

## Synthesis and Structure of *cis*-1,4-Di(1-pyrenyl)decamethylcyclohexasilane

Veronica E. M. Kaats-Richters,<sup>†</sup> Thomas J. Cleij,<sup>†,§</sup> Leonardus W. Jenneskens,<sup>†</sup> Martin Lutz,<sup>‡</sup> Anthony L. Spek,<sup>‡</sup> and Cornelis A. van Walree<sup>\*,†</sup>

Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received December 3, 2002

The synthesis and structure of *cis*-1,4-di(1-pyrenyl)decamethylcyclohexasilane (**2**), one of the first *cis*-1,4-substituted cyclohexasilanes, are reported. This isomer is unexpectedly formed as the major product in the reaction of a mixture of *trans*- and *cis*-1,4-dichlorodecamethylcyclohexasilane (**4a** and **4b**, respectively) with 1-pyrenyllithium. Reaction of **4a,b** with phenyllithium showed that preferential formation of the *cis*-product is a general feature of this kind of reaction. According to the X-ray crystal structures of two different solvates, the cyclohexasilane ring in **2** adopts a unique boatlike geometry, with the pyrenyl substituents occupying an equatorial or bisectonal position. <sup>1</sup>H NMR data indicate that a boatlike geometry also occurs in solution. Furthermore, the X-ray crystal structure of *trans*-1,4-dihydrodecamethylcyclohexasilane, which is an intermediate in the synthetic pathway to **2**, is reported.

### Introduction

The field of silicon-based chemistry has rapidly expanded in the last decades, and an impressive variety of silane structures have been prepared. This includes linear oligo- and polymers,<sup>1</sup> oligomeric<sup>2–4</sup> and polymeric branched or network structures,<sup>5–9</sup> cage compounds, and cyclic structures.<sup>10–13</sup> Research on these silicon-based compounds has been largely driven by the occurrence of  $\sigma$ -electron delocalization along the framework of sp<sup>3</sup>-hybridized silicon atoms. This  $\sigma$ -electron delocal-

ization leads to notable properties such as electronic transitions in the near-UV spectral region, relatively low ionization potentials, and pronounced interactions with aromatic moieties via  $\sigma$ – $\pi$  mixing,<sup>12</sup> and forms the basis for the application of silanes in materials science.

Cyclic alkyl-substituted silanes with ring sizes of up to 40 atoms have been prepared,<sup>10,12,13</sup> of which cyclopenta- and cyclohexasilanes are the best accessible homologues. Functionalized cyclopenta- and cyclohexasilanes can also be synthesized; mono- and multisubstituted halogen-, hydroxy-, methoxy-, triflate-, and phenyl-substituted cyclohexasilanes have been reported.<sup>11–13</sup> It is however not easy to isolate multisubstituted cyclohexasilanes in a pure state, since usually a variety of regio- and *cis*-*trans*-isomers are formed. Therefore, the number of well-characterized cyclohexasilane derivatives is still limited. Nevertheless, it can be stated that the cyclohexasilane ring strongly prefers a chair or chairlike geometry since in all 19 cyclohexasilane derivatives recorded in the Cambridge Structural Database<sup>14</sup> this ring geometry is found. Compounds included are, for example, dodecamethylcyclohexasilane, Si<sub>6</sub>Me<sub>12</sub>;<sup>15</sup> *trans*-1,4-Ph<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub>;<sup>16</sup> and 1,3,5-Ph<sub>3</sub>Si<sub>6</sub>Me<sub>9</sub>.<sup>17</sup> Not unexpectedly, the phenyl substituents tend to occupy an equatorial position.

Here we report on the synthesis and structure of *cis*-1,4-(*di*-1-pyrenyl)decamethylcyclohexasilane (**2**, Chart 1), a compound that possesses a number of novel and interesting features. For the first time the preparation of a *cis*-1,4-substituted decamethylcyclohexasilane in

\* Corresponding author. Tel: +3130 2531036. Fax: +3130 2534533. E-mail: c.a.vanwalree@chem.uu.nl.

<sup>†</sup> Debye Institute.

<sup>‡</sup> Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry.

<sup>§</sup> Present address: Gordon A. and Mary Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803.

(1) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(2) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195.

(3) Lambert, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98.

(4) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293.

(5) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342.

(6) Bianconi, P. A.; Schilling, F. C.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697.

(7) van Walree, C. A.; Cleij, T. J.; Jenneskens, L. W.; Vlietstra, E. J.; van der Laan, G. P.; de Haas, M. P.; Lutz, E. T. G. *Macromolecules* **1996**, *29*, 7362.

(8) Cleij, T. J.; Tsang, S. K. Y.; Jenneskens, L. W. *Macromolecules* **1999**, *32*, 3286.

(9) Maxka, J.; Chrusciel, J.; Sasaki, M.; Matyjaszewski, K. *Macromol. Symp.* **1994**, *77*, 79.

(10) Brough, L. F.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 3049.

(11) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, p 365.

(12) West, R. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 2, p 77.

(13) Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495.

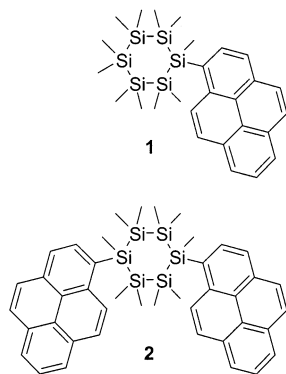
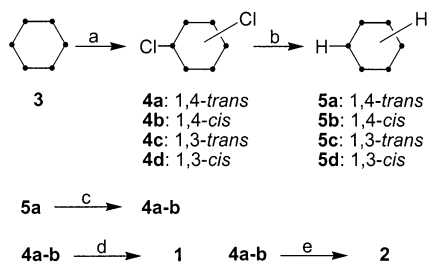
(14) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

(15) Carrell, H. L.; Donohue, J. *Acta Crystallogr.* **1972**, *B28*, 1566.

(16) Kumar, K.; Litt, M. H.; Chadha, R. K.; Drake, J. E. *Can. J. Chem.* **1987**, *65*, 437.

