# Silaheterocycles, 35[+]

# Carbon=Carbon Hydrogenation of Silicon-Functionalized Silaheterocycles

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*Dedicated to Prof. Dr. Drs. h.c. Hans Bock on the occasion of his 70th birthday*

**Keywords:** Silanorbornenes / Silanorbornanes / Silicon-functionalized olefins / Silacyclobutanes / Hydrogenations / Heterocycles

Catalytic hydrogenation of olefins containing functionalized silicon groups affords the saturated products in good yields. Chloro and alkoxy substituents at the silicon atom remain unaffected and, in the case of heterocyclic compounds, the cyclic or bicyclic moieties remain intact. The 2-silanorbornanes **4**, **5**, and **6** were synthesized from the corresponding 2-silanorbornenes **1**, **2**, and **3**, and organosilanes **13** and **14** possessing the cyclopentyl group, were prepared from the cyclopentenyl-substituted precursors **10** and **12**. The 3-vinyl-substituted silacyclobutanes **15**, **17**, and **18** were also hydrogenated in a simple apparatus with diethyl ether or THF as solvent, and Pd/C as a recoverable catalyst system. A basic organosilicon compound, trichloro(vinyl)silane, is hydrogenated in a nearly quantitative yield to form the saturated trichloro(ethyl)silane; this emphasizes the general applicability of this method.

## Introduction

Vinylsilanes are of great importance in organosilicon chemistry both for academic research and industrial applications.[2] This class of compounds[3] is available by large-scale processes (such as the cleveage of disilanes by vinylic chlorides,[4] the hydrosilylation of conjugated dienes or acetylenic derivatives,[5] and the thermal condensation of chlorohydridosilanes with vinylic chlorides[6]) and it′s members are commonly used as starting materials for the production of silicon-based polymers, the hydrosilylation reaction being widely used to crosslink silicon and carbon moieties.[2] Particularly in polymerization reactions, the defunctionalization of vinyl groups, directly attached to silicon centers or bound to carbon atoms in the polymeric backbone, is of importance in controlling the molecular mass or in preventing polymerization taking place. In this respect the hydrogenation of the vinylic unit could be a valuable method, but the reaction has to be very selective, forming the corresponding saturated derivatives in high yield, even in the presence of other functional groups, such as chlorine or alkoxy, at the silicon atom. In general, the direct synthesis of chloro(ethyl)silanes results in a complex mixture of differently substituted products with low yields.[7] Using catalysts for the hydrogenation of vinylsilanes the application is restricted to nonhalogenated derivatives, since the catalyst (e.g. Adam′s platinum or Raney′s nickel[8]) can affect the chlorine function or can be deactivated. Only Dunogues has reported on an efficient method using nickel chloride/triethylsilane as a catalyst,[9] but this method does not seem very practical for large-scale syntheses.[10] This paper reports on a synthetic route to transform unsaturated carbon−carbon moieties of organosilicon compounds into their corresponding saturated derivatives by use of Pd/C as a catalyst for a heterogeneous catalytic hydrogenation. This combination is well known to be cheap, easily available, and most effective in organic chemistry.[11] For these very basic studies we synthesized a series of silyl-functionalized silaheterocycles as model compounds containing both endo- or exocyclic vinyl subunits.[12] Carrying out the hydrogenation reactions, the chloro and alkoxy functionalities at the silicon atom and the cyclic carbon skeletons are preserved.

## Results and Discussion

The hydrogenation of carbon−carbon doubly bonded moieties is technologically a very important reaction[13] and requires the activation of molecular hydrogen and/or the unsaturated substrates by catalysts.[14] Heterogeneous hydrogenation uses Ni, Pd, Pt, and Rh metals supported on activated carbon, silica, aluminium oxides, and barium sulfate as catalysts.[15]

For the hydrogenation of a series of silaheterocycles Pd/C was used as a catalyst at room temperature in ether or THF as solvent. Starting from the 2-silanorbornenes **1**, and **2** (which were synthesized by the reaction of chlorodimethyl-(vinyl)silane,[16] trichloro(vinyl)silane,[17] and *tert*-butyllithium in the presence of cyclopentadiene) and from **3**, which

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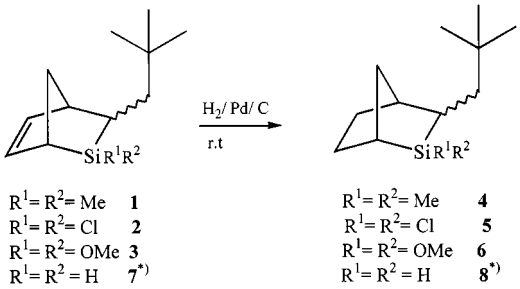
is easily available from **2** by a substitution reaction,[18] the corresponding 2-silanorbornanes are accessible in a yield of about 90% (after distillation) (see Scheme 1). The products were fully characterized by NMR and MS methods. In order to facilitate the NMR-spectroscopic assignments a semipreparative gas-chromatographic separation of the *exo*/*endo* diastereoisomers **4** was carried out (see Experimental Section).




$R^1 = R^2 = Me$ **1**
$R^1 = R^2 = Cl$ **2**
$R^1 = R^2 = OMe$ **3**
$R^1 = R^2 = H$ **7***)

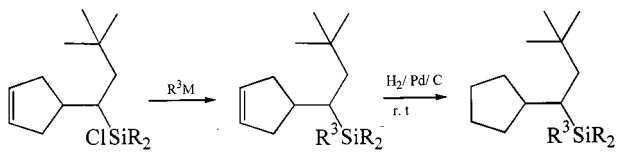
$R^1 = R^2 = Me$ **4**
$R^1 = R^2 = Cl$ **5**
$R^1 = R^2 = OMe$ **6**
$R^1 = R^2 = H$ **8***)

Scheme 1. Synthesis of silanorbornanes from silanorbornenes; *) formation of polymeric products from hydrosilylation

Surprisingly, hydrogenation of the *Si*-dihydro-substituted silanorbornene (**7**), which is available from **2** and $LiAlH_4$,[17] failed. Instead hydrosilylation took place, giving polymeric products, which have not been characterized in detail. Alternatively, the parent dihydro-substituted silanorbornane **8** can be synthesized from **5** by the use of $LiAlH_4$ as a reducing agent.

The hydrogenation reactions described in Scheme 1 provide another route for the synthesis of 2-silanorbornane skeletons: These bicyclic compounds are also available from both, the intramolecular hydrosilylation reaction of cyclopentenyl-substituted silanes $C_5H_7CH(HSiR_2)CH_2tBu$[18] and the reaction of the latter with catalytic amounts of trityl tetrakis(pentafluorophenyl)borate via the intermediacy of a silanorbornyl cation.[19][20] Furthermore, a carbon-functionalized 2-silanorbornane is easily available from silanorbornene **2** by the addition of hydrogen chloride to the carbon−carbon double bond.[18]

In contrast to compound **2**, the 2-silanorbornenes **1** and **3** do not add hydrogen chloride, but an allylic cleavage gives the cyclopentenyl-substituted chloro(organo)silanes **9**, and **11**.[18] The organo-substituted derivatives **10** and **12** were synthesized by the reactions of the chlorosilane precursors **9** and **11**, respectively, with fluorenyllithium and a 1-naphthyl Grignard reagent (see Scheme 2). After recrystallisation of **10** from ether/pentane (1:5), suitable single crystals were obtained for X-ray crystal analysis.



