Novel Tricyclic Sila-Heterocycles: Syntheses and Crystal Structure Analyses of *rac*-2,8-Diethoxy-6,6-diorganyl-3,9-diaza-6-silatricyclo[5.2.1.0^{4,8}]dec-2-enes

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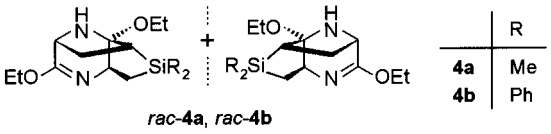
The novel tricyclic sila-heterocycles *rac*-2,8-diethoxy-6,6-diorganyl-3,9-diaza-6-silatricyclo-[5.2.1.0^{4,8}]dec-2-enes *rac*-**4a** (organyl = Me) and *rac*-**4b** (organyl = Ph) were synthesized in two-step, one-pot syntheses, starting from 3,6-diethoxy-2,5-dihydropyrazine (**1**). Metalation of **1** with 1 molar equiv of *n*-BuLi and subsequent treatment with 1 molar equiv of the (chloromethyl)silanes $R_2Si(CH{=}CH_2)CH_2Cl$ (R = Me, Ph) yielded the respective 2-$R_2Si(CH{=}CH_2)CH_2$-substituted 3,6-diethoxy-2,5-dihydropyrazines *rac*-**3a** (R = Me) and *rac*-**3b** (R = Ph). Treatment of *rac*-**3a** and *rac*-**3b** with 1 molar equiv of *n*-BuLi, followed by hydrolysis, finally yielded *rac*-**4a** and *rac*-**4b**, respectively. Compounds *rac*-**4a** and *rac*-**4b** were structurally characterized by multinuclear NMR studies and crystal structure analyses. In addition, some mechanistic aspects of the cyclization reactions *rac*-**3a** → *rac*-**4a** and *rac*-**3b** → *rac*-**4b** were investigated.

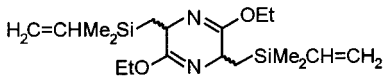
Introduction

In the course of our systematic studies in bioorganosilicon and bioorganogermanium chemistry,[1] we have synthesized a series of racemic and enantiomerically pure silicon- and germanium-containing α-amino acids of the formula type $H_2NCH(CH_2ElMe_2R)COOH$ (El = Si, Ge; R = Me, Ph).[1d,2−4] As demonstrated in Scheme 1, the synthesis of the racemic compounds could be accomplished by either a monoalkylation (method 1) or dialkylation (method 2) of the dihydropyrazine **1** with the respective CH_2ElMe_2R moiety.

In continuation of these studies, we attempted to synthesize the structurally related racemic α-amino acid $H_2NCH(CH_2SiMe_2CH{=}CH_2)COOH$ according to method 2. However, to our surprise the second metalation step with *n*-butyllithium, followed by treatment with $ClCH_2SiMe_2CH{=}CH_2$ and subsequent hydrolysis, afforded only traces of the expected dialkylated dihydropyrazine derivative **5** (detected by GC/MS analysis), and the tricyclic sila-heterocycle *rac*-**4a** was isolated as the main product.



rac-**4a**, *rac*-**4b**



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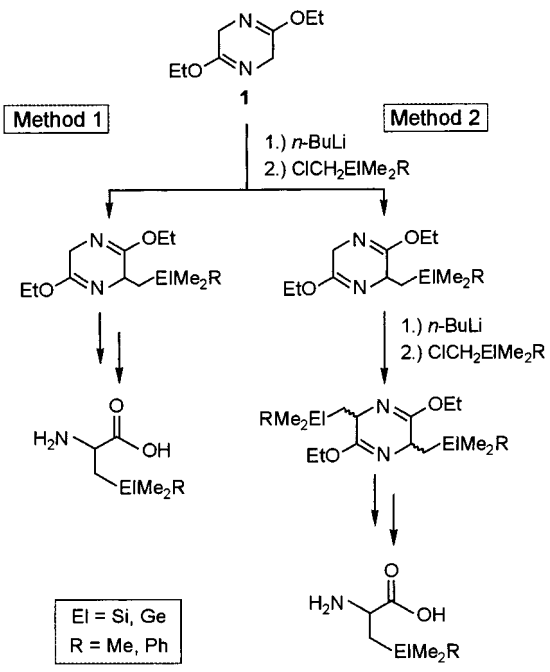
On the basis of these results, we have developed a two-step, one-pot synthesis for the preparation of race-

Scheme 1



* To whom correspondence should be addressed.

