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New *C*-functionalized silacycloalkanes $(CH_2)_nSi(CH_2X)_2$ and $(CH_2)_nSi(CH_2X)CH_2X'$ ($n = 3, 4$; X, X′ = functional group): Synthesis and reactivity studies of analogous silacyclobutanes and silacyclopentanes

Dennis Troegel, W. Peter Lippert, Frank Möller, Christian Burschka, Reinhold Tacke*

Universität Würzburg, Institut für Anorganische Chemie, Am Hubland, D-97074 Würzburg, Germany

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ABSTRACT

A series of novel bifunctional silacyclobutanes and silacyclopentanes of the formula types $(CH_2)_nSi(CH_2X)_2$ and $(CH_2)_nSi(CH_2X)CH_2X'$ ($n = 3, 4$; X, X′ = functional groups) was synthesized, starting from $(CH_2)_4Si(CH_2Cl)_2$ and $(CH_2)_3Si(CH_2Cl)_2$, respectively. The silacyclobutanes and silacyclopentanes were structurally characterized by elemental analyses (C, H, N, S) and multinuclear NMR spectroscopy, and their reactivity was explored. The aim of these investigations was to compare the different reactivity profiles of analogous silacyclobutanes and silacyclopentanes.

1. Introduction

Silacyclobutanes represent prominent small-membered heterocycles that are of great interest for organosilicon chemistry due to their unusual reactivity.[1] Since it was shown that 1,1-dimethylsilacyclobutane is much more reactive than ordinary tetraalkylsilanes,[2] many reactivity studies were carried out on the silacyclobutane ring system.[1] Apart from its synthetic use in organosilicon chemistry, the silacyclobutane skeleton might also be an interesting structural unit in silicon-containing drugs and odorants.

Recently, the synthesis of a series of bifunctional silacyclopentanes of the general formula type $(CH_2)_4Si(CH_2X)_2$ ($(CH_2)_4Si$ = silacyclopentane-1,1-diyl; X = functional group), e.g. compounds **1a**–**4a**, has been achieved.[3–5] In continuation of these studies, we were interested in the synthesis of 1,1-bis(chloromethyl)-1-silacyclobutane, $(CH_2)_3Si(CH_2Cl)_2$ (**1b**), and its synthetic potential for the preparation of new silacyclobutanes of the formula type $(CH_2)_3Si(CH_2X)_2$ ($(CH_2)_3Si$ = silacyclobutane-1,1-diyl; X = functional group), compounds **2b**–**5b**. Additionally, we were interested in the synthesis of the mixed functionalized derivatives **6a** and **6b** of the formula type $(CH_2)_nSi(CH_2NH_2)CH_2OH$ ($n = 3, 4$) as new potential building blocks for the preparation of silicon-containing drugs. We report here on the synthesis of compounds **1b**, **5a**, **5b**, and **6a**·*p*-TosOH (*p*-Tos = *p*-tolylsulfonyl) and their characterization by multinuclear NMR spectroscopy and single-crystal X-ray diffraction (compound **6a**·*p*-TosOH only). In addition, we report here on the failed syntheses of **2b**, **3b**, **4b**, and **6b**, emphasizing the significant differences in the reactivity of analogous silacyclobutanes and silacyclopentanes. In these studies, a series of novel bifunctional silacyclobutanes and silacyclopentanes were synthesized as intermediates and were also characterized by multinuclear NMR-spectroscopic studies and crystal structure analyses.

2. Results and discussion

2.1. Syntheses

1,1-Bis(chloromethyl)-1-silacyclobutane (**1b**) was prepared according to Scheme 1 by applying the same synthetic method as it was used for the synthesis of its silacyclopentane derivative **1a**.[4] Thus, treatment of 1,1-dichloro-1-silacyclobutane[6] with (chloromethyl)lithium, generated *in situ* from bromochloromethane and *n*-butyllithium in tetrahydrofuran,[7] afforded **1b** in 34% yield. The low yield of **1b** can be explained by the additional formation of the silacyclopentane derivative **1a** as the main product (detection by GC and ^{1}H NMR analyses), caused by a ring enlargement, and **1b** could only be separated by fractional distillation using a spinning band column due to the very similar boiling points of **1a** and **1b**. In the synthesis of **1a** from 1,1-dichloro-1-silacyclopentane, such kind of ring extension (formation of 1,1-bis(chloromethyl)-1-silacyclohexane) was not observed.[4]

* Corresponding author. Tel.: +49 931 31 85251; fax: +49 931 31 84609.
E-mail address: r.tacke@uni-wuerzburg.de (R. Tacke).

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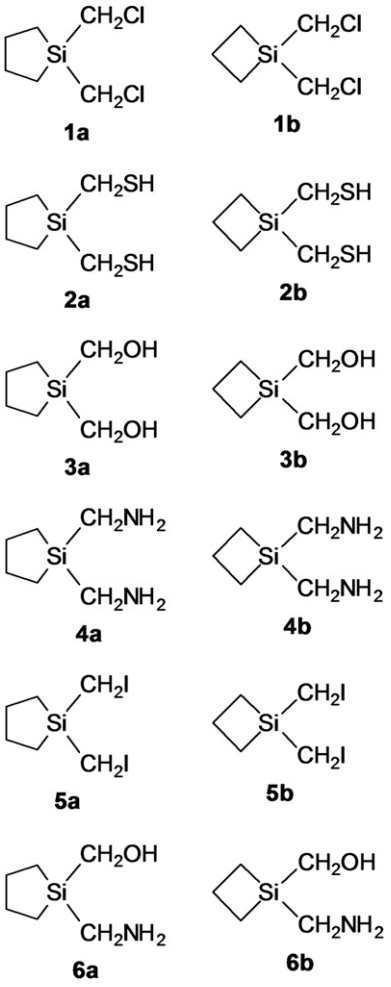
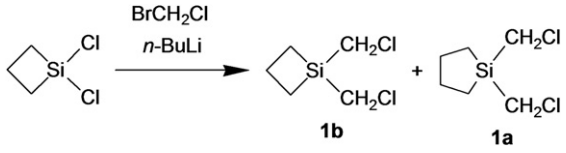