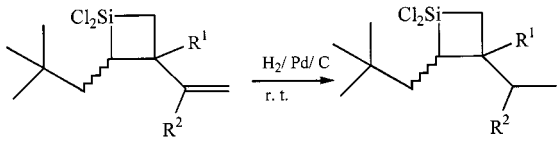

R= Me **9**
R= OMe **11**

R= Me, $R^3$= fluorenyl **10, 13**
R= OMe, $R^3$= 1- naphthyl **12, 14**

Scheme 2. Synthesis of cyclopentane-substituted organosilanes

Notably, the hydrogenation of the cyclopentenyl derivatives **10** and **12** gives the corresponding cyclopentane-substituted compounds **13** and **14** in high yields (**13**: 88%; **14**: 82%).

In order to prove the utility of the hydrogenation reaction for exocyclic vinyl groups, 1,1-dichloro-3-vinyl-1-silacyclobutanes **15**, **17**, and **18** were chosen as model compounds. These compounds are easily prepared by the reaction of trichloro(vinyl)silane, Li*t*Bu, and isoprene (**17**, **18** isomeric mixture) or 2,3-dimethylbutadiene (**15**).[21] The corresponding 3-ethyl-substituted derivatives **16**, and an isomeric product mixture of **19** and **20** were exclusively obtained from the catalyst-supported reaction at room temperature and were isolated in high yields (ca 75%) after distillation. The four-membered ring moieties remain stable and the same is true for the dichlorosilyl functionality (see Scheme 3).




$R^1 = R^2 = Me$ **15**
$R^1 = Me, R^2 = H$ **17**
$R^1 = H, R^2 = Me$ **18**

$R^1 = R^2 = Me$ **16**
$R^1 = Me, R^2 = H$ **19**
$R^1 = H, R^2 = Me$ **20**

Scheme 3. Synthesis of 3-ethyl-substituted silacyclobutanes from vinyl-substituted precursors

## Molecular Structure of 10

The crude slightly yellow crystalline organosilane **10** was recrystallized from an *n*-pentane/ether (5:1) mixture; a single crystal was used for X-ray diffraction analysis. In the solid state **10** forms a 1:1 inclusion compound with acetaldehyde, which was obviously introduced by an impurity within the solvents used for recrystallization (see Figure 2). No exceptionally short intermolecular distances indicating the presence of strong intermolecular interactions between silane **10** and the solvent molecule are observed. The packing of the silane and the disordered solvent molecules in the crystal structure is as close as possible and no further potentially solvent accessible cavities are left. The silicon atom is tetrahedrally surrounded by four carbon atoms of two methyl groups, the 5-fluorenyl, and the (3-cyclopentenyl)-3,3-dimethylbutyl substituent. Although sterically demanding ligands are present in the molecule, the bond angle C14−Si−C15 (113.26°) beween the methyl groups is the largest one at the silicon center. The mean distance $Si-C_{Me}$ is slightly shorter (187 pm) than the $Si-C_{fluorenyl}$ and the $Si-C_{butyl}$ bond length (191 pm) (see Figure 1). The fluorenyl ligand is mutually planar within the accuracy achieved and the observed range for the C−C bond lengths is characteristic for aromatic hydrocarbons in the solid state. The cyclopentenyl substituent adopts an envelope conformation with a carbon−carbon bond length of 130.4 pm. Due to the packing in the crystal structure the orientation of the *tert*-butyl group is ideally staggered with respect to

the C22−C23 bond (torsion angles: 61.8°, 63.3°, and 179.8°).

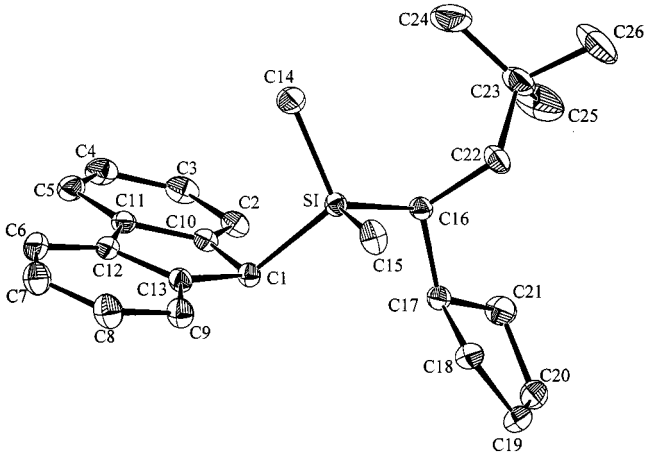



Figure 1. DIAMOND[22] drawing (30% envelopes) of 3-(3-cyclopentenyl)-2-fluorenyl-2,5,5-trimethyl-2-silahexane (**10**): Si−C1 191.41(14) pm, Si−C14 186.74(16), Si−C15 187.82(19), Si−C16 190.25(14); C14−Si−C15 106.85(9)°, C14−Si−C16 113.28(7), C15−Si−C16 111.16(7), C14−Si−C1 107.05(7), C15−Si−C1 109.78(7), C16−Si−C1 108.60(6)

## Conclusion

The Pd/C-catalyzed hydrogenation of endo- and exocyclic carbon−carbon doubly bonded moieties occurs under mild conditions, e.g. one atmosphere of hydrogen pressure and at room temperature, in nearly quantitative yields. Functional groups at the silicon atom, e.g. chlorine, alkoxy, or aryl substituents are preserved, as well as the mono- or bicyclic carbosilane skeletons. No side products can be detected, the yields for the hydrogenated compounds given in Table 1 in the Experimental Section are those after distillation.

To prove the whole range of applicability and to show the limitations of the discussed synthetic method, an industrially (economically) important chloro(vinyl)silane was used as a starting compound for hydrogenation: Within 24 h trichloro(vinyl)silane was completely converted into the corresponding ethylsilane, $Cl_3SiCH_2CH_3$. From this finding we conclude that the reaction may be widely used for the synthesis of chloro(ethyl)silanes from their vinyl-substituted precursors. However, the method does not work when the C=C bond is strongly shielded by sterically demanding substituents. Thus, treating 1,1-dichloro-2,3-diphenyl-4-neopentyl-1-silacyclobutene,[23] under comparable conditions, no hydrogenation occurs to form a silacyclobutane; the silacyclobutene is completely recovered from the reaction mixture. Further studies to expand this method using different vinylsilanes and a variety of functional groups at the silicon atom are currently being carried out in our laboratories.