(17) Eibl, M.; Katzenbeisser, U.; Hengge, E. *J. Organomet. Chem.* **1993**, *444*, 29.

Chart 1

Scheme 1. Synthetic Scheme for **1** and **2**<sup>a</sup>

<sup>a</sup> Reagents: (a) SbCl<sub>5</sub>; (b) LiAlH<sub>4</sub>; (c) CHCl<sub>3</sub>; (d) 1-pyrenyllithium, methyllithium; (e) 1-pyrenyllithium. Each dot represents a silicon atom, while methyl groups have been omitted for clarity.

pure form is reported. As far as we are aware the only *cis*-cyclohexasilane hitherto described is *cis*-1,4-dichlorodecaisopropylcyclohexasilane, Cl<sub>2</sub>Si<sub>6</sub>-*i*-Pr<sub>10</sub>.<sup>18</sup> Moreover, in **2** the cyclohexasilane ring uniquely adopts boatlike conformations.<sup>19,20</sup> In a separate publication we already reported the photophysical behavior of **2**, which comprises intramolecular excimer and exciplex formation.<sup>21</sup> In addition to the synthesis and structure of **2**, its NMR spectra are discussed and some surprising stereochemical aspects of reactions of cyclohexasilanes are described. The preparation of monosubstituted (1-pyrenyl)cyclohexasilane **1**, which is of interest for reasons of comparison, is reported as well.

## Results and Discussion

**Synthesis.** The mono- and 1,4-dipyranyl-substituted compounds **1** and **2** were synthesized as outlined in Scheme 1. Dichlorodecamethylcyclohexasilane (**4**) was prepared by reaction of dodecamethylcyclohexasilane **3** with antimony pentachloride and was obtained as a mixture predominantly consisting of *cis*- and *trans*-isomers of both the 1,3- and 1,4-disubstituted products.<sup>22</sup> This mixture was converted into the corresponding

dihydrides **5** by use of lithium aluminum hydride.<sup>22</sup> A single 1,4-substituted isomer could be isolated in pure form in 25% yield upon careful crystallization from ethyl acetate. An X-ray crystal structure determination revealed that this was *trans*-dihydride **5a** (vide infra). The crystallization of **5a** is a convenient method for the isolation of a 1,4-disubstituted cyclohexasilane isomer out of the mixture obtained by chlorination of dodecamethylcyclohexasilane. Other methods rely on the conversion of sulfur<sup>23</sup> or oxygen-bridged cyclosilanes into 1,4-dichlorides<sup>23</sup> or the fractional extraction of dicarbonylcyclopentadienylferrate complexes.<sup>22,25</sup> The simplicity and fair total yield of 25% renders the procedure described here the method of choice.

Dihydride **5a** was converted back into the chlorides **4a,b** in a mild reaction with chloroform. Although only 1,4-substituted product was formed, the pure *trans*-dihydride afforded both the *trans*- and *cis*-dichlorides **4a** and **4b**. The reaction was carried out several times, and <sup>1</sup>H NMR spectroscopy and GC showed that the **4a**:**4b** ratio reproducibly was 1.2:1 to 1.5:1.<sup>26</sup> This implies that both retention and inversion of the configuration at silicon must occur, but not in equal amounts. If the first and second substitution are independent of each other, two consecutive retentions or two consecutive inversions afford **4a**, while a retention followed by an inversion (or the other way around) gives **4b**. Starting from 100% *trans*-dihydride, the maximum amount of *cis*-product to be formed is 50%, which happens in the case that retention and inversion are equally likely. If either retention or inversion is dominant, two consecutive substitutions always lead to preferential formation of the *trans*-isomer. Thus, although one is initially inclined to think that a radical reaction like that of **5a** with chloroform would be completely nonstereoselective, some extent of stereoselectivity is present. This is in line with a report on the reaction of silicon hydrides with carbon tetrachloride, which was found to proceed mostly with retention of configuration.<sup>27</sup>

Monopyrenyl compound **1** was synthesized by reaction of dichlorides **4a,b** with 1 equiv of 1-pyrenyllithium followed by treatment with methyllithium. The dipyranyl product **2** was prepared by reaction of **4a,b** with excess 1-pyrenyllithium. Very surprisingly, a crystal structure determination revealed that the isolated form of **2** was the *cis*-isomer (vide infra). Usually, *trans*-isomers are obtained, as they crystallize much easier. Pure *trans*-1,4-Ph<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub> can for instance be crystallized from a mixture of many components (in 5% yield).<sup>16</sup> Similar behavior is observed for cyclohexanes: *trans*-1,4-diphenylcyclohexane can be crystallized from a mixture of isomers, whereas *cis*-1,4-diphenylcyclohexane has to be prepared via a stereospecific pathway.<sup>28</sup>

An intriguing question is why the *cis*-isomer **2** was obtained. Although a quantitative analysis of the crude

(18) Kyushin, S.; Yamaguchi, H.; Okayasu, T.; Yagihashi, Y.; Matsumoto, H.; Goto, M. *Chem. Lett.* **1994**, 221.

(19) Throughout this article, the terms boat and boatlike conformations are used to refer to a ring structure with a Cremer and Pople puckering parameter  $\theta$  close to 90°.

(20) One of the referees informed us that the structure of *cis*-1,4-diphenyldecamethylcyclohexasilane, which also possesses a boat-type ring geometry, was presented by Kleewein, Fischer, and Stüger at the 33rd American Organosilicon meeting in Saginaw in 2000. Hitherto this work has not been published.

(21) van Walree, C. A.; Kaats-Richters, V. E. M.; Jenneskens, L. W.; Williams, R. M.; van Stokkum, I. H. M. *Chem. Phys. Lett.* **2002**, 355, 65.

(22) Hengge, E.; Eibl, M. *J. Organomet. Chem.* **1992**, 428, 335.

(23) Wojnowski, W.; Dreczewski, B.; Herman, A.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem.* **1985**, 97, 978.