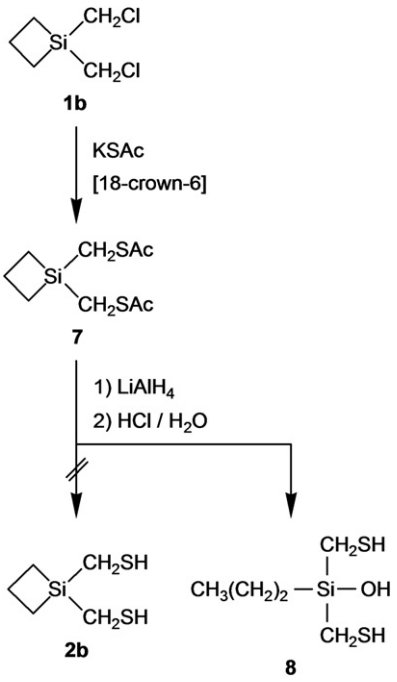
For the attempted synthesis of 1,1-bis(mercaptomethyl)-1-silacyclobutane (**2b**), in the first step **1b** was treated with potassium thioacetate and 18-crown-6 in toluene to furnish 1,1-bis(acetylthiomethyl)-1-silacyclobutane (**7**) in 72% yield (Scheme 2). However, subsequent treatment of **7** with lithium aluminum hydride in diethyl ether, followed by workup with hydrochloric acid, did not afford the target compound **2b**. Instead, ring opening occurred to give bis(mercaptomethyl)propylsilanol (**8**), which was isolated in 72% yield. It is interesting to note that the silacyclopentane derivate of **2b**, compound **2a**, can be easily prepared by using the strategy for the attempted synthesis of **2b**.[4]

The silanol **8** was found to be relatively stable against condensation. It could be stored at ambient temperature for two weeks without formation of the corresponding disiloxane.

The attempted synthesis of 1,1-bis(hydroxymethyl)-1-silacyclobutane (**3b**), following the strategy for the preparation of its silacyclopentane derivative **3a**,[5] also failed (Scheme 3). Thus,

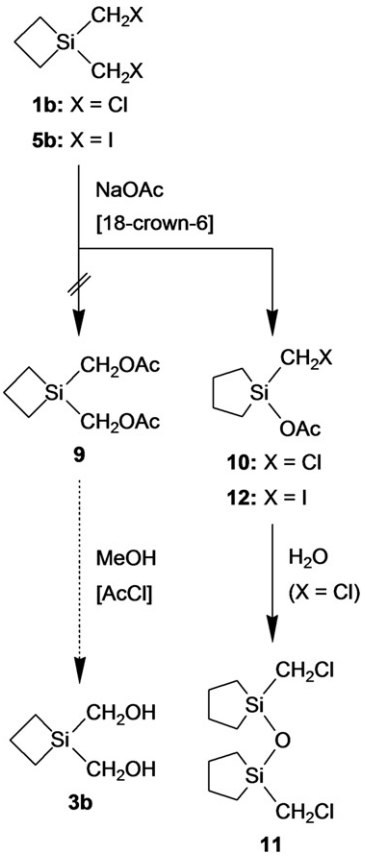


Scheme 1.



Scheme 2.

treatment of **1b** with sodium acetate and 18-crown-6 in toluene did not give 1,1-bis(acetoxymethyl)-1-silacyclobutane (**9**). Instead, the formation of 1-acetoxy-1-(chloromethyl)-1-silacyclopentane (**10**) via ring enlargement was observed. Compound **10** was isolated in



Scheme 3.

69% yield using a non-aqueous workup. When using an aqueous workup, the disiloxane 1,1'-oxybis[1-(chloromethyl)-1-silacyclopentane] (**11**) was obtained (75% yield). As can be seen from Scheme 3, treatment of 1,1-bis(iodomethyl)-1-silacyclobutane (**5b**) with sodium acetate and 18-crown-6 also resulted in a ring extension to give 1-acetoxy-1-(iodomethyl)-1-silacyclopentane (**12**), which was isolated in 50% yield.

Some years ago, the first synthesis of 1,1-bis(aminomethyl)-1-silacyclopentane (**4a**) has been reported.[3] Compound **4a** was obtained by treatment of **1a** with sodium azide and subsequent reaction of the resulting 1,1-bis(azidomethyl)-1-silacyclopentane with lithium aluminum hydride. As multifunctional (azidomethyl) silanes can be hazardous explosives,[3,8] an alternative synthetic route for the preparation of **4a** and its derivative 1,1-bis(aminomethyl)-1-silacyclobutane (**4b**) was studied by using the Gabriel synthesis (Scheme 4). Thus, treatment of **1a** with potassium phthalimide and 18-crown-6 in *N*,*N*-dimethylformamide yielded 1,1-bis(phthalimidomethyl)-1-silacyclopentane (**13a**) (77% yield), which, however, could not be converted into the corresponding diamine **4a**. Different synthetic methods for this transformation were applied (Scheme 4) using various reaction conditions, but in all cases Si—CH_2NH_2 bond cleavage was observed. The sensitivity of the Si—CH_2NH_2 group against nucleophiles has already been reported for some related (aminomethyl)silanes[3,9]; however, this reactivity profile is not yet fully understood. All attempts to synthesize the corresponding silacyclobutane derivative **4b** also failed. In this case, even the attempted intermediate, 1,1-bis-(phthalimidomethyl)-1-silacyclobutane (**13b**), could not be synthesized (Scheme 4). When using the same conditions as for the synthesis of **13a**, only a non-defined mixture of many products was obtained.

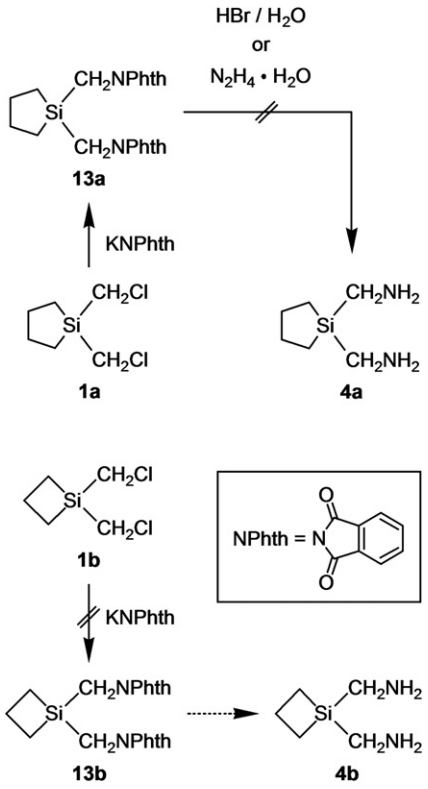
1,1-Bis(iodomethyl)-1-silacyclopentane (**5a**) and 1,1-bis(iodomethyl)-1-silacyclobutane (**5b**) were synthesized according to Scheme 5 by treatment of the corresponding 1,1-bis(chloromethyl)-1-silacycloalkanes **1a** and **1b**, respectively, with sodium iodide in acetone (yield: **5a**, 84%; **5b**, 93%).