## Experimental Section

**General Remarks:** All manipulations were performed under purified argon using standard Schlenk techniques. Solvents were dried by refluxing under nitrogen with the appropriate drying agent and were distilled prior before use. $CDCl_3$ was dried with molecular sieves, while [$D_6$]benzene was dried with potassium/sodium and distilled prior to NMR sample preparation. − NMR spectra: Bruker AM 300 ($^{29}$Si), DPX 300 ($^1$H, $^{13}$C) and AMX 600 ($^1$H, $^{13}$C), $^1$H- and $^{13}$C-NMR chemical shifts (δ) were internally referenced [δ(C*H*$Cl_3$) = 7.24, δ(*C*$DCl_3$) = 77.00, δ($C_6D_5$*H*) = 7.15, δ($C_6D_6$) = 128.00], $^{29}$Si-NMR shifts were externally referenced to TMS. − GC/MS: Chrompack CP 9000 (capillary column CP-SIL/5CB-MS, diameter 0.25 mm, 12.5 m length) coupled with a Finnigan MAT Ion Trap Detector 800 (electron impact, space current 3000 μA, ionisation energy 70 eV, ion-source temperature 250°C), for chemical ionisation methanol was used. − Elemental analyses: Microanalytical Laboratory of the Department of Chemistry, Humboldt-University, Berlin. Trichloro(vinyl)- and chlorodimethyl(vinyl)-silane were distilled from sodium carbonate prior before use. *tert*-Butyllithium was used as a 1.7 M solution in pentane. All other chemicals were used as purchased by Aldrich and Fluka.

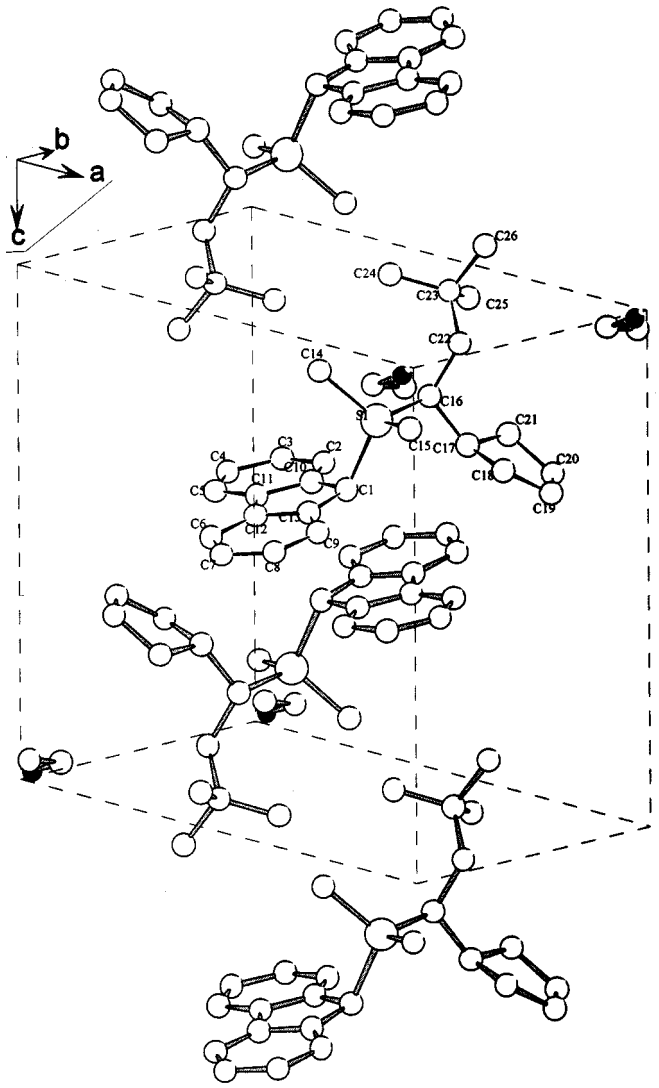



Figure 2. DIAMOND[22] representation of the crystal structure viewed along [100] showing the inclusion of acetaldehyde molecules

**Hydrogenation Apparatus:** A suitable reaction flask was connected to a set of two dropping funnels by a small glass tube. The two dropping funnels themselves were connected with a flexible tube

Table 1. Preparative details of the hydrogenation reactions

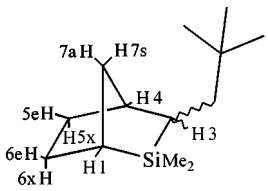
| Starting compound | Amount [g; mmol] | Pd/C [mol-%] | Solvent; amount [mL] | Product | Reaction time [h] | Yield [g;%] | Boiling point [°C/$10^{-2}$ mbar] |
|---|---|---|---|---|---|---|---|
| **1** | 1.4; 6.72 | 3.50 | THF; 20 | **4** | 16 | 1.3; 92 | 62 |
| **2** | 3.6; 14.52 | 1.62 | ether; 30 | **5** | 24 | 3.0; 82 | 58 |
| **3** | 5.2; 21.67 | 1.08 | ether; 50 | **6** | 16 | 4.1; 79 | 55 |
| **10** | 2.3; 6.23 | 3.77 | ether; 30 | **13** | 16 | 2.0; 88 | oil[a] |
| **12** | 1.9; 5.41 | 4.34 | THF; 30 | **14** | 16 | 1.7; 82 | oil[a] |
| **15** | 4.3; 16.21 | 1.45 | ether; 30 | **16** | 48 | 3.2; 73 | 73 |
| **17** + **18** | 10.2; 40.80 | 0.58 | THF; 50 | **19** + **20** | 24 | 7.7; 75 | 98 |

[a] A highly viscous residue, b.p. not determined.

and filled with silicone oil as sealing fluid. Then the oil in the first dropping funnel was displaced by hydrogen. The volume was marked before the tap of the reaction flask was opened. During the hydrogenation reaction the amount of hydrogen consumed was monitored as change in volume. For a sketch of the hydrogenation apparatus described see ref.[24]

**General Reaction Procedure:** The carbon−carbon unsaturated silaheterocycles or the vinylsilanes were placed in the reaction flask of the hydrogenation apparatus described and dissolved in THF or diethyl ether. 250 mg of Pd/C (10% on activated carbon) were added. Then the reaction mixture was stirred and allowed to react with hydrogen for 16 h. The volume of gas consumed indicated the end of the reaction. The catalyst Pd/C was filtered off, the solvent removed under reduced pressure, and the products distilled for purification at $10^{-2}$ mbar (Table 1).

For a semipreparative gas-chromatographic separation of the *exo*-/*endo*-3-neopentyl diastereomers **4** a packed column (10% OV 101 on 80−100 mesh Chromosorb W, HO, DMCS) was used in a Chromatron gas chromatograph. The column temperature was 110°C (isotherm) and the flow rate was set to 3.6 L $H_2$/h. A heat conductivity cell (Chromatron) was used for detection. The purity of the separation had been checked with a capillary gas chromatogaph and was detected to be 98.5% (2,2-dimethyl-*exo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane) and 98.7% (2,2-dimethyl-*endo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane). For the assignment of the NMR-chemical shifts of the silanorbornanes **4**−**6** and **8** the atoms are numbered as shown by the formula in Scheme 4.