(1) Reviews dealing with bioorganosilicon and/or bioorganogermanium chemistry: (a) Tacke, R.; Linoh, H. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 1143−1206. (b) Lukevics, E.; Ignatovich, L. *Appl. Organomet. Chem.* **1992**, *6*, 113−126. (c) Tacke, R.; Wagner, S. A. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 3, pp 2363−2400. (d) Tacke, R.; Heinrich, T.; Kornek, T.; Merget, M.; Wagner, S. A.; Gross, J.; Keim, C.; Lambrecht, G.; Mutschler, E.; Beckers, T.; Bernd, M.; Reissmann, T. *Phosphorus, Sulfur, Silicon* **1999**, *150/151*, 69−87.

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(3) Tacke, R.; Merget, M.; Bertermann, R.; Bernd, M.; Beckers, T.; Reissmann, T. *Organometallics* **2000**, *19*, 3486-3497.

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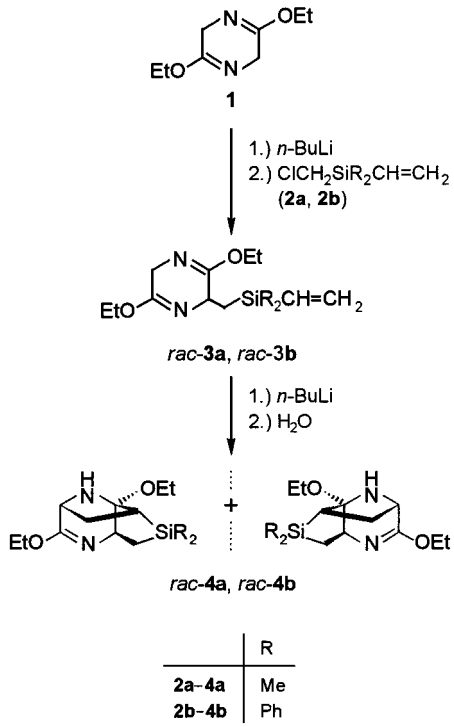
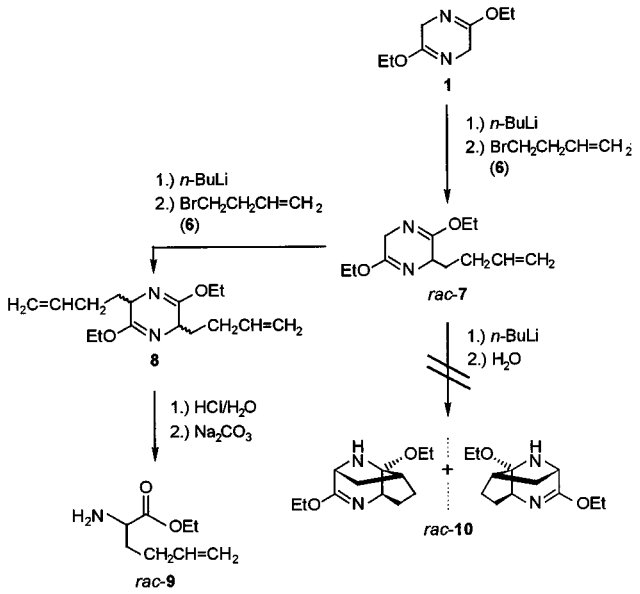
Scheme 2



	R
2a–**4a**	Me
2b–**4b**	Ph

Scheme 3



mic 2,8-diethoxy-6,6-diorganyl-3,9-diaza-6-silatricyclo-[5.2.1.0^{4,8}]dec-2-enes, starting from 3,6-diethoxy-2,5-dihydropyrazine (**1**). We report here the syntheses and crystal structure analyses of the tricyclic sila-heterocycles *rac*-**4a** and *rac*-**4b**.[5] Compounds of this particular formula type represent a novel class of sila-heterocycle.[6] As the tricyclic skeleton of these compounds resembles alkaloid-type structures, it may serve as a lead for the development of new biologically active organosilicon compounds.