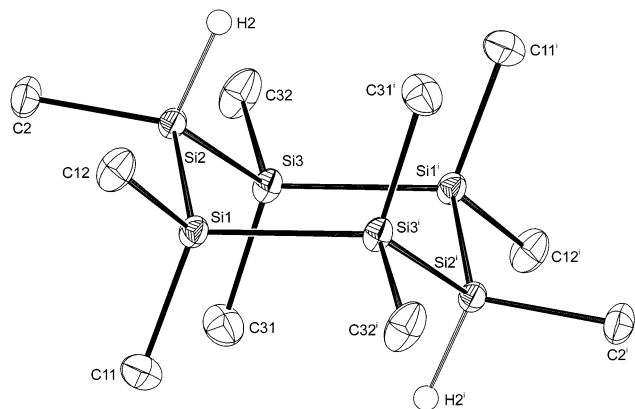
(24) Spielberger, A.; Gspaltl, P.; Siegl, H.; Hengge, E.; Gruber, K. *J. Organomet. Chem.* **1995**, 499, 241.

(25) In the articles cited, nothing is mentioned about the *cis*- or *trans*-nature of the isolated products.

(26) See the NMR Spectroscopy section for the identification of isomers **4a** and **4b**.

(27) Sakurai, H.; Murakami, M.; Kumada, M. *J. Am. Chem. Soc.* **1969**, 91, 519.

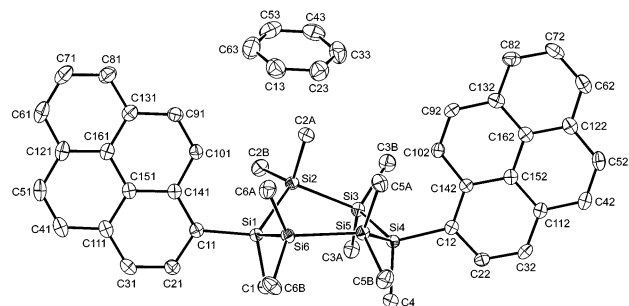
(28) Levine, S. G.; Ng, A. S. *J. Org. Chem.* **1985**, 50, 390.



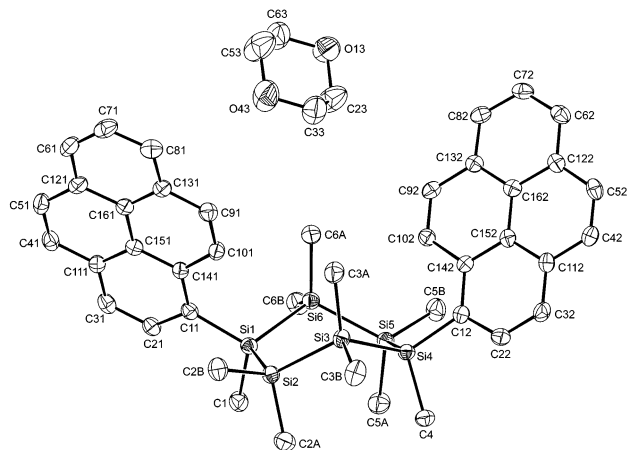
**Figure 1.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **5a**. Methyl hydrogen atoms were omitted for clarity.

product of the reaction of **4a,b** with 1-pyrenyllithium was not possible (see Experimental Section), the yield of 56% after purification indicates that the *cis*-isomer was formed in excess. To establish whether this is a more general feature, we reacted a *trans/cis*-1,4-dichloride mixture (composition 1.4:1 by GC, 1.3:1 by  $^1\text{H}$  NMR) with phenyllithium as well. Analysis of the homogeneous reaction mixture by GC revealed the presence of two products in a 2.3:1 ratio. After workup,  $^1\text{H}$  NMR of the product, which was obtained in quantitative yield, showed that it was the *cis*-isomer that was present in a 2.3-fold excess. Hereto use was made of the  $^1\text{H}$  NMR spectrum of *trans*-1,4- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$ , of which the identity has previously been established by X-ray diffraction.<sup>16</sup> Thus, in both cases the majority of *trans*-dichloride is converted into the *cis*-diaryl-substituted product. Although it is known that nucleophilic substitutions at silicon proceed with either inversion or retention of configuration,<sup>29,30</sup> it was described above that formation of more than 50% *cis*-product from an excess of *trans*-dichloride should not occur. This may imply that the two substitutions are not independent; once one substitution has taken place, the second one is directed toward the *cis*-product. An alternative explanation is that there is a difference in the inversion/retention behavior of **4a** and **4b**. Clearly, further research is required to understand the remarkable stereochemistry of reactions of cyclohexasilane derivatives.

**Crystal Structures.** As described above, (single-crystal) X-ray crystal structure determination was used to establish the nature of the isomers isolated from reactions b and e (Scheme 1). These studies showed that the *trans*-isomer **5a** (Figure 1) and the *cis*-isomer **2** (Figure 2) had been obtained. Moreover, Figure 2 demonstrates that the cyclohexasilane ring in **2** crystallized as benzene solvate adopts a screw boat structure. This is quite remarkable, since hitherto only crystal structures of chair cyclohexasilanes have been reported.<sup>20</sup> To verify whether the screw boat ring geometry is an intrinsic property and to what extent the presence of a cocrystallized benzene molecule affects the structure, the structure of **2** when crystallized as dioxane



**Figure 2.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **2** when crystallized from benzene. Hydrogen atoms were omitted for clarity.



**Figure 3.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **2** when crystallized from dioxane. Hydrogen atoms were omitted for clarity.

solvate was also determined (Figure 3). Here a boatlike ring structure is present as well. Crystal data for the three structures are given in Table 1. Selected bond lengths, bond angles, and torsion angles for **5a** are listed in Tables 1–3, while these data for the two solvates of **2** are compiled in Tables 4–6. Note that the benzene solvate of **2** is referred to as structure **2A**, while the dioxane solvate is labeled structure **2B**.