Scheme 4. Numbering scheme for **4**−**6** and **8**

**2,2-Dimethyl-*exo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*exo*-4):** $^1$H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, $SiCH_{3\ endo}$), 0.13 (s, 3 H, $SiCH_{3\ exo}$), 0.45 (m, 1 H, 3-H), 0.95 [s, 9 H, $C(CH_3)_3$], 1.21 (dddd, $^2J_{5x/5e}$ = 12.2 Hz, $^3J_{5x/6e}$ = 6.0 Hz, $^3J_{5x/6x}$ = 8.3 Hz, $^4J_{5x/7s}$ = 1.8 Hz, 1 H, 5x-H), 1.25 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 4.6 Hz, 1 H, $CH_aH_bt$Bu), 1.26 (m, 1 H, 1-H), 1.47 (dddd, $^2J_{7a/7s}$ = 10.8 Hz, $^3J_{7a/1}$ = 2.8 Hz, $^3J_{7a/4}$ = 2.8 Hz, $^4J_{7a/3}$ = 2.9 Hz, 1 H, 7a-H), 1.50 (dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, $CH_aH_bt$Bu), 1.60 (d, br., $^2J_{HH}$ = 10.8 Hz, 1 H, 7s-H), 1.63 (m, 1 H, 6x-H), 1.68 (dddd, $^2J_{6e/6x}$ = 12.0 Hz, $^3J_{6e/1}$ = 5.9 Hz, $^3J_{6e/5e}$ = 12.0 Hz, $^3J_{6e/5x}$ = 6.0 Hz, 1 H, 6e-H), 1.78 (dddd, $^2J_{5e/5x}$ = 12.2 Hz, $^3J_{5e/6e}$ = 12.0 Hz, $^3J_{5e/6x}$/$^3J_{5e/4}$ = 6.0, 4.0 Hz, 1 H, 5e-H), 2.15 (s, br., 1 H, 4-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 47.11 (C-4), 46.28 (C-8), 36.36 (C-7), 31.51 (C-9), 31.53 (C-5), 23.85 (C-6), 29.76 (C-10), 29.35 (C-1), 24.23 C-3), −4.21 [$SiCH_3$ (*exo*)], −4.35 [$SiCH_3$ (*endo*)]. − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 10.20. − MS (70 eV); *m*/*z* (%): 210 (0) [$M^+$], 153 (74.73) [$M^+ - t$Bu], 125 (98.91), 59 (100), 57 (33.15) [$t$Bu$^+$].

**2,2-Dimethyl-*endo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*endo*-4):** $^1$H NMR (600 MHz, $CDCl_3$): δ = 0.06 (s, 3 H, $SiCH_{3\ endo}$), 0.10 (s, 3 H, $SiCH_{3\ exo}$), 0.84 (m, 1 H, 3-H), 0.95 [s, 9 H, $C(CH_3)_3$], 1.29 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.0 Hz, 1 H, $CH_aH_bt$Bu), 1.29 (m, 1 H, 1-H), 1.42 (m, 2 H, 5e-H and 5x-H), 1.45 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 8.5 Hz, 1 H, $CH_aH_bt$Bu), 1.48 (d, br., $^2J_{7s/7a}$ = 10.8 Hz, 1 H, 7s-H), 1.57 (m, 1 H, 6x-H), 1.58 (m, 1 H, 7a-H), 1.68 (dddd, $^2J_{6e/6x}$ = 12.1 Hz, $^3J_{6e/1}$ = 5.9 Hz, $^3J_{6e/5e}$ = 12.0 Hz, $^3J_{6e/5x}$ = 6.0 Hz, 1 H, 6e-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 44.81 (C-4), 42.05 (C-8), 38.65 (C-7), 31.22 (C-9), 29.90 (C-10), 27.07 (C-3), 25.57 (C-1), 24.66, 23.94 (C-5/C-6), −1.82 [$SiCH_3$ (*exo*)], −6.25 [$SiCH_3$ (*endo*)]. − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 17.47. − MS (70 eV); *m*/*z* (%): 210 (0) [$M^+$], 153 (73.73) [$M^+ - t$Bu], 125 (95.47), 59 (100), 57 (31.73) [$t$Bu$^+$].

***exolendo*-4:** $C_{13}H_{26}Si$ (210.18): calcd. C 74.22, H 12.47; found C 73.99, H 12.41.

**2,2-Dichloro-*exo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*exo*-5):** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.86 (m, 1 H, 3-H), 0.92 (s, 9 H, $CH_2tBu$), 1.17 (dd, 1 H, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.8 Hz, $CH_aH_bt$Bu), 1.29 (m, 1 H, 5x-H), 1.52 (m, 1 H, 7s-H), 1.69 (m, 1 H, 1-H), 1.69−1.81 (m, 2 H, 6x-H, 6e-H), 1.72 (m, 1 H, 7a-H), 1.73 (dd, 1 H, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 7.9 Hz, $CH_aH_bt$Bu), 1.80 (m, 1 H, 5e-H), 2.21 (s, br., 1 H, 4-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 46.15 (C-4), 44.52 (C-8), 34.85 (C-3), 34.11 (C-7), 30.93 (C-9), 30.30 (C-5), 21.97 (C-6), 29.28 (C-10), 28.53 (C-1), 21.97 (C-6). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 40.60. − MS (70 eV); *m*/*z* (%): 240 (0) [$M^+$], 193 (30.33), 195 (19.78), 197 (3.96) [$M^+ - t$Bu] ($SiCl_2$ isotopic pattern), 67 (38.46) [$C_5H_7^+$], 57 (100) [$t$Bu$^+$].

**2,2-Dichloro-*endo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*endo*-5):** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.91 (s, 9 H, $CH_2tBu$), 1.20 (dd, 1 H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 6.8 Hz, $CH_aH_bt$Bu), 1.30 (m, 1 H, 3-H), 1.47 (m, 1 H), 1.62 (dd, 1 H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 8.4 Hz, $CH_aH_bt$Bu), 1.68−1.81 (m, 3 H), 1.71−1.74 (m, 2 H, 7s-H, 7a-H), 1.74 (m, 1 H, 1-H), 2.44 (s, br., 1 H, 4-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 43.57 (C-4), 40.43 (C-8), 36.35 (C-7), 32.79 (C-3), 30.66 (C-9), 23.23, 22.72 (C-5/C-6), 29.94 (C-1), 29.28 (C-10). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 37.57. − MS (70 eV); *m*/*z* (%): 240 (0) [$M^+$], 193 (37.14), 195 (28.12), 197 (3.98) [$M^+ - t$Bu] ($SiCl_2$ isotopic pattern), 67 (50.66) [$C_5H_7^+$], 57 (100) [$t$Bu$^+$].