Results and Discussion

Syntheses. The tricyclic sila-heterocycles *rac*-**4a** and *rac*-**4b** were prepared by a two-step, one-pot synthesis, starting from the dihydropyrazine **1** (Scheme 2). Thus, metalation of **1** with *n*-butyllithium and subsequent treatment with the silanes $ClCH_2SiMe_2CH{=}CH_2$ (**2a**) or $ClCH_2SiPh_2CH{=}CH_2$ (**2b**) yielded the respective dihydropyrazines *rac*-**3a** and *rac*-**3b** (not isolated), which upon treatment with *n*-butyllithium and subsequent hydrolysis finally afforded *rac*-**4a** (yield 50%) and *rac*-**4b** (yield[7] 21%). Both compounds were isolated as crystalline solids, and their identities were established by elemental analyses (C, H, N), NMR studies (^{1}H, ^{13}C, ^{29}Si), mass-spectrometric investigations, and crystal structure analyses.

Mechanistic Aspects. The formation of *rac*-**4a** and *rac*-**4b** may be described either as an (i) intramolecular [3+2] cycloaddition of a 2-azaallyl-type anion to the $SiCH{=}CH_2$ group or as an (ii) intramolecular nucleophilic attack of the carbon-centered lone pair at the terminal carbon atom of the $SiCH{=}CH_2$ moiety. As might have been expected, all attempts to prepare racemic 2,8-diethoxy-3,9-diazatricyclo[5.2.1.0^{4,8}]dec-2-ene (*rac*-**10**), a carbon analogue of the sila-heterocycles *rac*-**4a** and *rac*-**4b**, by this route failed. When using the alkylation agent $BrCH_2CH_2CH{=}CH_2$ (**6**) instead of the (chloromethyl)silanes **2a** and **2b**, the dihydropyrazine **1** could not be transformed into *rac*-**10** (identical reaction conditions as used for the syntheses of *rac*-**4a** and *rac*-**4b**). A 2-fold metalation/alkylation procedure according to Scheme 3 rather afforded the dialkylated dihydropyrazine **8** (*rac*-**7** and **8** not isolated), which upon hydrolysis with hydrochloric acid gave the α-amino acid ester *rac*-**9** (yield 62%; relative to the 2-fold amount of **1**). These results support the idea that the formation of *rac*-**4a** and *rac*-**4b** is based on an intramolecular cyclization process (via a nucleophilic attack of the carbanion at the terminal carbon atom of the $SiCH{=}CH_2$ group) that is favored by the silicon atom.[8] However, further detailed studies are necessary to clarify this reaction mechanism unequivocally.

Crystal Structure Analyses. The crystal structures of *rac*-**4a** and *rac*-**4b** were determined by single-crystal X-ray diffraction. Both compounds crystallize in the space group $P\bar{1}$. The molecular structures of these compounds in the crystal are depicted in Figures 1 and 2. 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 Table 2.

As can be seen from Figures 1 and 2 and Table 2, the tricyclic skeletons of *rac*-**4a** and *rac*-**4b** are almost

(5) Report on preliminary results of these studies: Merget, M.; Wagner, B.; Tacke, R. *12th International Symposium on Organosilicon Chemistry*; Sendai, Japan, 1999; Abstracts, p 180.

(6) Reviews dealing with sila-heterocycles: (a) Lukevics, E.; Pudova, O. *Main Group Met. Chem.* **1998**, *21*, 649−727. (b) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2209−2230. (c) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1999**, 81−102.

(7) GC analysis of the reaction mixture demonstrated compound *rac*-**4b** to be the main product (>90%). The low yield of the isolated product can be explained by partial thermal decomposition during distillation.

(8) The especially favorable nucleophilic attack of organolithium reagents on vinylsilanes due to stabilization of the resulting α-negative charge by silicon is a well-known phenomenon: (a) Cason, L. F.; Brooks, H. G. *J. Am. Chem. Soc.* **1952**, *74*, 4582−4583. (b) Cason, L. F.; Brooks, H. G. *J. Org. Chem.* **1954**, *19*, 1278−1282. (c) Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, 1137−1140. (d) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264−3268. (e) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 1133−1136.