**Structure of 5a.** In its crystalline state, **5a** possesses an exact, crystallographic  $C_i$  symmetry. Consequently, the cyclohexasilane ring adopts a perfect chair conformation. This is shown by the Cremer and Pople puckering parameters  $Q = 0.9450(1)$  Å,  $\theta = 180^\circ$ , and  $\phi = 0^\circ$ ;  $Q$  denotes the total puckering amplitude, and the angles  $\theta$  and  $\phi$  locate the ring conformation on the puckering sphere surface.<sup>31</sup> In an alternative approach by Evans and Boeyens,<sup>32</sup> the ring puckering is expressed as a linear combination of the primitive forms  $E_{2u} \cos$  (boat),  $E_{2u} \sin$  (twist boat), and  $B_{2g}$  (chair). In **5a** the coefficients are 0, 0, and 1, implying a 100% chair conformation. With the angles of the Si–H bonds with the normal to the ring plane being  $6.6(4)^\circ$ , the hydrogen atoms H2 and H2' are in an axial position. All methyl groups occupy either an equatorial or axial position.

The structure of **5a** is similar to that of  $\text{Si}_6\text{Me}_{12}$ ,<sup>15</sup> but differs in the details. In this connection it should be noted that the atomic positions in **5a** were determined at the higher resolution of  $(\sin\theta/\lambda)_{\text{max}} = 1.09$  Å<sup>-1</sup>, as

(29) Barton, T. J.; Boudjouk, P. In *Silicon-Based Polymer Science*; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; Vol. 224, p 3.

(30) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17.

(31) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

(32) Evans, D. G.; Boeyens, J. C. A. *Acta Crystallogr.* **1989**, *B45*, 581.



**Table 1. Crystallographic Data for 5a and 2 Crystallized from Benzene (2A) and Dioxane (2B)**

	5a	2A	2B
formula	C <sub>10</sub> H <sub>32</sub> Si <sub>6</sub>	C <sub>42</sub> H <sub>48</sub> Si <sub>6</sub> ·C <sub>6</sub> H <sub>6</sub>	C <sub>42</sub> H <sub>48</sub> Si <sub>6</sub> ·C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>
M <sub>r</sub>	320.90	799.45	809.45
cryst size [mm <sup>3</sup> ]	0.50 × 0.30 × 0.12	0.54 × 0.12 × 0.12	0.48 × 0.06 × 0.03
cryst color	colorless	colorless	colorless
temp [K]	100(2)	125(2)	150(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)
a [Å]	6.6648(1)	20.8757(5)	12.3565(4)
b [Å]	15.8086(2)	10.0414(2)	23.1823(7)
c [Å]	11.0109(1)	23.4955(6)	15.4010(4)
β [deg]	115.8371(7)	115.4781(8)	93.8309(16)
V [Å <sup>3</sup> ]	1044.15(2)	4446.18(18)	4401.8(2)
Z	2	4	4
ρ [g/cm <sup>3</sup> ]	1.021	1.194	1.221
μ [mm <sup>-1</sup> ]	0.38	0.22	0.23
(sin θ/λ) <sub>max</sub> [Å <sup>-1</sup> ]	1.09	0.61	0.53
no. of reflns (measd/unique)	107 086/11 081	65 227/8270	43 985/5365
abs corr	PLATON (MULABS)	PLATON (MULABS)	PLATON (MULABS)
transmn	0.89–0.98	0.90–1.09	0.91–1.13
no. of params	137	497	497
R1/wR2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0276/0.0660	0.0382/0.0807	0.0390/0.0914
R1/wR2 [all reflns]	0.0388/0.0710	0.0581/0.0881	0.0586/0.1000
S	1.043	1.017	1.017
res dens [e/Å <sup>3</sup> ]	–0.46/0.34	–0.27/0.36	–0.22/0.38

**Table 2. Selected Bond Lengths (Å) for 5a with SD's in Parentheses**

Si1–Si2	2.34017(14)	Si1–Si3 <sup>a</sup>	2.34306(14)	Si1–C11	1.8875(4)
Si1–C12	1.8893(4)	Si2–C2	1.8899(4)	Si2–Si3	2.34294(14)
Si3–C31	1.8863(4)	Si3–C32	1.8865(4)	Si2–H2 <sup>b</sup>	1.423(9)

<sup>a</sup> Symmetry operation 1–*x*, 1–*y*, 1–*z*. <sup>b</sup> Hydrogen atoms of **5a** were refined freely with isotropic displacement parameters.

**Table 3. Selected Bond Angles (deg) for 5a with SD's in Parentheses**

Si2–Si1–Si3 <sup>a</sup>	107.121(5)	Si2–Si1–C11	111.911(18)
Si2–Si1–C12	108.430(15)	Si3 <sup>a</sup> –Si1–C11	111.015(17)
Si3 <sup>a</sup> –Si1–C12	109.707(16)	C11–Si1–C12	108.61(2)
Si1–Si2–C2	111.972(15)	Si1–Si2–Si3	113.373(5)
C2–Si2–Si3	112.156(14)	Si1 <sup>a</sup> –Si3–C31	109.148(16)
Si1 <sup>a</sup> –Si3–C32	110.720(17)	Si1 <sup>a</sup> –Si3–Si2	108.559(5)
C31–Si3–C32	108.27(3)	C31–Si3–Si2	111.312(15)
C32–Si3–Si2	108.834(16)	Si1–Si2–H2 <sup>b</sup>	106.3(4)
C2–Si2–H2 <sup>b</sup>	106.6(4)	H2 <sup>b</sup> –Si2–Si3	105.9(4)

<sup>a</sup> Symmetry operation 1–*x*, 1–*y*, 1–*z*. <sup>b</sup> Hydrogen atoms of **5a** were refined freely with isotropic displacement parameters.

compared to (sin θ/λ)<sub>max</sub> = 0.58 Å<sup>-1</sup> for Si<sub>6</sub>Me<sub>12</sub>. The Si–Si bonds lengths of 2.34017(14)–2.34306(14) Å in **5a** are within the standard deviation equal to the distances of 2.332(1)–2.342(1) Å in Si<sub>6</sub>Me<sub>12</sub>. There is a small variation in the ring bond angles in **5a**. They are 113.373(5)° (Si1–Si2–Si3), 107.121(5)°, or 108.559(5)°. For Si<sub>6</sub>Me<sub>12</sub> much more uniform Si–Si–Si bond angles in the range 111.64(5)–112.40(5)° were found. Apparently, the presence of the hydrogen atom somewhat widens the Si–Si–Si bond angle. In addition, the ring puckering amplitude in **5a** of *Q* = 0.9450(1) is significantly larger than that in Si<sub>6</sub>Me<sub>12</sub> (*Q* = 0.8326(11)), which may be the consequence of thermal motion in the room-temperature structure of Si<sub>6</sub>Me<sub>12</sub> (the structure of **5a** was determined at 100 K). The observation made for Si<sub>6</sub>Me<sub>12</sub> that equatorial Si–Me bonds are longer than axial Si–Me bonds<sup>15</sup> is not valid for **5a** and might again result from thermal motion in the room-temperature structure. In **5a**, the Si–C bond lengths are all equal within standard deviations (1.8875(4)–1.8899(4) Å).