***exolendo*-5:** $C_{11}H_{20}Cl_2Si$ (250.07): calcd. C 52.58, H 8.02, Cl 28.22; found C 51.61, H 8.08, Cl 28.94.

**2,2-Dimethoxy-*exo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*exo*-6):** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.39 (m, 1 H, 3-H), 0.78 (s, 9 H, $CH_2tBu$), 1.01 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.5 Hz, 1 H, $CH_aH_btBu$), 1.21 (m, 1 H, 5x-H), 1.25 (m, 1 H, 1-H), 1.30 (m, 1 H, 7-H), 1.31−1.67 (m, 2 H, 6x-H, 6e-H), 1.54 (m, 1 H, 7-H), 1.56 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.9 Hz, 1 H, $CH_aH_btBu$), 1.65 (m, 1 H, 5e-H), 2.01 (s, br., 1 H, 4-H), 3.43 (s, 3 H, $SiOCH_3$), 3.44 (s, 3 H, $SiOCH_3$). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 51.27 ($SiOCH_3$), 50.77 ($SiOCH_3$), 45.41 (C-4), 43.60 (C-8), 34.80 (C-7), 31.23 (C-9), 30.53 (C-5), 29.33 (C-10), 27.99 (C-3), 21.83 (C-6), 19.14 (C-1). − $^{29}$Si NMR (59.45 MHz, $CDCl_3$): δ = 4.55. − MS (70 eV); *m/z* (%): 242 (7.60) [$M^+$], 210 (13.90) [$M^+ - CH_3OH$], 185 (68.40) [$M^+ - t$Bu], 157 (100), 91 (40.30), 57 (16.55) [$t$Bu$^+$].

**2,2-Dimethoxy-*endo*-3-neopentyl-2-silabicyclo[2.2.1]silaheptane (*endo*-6):** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 9 H, $CH_2tBu$), 0.89 (m, 1 H, 3-H), 1.11 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, $CH_aH_btBu$), 1.31−1.67 (m, 5 H, 5x-H, 5e-H, 6x-H, 6e-H, 1-H), 1.41 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 7.5 Hz, 1 H, $CH_aH_btBu$), 1.46 (m, 2 H, 7a-H, 7s-H) 2.27 (s, br., 1 H, 4-H), 3.43 (s, 3 H, $SiOCH_3$), 3.44 (s, 3 H, $SiOCH_3$). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 50.98 ($SiOCH_3$), 50.67 ($SiOCH_3$), 42.43 (C-4), 40.13 (C-8), 37.24 (C-7), 31.00 (C-9), 29.46 (C-10), 26.09 (C-1), 22.61, 23.49 (C-5/C-6). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 0.34. − MS (70 eV); *m/z* (%): 242 (5.84) [$M^+$], 210 (15.00) [$M^+ - OCH_3$], 185 (84.52) [$M^+ - t$Bu], 157 (100), 91 (54.32), 57 (19.09) [$t$Bu$^+$].

***exolendo*-6:** $C_{13}H_{26}SiO_2$ (242.45): calcd. C 64.41, H 10.81; found C 64.28, H 10.91.

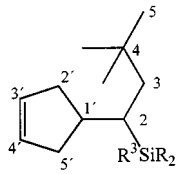
**Synthesis of *exolendo*-3-Neopentyl-2-silabicyclo[2.2.1]silaheptane (*exolendo*-8):** 1.61 g (42.34 mmol) of $LiAlH_4$ and 80 mL of diethyl ether were placed in a flask. The suspension was cooled to 0°C and 5.32 g (21.17 mmol) of **5** added dropwise. The reaction mixture was heated under reflux for 5 h. The solvent was removed by evaporation in vacuo. The product was then extracted with 60 mL of *n*-pentane, excess lithium alanate filtered off, and washed with pentane (2 × 10−15 mL). After removing the solvent, the mixture was distilled at $10^{-2}$ mbar to give 3.40 g of **8** (88%). The product is a colourless, viscous liquid; b.p. 67°C/$10^{-2}$ mbar.

***exo*-8:** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.77 (m, 1 H, 3-H), 0.90 (s, 9 H, $CH_2tBu$), 1.15 (m, 1 H, 5x-H), 1.57 (m, 1 H, 1-H), 1.41 (m, 1 H, 7a-H), 1.41 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 3.7 Hz, 1 H, $CH_aH_btBu$), 1.45 (m, 1 H, 6x-H), 1.46 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 5.5 Hz, 1 H, $CH_aH_btBu$), 1.49 (m, 1 H, 7s-H), 1.64 (m, 1 H, 6e-H), 1.65 (m, 1 H, 5e-H), 2.16 (s, br., 4-H), 3.36 [dm, $^2J_{HH}$ = 11.9 Hz, 1 H, SiH (*exo*)], 3.78 [dm, $^2J_{HH}$ = 11.9 Hz, 1 H, SiH (*endo*)]. − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 49.02 (C-8), 45.44 (C-4), 35.88 (C-7), 31.87 (C-9), 31.11 (C-5), 29.77 (C-10), 24.74 (C-6), 24.32 (C-1), 20.98 (C-3). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = −10.23 ($^1J_{SiH}$ = 203 Hz). − MS (70 eV); *m/z* (%): 181 (3.16) [$M^+$ − H], 125 (38.14) [$M^+ - t$Bu], 97 (100), 57 (23.00) [$t$Bu$^+$].

***endo*-8:** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.90 (s, 9 H, $CH_2tBu$), 1.16 (m, 1 H, 3-H), 1.36 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.2 Hz, 1 H, $CH_aH_btBu$), 1.37 (m, 1 H, 7-H), 1.40 (m, 1 H, 5x-H), 1.47 (m, 1 H, 6x-H), 1.48 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, $CH_aH_btBu$), 1.52 (m, 1 H, 5e-H), 1.53 (m, 1 H, 1-H), 1.73 (m, 1 H, 6e-H), 2.36 (s, br., 4-H), 3.36 (dm, $^2J_{HH}$ = 11.9 Hz, 1 H, SiH), 3.88 (dm, $^2J_{HH}$ = 11.9 Hz, SiH). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 44.20 (C-8), 43.44 (C-4), 39.19 (C-7), 31.32 (C-9), 29.77 (C-10), 26.51 (C-6), 23.91 (C-5), 22.75 (C-3), 22.01 (C-1). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = −16.03 ($^1J_{SiH}$ = 206 Hz). − MS (70 eV); *m/z* (%): 181 (3.21) [$M^+$ − H], 125 (40.00) [$M^+ - t$Bu], 97 (100), 67 (17.01) [$C_5H_7$+], 57 (26.26) [$t$Bu$^+$].