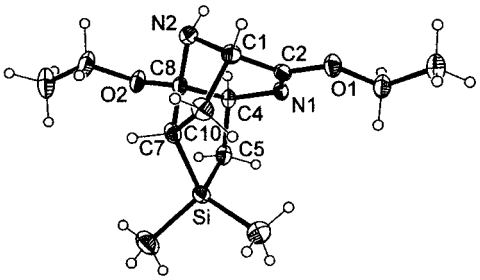


Figure 1. Molecular structure of one of the two enantiomers in the crystal of *rac*-**4a** (probability level of displacement ellipsoids 50%). For selected distances and angles, see Table 2.

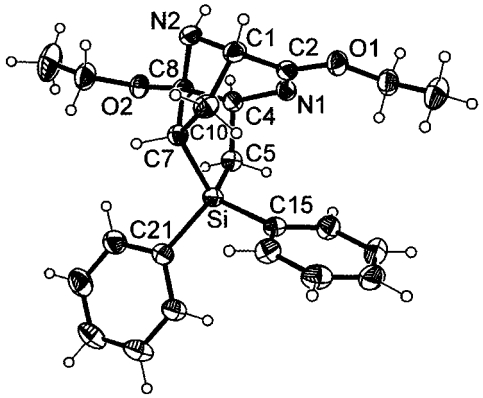


Figure 2. Molecular structure of one of the two enantiomers in the crystal of *rac*-**4b** (probability level of displacement ellipsoids 50%). For selected distances and angles, see Table 2.

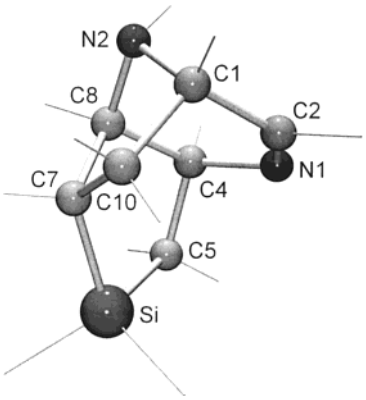


Figure 3. Tricyclic skeleton of one of the two enantiomers in the crystal of *rac*-**4a** and *rac*-**4b**.

identical. This common structural feature is depicted in Figure 3. The tricyclic framework is composed of one six-membered ring and two five-membered rings, which are connected with each other by the brigdehead atoms C1, C4, C7, and C8. In the six-membered ring the nitrogen atom N2 deviates by 0.81 Å from the plane generated by the atoms N1, C1, C2, C4, and C8. The five-membered ring that contains the atoms Si, C4, C5, C7, and C8 adopts an envelope conformation, the atom C4 deviating by 0.61 Å from the plane generated by the other four atoms. The five-membered ring that contains the atoms N2, C1, C7, C8, and C10 adopts a half-chair conformation.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of *rac*-4a and *rac*-4b

	rac-**4a**	*rac*-**4b**
empirical formula	$C_{13}H_{24}N_2O_2Si$	$C_{23}H_{28}N_2O_2Si$
formula mass, g mol^{-1}	268.43	392.56
collection T, K	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group (no.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a, Å	8.0267(16)	7.0707(14)
b, Å	8.4744(17)	10.435(2)
c, Å	11.835(2)	14.556(3)
α, deg	70.98(3)	93.34(3)
β, deg	74.23(3)	94.85(3)
γ, deg	87.93(3)	99.53(3)
V, Å^3	731.2(3)	1052.5(4)
Z	2	2
D(calcd), g cm^{-3}	1.219	1.239
μ, mm^{-1}	0.158	0.132
F(000)	292	420
cryst dimens, mm	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.4
2θ range, deg	5.26−49.42	4.70−56.26
index ranges	$-9 \le h \le 9$, $-9 \le k \le 9$, $-13 \le l \le 13$	$-9 \le h \le 9$, $-13 \le k \le 13$, $-19 \le l \le 19$
no. of collected reflns	7714	12 364
no. of ind reflns	2411	4719
R_{int}	0.0785	0.0302
no. of reflns used	2411	4719
no. of params	259	259
S^a	1.062	1.017
weight params a/b^b	0.0642/0.1558	0.0608/0.0872
$R1^c$ [$I > 2\sigma(I)$]	0.0382	0.0370
$wR2^d$ (all data)	0.1050	0.1013
max/min residual electron density, e Å^{-3}	+0.354/−0.240	+0.365/−0.321