**Structure of 2.** In structure **2A**, the screw boat conformation of the silicon ring is characterized by the Cremer and Pople puckering parameters *Q* = 1.0930(7) Å, *θ* = 105.11(4)°, and *φ* = 211.30(4)°. Description

as a linear combination of E<sub>2u</sub> cos (boat), E<sub>2u</sub> sin (twist boat), and B<sub>2g</sub> (chair) forms results in coefficients of 0.04, 0.75, and 0.21, respectively. The two pyrenyl substituents adopt an equatorial position, the angles of the Si1–C11 and Si4–C12 bonds with the normal to the silicon ring plane being 89.95(6)° and 70.25(6)°, respectively. Most methyl groups are found in either an equatorial or an axial position, but the C3B, C5B, C6A, and C6B methyl groups occupy a bisectonal position.

Si–Si bond lengths range from 2.3440(8) to 2.3728(7) Å. They are somewhat longer than in Si<sub>6</sub>Me<sub>12</sub> (2.332(1)–2.342(1) Å)<sup>15</sup> and **5a** (2.34017(14)–2.34306(14) Å) but similar to bond lengths in phenyl-substituted cyclohexasilanes.<sup>9,12,16</sup> It is however noteworthy that the Si3–Si4, Si4–Si5, and Si5–Si6 bonds are longer than the other Si–Si bond lengths. There is also a quite large variation in Si–Si–Si bond angles. Whereas the Si2–Si1–Si6 angle of 106.78(3)° is relatively small, Si–Si–Si bond angles involving both Si4 and Si5 are as large as 117.54(3)° and 115.58(3)°. This is substantially larger than the 110–111° bond angle usually found in other cyclohexasilanes<sup>15,16</sup> and cyclohexanes.<sup>33</sup> Hence, the local structure of the silicon ring at Si4 and Si5 is subject to deviations from standard Si–Si bond lengths and Si–Si–Si bond angles. At first sight, this may be thought to be a consequence of the small Si2–Si3–Si4–Si5 dihedral angle of –8.77(4)°. However, in structure **2B** (vide infra) dihedral angles of the same order of magnitude occur without large distortion of bond lengths and angles, indicating that the structure of silicon ring systems is not necessarily perturbed by the presence of small dihedral angles.

As the torsion angle C4–Si4–C12–C22 is –4.07(18)°, the pyrenyl substituent attached to Si4 is in an eclipsed-

(33) Leong, M. K.; Mastryukov, V. S.; Boggs, J. E. *J. Phys. Chem.* **1994**, *98*, 6961.

**Table 4. Selected Torsion Angles (deg) for 5a with SD's in Parentheses**

Si3 <sup>a</sup> -Si1-Si2-C2	-171.605(15)	Si3 <sup>a</sup> -Si1-Si2-Si3	60.269(7)
C11-Si1-Si2-Si3	-61.626(18)	C12-Si1-Si2-Si3	178.600(17)
Si2 <sup>a</sup> -Si1 <sup>a</sup> -Si3-C31	-64.27(2)	Si2-Si1-Si3 <sup>a</sup> -C32 <sup>a</sup>	-176.64(2)
Si2 <sup>a</sup> -Si1 <sup>a</sup> -Si3-Si2	57.23(1)	C11-Si1-Si3 <sup>a</sup> -Si2 <sup>a</sup>	65.23(2)
C12 <sup>a</sup> -Si1 <sup>a</sup> -Si3-Si2	174.73(2)	Si1-Si2-Si3-Si1 <sup>a</sup>	-61.092(7)
Si1-Si2-Si3-C31	59.066(18)	Si1-Si2-Si3-C32	178.32(2)
C2-Si2-Si3-Si1 <sup>a</sup>	170.877(15)	Si3 <sup>a</sup> -Si1-Si2-H2 <sup>b</sup>	-55.6(4)
C11-Si1-Si2-H2 <sup>b</sup>	-177.5(4)	C12-Si1-Si2-H2 <sup>b</sup>	62.7(4)
H2 <sup>b</sup> -Si2-Si3-Si1 <sup>a</sup>	55.1(4)	H2 <sup>b</sup> -Si2-Si3-C31	175.2(4)
H2 <sup>b</sup> -Si2-Si3-C32	-65.5(4)		

<sup>a</sup> Symmetry operation 1-x, 1-y, 1-z. <sup>b</sup> Hydrogen atoms of **5a** were refined freely with isotropic displacement parameters.