To synthesize 1-(aminomethyl)-1-(hydroxymethyl)-1-silacyclopentane (**6a**), two different routes were studied, starting from 1-(acetoxymethyl)-1-(chloromethyl)-1-silacyclopentane (**14**) and 1-(acetoxymethyl)-1-(iodomethyl)-1-silacyclopentane (**15**) (Scheme 6). Compounds **14** and **15** were obtained by treatment of **1a** and **5a**, respectively, with one molar equivalent of sodium acetate and 18-crown-6 in *N*,*N*-dimethylformamide. Under the reaction conditions chosen (temperature, 20 °C; reaction time, 4 days), a mixture of the starting material **1a** (21 mol%), the target compound **14** (58 mol%), and the disubstituted product $(CH_2)_4Si(CH_2OAc)_2$ (21 mol%) (GC analysis) was obtained, which upon chromatographic separation and purification on silica gel afforded **14** in 45% yield. When using **5a** as the starting material (temperature, 20 °C; reaction time, 2 days), a mixture of **5a** (29 mol%), **15** (42 mol%), and $(CH_2)_4Si(CH_2OAc)_2$ (29 mol%) was obtained, which upon separation on silica gel gave the target compound **15** in 36% yield. Subsequent treatment of **14** with potassium pthalimide furnished 1-(acetoxymethyl)-1- (phthalimidomethyl)-1-silacyclopentane (**16**) in 79% yield. However, all attempts to convert **16** into the target compound **6a** failed due to the same reasons as described for the failed synthesis of **4a**. Alternatively, compound **14** was then treated with sodium azide to afford 1-(acetoxymethyl)-1-(azidomethyl)-1-silacyclopentane (**17**) in 81% yield. Subsequent treatment of **17** with triphenylphosphine, followed by hydrolysis with hydrochloric acid,[10] was expected to afford **6a**·HCl. However, under the reaction conditions applied (see Experimental Section), an additional transformation of the (hydroxymethyl) group into a (chloromethyl) moiety occurred to give 1-(aminomethyl)-1-(chloromethyl)-1-silacyclopentane hydrochloride (**18**·HCl) (40% yield). To prevent this OH/Cl exchange, the aqueous workup was performed by using the non-nucleophilic *p*-toluenesulfonic acid (*p*-TosOH) to give the target compound **6a** as the salt **6a**·*p*-TosOH in 42% yield. All attempts to transform this salt into **6a** failed due to decomposition.

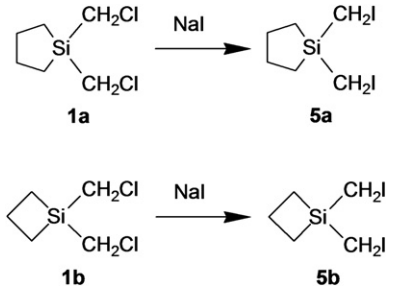
Compounds **1b**, **5a**, **5b**, **7**, **8**, **10**—**12**, **14**, **15**, and **17** were isolated as liquids, whereas **6a**·*p*-TosOH, **13a**, **16**, and **18**·HCl were obtained as crystalline solids. The identities of all these compounds were established by elemental analyses (C, H, N, S) and NMR studies (^1H, ^{13}C, ^{15}N (**6a**·*p*-TosOH, **17**, and **18**·HCl only), ^{29}Si). In addition, compounds **6a**·*p*-TosOH, **13a**, and **18**·HCl were characterized by crystal structure analyses.

2.2. Crystal structure analyses

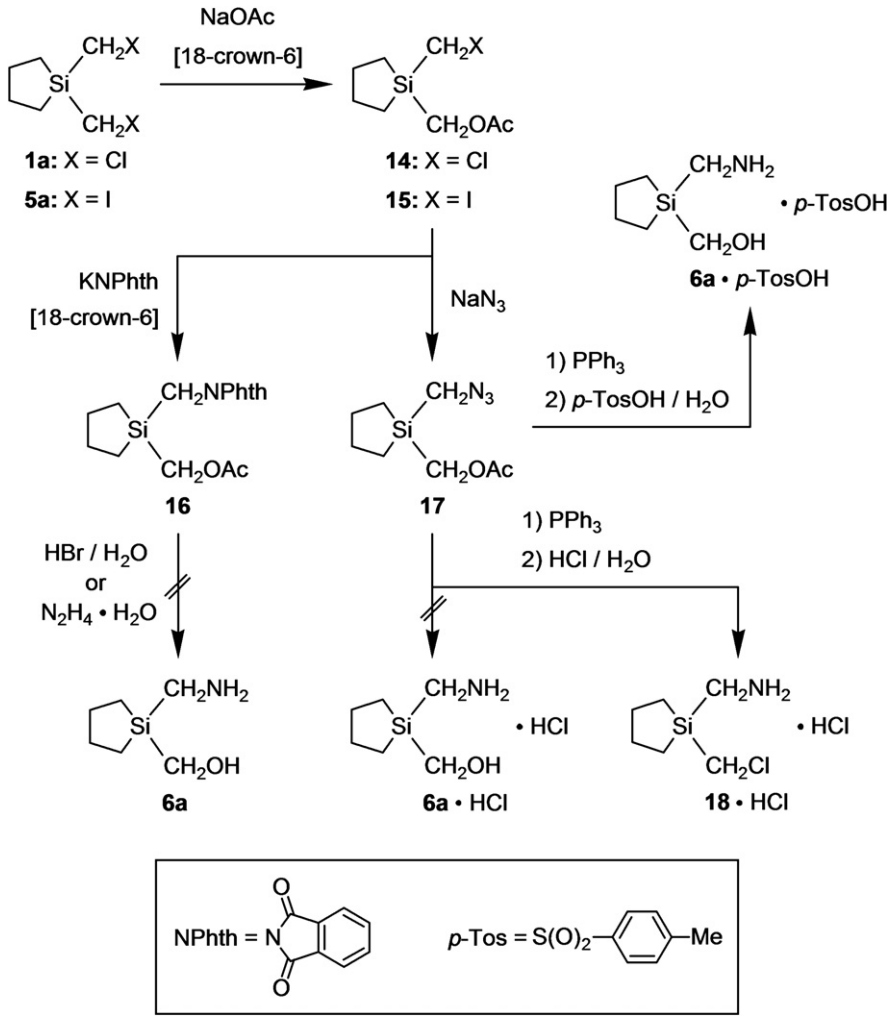
Compounds **6a**·*p*-TosOH, **13a**, and **18**·HCl were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these studies are given in Table 1. The molecular structure of the cation of **6a**·*p*-TosOH is



Scheme 4.



