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Synthesis and Solid-State Molecular Structure of Bi(silacyclohexyls) C5H10SiX-XSiC5H10 with X = H, PH, F, CL, BR, and I

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SYNTHESIS AND SOLID-STATE MOLECULAR STRUCTURE OF BI(SILACYCLOHEXYLS) C5H10SIX-XSIC5H10 WITH X = H, PH, F, CL, BR, AND I

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The synthesis and purification of novel bi(silacyclohexyls) $C_5H_{10}SiX$ -XSi C_5H_{10} with X = H(1), Ph (2), F (3), Cl (4), Br (5), and I (6), which are composed of two silacyclohexyl rings connected by a silicon–silicon single bond, is described. Molecular structures for 2, 4, 5, and 6 were determined employing X-ray crystallography. Surprisingly, the SiSi bond lengths increase in the order I < Br < Cl, contrary to what is observed for methylated disilanes Me₂XSiSiXMe₂. The bond lengthening can be traced back to 1, 3 nonbonded interactions between the halogen atoms and the axial hydrogen atoms in the SiC₅ ring, which also cause a decrease of the SiSiX bond angles with increasing size of the halogen atom. Both rings substitute each other in the equatorial position for 4, 5, and 6, but in the axial position for 2.

Keywords Silacyclohexanes; synthesis; x-ray diffraction

INTRODUCTION

Cyclohexane C_6H_{12} has been and still is the archetype and cornerstone for discussing and comparing the conformational equilibria of saturated heterocyclic six-membered rings composed of main group elements such as carbon, silicon, germanium, oxygen, sulfur, nitrogen, or phosphorus. Not surprisingly, a huge number of studies on the conformational properties of cyclohexanes composed of second row elements C, O, and N have been published in the literature.¹ Much less effort has been directed toward heterocycles whose backbones incorporate third or fourth row elements. Most intensely studied rings are silacyclohexanes with up to three silicon atoms and thiacyclohexanes with up to five sulfur atoms.¹

Our group focuses on conformational equilibria of cyclohexanes composed of just third or fourth row elements such as cyclohexasilanes Si_6R_{12} , cyclohexagermanes Ge_6R_{12} or silicon–sulfur and germanium–sulfur rings such as $Si_3S_3R_6$ and $Ge_3S_3R_6$.² Just as in cyclohexane, these rings are characterized by the presence of chair, boat, and twist conformations, albeit with smaller energy differences between conformers and smaller

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barriers that separate them. Interconversions of conformers on the time-scale of NMR-spectroscopy therefore are fast, and very low temperatures are needed to slow them down sufficiently. For instance, a temperature of about -160 °C had to be used for investigating the chair to chair interconversion of Si₆Me₁₂ with ¹³C-NMR spectroscopy, with all the problems caused by the low solubility at that temperature.³ A spectroscopic method with a shorter timescale such as vibrational Raman spectroscopy coupled with quantum chemical calculations therefore is a much more convenient method for investigating these rings, as we have shown with Si₆Me₁₂,⁴Si₆Me₁₁X (X = F, Cl, Br, and I)⁵ and Ge₆Me₁₂.⁶ It is therefore quite natural to apply the method to larger systems, such as bi(cyclohexasilanyls) Si₁₂H₂₂ and Si₁₂Me₂₂ as shown in Scheme 1, which we are investigating currently. Si₁₂Me₂₂ is a formidable conformational problem, because each Si₆ ring can adopt chair, twist, and boat conformation. Moreover, rotational isomerism around the pivot SiSi bond is present with the further complication that methylated oligosilanes display SiSiSiSi dihedral angle minima at \approx 90 °, termed ortho conformations, besides the usual \approx 180 ° and $\approx \pm 60$ ° anti and gauche minima.⁷



Scheme 1 Molecular structures of bicyclohexyl, bi(silacyclohexyl) and bi(cyclohexasilanyl). H-atoms have been omitted for clarity.

We therefore decided to include 1,1'-bi(silacyclohexyl) derivatives $C_5H_{10}SiX-XSiC_5H_{10}$ with X = hydrogen or halogen (Scheme 1) in the study, as these represent simpler systems due to the fact that twisted conformers of the SiC₅ rings have large relative energies of about 16 kJmol⁻¹.⁸ At ambient temperatures, these states are populated to an almost negligible extent, thereby simplifying the conformational problem. However, rotational isomerism of the pivot SiSi bond is maintained.