**Table 5. Selected Bond Lengths (Å) for 2 in Solvates 2A and 2B with SD's in Parentheses**

	2A	2B
Si1-Si2	2.3525(8)	2.3642(11)
Si1-C11	1.907(2)	1.897(3)
Si2-C2B	1.881(2)	1.887(3)
Si3-C3B	1.891(2)	1.888(3)
Si4-C12	1.902(2)	1.898(3)
Si5-C5B	1.893(2)	1.888(3)
Si1-Si6	2.3494(8)	2.3621(12)
Si2-Si3	2.3440(8)	2.3532(11)
Si3-Si4	2.3728(7)	2.3584(11)
Si4-Si5	2.3652(8)	2.3687(11)
Si5-Si6	2.3679(8)	2.3566(11)
Si6-C6A	1.880(2)	1.890(3)
Si1-C1	1.891(2)	1.891(3)
Si2-C2A	1.895(2)	1.890(3)
Si3-C3A	1.887(2)	1.883(3)
Si4-C4	1.892(2)	1.892(3)
Si5-C5A	1.884(2)	1.883(3)
Si6-C6B	1.884(2)	1.881(3)

**Table 6. Selected Bond Angles (deg) for 2 in Solvates 2A and 2B with SD's in Parentheses**

	2A	2B
Si2-Si1-Si6	106.78(3)	113.79(4)
Si6-Si1-C1	111.26(7)	106.09(10)
Si1-Si2-Si3	109.23(3)	114.50(4)
Si3-Si2-C2A	103.50(7)	106.02(10)
Si2-Si3-Si4	110.00(3)	108.77(4)
Si4-Si3-C3A	109.26(7)	112.23(11)
Si3-Si4-Si5	117.54(3)	113.65(4)
Si5-Si4-C4	103.88(7)	106.51(10)
Si4-Si5-Si6	115.58(3)	114.51(4)
Si6-Si5-C5A	107.64(7)	106.37(10)
Si1-Si6-Si5	112.85(3)	108.54(4)
Si5-Si6-C6A	108.82(7)	114.21(10)
Si1-C11-C21	118.48(15)	118.6(2)
Si4-C12-C22	119.55(15)	119.8(2)
Si2-Si1-C1	105.98(7)	106.72(10)
Si6-Si1-C11	109.67(6)	111.31(9)
Si1-Si2-C2A	112.98(7)	107.53(10)
Si3-Si2-C2B	109.36(7)	111.61(10)
Si2-Si3-C3A	111.05(7)	114.04(10)
Si4-Si3-C3B	113.68(7)	107.39(11)
Si3-Si4-C4	106.27(7)	106.94(10)
Si5-Si4-C12	108.99(6)	112.03(9)
Si4-Si5-C5A	113.87(7)	106.40(11)
Si6-Si5-C5B	108.43(8)	110.87(10)
Si1-Si6-C6A	109.04(8)	113.57(10)
Si5-Si6-C6B	108.58(8)	107.10(11)
Si1-C11-C141	124.45(15)	124.3(2)
Si4-C12-C142	122.94(14)	123.2(2)
Si2-Si1-C11	117.68(6)	111.78(9)
C1-Si1-C11	105.43(9)	106.61(13)
Si1-Si2-C2B	110.78(7)	110.33(10)
C2A-Si2-C2B	110.70(10)	106.33(14)
Si2-Si3-C3B	105.69(7)	106.17(11)
C3A-Si3-C3B	107.11(10)	107.85(14)
Si3-Si4-C12	112.86(6)	110.50(9)
C4-Si4-C12	106.28(9)	106.76(13)
Si4-Si5-C5B	103.29(8)	111.76(10)
C5A-Si5-C5B	107.59(10)	106.34(15)
Si1-Si6-C6B	109.44(7)	106.56(10)
C6A-Si6-C6B	107.98(11)	106.36(14)
C21-C11-C141	117.07(18)	117.1(3)
C22-C12-C142	117.51(17)	117.0(3)

like arrangement with the C4 methyl group. Hereby the orientation of the pyrenyl group is such that the hydrogen at C22 is in the vicinity of the C4 methyl group. Geometrical inspection shows that a 180° rotation of the pyrenyl group would lead to a more unfavorable situation in which the pyrenyl hydrogen at C102 conflicts with the C4 methyl group. Owing to the eclipsed-like arrangement of the pyrenyl group, the position of C102 is nearly equidistant from the C3B and C5A methyl groups; the C102-C3B and C102-C5A distances are 3.343(3) and 3.411(3) Å, respectively.

The pyrenyl substituent at Si1 is essentially coplanar with the pyrenyl substituent at Si4, the interplanar angle being 3.83(3)°. The screw boat conformation of the silicon ring then results in a torsion angle C1-Si1-C11-C21 of 26.25(18)°, so that the arrangement with the C1 methyl group is not eclipsed. Another consequence is the asymmetry in the distances of C101 to the methyl groups containing C2A and C6A of 3.569(3) and 3.769(3) Å, respectively. The short C101-C2A separation finds expression in five close contacts between C101 or H101 and Si1, Si2, C2A, or H2C. For instance, the Si2-H101 distance is 2.80 Å, 0.50 Å less than the sum of the van der Waals radii. Only one very close contact involving H102 or C102 (viz., H102-Si4) is found. Although also a close contact between C4 and H22 is present, there seems to be more space for the pyrenyl group near the distorted part of the silicon ring than for the pyrenyl group in whose vicinity Si-Si bond lengths and Si-Si-Si bond angles are of usual magnitude. It therefore appears that **2** has the choice to either contain some very close contacts or adopt an irregular ring conformation in order to accommodate the large pyrenyl substituents.

The molecular structure of **2** crystallized as dioxane solvate, structure **2B**, is depicted in Figure 3. A pseudo C<sub>2</sub>-axis is present which percolates through the center of the silicon ring and is oriented perpendicular to the ring plane. Cremer and Pople puckering parameters for the silicon ring are Q = 1.13(1) Å, θ = 89.9(1)°, and φ = 287.54(4)°. The respective coefficients for the E<sub>2u</sub> cos (boat), E<sub>2u</sub> sin (twist boat), and B<sub>2g</sub> (chair) primitive forms are 0.582, 0.417, and 0.001. Thus, the structure of the silicon ring in structure **2B** is approximately midway between a boat and a twist boat geometry. Though not identical to the ring structure in **2A**, the structure is definitely boatlike. The occurrence of a boatlike ring structure in two different solvates of **2** strongly suggests that this is the preferred conformation