Scheme 5.



Scheme 6.

depicted in Fig. 1; selected bond distances and angles are given in the figure legend (for further details concerning the crystal structure analyses, see the Supporting Information).

The bond lengths and angles of **6a**·*p*-TosOH, **13a**, and **18**·HCl are all in the expected ranges and therefore do not need any further comments, except for the hydrogen-bonding system in the crystal of **6a**·*p*-TosOH, where the ammonium cations are connected with the *p*-tosylate anions via hydrogen bonds. All three N*H* units and the O*H* group of the cation act as proton donors, and the oxygen atom of the cation and the three oxygen atoms of the anion act as proton acceptors to form a three-dimensional hydrogen-bonding network consisting of intermolecular O—H···O and N—H···O hydrogen bonds.[11]

3. Conclusions

Multifunctional tetraorganylsilanes are versatile building blocks for synthetic organosilicon chemistry. In this study, we have evaluated the synthetic potential of 1,1-bis(chloromethyl)-1-silacyclobutane (**1b**) and 1,1-bis(chloromethyl)-1-silacyclopentane (**1a**) as starting materials for the preparation of a series of new bifunctional silacyclobutanes and silacyclopentanes of the formula type $(CH_2)_nSi(CH_2X)_2$ (n = 3, 4; X = functional group). In almost all cases, the silacyclobutanes displayed a different reactivity profile than their corresponding silacyclopentane analogues, leading to unexpected products which were formed by opening or enlargement of the silacyclobutane ring system or by Si—C cleavage of the Si—CH_2X moieties. Only in the case of soft nucleophiles (thioacetate, iodide), compounds **1a** and **1b** reacted analogously. Additionally, some bifunctional silacyclopentanes of the formula type $(CH_2)_4Si(CH_2X)CH_2X'$ with two different functional groups were synthesized, starting from **1a**. With these studies, valuable information about the synthetic potential of 1,1-bis(chloromethyl)-1-silacyclobutane (**1b**) and 1,1-bis(chloromethyl)-1-silacyclopentane (**1a**) for synthetic organosilicon chemistry was obtained.

4. Experimental

4.1. General procedures

All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR-51 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed glass capillaries. The ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectra were recorded at 23 °C on a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{15}N, 30.4 MHz; ^{29}Si, 59.6 MHz) or a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). $CDCl_3$ or [D_6]DMSO was used as the

Table 1
Crystal data and experimental parameters for the crystal structure analyses of **6a**·*p*-TosOH, **13a**, and **18**·HCl

	6a·*p*-TosOH	**13a**	**18**·HCl
Formula	$C_{13}H_{23}NO_4SSi$	$C_{22}H_{20}N_2O_4Si$	$C_6H_{15}Cl_2NSi$
Formula mass (g mol^{-1})	317.47	404.49	200.18
Collection T (K)	193(2)	193(2)	193(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/\mathbf{c}$ (14)
a (Å)	15.999(2)	7.4553(15)	14.086(2)
b (Å)	6.2974(6)	16.489(3)	6.3760(7)
c (Å)	16.875(2)	15.874(3)	11.5278(17)
β (°)	112.411(14)	99.11(3)	95.894(18)
V (Å^3)	1571.8(3)	1926.8(7)	1029.8(2)
Z	4	4	4
$\rho_{calc.}$ (g cm^{-3})	1.342	1.394	1.291
μ (mm^{-1})	0.294	0.155	0.685
F(000)	680	848	424
Crystal size (mm)	0.5 × 0.4 × 0.4	0.5 × 0.3 × 0.3	0.4 × 0.3 × 0.05
2θ Range(°)	5.22–58.18	4.94–58.20	5.82–58.16
Index ranges	$-21 \le h \le 21$, $-8 \le k \le 8$, $-23 \le l \le 23$	$-10 \le h \le 10$, $-22 \le k \le 22$, $-21 \le l \le 21$	$-19 \le h \le 19$, $-8 \le k \le 8$, $-14 \le l \le 14$
No. of collected reflections	15189	26763	14373
No. of independent reflections	4159	5086	2591
R_{int}	0.0412	0.0325	0.0443
No. of reflections used	4159	5086	2591
No. of parameters	194	262	100
S[a]	1.066	1.039	1.051
Weight parameters a/b[b]	0.0582/0.4008	0.0521/0.4923	0.0443/0.2844
$R1$[c] [$I > 2\sigma(I)$]	0.0347	0.0354	0.0319
$wR2$[d] (all data)	0.0989	0.0963	0.0820
Max./min. residual electron density, e Å^{-3}	+0.524/−0.416	+0.295/−0.209	+0.323/−0.306

[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 $P = [\max(F_o^2,0) + 2F_c^2]/3$.
[c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), internal $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), internal $[D_5]$DMSO (^{1}H, δ 2.49; $[D_6]$DMSO), internal $[D_6]$DMSO (^{13}C, δ 39.5; $[D_6]$DMSO), external $H_2NC(O)H$ (90% in $[D_6]$DMSO; ^{15}N, δ −268.0; $CDCl_3$, $[D_6]$DMSO), or external TMS (^{29}Si, δ 0; $CDCl_3$, $[D_6]$DMSO). Analysis and assignment of the ^{1}H NMR data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HMQC, and ^{13}C,^{1}H HMBC experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135, ^{13}C,^{1}H HMQC, and ^{13}C,^{1}H HMBC experiments. Assignment of the ^{15}N NMR data was supported by ^{15}N,^{1}H HMQC and ^{15}N,^{1}H HMBC experiments. The elemental analyses were performed by using an VarioMicro apparatus. (Elementar Analysensysteme GmbH)

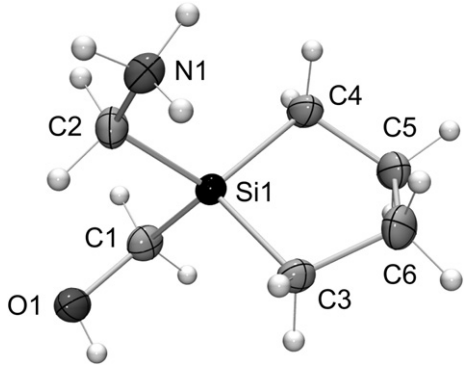


Fig. 1. Molecular structure of the cation of **6a**·*p*-TosOH in the crystal (probability level of displacement ellipsoids 50%). Bond distances (Å) and angles (°): Si–C1 1.8887(14), Si1–C2 1.8965(13), Si1–C3 1.8748(13), Si1–C4 1.8826(13), O1–C1 1.4443(17), N1–C2 1.4930(17), C3–C6 1.5434(19), C4–C5 1.5367(19), C5–C6 1.530(2); C1–Si1–C2 104.87(6), C1–Si1–C3 115.11(6), C1–Si1–C4 112.13(7), C2–Si1–C3 112.86(6), C2–Si1–C4 116.12(6), C3–Si1–C4 96.12(6), Si1–C1–O1 112.84(9), Si1–C2–N1 116.73(9), Si1–C3–C6 104.40(9), Si1–C4–C5 102.88(9), C4–C5–C6 108.79(12).