Much to our surprise, no such compounds have been described in the literature yet. We therefore have set out to develop a synthetic method for their preparation and to compare their structures and conformations with bicyclohexyl C_6H_{11} - C_6H_{11} , which is also shown in Scheme 1. So far, bicyclohexyl has been investigated with gas phase electron diffraction,⁹ and the solid state molecular structure of $Si_{12}Me_{22}$ has been elucidated with X-ray crystallography.¹⁰

RESULTS AND DISCUSSION

Synthesis

Compounds 1-6 were synthesized following two different routes as shown in Scheme 2. The first one starts from 1,5-dichloropentane, which with magnesium gives dichloro- μ -1,5-pentanediyldimagnesium. Its reaction with hexachlorodisilane affords



Scheme 2 Synthesis of $C_5H_{10}SiPh$ -PhSi C_5H_{10} (2) and $C_5H_{10}SiCl$ -ClSi C_5H_{10} (4).

a mixture of $C_5H_{10}SiCl(SiCl_3)$ and **4**, from which **4** can be separated by fractional crystallization. The reaction of Si_2Cl_6 with dibromo- μ -1,5-pentanediyldimagnesium has been described previously.¹¹ Due to bromine/chlorine exchange a mixture of partially brominated chlorosilanes was obtained from which no pure compounds could be separated.

The second route starts from known 1-chloro-1-phenylsilacyclohexane $C_5H_{10}SiPhCl$, which was reduced to 2 by the use of sodium.

As shown in Scheme 3, 2 and 4 were transformed into 1, 3, and 5 employing standard methods used for the synthesis of alkyldisilanes such as reduction with LiAlH₄ or removal of the phenyl groups with trifluoromethanesulfonic acid and subsequent transformation of the trifluoromethanesulfonyloxysilane into a halosilane with an alkali metal halide.¹² 6 was synthesized from 1 by hydrogen/halogen exchange with CHI₃.



Scheme 3 Synthesis of 1, 3, 5 and 6.



Scheme 4 1, 3-steric interaction between hydrogen atoms on C2 and C4 and halogen atom X.

X-Ray Crystallography

We were able to grow crystals of **2**, **4**, **5**, and **6** from various solvents with a quality suitable for X-ray analysis. ORTEP drawings of the molecular structures are presented in Figure 1, and relevant structural parameters are summarized in Table 1. In all compounds, the silacyclohexane rings possess the chair conformation. A substituent on the silicon atom thus can adopt either the equatorial (e) or axial (a) position. The conformers therefore can be classified as either aa (both rings adopt the axial position relative to each other), ae, or ee.



Figure 1 ORTEP plots (30% probabilities) of the solid state molecular structures of 2 (top left), 4 (top right), 5 (bottom left) and 6 (bottom right) (Color figure available online).

	2	4	5	6
Sil-SilA	235.90(5)	234.55(12)	234.09(12)	231.77(10)
Sil-Xl	188.03(9)	209.53(9)	225.75(3)	248.48(5)
Sil-Cl	188.18(9)	186.31(19)	186.27(9)	186.28(19)
Sil-C5	188.23(9)	186.2(2)	186.47(9)	186.28(19)
SilA-Sil-Xl	109.47(3)	105.73(4)	104.95(15)	103.34(3)
SilA-Sil-Cl	112.22(3)	116.52(7)	116.74(3)	114.26(7)
SilA-Sil-C5	111.21(3)	114.78(7)	115.35(3)	115.77(7)

Table 1 Selected bond lengths [pm] and bond angles [°] for 2, 4, 5, and 6

As a silacyclohexyl substituent is quite bulky, the ee conformer is expected to constitute the energetic global minimum for all compounds. Interestingly, the phenyl compound 2 shows the SiC₅ rings in the axial positions, which seems to be an effect of the crystal packing forces.

Quite surprisingly, the SiSiX bond angles in the series $CI \rightarrow Br \rightarrow I$ decrease from 105.73(4) ° for Cl to 103.34(3) ° for I, despite an increase of the size of the halogen atom. We attribute this to the repulsive 1,3-steric interaction of X with the two axial hydrogen atoms on C-atoms 2 and 4, as shown in Scheme 4.