**Table 7. Selected Torsion Angles (deg) for 2 in Solvates 2A and 2B with SD's in Parentheses**

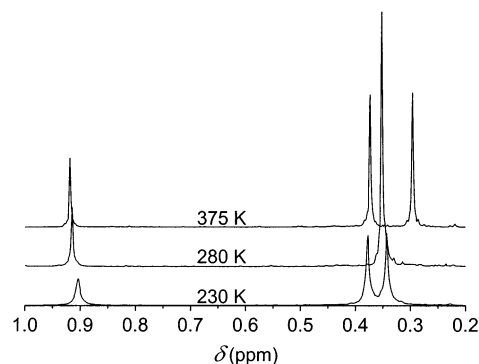
	2A	2B
Si6–Si1–Si2–Si3	76.64(3)	13.46(6)
C1–Si1–Si2–C2A	–156.68(10)	12.60(15)
Si6–Si1–C11–C21	–93.63(15)	107.9(2)
C1–Si1–C11–C21	26.25(18)	–7.4(3)
Si1–Si2–Si3–Si4	–47.44(4)	–57.59(6)
Si3–Si4–Si5–Si6	38.99(4)	13.62(6)
C4–Si4–Si5–C5A	156.59(10)	13.90(15)
Si4–Si5–Si6–Si1	–10.22(4)	–57.58(5)
C1–Si1–Si2–Si3	–42.06(8)	130.12(11)
Si2–Si1–C11–C21	144.11(14)	–123.6(2)
Si6–Si1–C11–C141	86.08(17)	–72.7(2)
C1–Si1–C11–C141	–154.04(17)	172.0(2)
Si2–Si3–Si4–Si5	–8.77(4)	42.66(6)
C4–Si4–Si5–Si6	–78.02(7)	131.11(10)
C4–Si4–C12–C22	–4.07(18)	–12.2(3)

of the hexasilane ring in **2**. It is noteworthy that in *cis*-Cl<sub>2</sub>Si<sub>6</sub>-*i*-Pr<sub>10</sub> a chair hexasilane ring is found.<sup>18</sup>

In contrast to structure **2A**, in structure **2B** the pyrenyl substituents occupy a bisectonal position as indicated by the angles of the Si1–C11 and Si4–C12 bonds with the ring plane normal of 57.42(9)° and 56.43(9)°, respectively. All Si–Me groups adopt either an equatorial or axial position. Si–Si bond lengths (2.3532(11)–2.3687(11) Å) and Si–Si–Si bond angles (108.54(4)–114.51(4)°) are much more uniform than in structure **2A**.

In common with structure **2A**, the pyrenyl substituents are oriented with the C21/22 and H21/22 atoms located in the vicinity of the C1 and C4 methyl groups. The C1–Si1–C11–C21 and C4–Si4–C12–C22 torsion angles are small, –7.4(3)° and –12.2(3)°, respectively, suggesting that the pyrenyl substituents preferably occupy the plane set up by the Si–pyrenyl and the adjacent Si–Me bonds and that there is not much rotational freedom for the pyrenyl groups. The two pyrenyl groups are not situated in a single plane, as was found for structure **2A**. Very short contacts are present between H101–Si1, H101–Si2, H102–Si4, C102–Si5, H102–Si5, H21–C1, and H22–C4. This is another illustration of what was deduced already above: a ring structure with regular bond lengths and bond angles leads to close contacts with the pyrenyl substituents.

A conspicuous aspect of structure **2B** is that the Si3–C3A and Si6–C6A bonds are virtually located in a single plane; the C3A–Si3–Si6–C6A torsion angle is only 5.96(16)°. The shortest distance between hydrogen atoms of the flagpole methyl groups amounts to 2.41 Å (for H3A and H6A), which is equal to the sum of the contact radii of two hydrogen atoms (2.40 Å). Flagpole methyl groups thus can be easily accommodated in the cyclohexasilane geometry of structure **2B**. The situation is different for structure **2A**. The shortest distance between C1 methyl and C4 methyl hydrogen atoms, H1B–H4B, is 2.26 Å, significantly shorter than the sum of the contact radii. Here the axial methyl groups are pushed toward each other as a consequence of the equatorial position of the pyrenyl groups. This leads to the conclusion that the occurrence of a near-boat structure for **2B** is facilitated by the bisectonal position of the pyrenyl substituents. In **2** there seems to be a balance between the tendency of the pyrenyl groups to occupy an equatorial position and the tendency of the silicon ring to adopt a regular structure.

**Figure 4.** Si–Me region of the <sup>1</sup>H NMR spectra of **2** in toluene-*d*<sub>8</sub> at 230, 280, and 375 K.

A point to be considered is to what extent the molecular structure of **2** in both **2A** and **2B** is dictated by the presence of cocrystallized solvent molecules. One can imagine that the benzene and dioxane molecules have a strong effect on the molecular structure of **2** via intermolecular (solvent-**2**) forces. However, in both structures no evidence is found for significant intermolecular interactions, e.g., in the form of short contacts or by the mode of packing. Moreover, the solvent molecules are always positioned between several molecules so that they rather seem to be a factor of interest for the intermolecular packing than for the molecular structure. They may well fill the voids present in the structure.

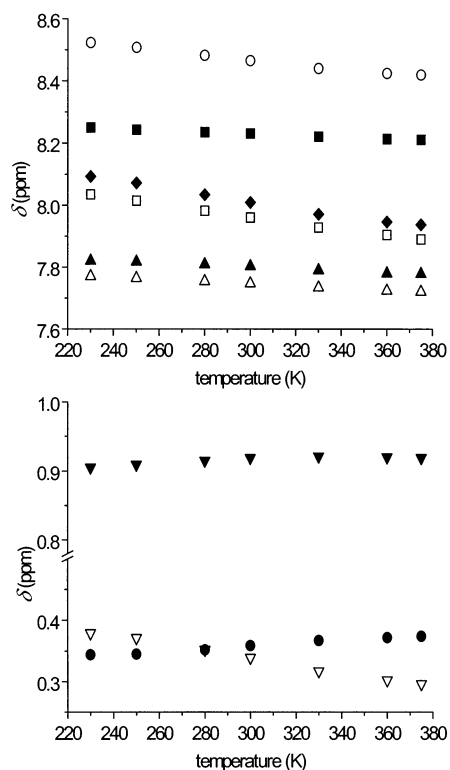
**NMR Spectroscopy.** NMR spectroscopy was applied to obtain information on the conformational behavior of mono- and dipyrenyl-substituted compounds **1** and **2** in solution. In both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** three signals are observed for the methyl groups attached to the silicon ring. One stems from the C1/C4 methyl groups; in CDCl<sub>3</sub> it is found at 1.01 ppm in <sup>1</sup>H NMR and at –4.4 ppm in <sup>13</sup>C NMR (see also Figure 4 and the Experimental Section). The other two signals originate from the C2/3/5/6 methyl groups. The presence of three methyl signals in <sup>1</sup>H and <sup>13</sup>C NMR indicates that rapid interconversion between two or more conformations takes place, leading to average chemical shift values for three pairs of interconverting methyl groups. The occurrence of rapid interconversion is supported by the known highly flexible character of cyclohexasilanes.<sup>33,34</sup> In fact, from time-resolved fluorescence studies it was inferred that the silicon ring in **2** undergoes conformational changes on the 10<sup>–7</sup>–10<sup>–8</sup> s time scale.<sup>21</sup>