4.2. 1,1-Bis(chloromethyl)-1-silacyclopentane (**1a**)

This compound was synthesized according to ref. [4].

4.3. Preparation of 1,1-bis(chloromethyl)-1-silacyclobutane (**1b**)

A 2.5 M solution of *n*-butyllithium in hexanes (151 mL, 378 mmol of *n*-BuLi) was added dropwise at −73 °C (±3 °C, temperature measurement within the flask) within 7 h to a stirred mixture of 1,1-dichloro-1-silacyclobutane[6] (26.7 g, 189 mmol), bromochloromethane (73.4 g, 567 mmol), and tetrahydrofuran (200 mL) (the *n*-butyllithium solution was added via a special horizontally elongated side neck of the three-necked flask, which itself was immersed in the cooling bath to ensure precooling of the *n*-butyllithium solution before making contact with the reaction mixture). After the addition was complete, the mixture was stirred at −78 °C for 5 h and was then warmed to 20 °C within 17 h. The solvent was removed under reduced pressure (formation of a precipitate), and the residue was extracted with water (300 mL) and diethyl ether (300 mL). The organic extract was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by fractional distillation using a spinning band column to give **1b** in 34% yield as a colorless liquid (10.8 g, 63.9 mmol). Bp.: 76 °C/10 mbar. Anal. Calc. ($C_5H_{10}Cl_2Si$): C, 35.51; H, 5.96; *M*, 169.13. Found: C, 35.5; H, 5.9%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.26–1.31 (4 H, m, SiCH_2C), 2.09–2.20 (2 H, m, CCH_2C), 3.08 (4 H, s, SiCH_2Cl). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ 12.1 (SiCH_2C), 17.7 (CCH_2C), 27.1 (SiCH_2Cl). ^{29}Si NMR (59.6 Hz, $CDCl_3$): δ 14.9.

4.4. Preparation of 1,1-bis(iodomethyl)-1-silacyclopentane (**5a**)

Compound **1a** (1.03 g, 5.62 mmol) was added in a single portion at 20 °C to a stirred solution of sodium iodide (3.27 g, 21.8 mmol) in acetone (30 mL), and the resulting mixture was then stirred at 20 °C for 18 h. The solvent was removed under reduced pressure, *n*-pentane (150 mL) and water (150 mL) were added to the residue, the organic layer was separated, and the aqueous phase was extracted with *n*-pentane (2 × 150 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (100 °C/0.2 mbar) to give **5a** in 84% yield as a yellowish liquid (1.72 g, 4.70 mmol). Anal. Calc. ($C_6H_{12}I_2Si$): C, 19.69; H, 3.30; *M*, 366.06. Found: C, 20.0; H, 3.4%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.77–0.82 (4 H, m, SiCH_2C), 1.67–1.72 (4 H, m, CCH_2C), 2.19 (4 H, s, SiCH_2I). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −17.0 (SiCH_2I), 11.6 (SiCH_2C), 26.9 (CCH_2C). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 23.9.

4.5. Preparation of 1,1-bis(iodomethyl)-1-silacyclobutane (**5b**)

Compound **1b** (1.53 g, 9.05 mmol) was added in a single portion at 20 °C to a stirred solution of sodium iodide (5.43 g, 36.2 mmol) in acetone (50 mL), and the resulting mixture was then stirred at 20 °C for 24 h. The solvent was removed under reduced pressure, *n*-pentane (250 mL) and water (250 mL) were added to the residue,

the organic layer was separated, and the aqueous phase was extracted with *n*-pentane (2 × 250 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (140 °C/8 mbar) to give **5b** in 93% yield as a yellowish liquid (2.95 g, 8.38 mmol). Anal. Calc. ($C_5H_{10}I_2Si$): C, 17.06; H, 2.86; *M*, 352.03. Found: C, 17.2; H, 2.7%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.22–1.30 (4 H, m, SiCH_2C), 1.93–2.04 (2 H, m, CCH_2C), 2.31 (4 H, s, SiCH_2I). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −15.9 (SiCH_2I), 16.07 (SiCH_2C), 16.13 (CCH_2C). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 17.4.

4.6. Preparation of 1-(aminomethyl)-1-(hydroxymethyl)-1-silacyclopentane hydro-p-tosylate (**6a**·*p*-TosOH)

Compound **17** (1.69 g, 7.92 mmol) was added at 20 °C in a single portion to a solution of triphenylphosphine (2.34 g, 8.92 mmol) in toluene (16 mL), and the mixture was then stirred at 20 °C for 24 h. The solvent was removed under reduced pressure, a solution of *p*-toluenesulfonic acid monohydrate (1.70 g, 8.94 mmol) in water (8 mL) was added to the residue, and the mixture was then heated under reflux for 4 h, cooled to 20 °C, and stirred for a further 15 h at 20 °C. Subsequently, the mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 25 mL). The solvent of the aqueous phase was removed under reduced pressure, the residue was dissolved in methanol (15 mL), and the mixture was then heated under reflux for 7 h. The solvent was removed under reduced pressure, and the residue was crystallized from acetonitrile (5 mL; slow cooling to −20 °C and crystallization over a period of 6 days). The product was isolated by removal of the mother liquor via a syringe, washed with *n*-pentane (3 × 2 mL), and dried in vacuo (0.04 mbar, 20 °C, 3 h) to give **6a**·HOTos in 42% yield as a colorless crystalline solid (1.05 g, 3.31 mmol). Mp.: 93–94 °C. Anal. Calc. ($C_{13}H_{23}NO_4SSi$): C, 49.18; H, 7.30; N, 4.41; S, 10.10; *M*, 317.48. Found: C, 48.8; H, 7.3; N, 4.6; S, 10.3%. ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ 0.59–0.74 (4 H, m, SiCH_2C), 1.48–1.59 (4 H, m, CCH_2C), 2.28 (3 H, s, CH_3), 2.38 (2 H, q, $^3J_{HH}$ = 6.2 Hz, SiCH_2N), 3.36 (2 H, s, SiCH_2O), 4.22 (1 H, br. s, O*H*), 7.10–7.13 (2 H, m, *H*-3/*H*-5, C_6H_4), 7.47–7.49 (2 H, m, *H*-2/*H*-6, C_6H_4), 7.56 (3 H, br. s, NH_3). ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ 8.0 (SiCH_2C), 20.8 (CH_3), 24.4 (SiCH_2N), 26.4 (CCH_2C), 49.9 (SiCH_2O), 125.5 (*C*-2/*C*-6, C_6H_4), 128.1 (*C*-3/*C*-5, C_6H_4), 137.8 (*C*-1, C_6H_4), 145.4 (*C*-4, C_6H_4). ^{15}N NMR (30.4 MHz, [D$_6$]DMSO): δ −358.5. ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ 15.5.