***exolendo*-8:** $C_{11}H_{22}Si$ (182.15): calcd. C 72.44, H 12.16; found C 72.55, H 12.65.

**Synthesis of 3-(3-Cyclopentenyl)-2-fluorenyl-2,5,5-trimethyl-2-silahexane (10):** Fluorenyllithium was synthesized by the dropwise addition of 7.8 mL *n*BuLi (1.7 M in hexane) to a solution of 2.12 g (12.77 mmol) of fluorene in 40 mL of *n*-pentane and 10 mL of diethyl ether at 0°C. The yellow precipitate was stirred vigorously for 1 h and then 2.12 g (12.77 mmol) of **9** was added slowly. After stirring for 1 h, the solution was filtered off from LiCl. The solvent was removed in vacuo and **10** was isolated as a crude (slightly yellow) crystalline solid. After recrystallisation from pentane/ether (5:1), a white solid was obtained [yield: 3.01 g (63%)]; m.p. 57°C. For the assignment of the NMR chemical shifts in **10** the atoms are numbered as expressed by the formula in Scheme 5. − $^1$H NMR ($CDCl_3$): δ = −0.12 (s, 3 H, $SiCH_3$); 0.07 (s, 3 H, $SiCH_3$); 0.96 (s, 9 H, $CH_2tBu$), 1.21−1.52 (m, 3 H, $CH_2t$Bu and C*H*−Si), 2.24−2.38 [m, 2 H, $CH_2$ (cyclopentenyl)], 2.42−2.58 [m, 2 H, $CH_2$ (cyclopentenyl)], 2.77 [m, 1 H, CH (cyclopentenyl)], 4.11 [s, br., 1 H, aliphatic CH group (fluorenyl)], 5.82 (s, br., 2 H, 2 CH olefin.), 7.43−7.46 (m, 4 H, 4 aromatic CH groups), 7.68 ( m, 2 H, aromat.), 7.96 (m, 2 H, aromat.). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 130.78 (C-3′), 130.78 (C-4′), 41.90 (C-1′), 41.25 (C-4), 40.71 [C-7′′ (fluorenyl)], 38.29, 38.21 (C-2′/C-5′), 31.67 (C-5), 30.53 (C-6), 23.11 (C-3), −3.01, 3.01 (C-1/$SiCH_3$). − **10** has 12 diastereotopic aromatic carbon atoms, their $^{13}$C-chemical shifts are: δ = 146.26, 146.01, 140.84, 140.79 (4 $C_q$, fluorenyl), 126.06 (CH intensity 2), 125.40 (CH intensity 2), 120.06 (CH intensity 2), 124.33, 124.26 (in total 8 aromatic CH groups). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 8.27. − MS(CI); *m/z* (%): 375 (0) [(M + 1)$^+$], 358 (31.00) [$M^+ - CH_4$], 209 (100) [$M^+ - C_{13}H_9$ (fluorenyl)], 165 (22.54) [$C_{13}H_9^+$ (fluorenyl)], 194 (8.19) [$M^+ - CH_3 - C_{13}H_9$], 223 (27.26) [$SiMe_2$fluorenyl$^+$]. − $C_{26}H_{34}Si$ (374.644): calcd. C 83.36, H 9.15; found C 80.94, H 10.25.




Scheme 5. Numbering scheme of **10** and **12**

**X-ray Structure Determination of 10:** The single crystal was mounted on the glass fibre tip, glued with silicone grease (Wacker AG, FRG), and transfered to the goniometer. The crystal was cooled to 180 K (Oxford Cryo Stream, UK) for all subsequent manipulations. The data collection was performed by means of a four-circle diffractometer (Stoe Stadi4, Darmstadt, FRG) equipped with a fine focus sealed X-ray tube (Mo-$K_\alpha$ radiation, 50 kV, 35 mA), a graphite monochromator and an eulerian cradle. The initial lattice constants were determined by indexing 16 accurately centered, independant reflections (15° < 2Θ < 25°). The initial orientation matrix was refined by centering 32 strong reflections measured at large angles in 2Θ (35° < 2Θ < 45°). To obtain accurately scaled raw intensities, the intensity data collection (3° < 2Θ < 60°) was monitored by the repeated (every 12 h) measurement of three medium strong control reflections taken from the strong reflection set found. 7403 reflections were collected and corrected for Lorentz and polarisation effects. To refine the lattice constants 13 large angle reflections (45° < 2Θ < 49°) were recentered to estimate the final lattice constants. The atom form factors[25] were implemented in the used program system. The crystal structure was solved by Direct Methods (SHELXS86).[26] After two cycles of difference

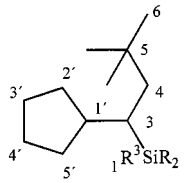
Fourier syntheses and subsequent full-matrix least-squares refinement (SHELXL93)[27] the structure model was complete. All non-hydrogen atoms were assigned as anisotropic, no absortion or extinction correction was done. 20 reflections seemed to be disturbed by a strong extinction and were therefore excluded from the refinement calculations. Hydrogen atoms were calculated in their ideal positions and allowed to ride on their pivot atom. Further details of the crystal structure analysis are given in Table 2. Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103265. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinement of **10**

| | |
|---|---|
| Empirical formula | $C_{27.39}H_{36.77}O_{0.69}Si$ |
| Molecular mass | 405.09 |
| Temperature [K] | 180(2) |
| Wavelength [pm] | 71.069 |
| Space group | $P-1$ (no. 2) |
| Unit cell dimensions | $a$ = 1018.0(2) pm, α = 88.63(3)°<br>$b$ = 1064.3(7) pm, β = 77.180(10)°<br>$c$ = 1276.6(2) pm, γ = 71.22(3)° |
| Volume [nm$^3$] | 1.2752(9) |
| $Z$ | 2 |
| Density (calcd.) [Mg/m$^3$] | 1.055 |
| Absorption coefficient [mm$^{-1}$] | 0.105 |
| $F$(000) | 441 |
| Crystal size [mm$^3$] | 0.80 × 0.40 × 0.04 |
| Φ range for data collection [°] | 1.64 to 29.97 |
| Index ranges | $-13 \le h \le 14$, $-14 \le k \le 14$, $0 \le l \le 17$ |
| Reflections collected | 7374 |
| Independent reflections | 7374 [$R$(int) = 0.0000] |
| Completeness to Φ = 29.97° | 99.4% |
| Refinement method | Full-matrix least squares on $F^2$ |
| Data/restraints/parameters | 7374/0/285 |
| Goodness-of-fit on $F^2$ | 1.021 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0575, $wR2$ = 0.1616 |
| $R$ indices (all data) | $R1$ = 0.0672, $wR2$ = 0.1728 |
| Largest diff. peak and hole [eÅ$^{-3}$] | 0.725 and −0.578 |