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = number of reflections; p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. Tetrahydrofuran (THF) and diethyl ether were dried and purified according to standard procedures and stored under nitrogen. The concentrations of the *n*-BuLi solutions were determined according to ref 9. ^{1}H NMR spectra were recorded at 22 °C on a Bruker DMX-600 (^{1}H, 600.1 MHz) or a Bruker AMX-400 NMR spectrometer (^{1}H, 400.1 MHz). ^{13}C NMR spectra were recorded at 22 °C on a Bruker AMX-400 (^{13}C, 100.6 MHz) or a Bruker DRX-300 NMR spectrometer (^{13}C, 75.5 MHz). ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{29}Si, 59.6 MHz). $CDCl_3$ was used as solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24), $CDCl_3$ (^{13}C, δ 77.0), and external TMS (^{29}Si, δ 0). Assignment of the ^{1}H NMR data of *rac*-**4a** and *rac*-**4b** was supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HMQC, ^{13}C,^{1}H HMBC, ^{15}N,^{1}H HMBC, and ^{29}Si,^{1}H HMBC experiments. The ^{1}H spin systems were analyzed by simulations using the Bruker software program *WIN-DAISY* 4.05.[10] Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C,^{1}H HMQC experiments. Mass spectra were obtained with a ThermoQuest TRIO 1000 mass spectrometer (EI MS, 70 eV). The selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, and ^{28}Si.

Preparation of 3,6-Diethoxy-2,5-dihydropyrazine (1). This compound was synthesized according to ref 11.

(9) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879−1880.

(10) Weber, U.; Thiele, H.; Spiske, R.; Höffken, H.-W.; Hägele, G. *WIN-DAISY* 4.05; Bruker-Franzen GmbH: Bremen, Germany, 1998.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for *rac*-4a and *rac*-4b

	rac-**4a**	*rac*-**4b**		*rac*-**4a**	*rac*-**4b**
Si−C5	1.8870(17)	1.8783(15)	C1−C2	1.517(2)	1.504(2)
Si−C7	1.8941(17)	1.8908(15)	C1−C10	1.539(2)	1.535(2)
N1−C2	1.268(2)	1.2754(19)	C4−C5	1.535(2)	1.5380(19)
N1−C4	1.4857(19)	1.4824(16)	C4−C8	1.552(2)	1.538(2)
N2−C1	1.467(2)	1.4655(17)	C7−C8	1.565(2)	1.5668(19)
N2−C8	1.465(2)	1.4730(18)	C7−C10	1.552(2)	1.5514(18)
C5−Si−C7	95.30(7)	95.77(7)	C5−C4−C8	107.82(12)	108.63(11)
C2−N1−C4	117.65(13)	117.35(12)	Si−C5−C4	103.84(10)	102.87(9)
C1−N2−C8	100.56(12)	100.56(10)	Si−C7−C8	104.62(10)	104.55(10)
N2−C1−C2	109.07(12)	109.41(12)	Si−C7−C10	120.26(12)	118.71(10)
N2−C1−C10	102.70(13)	101.88(11)	C8−C7−C10	103.54(12)	103.50(10)
C2−C1−C10	108.33(13)	109.49(11)	N2−C8−C4	111.61(12)	111.34(11)
N1−C2−C1	126.05(14)	125.92(12)	N2−C8−C7	103.89(12)	103.39(11)
N1−C4−C5	108.74(12)	107.57(11)	C4−C8−C7	108.74(12)	109.04(11)
N1−C4−C8	112.31(11)	112.74(11)	C1−C10−C7	102.18(12)	102.13(11)

Preparation of (Chloromethyl)dimethyl(vinyl)silane (2a). This compound was synthesized according to ref 12.

Preparation of (Chloromethyl)diphenyl(vinyl)silane (2b). This compound was synthesized according to ref 13.