We do not attribute the decrease of the XSiSi bond angle to crystal packing forces because it is reproduced quite nicely by preliminary quantum chemical DFT calculations, which we will describe in a forthcoming article. They predict values of 105.4 ° (Cl), 104.7 ° (Br), and 104.3 ° (I). The calculated HX distances marked by arrows in Scheme 4 are 328.8 pm, 337.2 pm, and 351.3 pm for X = Cl, Br, and I, respectively. They compare well with the sum of the van der Waals radii, listed in the literature (H: 120–145 pm, Cl: 170–190 pm, Br: 180–200 pm, I: 195–210 pm).^{13,14} It is worth mentioning that for substituted cyclohexanes $C_6H_{11}R$ with R = H, Cl, Me, and *tert*-Bu, the so called 1,3*-syn*-diaxial interaction has been shown to be attractive rather than repulsive by quantum chemical calculations.¹⁵ The long SiCl bond (as compared to CCl) can serve as an explanation for why an attractive interaction turns into a repulsive one. Moreover, the van der Waals radius of a chlorine atom bonded to silicon certainly is larger than in a CCl bond due to the differing electronegativities of C and Si.

The SiSi bonds of **3**, **4**, and **5** shorten in the order $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$, which is quite unusual for disilanes. Normally, SiSi bond lengths of halogenated disilanes decrease with increasing electronegativities of the halogen atoms, for instance in the hexahalodisilanes $X_3\text{SiSiX}_3$.^{16a,16b} The effect can be rationalized using Bent's rule, which is an extension of the VSEPR model, stating that bonds to electronegative substituents use more p-character due to the shift of the electron cloud toward the electronegative atom.¹⁷ The bond to the most electropositive substituent, which is the other silicon atom, thus gains more s-character, an effect which is maximized for X = F. An increased s-character usually means a stronger and consequently shortened bond.

The trend of bond shortening observed in the solid state, which contradicts simple VSEPR theory, is also predicted by the preliminary quantum chemical calculations mentioned previously, suggesting that it originates from electronic causes. Detailed results of the calculations including the influences of conformations on the bond lengths will be published elsewhere.

Compound	2	4	o,	6
Empirical formula	C ₂₂ H ₃₀ Si ₂	Ci ₀ H ₂ o Cl ₂ Si ₂	$C_{10} H_{20} Br_2 Si_2$	C ₁₀ H ₂₀ I ₂ Si ₂
Formula weight	350.64	267.34	356.26	450.24
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Ortho rhombic
Space group	P2(1)/c	C2/c	C2/c	Pbca
Unit cell dimensions	a = 9.6881(4) Å	a = 19.043(6) Å	a = 18.8490(9) Å	a = 7.6651(6) Å
	b = 11.4676(5) Å	b = 6.220(2) Å	b = 6.2696(3) Å	b = 13.8941(11) Å
	c = 9.0679(3) Å	c = 11.254(4) Å	c = 11.7133(6) Å	c = 14.2064(10) Å
Volume	998.55(7) Å ³	1328.6(8) Å ³	1379.19(12) Å ³	1513.0(2) Å ³
z	2	4	4	4
Density (calculated)	1.166 Mg/m ³	1.337 Mg/m ³	1.716 Mg/m ³	1.977 Mg/m ³
Absorption coefficient	0.179 mm^{-1}	0.633 mm^{-1}	6.017 mm^{-1}	4.285 mm^{-1}
F(000)	380	568	712	856
Crystal size	$0.62 \times 0.49 \times 0.11 \text{ mm}^3$	$0.33 \times 0.19 \times 0.02 \text{ mm}^3$	$0.31 \times 0.29 \times 0.09 \text{ mm}^3$	$0.213 \times 0.178 \times 0.154 \mathrm{mm^3}$
Theta range for data	2.77 to 30.00° .	$3.45 \text{ to } 24.97^{\circ}.$	2.17 to 33.34°.	2.87 to 33.00° .
collection				
Index ranges	-13 < h < 13, -16 < k <	-22 < h < 22, -7 < k < 7,	-28 < h < 28, -9 < k < 8,	-11 < h < 11, -21 < k <
	16, -11 < 1 < 12	-13 < 1 < 11	-18 < 1 < 18	21, -21 < 1 < 21
Reflections collected	24017	7704	29167	57382
Independent reflections	2920 [R(int) = 0.0280]	1164 [R(int) = 0.0311]	2672 [R(int) = 0.0272]	2854 [R(int) = 0.0467]
Completeness to thetamax.	96.66	99.6%	99.8%	100.0%
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max. and min. transmission	0.9813 and 0.8978	0.9856 and 0.8192	0.6226 and 0.2538	
Refinement method	Full-matrix least-squares on E ²	Full-matrix least-squares on E ²	Full-matrix least-squares on E2	Full-matrix least-squares on E ²
Data /restraints /no rameters	2020/0/100	1 116/10/6/		785410164
Goodness-of-fit on F ²	1.076	1.085	1,060	1.186
Final R indices	RI = 0.0284, $wR2 = 0.0807$	Rl = 0.0265, w $R2 = 0.0629$	RI = 0.0145, $wR2 = 0.0367$	Rl = 0.0184, w $R2 = 0.0399$
[I>2sigma(I)]				
R indices (all data) Largest diff. peak and hole	R1 = 0.0318, wR2 = 0.0851 0.426 and $-0.160 \text{ e.}\text{Å}^{-3}$	RI = 0.0359, wR2 = 0.0687 0.374 and $-0.178 \text{ e.}\text{Å}^{-3}$	R1 = 0.0174, wR2 = 0.0376 0.442 and $-0.297 \text{ e.}\text{Å}^{-3}$	RI = 0.0303, wR2 = 0.0481 1.027 and $-0.564 \text{ e.} \text{Å}^{-3}$