**Synthesis of 2-(3-Cyclopentenyl)-1,1-dimethoxy-4,4-dimethyl-1-naphthyl-1-silapentane (12):** 570 mg (13.10 mmol, 30% excess) of magnesium and 150 mL of diethyl ether were placed into a 250-mL 3-necked flask with a dropping funnel and a reflux condenser. 4.94 mL (13.10 mmol, 30% excess) of 1-bromonaphthalene was added dropwise. The mixture was refluxed for 3 h. After cooling to room temperature, 3.04 g (10.08 mmol) of **11** was slowly added. The reaction mixture was then refluxed for 2 h. The solvent was removed in vacuo, the residue dissolved in 50 mL of pentane, and the magnesium salts were filtered off and extracted with pentane (2 × 15 mL). After removing the solvent, **12** (2.30 g) was isolated as a slightly yellow viscous oil (57%). For the assignment of the NMR chemical shifts the atoms are numbered as expressed by the formula in Scheme 5. − $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 9 H, $CH_2tBu$), 1.07−1.25 (m, 1 H, CHSi), 1.58 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 5.1 Hz, 1 H, C$H_a$H$_b$tBu), 2.10 (dd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 4.9 Hz, 1 H, CH$_a$$H_b$tBu), 2.40−2.46 [m, 2 H, $CH_2$ (cyclopentenyl)], 2.52−2.57 [m, 2 H, $CH_2$ (cyclopentenyl)], 2.74−2.84 [m, 1 H, CH (cyclopentenyl)], 3.81 (s, 3 H, $SiOCH_3$), 3.82 (s, 3 H, $SiOCH_3$), 5.78−5.80 (m, 2 H, 2 CH olefin.), 7.61−7.73 (m, 3 H, aromat.), 7.97−8.05 (m, 2 H, aromat.), 8.18−8.25 (d, $^3J_{HH}$ = 6.8 Hz, 1 H, aromat.), 8.61 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, aromat.). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 130.71 (C-3′), 130.64 (C-4′), 51.37 ($SiOCH_3$), 51.02 ($SiOCH_3$), 40.41 (C-1′), 40.28 (C-3), 38.29 (C-2′), 37.86 (C-5′), 30.66 (C-4), 30.11 (C-5), 25.98 (C-2). − **12** contains 10 diastereotopic aromatic carbon atoms, their $^{13}$C chemical shifts are: 137.37, 133.27, 132.49 (3 $C_q$); 136.30, 130.81, 129.12, 128.28, 126.27, 125.62, 125.29 (7 CH aromatic). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = −18.61. − MS (70 eV); *m/z* (%): 368 (2.65) [$M^+$], 337 (7.63) [$M^+ - OCH_3$], 241 (100) [$M^+ - C_{10}H_7$ (naphthyl)], 217 (18.80) [$Si(OCH_3)_2$naphthyl$^+$], 67 (6.25) [$C_5H_7^+$], 57 (26.16) [$t$Bu$^+$]. − $C_{23}H_{32}SiO_2$ (368.59): calcd. C 74.95, H 8.75; found C 74.78, H 8.69.

**3-Cyclopentyl-2-fluorenyl-2,5,5-trimethyl-2-silahexane (13):** For the assignment of the NMR chemial shifts in **13** the atoms are numbered as expressed by the formula in Scheme 6. − $^1$H NMR (300 MHz, $CDCl_3$): δ = −0.42 (s, 3 H, $SiCH_3$), −0.06 (s, 3 H, $SiCH_3$), 0.80 (s, 9 H, $CH_2tBu$), 0.84−0.86 (m, 2 H), 1.10−1.33 (m, 5 H), 1.37−1.75 (m, 4 H), 1.97−2.03 [m, 1 H, CH (cyclopentyl)], 4.02 (s, 1 H, fluorenyl−CH), 7.27−7.35 (m, 4 H, aromatic), 7.54 (dm, $J_{HH}$ = 6.8 Hz, 2 H, aromatic), 7.84 (dm, $J_{HH}$ = 7.8 Hz, 2 H, aromatic). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 43.98 (fluorenyl−CH), 41.64 (C-1′), 40.83 (C-4), 32.60, 31.14 (C-2′/C-5′), 31.49 (C-5), 29.73 (C-6), 25.10, 24.48 (C-3′/C-4′), 21.89 (C-3), −3.26 ($SiCH_3$), −3.74 ($SiCH_3$). − Aromatic $^{13}$C shifts: 146.16, 145.96, 140.70, 140.63 (4 $C_q$), 125.89 (intensity 2), 125.17 (intensity 2), 124.22, 124.17, 119.83 (intensity 2) (in total 8 CH aromatic). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 8.43. − MS (70 eV); *m/z* (%): 376 (0) [$M^+$], 211 (26.05) [$M^+ - C_{13}H_9$ (fluorenyl)], 165 (33.33) [$C_{13}H_9^+$ (fluorenyl)], 73 (100), 67 (12.01) [$C_5H_7^+$], 59 (61.00), 57 (56.01) [$t$Bu$^+$]. − $C_{26}H_{36}Si$ (376.66): calcd. C 82.91, H 9.63; found C 83.07, H 9.72.

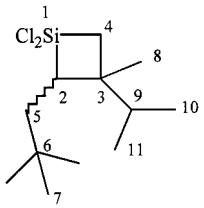



Scheme 6. Numbering scheme of **13** and **14**

**2-Cyclopentyl-1,1-dimethoxy-4,4-dimethyl-1-naphthylsilapentane (14):** For the assignment of the NMR chemial shifts in **14** the atoms are numbered as expressed by the formula in Scheme 6. − $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.94 (s, 9 H, $CH_2t$Bu), 1.02−1.08 (m, 1 H, CHSi), 1.28−1.68 (m, 6 H), 1.82−1.83 [m, 2 H, $CH_2$ (cyclopentyl)], 2.01−2.29 [m, 3 H, $CH_2$ and CH (cyclopentyl)], 3.73 (s, 3 H, $SiOCH_3$), 3.75 (s, 3 H, $SiOCH_3$), 7.49−7.66 (m, 3 H, aromat.), 7.87−7.95 (2 H, aromat.), 8.14−8.16 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, aromat.), 8.55 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, aromat.). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 50.73 ($SiOCH_3$), 50.31 ($SiOCH_3$), 42.82 (C-1′), 40.07 (C-3), 32.37, 31.17 (C-2′/C-5′), 31.53 (C-4), 29.49 (C-5), 25.00, 24.99 (C-3′/C-4′), 24.99 (C-2). − Aromatic $^{13}$C shifts: 136.97, 133.13, 132.21 (3 $C_q$ aromatic), 135.74, 130.26, 128.58, 127.74, 125.89, 125.08, 124.75 (in total 7 aromatic CH groups). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = −21.71. − MS (CI); *m/z* (%): 371 (1.81) [(M + 1)$^+$], 339 (75.81) [$M^+ - OCH_3$], 243 (100) [$M^+ - C_{10}H_7$ (naphthyl)], 128 (12.24) [$C_{10}H_8^+$], 57 (22.22) [$t$Bu$^+$]. − $C_{23}H_{34}SiO_2$ (370.61): calcd. C 74.54, H 9.25; found C 74.39, H 9.13.