Preparation of *rac*-2,8-Diethoxy-6,6-dimethyl-3,9-diaza-6-silatricyclo[5.2.1.0^{4,8}]dec-2-ene (*rac*-4a). A 1.6 M solution of *n*-butyllithium in *n*-hexane (3.00 mL, 4.80 mmol *n*-BuLi) was added dropwise at −10 °C during 15 min to a stirred solution of **1** (5.00 g, 29.4 mmol) in THF (350 mL). After the reaction mixture was cooled to −70 °C, a 1.6 M solution of *n*-butyllithium in *n*-hexane (15.4 mL, 24.6 mmol *n*-BuLi) was added dropwise over a period of 30 min. The resulting mixture was stirred at −70 °C for 15 min, and then a solution of **2a** (3.96 g, 29.4 mmol) in THF (20 mL) was added dropwise at this temperature within 30 min. After the mixture was stirred at −70 °C for 2 h, it was warmed to room temperature within 12 h. The mixture was cooled again to −70 °C and then treated dropwise with a 1.6 M solution of *n*-butyllithium in *n*-hexane (18.4 mL, 29.4 mmol *n*-BuLi). The resulting mixture was stirred at −70 °C for 2 h and then warmed to room temperature within 12 h, followed by addition of diethyl ether (300 mL) and water (300 mL). The organic phase was separated, the aqueous layer was extracted with diethyl ether (3 × 300 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the oily residue distilled in a Kugelrohr apparatus (oven temperature 220 °C, 0.01 mbar). The solid product (crystallization of the distillate at room temperature) was purified by recrystallization from diethyl ether at −20 °C to give *rac*-**4a** in 50% yield (relative to **1**) as a colorless crystalline solid (3.95 g, 14.7 mmol); mp 75 °C. ^{1}H NMR (400.1 MHz): δ −0.04 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.93 (δ_D), 1.13 (δ_E), 1.33 (δ_K), 1.61 (δ_A), 2.18 (δ_B), 3.57 (δ_Q), and 3.87 (δ_T) [N(H)CH_Q(C)$CH_AH_BCH_K$(Si)$CCH_TCH_DH_E$, $^2J_{AB}$ = −12.3 Hz, $^3J_{AK}$ = 3.2 Hz, $^3J_{BK}$ = 13.0 Hz, $^3J_{BQ}$ = 6.1 Hz, $^2J_{DE}$ = −14.4 Hz, $^3J_{ET}$ = 6.3 Hz, $^3J_{DT}$ = 1.3 Hz, $^4J_{KT}$ = 1.9 Hz], 1.12 (δ_X), 3.49 (δ_A), and 3.68 (δ_B) [N(H)$COCH_AH_BCH_{X3}$, $^2J_{AB}$ = −9.5 Hz, $^3J_{AX}$ = 7.2 Hz, $^3J_{BX}$ = 6.9 Hz], 1.21 (δ_X), 3.95 (δ_A), and 3.98 (δ_B) [N=$COCH_AH_BCH_{X3}$, $^2J_{AB}$ = −10.6 Hz, $^3J_{AX}$ = 7.0 Hz, $^3J_{BX}$ = 7.3 Hz], 2.02 (s, 1 H, NH). ^{13}C NMR (100.6 MHz): δ −2.9 ($SiCH_3$), −0.7 ($SiCH_3$), 14.4 [(C-2)OCH_2CH_3], 16.2 [(C-8)-OCH_2CH_3], 19.8 (C-5), 23.8 (C-7), 31.4 (C-10), 55.3 (C-1), 57.1 [(C-8)OCH_2CH_3], 61.0 [(C-2)OCH_2CH_3], 65.8 (C-4), 102.4 (C-8), 167.3 (C-2). ^{29}Si NMR: δ 24.3. EI MS: *m*/*z* 268 [3%, M^+], 253 [2%, M^+ − Me], 239 [59%, M^+ − Et], 223 [8%, M^+ − OEt], 75 [100%]. Anal. Calcd for $C_{13}H_{24}N_2O_2Si$: C, 58.17; H, 9.01; N, 10.44. Found: C, 57.9; H, 8.8; N, 10.2.