4.7. Preparation of 1,1-bis(acetylthiomethyl)-1-silacyclobutane (**7**)

Compound **1b** (1.01 g, 5.97 mmol) was added in a single portion at 20 °C to a stirred mixture of potassium thioacetate (2.02 g, 17.7 mmol), 18-crown-6 (60.0 mg, 227 μmol), and toluene (20 mL), and the resulting mixture was then stirred at 20 °C for 24 h. The solvent was removed under reduced pressure, diethyl ether (100 mL) and water (75 mL) were added, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2 × 100 mL). The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (oven temperature 95 °C, 0.01 mbar) to give **7** in 72% yield as a yellowish liquid (1.06 g, 4.27 mmol). Anal. Calc. ($C_9H_{16}O_2S_2Si$): C, 43.51; H, 6.49; S, 25.81; *M*, 248.44. Found: C, 43.4; H, 6.5; S, 25.7%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.06–1.14 (4 H, m, SiCH_2C), 1.96–2.08 (2 H, m, CCH_2C), 2.28 (4 H, s, SiCH_2S), 2.31 (6 H, s, C(O)CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.5 (SiCH_2S), 14.0 (SiCH_2C), 17.6 (CCH_2C), 29.9 (C(O)CH_3), 196.5 (*C*(O)CH_3). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 16.2.

4.8. Preparation of bis(mercaptomethyl)propylsilanol (**8**)

A solution of **7** (962 mg, 3.87 mmol) in diethyl ether (10 mL) was added dropwise at 0 °C within 10 min to a stirred suspension of lithium aluminum hydride (747 mg, 19.7 mmol) in diethyl ether (22 mL), and the resulting mixture was stirred at 0 °C for 90 min and then at 20 °C for a further 17 h. Subsequently, hydrochloric acid (2 M, 15 mL) was added dropwise under stirring at 0 °C within 15 min, and the resulting mixture was then warmed to 20 °C, followed by the addition of water (120 mL) and diethyl ether (120 mL). The organic phase was separated, the aqueous phase was extracted with diethyl ether (2 × 120 mL), the combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (oven temperature 80–85 °C, 0.2 mbar) to give **8** in 65% yield as a colorless liquid (457 mg, 2.51 mmol). Anal. Calc. ($C_5H_{14}OS_2Si$): C, 32.93; H, 7.74; S, 35.16; *M*, 182.38. Found: C, 32.9; H, 7.6; S, 35.2%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.76–0.82 (2 H, m, SiCH_2C), 0.98 (3 H, t, $^3J_{HH}$ = 7.3 Hz, CCH_3), 1.30 (δ_X), 1.79 (δ_A), and 1.81 (δ_B) (6 H, $^2J_{AB}$ = 14.4 Hz, $^3J_{AX}$ = 7.5 Hz, $^3J_{BX}$ = 7.4 Hz, Si$CH_AH_BSH_X$), 1.37–1.50 (2 H, m, CCH_2C), 2.55 (1 H, s, SiO*H*). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 5.2 (SiCH_2S), 15.3 (SiCH_2C), 16.4 (CCH_2C), 18.0 (CCH_3). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 7.6.

4.9. Preparation of 1-acetoxy-1-(chloromethyl)-1-silacyclopentane (**10**)

Compound **1b** (2.93 g, 17.3 mmol) was added in a single portion at 20 °C to a stirred mixture of sodium acetate (1.42 g, 17.3 mmol), 18-crown-6 (56.0 mg, 212 μmol), and toluene (30 mL), and the resulting mixture was then stirred at 20 °C for 4 days. The precipitate was removed by filtration, washed with toluene (20 mL), and discarded. The filtrate and wash solutions were combined, the solvent was removed under reduced pressure, and the residue was purified by distillation (Vigreux column) to give **10** in 69% yield as a colorless liquid (2.30 g, 11.9 mmol). Bp.: 29 °C/0.1 mbar. Anal. Calc. ($C_7H_{13}ClO_2Si$): C, 43.63; H, 6.80; *M*, 192.72. Found: C, 43.6; H, 6.9%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.73–0.92 (4 H, m, SiCH_2C), 1.55–1.77 (4 H, m, CCH_2C), 2.05 (3 H, s, C(O)CH_3), 3.06 (2 H, s, SiCH_2Cl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.6 (SiCH_2C), 22.3 (C(O)CH_3), 25.7 (CCH_2C), 26.9 (SiCH_2Cl), 171.9 (*C*(O)CH_3). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 32.2.

4.10. Preparation of 1,1'-oxybis[1-(chloromethyl)-1-silacyclopentane] (**11**)

Compound **1b** (2.00 g, 11.8 mmol) was added in a single portion at 20 °C to a stirred mixture of sodium acetate (970 mg, 11.8 mmol), 18-crown-6 (31.0 mg, 117 μmol), and toluene (20 mL), and the resulting mixture was then stirred at 20 °C for 7 days. The solvent was removed under reduced pressure, diethyl ether (100 mL) and water (100 mL) were added to the residue, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (3 × 100 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was stored at 20 °C for 4 days (formation of water drops) and then purified by bulb-to-bulb distillation (oven temperature 85–100 °C, 0.3 mbar) to give **11** in 75% yield as a colorless liquid (1.26 g, 4.45 mmol). Anal. Calc. ($C_{10}H_{20}Cl_2OSi_2$): C, 42.39; H, 7.11; *M*, 283.34. Found: C, 42.4; H, 7.3%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.53–0.79 (8 H, m, SiCH_2C), 1.50–1.73 (8 H, m, CCH_2C), 2.85 (4 H, s, SiCH_2Cl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 11.4 (SiCH_2C), 25.8 (CCH_2C), 29.0 (SiCH_2Cl). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 20.9.