Table 2Crystallographic data for compounds 2, 4, 5, and 6

CONCLUSIONS

In this article, we describe preparative procedures for the synthesis and purification of novel bi(silacyclohexyls) $C_5H_{10}SiX-XSiC_5H_{10}$ with X = Ph, H, F, Cl, Br, and I, which are composed of two silacyclohexyl rings connected with a silicon–silicon bond. The compounds with X = Ph, Cl, Br, and I crystallize readily, and X-ray diffraction experiments show that the two rings substitute each other in an equatorial position for X = Cl, Br, and I (ee isomer), but in axial position for X = Ph (aa isomer) caused by crystal packing forces. Moreover, the SiSi bond lengths increase in the order $I \rightarrow Br \rightarrow Cl$, just opposite to what has been found for other halogenated disilanes, for instance MeX₂SiSiX₂Me.²³ This is due to 1,3-nonbonded interactions between the halogen atoms and the axial hydrogen atoms in the ring, which can be relieved in methylated disilanes by internal rotation of the methyl groups.

EXPERIMENTAL PART

General

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were deoxygenated and dried prior to use with Al₂O₃, using a column purification system from Innovative Technology. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded in solutions of C₆D₆ employing a INOVA 300 spectrometer (299.953 MHz for ¹H, 59.592 MHz for ²⁹Si, and 75.430 MHz for ¹³C). Standard INEPT pulse sequences were used for recording the ²⁹Si{¹H} and ¹³C{¹H} spectra. All shifts are referenced against TMS. Due to ring inversion, r.t. proton signals generally are broad, sometimes splitting into broad doublets. ¹³C and ²⁹Si nuclei produce sharp signals due to lower resonance frequencies.

Synthesis of 1,1'-Dichloro-bi(silacyclohexyl) (4)

A solution of of dichloro- μ -pentanediylmagnesium (35.05 g, 185 mmol) in diethylether (100 mL), which was prepared from Cl(CH₂)₅Cl (154.05 g) and of Mg (8.99 g) according to the literature,¹⁸ was added dropwise to a solution of hexachlorodisilane (24.85 g, 92 mmol) in diethylether (400 mL) at a temperature of 0 °C. After completion, the reaction mixture was stirred for 2 h. Diethylether was then replaced by toluene, and the solution was separated from the salts by filtration. Toluene was then removed by evaporation in vacuo (i.v.) Crude **4** crystallized from the oily and colorless residue and was separated by decantation. A further crystallization from toluene afforded pure **4** (5.05 g, 18.7 mmol, 20.3%) with a crystal quality sufficient for X-ray analysis.

Elemental analysis $C_{10}H_{20}Si_2Cl_2$ (267.34): calc. C 44.93, H 7.54%; found C 44.95, H 7.48% ¹H-NMR: $\delta = 1.75-1.56$ ppm (m, 8H), $\delta = 1.39-1.27$ ppm (m, 2H), $\delta = 1.18-1.05$ ppm (m, 2H), $\delta = 0.98-0.86$ ppm (m, 8H).