Preparation of *rac*-2,8-Diethoxy-6,6-diphenyl-3,9-diaza-6-silatricyclo[5.2.1.0^{4,8}]dec-2-ene (*rac*-4b). This compound was prepared analogously to the synthesis of *rac*-**4a** by addition of a 1.6 M solution of *n*-butyllithium in *n*-hexane (9.00 mL, 14.4 mmol *n*-BuLi) to a solution of **1** (2.43 g, 14.3 mmol) in THF (125 mL), followed by treatment with a solution of **2b** (3.70 g, 14.3 mmol) in THF (10 mL). After treatment with a 1.6 M solution of *n*-butyllithium in *n*-hexane (9.00 mL, 14.4 mmol *n*-BuLi) and subsequent aqueous workup, the crude product was distilled in a Kugelrohr apparatus (oven temperature 250 °C, 0.01 mbar). The solid product (crystallization of the distillate at room temperature) was purified by recrystallization from diethyl ether at −20 °C to give *rac*-**4b** in 21% yield (relative to **1**) as a colorless crystalline solid (1.20 g, 3.06 mmol); mp 128 °C. ^{1}H NMR (400.1 MHz): δ 1.01 (δ_X), 3.78 (δ_A), and 3.91 (δ_B) (N=$COCH_AH_BCH_{X3}$, $^2J_{AB}$ = −10.4 Hz, $^3J_{AX}$ = 7.1 Hz, $^3J_{BX}$ = 7.1 Hz), 1.24 (δ_X), 3.63 (δ_A), and 3.85 (δ_B) [N(H)$COCH_AH_BCH_{X3}$, $^2J_{AB}$ = −9.5 Hz, $^3J_{AX}$ = 7.1 Hz, $^3J_{BX}$ = 7.1 Hz], 1.52 (δ_A), 1.65 (δ_E), 1.75 (δ_D), 1.91 (δ_K), 2.19 (δ_B), 3.51 (δ_Q), and 4.14 (δ_T) [N(H)CH_Q(C)$CH_AH_BCH_K$(Si)$CCH_TCH_DH_E$, $^2J_{AB}$ = −12.3 Hz, $^3J_{AK}$ = 3.4 Hz, $^3J_{BK}$ = 13.3 Hz, $^3J_{BQ}$ = 6.1 Hz, $^2J_{DE}$ = −15.1 Hz, $^3J_{ET}$ = 6.3 Hz, $^3J_{DT}$ = 1.3 Hz, $^4J_{KT}$ = 2.0 Hz], 1.66 (s, 1 H, NH), 7.32−7.38 and 7.50−7.58 (m, 10 H, SiC_6H_5). ^{13}C NMR (100.6 MHz): δ 14.1 [(C-2)OCH_2CH_3], 16.1 [(C-8)OCH_2CH_3], 18.8 (C-5), 25.0 (C-7), 31.7 (C-10), 55.4 (C-1), 57.4 [(C-8)OCH_2CH_3], 60.8 [(C-2)OCH_2CH_3], 65.9 (C-4), 102.7 (C-8), 127.7 (C-meta, SiC_6H_5), 127.8 (C-meta, SiC_6H_5), 129.3 (C-para, SiC_6H_5), 129.5 (C-para, SiC_6H_5), 132.7 (C-ipso, SiC_6H_5), 134.8 (C-ortho, SiC_6H_5), 136.0 (C-ortho, SiC_6H_5), 136.7 (C-ipso, SiC_6H_5), 167.4 (C-2). ^{29}Si NMR: δ 16.3. EI MS: *m*/*z* 392 [4%, M^+], 377 [3%, M^+ − Me], 363 [100%, M^+ − Et], 347 [17%, M^+ − OEt]. Anal. Calcd for $C_{23}H_{28}N_2O_2Si$: C, 70.37; H, 7.19; N, 7.14. Found: C, 70.4; H, 7.2; N, 7.1.

4-Bromo-1-butene (6). This compound was commercially available (Aldrich).

Preparation of *rac*-2-Amino-5-hexenoic Acid Ethyl Ester (*rac*-9). A 1.6 M solution of *n*-butyllithium in *n*-hexane (3.00 mL, 4.80 mmol *n*-BuLi) was added dropwise at −10 °C within 10 min to a stirred solution of **1** (5.00 g, 29.4 mmol) in THF (150 mL). After the reaction mixture was cooled to −70 °C, a 1.6 M solution of *n*-butyllithium in *n*-hexane (15.4 mL, 24.6 mmol *n*-BuLi) was added dropwise over a period of 20 min. The resulting mixture was stirred at −70 °C for 15 min, and then a solution of **6** (3.97 g, 29.4 mmol) in THF (15 mL) was added dropwise at this temperature within 30 min. After the mixture was stirred at −70 °C for 2 h, it was warmed to room temperature within 12 h. The mixture was cooled again to −70 °C and then treated dropwise with a 1.6 M solution of *n*-butyllithium in *n*-hexane (18.4 mL, 29.4 mmol *n*-BuLi). After the mixture was stirred at −70 °C for 30 min, a solution of **6** (3.97 g, 29.4 mmol) in THF (15 mL) was added dropwise at this temperature within 30 min. The resulting mixture was stirred at −70 °C for 2 h and then warmed to room temper-