**(*E*)-1,1-Dichloro-3-isopropyl-3-methyl-2-neopentyl-1-silacyclobutane (*E*-16):** For the assignment of the NMR chemical shifts in **16** the atoms are numbered as expressed by the formula in Scheme 7. − $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.86−0.90 (m, 6 H, 10-H and 11-H), 0.91 [s, 9 H, C(C$H_3$)$_3$], 0.99 (s, 3 H, 8-H), 1.33 (dd, $^2J_{HH}$ =

13.2 Hz, $^3J_{HH}$ = 2.6 Hz, 1 H, C$H_a$H$_b$*t*Bu), 1.54 (m, 1 H, 4-H), 1.60 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 12.8 Hz, 1 H, CH$_a$$H_b$*t*Bu), 1.64 (m, 1 H, 9-H), 1.76 (m, 1 H, 4-H), 1.96 (dd, $^3J_{HH}$ = 12.8 Hz, $^3J_{HH}$ = 2.6 Hz, 1 H, 2-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 46.37 (C-2), 42.60 (C-6), 40.87 (C-3), 40.40 (C-9), 38.50 (C-4), 30.53 (C-10), 29.51 (C-11), 28.73 (C-4), 17.77 (C-7), 17.95 (C-8). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 19.65.




Scheme 7. Numbering scheme of **16**, **19**, and **20**

**(*Z*)-1,1-Dichloro-3-isopropyl-3-methyl-2-neopentyl-1-silacyclobutane (*Z*-16):** $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.86−0.90 (m, 6 H, 10-H and 11-H), 0.90 [s, 9 H, C(C$H_3$)$_3$], 1.18 (s, 3 H, 8-H), 1.34 (m, 1 H, 9-H), 1.46 (dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 2.3 Hz, 1 H, C$H_a$H$_b$*t*Bu), 1.57 (m, 1 H, 4-H), 1.61(dd, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 12.6 Hz, 1 H, CH$_a$$H_b$*t*Bu), 1.88 (m, 1 H, 2-H), 2.14 (m, 1 H, 4-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 49.53 (C-2), 41.43 (C-3), 38.23 (C-9), 36.26 (C-4), 32.92 (C-6), 30.60 (C-10), 29.45 (C-11), 27.40 (C-5), 18.86 (C-8), 18.70 (C-7). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$ ): δ = 19.35. − MS (70 eV) of (***E*/*Z*)-16**; *m*/*z* (%): 266 (4.65), 268 (3.37), 270 (0.71) [$M^+$] (isotopic pattern $SiCl_2$), 251 (1.17), 253 (1.27) [$M^+ - CH_3$] (isotopic pattern $SiCl_2$), 235 (0.56) [$M^+$ − Cl], 209 (9.35)/211 (7.34) [$M^+$ − *t*Bu] (isotopic pattern $SiCl_2$). − $C_{12}H_{24}Cl_2Si$ (267.32): calcd. C 53.92, H 9.05, Cl 26.53; found C 53.95, H 10.29, Cl 26.04.

**(*E*)-1,1-Dichloro-3-ethyl-3-methyl-2-neopentyl-1-silacyclobutane (*E*-19):** Numbering of atoms in *E*-**19** see Scheme 7, 11 = H. − $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.84−0.89 (m, 3 H, 10-H), 0.91 [s, 9 H, C(C$H_3$)$_3$], 1.16 (s, 3 H, 8-H), 1.24 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 3.0 Hz, 1 H, C$H_a$H$_b$*t*Bu), 1.46 (m, 1 H, 9-H), 1.55 (m, 1 H, 4-H), 1.59 (m, 1 H, 9-H), 1.66 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 12.1 Hz, 1 H, CH$_a$$H_b$*t*Bu), 1.92 (m, 1 H, 4-H), 1.94 (dd, $^3J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 3.0 Hz, 1 H, 2-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 50.65 (C-2), 39.64 (C-8), 38.48 (C-3), 38.33 (C-4), 30.22 (C-9), 29.53 (C-10), 28.86 (C-5), 28.82 (C-6), 8.41 (C-7). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 18.88.

**(*Z*)-1,1-Dichloro-3-ethyl-3-methyl-2-neopentyl-1-silacyclobutane (*Z*-19):** Numbering of atoms in *Z*-**19** see Scheme 7, 11 = H. − $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.84−0.89 (m, 3 H, 10-H), 0.91 [s, 9 H, C(C$H_3$)$_3$], 1.07 (s, 3 H, 8-H), 1.28 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 3.0 Hz, 1 H, C$H_a$H$_b$*t*Bu), 1.44 (m, 1 H, 9-H), 1.52 (m, 1 H, 4-H), 1.60 (m, 1 H, 9-H), 1.62 (dd, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 12.6 Hz, 1 H, CH$_a$$H_b$*t*Bu), 1.88 (dd, $^3J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 3.0 Hz, 1 H, 2-H), 1.92 (m, 1 H, 4-H). − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 47.17 (C-2), 38.95 (C-8), 37.95 (C-3), 37.77 (C-4), 35.43 (C-6), 30.22 (C-9), 29.53 (C-10), 22.33 (C-5), 9.10 (C-7). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 18.12. − Mass spectra and elemental analysis of ***E*/*Z*-19** together with ***E*/*Z*-20**. The isomeric mixture could not be seperated by distillation.

**(*E*/*Z*)-1,1-Dichloro-3-isopropyl-2-neopentyl-1-silacyclobutane (*E*/*Z*-20):** A detailed interpretation of the $^1$H-NMR spectra was avoided because of small signal intensities and complex superpositions of NMR signals.

**(E)-1,1-Dichloro-3-isopropyl-2-neopentyl-1-silacyclobutane (*E*-20):** Numbering of atoms in *E*-**20** see Scheme 7, 8 = H. − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 43.74 (C-9), 42.09 (C-2), 41.98 (C-3), 30.62 (C-10), 29.46 (C-11), 27.33 (C-4), 22.33 (C-6), 21.04 (C-7), 19.03 (C-5). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 16.13.

**(*Z*)-1,1-Dichloro-3-isopropyl-2-neopentyl-1-silacyclobutane (*Z*-20):** Numbering of atoms in *Z*-**20** see Scheme 7, 8 = H. − $^{13}$C NMR (75.40 MHz, $CDCl_3$): δ = 42.85 (C-9), 41.98 (C-2), 40.78 (C-3), 31.97 (C-4), 30.38 (C-10), 29.46 (C-11), 21.28 (C-6), 20.26 (C-7), 19.45 (C-5). − $^{29}$Si NMR (59.25 MHz, $CDCl_3$): δ = 17.07. − MS (70 eV) of **19** and **20**; *m*/*z* (%): 252 (3.58), 254 (2.59), 256 (0.58) [$M^+$] (isotope pattern of $SiCl_2$), 237 (0.91), 239 (0.96) [$M^+ - CH_3$] (isotope pattern of $SiCl_2$), 217 (0.35) [$M^+$ − Cl], 195 (7.11), 197 (5.66) [$M^+$ − *t*Bu]. − Elemental analysis of **19** and **20**; $C_{11}H_{22}Cl_2Si$ (253.29): calcd. C 52.16, H 8.75, Cl 27.99; found C 52.44, H 9.85, Cl 26.35.

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