¹³C{¹H}-NMR: δ = 29.1 ppm, δ = 23.3 ppm, δ = 15.3 ppm.

²⁹Si{¹H}-NMR: $\delta = 11.3$ ppm.

The measured ¹H-, ¹³C{¹H}-, and ²⁹Si{¹H}-NMR spectra of **4** are presented in the supplemental materials available online (Figures S1, S2, and S3) to illustrate their general appearance, which is also typical for the other compounds described in this publication.

Synthesis of 1, 1'-diphenyl-bi(silacyclohexyl) (2)

A solution of 1-chloro-1-phenylsilacyclohexane (18.65 g, 88.5 mmol) prepared by following the literature procedure was dissolved in of toluene (100 mL).¹⁹ An excess of sodium (5.6 g, 243.5 mmol) was added, and the reaction mixture was refluxed for 3 days (72 h). The resulting greenish solution was separated from the salts by decantation, and the solvent was removed by evaporation i.v. The resulting oily residue was fractionated by a Kugelrohr distillation, giving **2** (6.1 g, 17.4 mmol, 20%) as a colorless oil, which crystallized slowly at r.t. The quality of the crystals turned out to be sufficient for an X-ray analysis.

Elemental analysis $C_{22}H_{30}Si_2$ (350.65): calc. C 75.36, H 8.62%; found C 75.60 H 8.83%.

¹H-NMR: $\delta = 7.39-7.35$ ppm (m, aromatic 4H), $\delta = 7.23-7.13$ ppm (m, aromatic 6H), $\delta = 7.39-7.35$ ppm (m, 4H), $\delta = 1.74-1.55$ ppm (m, 8H), $\delta = 1.41-1.23$ ppm (m, 4H), $\delta = 1.06-0.90$ ppm (m, 8H).

¹³C{¹H}-NMR: $\delta = 134.6$ ppm (aromatic C), $\delta = 133.2$ ppm (aromatic C), $\delta = 130.3$ ppm (aromatic C), $\delta = 128.0$ ppm (aromatic C), $\delta = 30.1$ ppm, $\delta = 24.6$ ppm, $\delta = 10.9$ ppm.

²⁹Si{¹H}-NMR: $\delta = -25.6$ ppm.

Synthesis of bi(silacyclohexyl) (1)

To a solution of **4** (2.17 g, 8.1 mmol) in diethyl ether (50 mL) was added a solution of LiAlH₄ (0.30 g, 8 mmol) in diethyl ether (30 mL) at a temperature of 0 °C. After completion, the reaction mixture was stirred overnight and then added dropwise to an ice-cooled aqueous solution of H₂SO₄ (2N). The aqueous phase was separated with the help of a separatory funnel, and washed twice with diethyl ether. The combined organic phases were then dried with Na₂SO₄. The oily residue that was obtained after the removal of the diethyl ether was fractionated with a Kugelrohr distillation, giving pure **1** (1.57 g, 7.94 mmol, 98%) as a colorless oil (Kp_{0.1} \approx 65 °C). Attempts to obtain crystals at low temperatures failed. Therefore, the purity of the compound was checked with NMR spectroscopy.

¹H-NMR: $\delta = 4.0$ ppm (s, 2H), $\delta = 1.96-1.87$ ppm (m, 8H), $\delta = 1.66-1.57$ ppm (m, 4H), $\delta = 1.07-0.92$ ppm (m, 8H).

¹³C{¹H}-NMR: δ = 30.4 ppm, δ = 26.6 ppm, δ = 9.3 ppm. ²⁹Si{¹H}-NMR: δ = -39.7 ppm (s), ¹J(SiH) = 195 ± 5 Hz.

Synthesis of 1, 1'-Difluorobi(silacyclohexyl) (3) and 1, 1'-dibromo-bi(silacyclohexyl) (5)

2 (1.32 g, (3.76 mmol) was dissolved in toluene (60 mL). The solution was cooled to $-30 \,^{\circ}$ C, and CF₃SO₃H (0.68 mL, 7.71 mmol) was added with a syringe. After about 2 h, C₅H₁₀Si(OTf)-(TfO)SiC₅H₁₀ had formed quantitatively as checked with ²⁹Si-NMR spectroscopy (δ (²⁹Si) = +18.7 ppm). Toluene and the excess of CF₃SO₃H were then removed by evaporation i.v. The oily residue was then dissolved in diethyl ether (30 mL), and an ample excess of an alkali metal halide was added (for **3**: LiF; for **5**: LiBr). The resulting suspension was stirred at r.t. for 3 days. Then diethyl ether was removed by evaporation i.v., and the residue was suspended in dry toluene. The solution that was

decanted from the residual salts contained the desired compounds, which were purified further by either fractional distillation (3) or crystallization (5).