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ature within 12 h, followed by addition of diethyl ether (100 mL) and water (100 mL). The organic phase was separated, the aqueous layer was 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 distilled in a Kugelrohr apparatus (oven temperature 120 °C, 0.01 mbar) to give a 8:92 mixture (7.11 g) of *rac*-**7** and **8**. Hydrochloric acid (3 M, 70 mL) was added dropwise at 0 °C within 15 min to a stirred solution of *rac*-**7**/**8** in ethanol (40 mL). After the mixture was stirred at 0 °C for 2 h, the solvent was removed in vacuo (0.1 mbar, 20 °C), the residue dissolved in dichloromethane (175 mL), and the resulting solution extracted with a saturated aqueous Na_2CO_3 solution (140 mL). After the organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure (rotary evaporator) and the residue purified by distillation in a Kugelrohr apparatus (oven temperature 60 °C, 0.1 mbar) to give *rac*-**10** in 62% yield (relative to the 2-fold molar amount of **1**) as a colorless liquid (5.75 g, 36.6 mmol). ^{1}H NMR (600.1 MHz): δ 1.17 (δ_X), 4.06 (δ_A), and 4.08 (δ_B) ($OCH_AH_BCH_{X3}$, $^2J_{AB} = -10.7$ Hz, $^3J_{AX} = 7.2$ Hz, $^3J_{BX} = 7.2$ Hz), 1.42 (s, 2 H, NH_2), 1.53 (δ_N), 1.73 (δ_M), 2.05 (δ_L), 2.08 (δ_K), 3.33 (δ_Q), 4.88 (δ_A), 4.95 (δ_B), and 5.71 (δ_C) [$CH_AH_B{=}CH_C$-$CH_KH_LCH_MH_NCH_Q$(COOEt)NH_2, $^2J_{AB} = 1.4$ Hz, $^3J_{AC} = 10.2$ Hz, $^4J_{AK} = 2.1$ Hz, $^4J_{AL} = 1.1$ Hz, $^3J_{BC} = 17.1$ Hz, $^4J_{BK} = 2.0$ Hz, $^4J_{BL} = 1.7$ Hz, $^3J_{CK} = 6.4$ Hz, $^3J_{CL} = 6.8$ Hz, $^2J_{KL} = -14.5$ Hz, $^3J_{KM} = 6.5$ Hz, $^3J_{KN} = 9.0$ Hz, $^3J_{LM} = 9.5$ Hz, $^3J_{LN} = 6.0$ Hz, $^2J_{MN} = -13.6$ Hz, $^3J_{MQ} = 5.3$ Hz, $^3J_{NQ} = 7.8$ Hz]. ^{13}C NMR (75.5 MHz): δ 14.2 (OCH_2CH_3), 29.8 ($CH_2CH{=}CH_2$), 34.0 (CH_2-$CHNH_2$), 53.9 (CH_2CHNH_2), 60.8 (OCH_2CH_3), 115.3 ($CH{=}CH_2$), 137.5 ($CH{=}CH_2$), 176.0 (C=O). EI MS: *m*/*z* 102 [6, $M^+ - CH_2CH_2CH{=}CH_2$], 84 [100, $M^+ - CO_2Et$]. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.0; H, 9.4; N, 9.0.

Crystal Structure Analyses of *rac*-4a and *rac*-4b. Suitable single crystals were obtained by crystallization from the oily crude product (*rac*-**4a**) or from diethyl ether (*rac*-**4b**, slow evaporation of the solvent at room temperature). The crystals were mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [Stoe IPDS diffractometer; graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å)]. Both structures were solved by direct methods.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of *rac*-**4a** and the NH hydrogen atom of *rac*-**4b** were localized in difference Fourier syntheses and refined freely.[15,16] For the refinement of the CH hydrogen atoms of *rac*-**4b** a riding model was applied.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for *rac*-**4a** and *rac*-**4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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