4.11. Preparation of 1-acetoxy-1-(iodomethyl)-1-silacyclopentane (**12**)

Compound **5b** (4.19 g, 11.9 mmol) was added in a single portion at 20 °C to a stirred mixture of sodium acetate (4.46 g, 54.4 mmol), 18-crown-6 (206 mg, 779 μmol), and toluene (30 mL), and the resulting mixture was then stirred at 20 °C for 2 days. The precipitate was removed by filtration, washed with toluene (15 mL), and discarded. The filtrate and wash solutions were combined, the solvent was removed under reduced pressure, and the residue was purified by distillation (Vigreux column) to give **12** in 50% yield as a colorless liquid (1.68 g, 5.91 mmol). Bp.: 62 °C/0.6 mbar. Anal. Calc. ($C_7H_{13}IO_2Si$): C, 29.59; H, 4.61; *M*, 284.17. Found: C, 30.0; H, 4.7%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.80–0.91 (4 H, m, Si*CH*$_2$C), 1.61–1.76 (4 H, m, CC*H*$_2$C), 2.06 (3 H, s, C(O)C*H*$_3$), 2.27 (2 H, s, Si*CH*$_2$I). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −18.5 (Si*C*H$_2$I), 10.7 (Si*C*H$_2$C), 22.4 (C(O)*C*H$_3$), 25.8 (CC*H*$_2$C), 171.9 (*C*(O)CH$_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 33.8.

4.12. Preparation of 1,1-bis(phthalimidomethyl)-1-silacyclopentane (**13a**)

Compound **1a** (3.00 g, 16.4 mmol) was added in a single portion to a stirred mixture of potassium phthalimide (6.07 g, 32.8 mmol), 18-crown-6 (335 mg, 1.27 mmol), and *N*,*N*-dimethylformamide (60 mL), and the resulting mixture was then stirred at 20 °C for 19 h. The solvent was removed by distillation (45 °C/10 mbar), diethyl ether (200 mL) and water (200 ml) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 × 100 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was crystallized from dichloromethane (40 mL; crystallization by slow evaporation of the solvent at 20 °C over a period of 2 days). The product was isolated by removal of the mother liquor via a syringe and then dried in vacuo (0.1 mbar, 20 °C, 2 h) to give **13a** in 77% yield as a colorless crystalline solid (5.14 g, 12.7 mmol). Mp.: 148–149 °C. Anal. Calc. ($C_{22}H_{20}N_2O_4Si$): C, 65.33; H, 4.98; N, 6.93; *M*, 404.50. Found: C, 65.0; H, 4.9; N, 7.0%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.71–0.76 (4 H, m, Si*CH*$_2$C), 1.53–1.57 (4 H, m, CC*H*$_2$C), 3.32 (4 H, s, Si*CH*$_2$N), 7.62–7.65 (4 H, m, *H*-5/*H*-6, Phth (= phthalimido)), 7.72–7.75 (4 H, m, *H*-4/*H*-7, Phth). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 11.2 (Si*C*H$_2$C), 26.7 (Si*C*H$_2$N), 26.8 (*C*CH$_2$C), 123.0 (*C*-4/*C*-7, Phth), 132.1 (*C*-3a/*C*-7a, Phth), 133.7 (*C*-5/*C*-6, Phth), 168.6 (*C*-1/*C*-3, Phth). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 19.0.

4.13. Preparation of 1-(acetoxymethyl)-1-(chloromethyl)-1-silacyclopentane (**14**)

Compound **1a** (3.00 g, 16.4 mmol) was added in a single portion to a stirred mixture of sodium acetate (1.34 g, 16.3 mmol), 18-crown-6 (62.0 mg, 235 μmol), and *N*,*N*-dimethylformamide (30 mL), and the resulting mixture was then stirred at 20 °C for 4 days. The solvent was removed by distillation (45 °C/10 mbar), diethyl ether (100 mL) and water (100 mL) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2 × 100 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (silica gel, 32–63 μm (ICN 02826); eluent, *n*-hexane/ethyl acetate (9:1 (v/v))). The relevant fractions (GC analysis) were combined, and the solvent was removed under reduced pressure to give **14** in 45% yield as a colorless liquid (1.51 g, 7.30 mmol). Anal. Calc. ($C_8H_{15}ClO_2Si$): C, 46.48; H, 7.31; *M*, 206.74. Found: C, 46.3; H, 7.4%. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.64–0.79 (4 H, m, Si*CH*$_2$C), 1.56–1.65 (4 H, m, CC*H*$_2$C), 2.01 (3 H, s, C(O)C*H*$_3$), 2.92 (2 H, s, Si*CH*$_2$Cl), 3.91 (2 H, s, Si*CH*$_2$O). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.7 (Si*C*H$_2$C), 20.6 (C(O)*C*H$_3$), 26.9 (*C*CH$_2$C), 27.1 (Si*C*H$_2$Cl), 54.4 (Si*C*H$_2$O), 171.7 (*C*(O)CH$_3$). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ 17.7.

4.14. Preparation of 1-(acetoxymethyl)-1-(iodomethyl)-1-silacyclopentane (**15**)

Compound **5a** (10.0 g, 27.3 mmol) was added in a single portion to a stirred mixture of sodium acetate (2.24g, 27.3 mmol), 18-crown-6 (96.0 mg, 363 μmol), and *N*,*N*-dimethylformamide (50 mL), and the resulting mixture was then stirred at 20 °C for 2 days. The solvent was removed by distillation (45 °C/10 mbar), diethyl ether (150 mL) and water (150 mL) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (2 × 150 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (silica gel, 32–63 μm (ICN 02826); eluent, *n*-hexane/ethyl acetate (9:1 (v/v))). The relevant fractions (GC analysis) were combined, and the solvent was removed under reduced pressure to give **15** in 36% yield as a colorless liquid (2.94 g, 9.86 mmol). Anal. Calc. ($C_8H_{15}IO_2Si$): C, 32.22; H, 5.07; *M*, 298.20. Found: C, 32.1; H, 5.0%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.69–0.74 (4 H, m, Si*CH*$_2$C), 1.55–1.71 (4 H, m, CC*H*$_2$C), 2.02 (3 H, s, C(O)C*H*$_3$), 2.10 (2 H, s, Si*CH*$_2$I), 3.92 (2 H, s, Si*CH*$_2$O). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ −18.9 (Si*C*H$_2$I), 10.4 (Si*C*H$_2$C), 20.7 (C(O)*C*H$_3$), 26.9 (*C*CH$_2$C), 55.4 (Si*C*H$_2$O), 171.6 (*C*(O)CH$_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 19.5.

