{1}H-NMR (300.1 MHz): δ 3.43 (s, 4H; $SiCH_2Cl$), 7.35–7.67 (m, 10H; SiC_6H_5). ^{13}C-NMR: δ 25.9 ($SiCH_2Cl$), 128.2 (C-2/C-6 or C-3/C-5, SiC_6H_5), 130.4 (C-1, SiC_6H_5), 130.7 (C-4, SiC_6H_5), 135.2 (C-2/C-6 or C-3/C-5, SiC_6H_5). ^{29}Si-NMR: δ −12.3. Anal. Calc. for $C_{14}H_{14}Cl_2Si$ (281.3): C, 59.79; H, 5.02; Cl, 25.21. Found: C, 59.8; H, 5.2; Cl, 25.2%.

3.2. Crystal structure analyses

Suitable single crystals of *rac*-**2b** (*rac*-**3a**) were obtained by cooling a saturated solution in *n*-hexane (*n*-hexane–diethyl ether) to −20°C (−10°C). Suitable single crystals of *rac*-**3b** were obtained by crystallization from *n*-hexane–diethyl ether by slow evaporation of the solvent at room temperature. The crystals were mounted in inert oil (perfluoroalkylether, ABCR) on a glass fiber and then transferred to the cold gas stream of the diffractometer [Stoe IPDS; graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å)]. The structures were solved by direct methods [12,13]. All non-hydrogen atoms were refined anisotropically [14]. A riding model was employed in the refinement of the hydrogen atoms.

3.3. Kinetic studies

A stirred solution of *rac*-**2a** (152 mg, 523 μmol) in C_6D_6 (14 ml) was heated at 80°C for 7 days. In order to study the kinetics of the reaction *rac*-**2a** → *rac*-**3a**, samples (0.5 ml) were taken from the reaction mixture at *t* = 1 h, 2 h, 2.5 h, 3 h, 3.5 h, 4 h, 5 h, 6 h, 8.5 h, 11 h, 14.5 h, 19.5 h, 23.5 h 27 h, 72.5 h, and 7 days and were immediately cooled down in liquid nitrogen. These samples were subsequently studied by ^{1}H-NMR spectroscopy (300.1 MHz) at 10°C, and the kinetics were analyzed by integration of the $SiCH_2Cl$ (*rac*-**2a**) and $SiCH_2N$ (*rac*-**3a**) resonance signals.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 143362 (*rac*-**2b**), CCDC 143360 (*rac*-**3a**), and CCDC 143361 (*rac*-**3b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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