 $C_{10}H_{20}Si_2F_2$, **3**: (234.44): After removal of toluene by evaporation i.v., **3** was purified by a Kugelrohr distillation (Kp_{0.1} \approx 70 °C). **3** (0.75g, 3.19 mmol, 84.9%) was obtained as a colorless liquid, whose purity was checked with multinuclear NMR-spectroscopy. All attempts to grow crystals failed.

¹H-NMR: $\delta = 1.78-1.56$ ppm (m, 8H), $\delta = 1.56-1.53$ ppm (m, 4H), $\delta = 1.03-0.93$ ppm (m, 8H).

¹³C{¹H}-NMR: δ = 29.6 ppm (s), δ = 23.5 ppm (s), δ = 14.8 ppm (dd), ²J(CF) = 7.0Hz, ³J(CF) = 2.2 Hz.

²⁹Si{¹H}-NMR: $\delta = 21.1$ ppm (dd), ¹J(SiF) = 318.5 Hz, ²J(SiF) = 32.8 Hz.

 $C_{10}H_{20}Si_2Br_2$, 5:

Elemental analysis $C_{10}H_{20}Si_2Br_2$ (356.25): calc. C 33.72, H 5.66%; found C 34.23, H 5.65%.

¹H-NMR: $\delta = 1.69-1.59$ ppm (m, 8H), $\delta = 1.34-1.29$ ppm (m, 4H), $\delta = 1.11-0.97$ ppm (m, 8H).

¹³C{¹H}-NMR: $\delta = 28.7$ ppm, $\delta = 23.1$ ppm, $\delta = 14.6$ ppm.

²⁹Si{¹H}-NMR: $\delta = 7.9$ ppm.

Synthesis of 1, 1'-Diiodo-bi(silacyclohexyl) (6)

1 (2.83 g, 14.3 mmol) was dissolved in heptane (200 mL). CHI₃ (5.0 g, 12.6 mmol) was then added under vigorous stirring, and the reaction mixture was kept at 90 °C for a period of 20 h. The mixture was then allowed to come to r.t. Subsequently, the solution was decanted from the excess of CHI₃. The compound was then purified by fractional crystallization from toluene giving **6** (about 1 g, 15%) as colorless crystals.

Elemental analysis C₁₀H₂₀Si₂I₂ (450.25): calc. H 4.48%; found 4.48%

¹H-NMR: $\delta = 1.66-1.41$ ppm (m, 8H), $\delta = 1.25-1.19$ ppm (m, 4H), $\delta = 1.10-0.55$ ppm (m, 8H).

¹³C{¹H}-NMR: $\delta = 26.2$ ppm, $\delta = 21.1$ ppm, $\delta = 11.4$ ppm. ²⁹Si{¹H}-NMR: $\delta = -10.4$ ppm.

X-Ray Structure Determination

Crystals suitable for X-ray structural analyses were immersed in inert oil under a nitrogen atmosphere, selected and mounted on the tip of a glass fibre. Diffraction data were collected at 100 K on a Bruker D8 Kappa diffractometer equipped with a SMART APEX II CCD detector with Mo K α ($\lambda = 0.71073$ Å) radiation.

Data were integrated with SAINT²⁰ and empirical methods as implemented in SAD-ABS²¹ were used to correct for absorption effects. Structures were solved with direct methods using SHELXS-97. SHELXL-97 was used for refinement against all data by full-matrix least-squares methods on $F^{2,22}$ All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically on calculated positions using the riding model implemented in SHELXL-97. All diagrams were draw with 30% probability thermal ellipsoids and all hydrogen atoms were omitted for clarity.

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **4**, **5**, and **6** reported in this article are summarized in Table 2 and have also been deposited

with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-868302 (2), CCDC-868300 (4), CCDC-868299 (5), and CCDC- 868301 (6). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax +44 1223 336033; E-mail deposit@ ccdc.cam.ac.uk).

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