4.15. Preparation of 1-(acetoxymethyl)-1-(phthalimidomethyl)-1-silacyclopentane (**16**)

Compound **14** (1.51 g, 7.30 mmol) was added in a single portion at 20 °C to a mixture of potassium phthalimide (1.36 g, 7.34 mmol), 18-crown-6 (35.0 mg, 132 μmol), and dimethylformamide (15 mL), and the resulting mixture was then stirred at 20 °C for 20 h. The solvent was removed by distillation (45 °C/10 mbar), water (100 mL) and diethylether (100 mL) were added to the residue, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 100 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give **16** in 79% yield as a colorless crystalline solid (1.83 g, 5.77 mmol). Anal. Calc. ($C_{16}H_{19}NO_4Si$): C, 60.54; H, 6.03; N, 4.41; *M*, 317.42. Found: C, 60.4; H, 5.9; N, 4.5%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.68–0.73 (4 H, m, Si*CH*$_2$C), 1.54–1.59 (4 H, m, CC*H*$_2$C), 1.93 (3 H, s, C(O)C*H*$_3$), 3.26 (2 H, s, Si*CH*$_2$N), 3.93 (2 H, s, Si*CH*$_2$O), 7.65–7.68 (2 H, m, *H*-5/*H*-6, Phth), 7.77–7.80 (2 H, m, *H*-4/*H*-7, Phth). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 10.1 (Si*C*H$_2$C), 20.5 (C(O)*C*H$_3$), 25.6 (Si*C*H$_2$N), 26.8 (*C*CH$_2$C), 55.8 (Si*C*H$_2$O), 123.0 (*C*-4/*C*-7, Phth), 132.1 (*C*-3a/*C*-7a, Phth), 133.8 (*C*-5/*C*-6, Phth), 168.6 (*C*-1/*C*-3, Phth), 171.7 (*C*(O)CH$_3$). ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 16.9.

4.16. Preparation of 1-(acetoxymethyl)-1-(azidomethyl)-1-silacyclopentane (**17**)

Compound **14** (4.29 g, 20.8 mmol) was added in a single portion at 20 °C to a stirred suspension of sodium azide (4.63 g, 71.2 mmol) and sodium carbonate (280 mg, 2.64 mmol) in acetone (25 mL), and the resulting mixture was then stirred at 20 °C for 10 days. The precipitate was removed by filtration, washed with acetone (20 ml), and discarded. The filtrate and the wash solution were combined, the solvent was removed under reduced pressure, and the residue

was purified by column chromatography on silica gel (silica gel, 32–63 μm (ICN 02826); eluent, *n*-hexane/ethyl acetate (9:1 (v/v))). The relevant fractions (GC analysis) were combined, and the solvent was removed under reduced pressure to give **17** in 81% yield as a yellowish liquid (3.61 g, 16.9 mmol). Anal. Calc. ($C_8H_{15}N_3O_2Si$): C, 45.05; H, 7.09; N, 19.70; *M*, 213.31. Found: C, 45.2; H, 7.0; N, 19.5%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.67–0.73 (4 H, m, SiCH_2C), 1.58–1.63 (4 H, m, CCH_2C), 2.03 (3 H, s, C(O)CH_3), 2.97 (2 H, s, SiCH_2N), 3.87 (2 H, s, SiCH_2O). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 8.9 (SiCH_2C), 20.6 (C(O)CH_3), 26.8 (CCH_2C), 38.4 (SiCH_2N), 54.6 (SiCH_2O), 171.7 (*C*(O)CH_3). ^{15}N NMR (30.4 MHz, $CDCl_3$): δ −319.7 (CH_2*N*NN; lower intensity), −129.8 (CH_2N*N*N; higher intensity), CH_2NN*N* not detected. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ 16.9.

*4.17. Preparation of 1-(aminomethyl)-1-(chloromethyl)-1-silacyclopentane hydrochloride (**18**·HCl)*

Compound **17** (1.79 g, 8.39 mmol) was added at 20 °C in a single portion to a solution of triphenylphosphine (2.43 g, 9.26 mmol) in toluene (17 mL), and the resulting mixture was then stirred at 20 °C for 23 h. The solvent was removed under reduced pressure, 6 M hydrochloric acid (32 mL) was added to the residue, and the mixture was then heated under reflux for 2 h, cooled to 20 °C, and extracted with dichloromethane (3 × 30 mL). The aqueous phase was concentrated under reduced pressure to a volume of ca. 20 mL and was then stored at −20 °C for 24 h. The resulting precipitate was isolated by filtration and dried in vacuo (0.4 mbar, 20 °C, 2 h) to give **18**·HCl in 40% yield as a colorless crystalline solid (672 mg, 3.36 mmol). Mp.: 223–223 °C (dec.). Anal. Calc. ($C_6H_{15}Cl_2NSi$): C, 36.00; H, 7.55; N, 7.00; *M*, 200.18. Found: C, 36.0; H, 7.5; N, 7.0%. ^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ 0.65–0.89 (4 H, m, SiCH_2C), 1.54–1.63 (4 H, m, CCH_2C), 2.40 (2 H, q, $^3J_{HH}$ = 6.1 Hz, SiCH_2N), 3.24 (2 H, s, SiCH_2Cl), 8.14 (3 H, br. s, NH_3). ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ 8.5 (SiCH_2C), 23.8 (SiCH_2N), 26.4 (CCH_2C), 27.8 (SiCH_2Cl). ^{15}N NMR (30.4 MHz, [D$_6$]DMSO): δ −354.7. ^{29}Si NMR (99.4 MHz, [D$_6$]DMSO): δ 19.5.

4.18. Crystal structure analyses

Suitable single crystals of **6a**·*p*-TosOH, **13a**, and **18**·HCl were obtained directly from the preparation of the respective compounds (see 4.1; Syntheses). The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)). The structures were solved by direct methods (SHELXS-97).[12] All non-hydrogen atoms were refined anisotropically (SHELXL-97).[12] A riding model was employed in the refinement of the Hydrogen atoms.

Appendix. Supplementary data

Supporting information available: Crystallographic data for **6a**·*p*-TosOH, **13a**, and **18**·HCl.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.024

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