For monopyrenyl compound **1** separate <sup>1</sup>H signals are observed for the two methyl groups at Si4.<sup>35</sup> In addition, of the methyl groups at Si2/6 and Si3/5 one set has a distinctly separate chemical shift at 0.37 ppm. In the <sup>13</sup>C NMR spectrum, six different signals are found for the Si–Me signals (an expected seventh one most probably overlaps with one of the other signals). All these data imply that axial and equatorial methyl groups do not interconvert on the NMR time scale and that this silicon ring occurs in a single conformation. This is easily rationalized by a preference

(34) Casarini, N.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1998**, *63*, 9125.

(35) For **1**, an atom-numbering system analogous to that of **2** (Figure 2) has been adopted. The silicon atom bearing the pyrenyl substituent is Si1. In the description of NMR spectra, the standard numbering of pyrenyl hydrogen atoms (H1–H10) is used for both **1** and **2**.





**Figure 5.** Temperature dependence of  $^1\text{H}$  NMR signals of **2** in toluene- $d_8$ . The top and bottom panels display the pyrenyl and Si-Me H shifts, respectively. Legend:  $\circ$  H10,  $\blacksquare$  H2,  $\blacklozenge$  H9,  $\square$  H3,  $\blacktriangle$  H4/5,  $\triangle$  H7,  $\blacktriangledown$  Si1/4-Me,  $\triangledown$  Si2/3/5/6-Me,  $\bullet$  Si2/3/5/6-Me.

of the pyrenyl group for an equatorial position. The conformation with an axial pyrenyl substituent must be higher in energy.

More insight into the structure of **2** in solution was obtained from temperature-dependent  $^1\text{H}$  NMR spectroscopy in toluene- $d_8$ . Spectra were recorded in the temperature range 230–375 K (Figures 4 and 5). At 230 K, the signals in the Si-Me region are broad in comparison to signals at higher temperatures. Since the solvent and pyrenyl signals were not found to be as strongly broadened as the Si-Me signals,<sup>36</sup> this broadening is possibly caused by decoalescence. In view of the symmetric band shape, this decoalescence probably involves the interconversion between two chair conformations, which are isoenergetic since they both carry an equatorial and an axial pyrenyl group.

Upon going from 230 K to higher temperatures, signals undergo a continuous shift. In the Si-Me spectral region, the C1/4 methyl signal very slowly shifts to higher  $\delta$ -values with increasing temperature. The shift difference between 230 and 375 K is small, 0.015 ppm. The positions of the C2/3/5/6 methyl singlets are much more sensitive to temperature. At 230 K,  $\delta$ -values are 0.379 and 0.344 ppm. Upon raising the temperature, the former signal shifts to lower  $\delta$ -values, whereas the latter shifts to higher  $\delta$ -values. This has the conse-

quence that at 280 K the two signals coincide, at 0.35 ppm. Above 280 K the signals continue to shift in opposite directions. At 375 K, the final chemical shifts are 0.296 and 0.374 ppm. It is clear that the larger change with temperature is found for the former signal.

This temperature behavior is rationalized as arising from a shift of an equilibrium between two (or more) conformations which rapidly interconvert and are not equal in energy. This implies that **2** cannot exclusively occur in a chair conformation because the two possible chair forms are degenerate. Consequently, at least one nonchair conformation of the cyclohexasilane ring must be involved in the equilibrium. The energy of this nonchair conformation cannot be very much higher than that of a chair, since there must be sufficient amounts of it present to cause the observed temperature-induced shifts. It is most probable that it concerns a boatlike conformation such as found in the solid state. For cyclohexasilane  $\text{Si}_6\text{H}_{12}$  electron diffraction studies<sup>37</sup> and ab initio calculations at the MP2/6-31G\* level<sup>33</sup> have indicated that the twist boat ( $\theta = 90^\circ$ ,  $\phi = n \times 60 + 30^\circ$ ) and boat forms are only 1.3–1.9 and 2.1–2.5 kcal·mol<sup>-1</sup> above the ground state, respectively. Although it is not known how the presence of methyl groups instead of hydrogen atoms affects the energies of the different conformations, the loss of energy upon adaptation of a boatlike geometry in **2** must be so small that, despite the chair form being lower in energy, a boatlike conformation is present in significant amounts at ambient temperatures. We note that boatlike geometries of **2** may be particularly stable since the large pyrenyl substituents adopt an equatorial position. Thus, the temperature-dependent NMR data show that above 230 K **2** is subject to a conformational equilibrium involving two chair forms and a boatlike structure. This strongly suggests that the X-ray structures of **2** are not the result of solid-state phenomena such as packing effects, but represent real low-energy conformations.

Additional evidence for the existence of a dynamic equilibrium between different ring forms is obtained from temperature-induced chemical shift changes of some diagnostic pyrenyl hydrogen atoms (7.6–8.6 ppm region, Figure 5).<sup>38</sup> It is evident that the signals of all hydrogen atoms shift to lower  $\delta$ -values with increasing temperature. However, the effect is small for H2, H4/H5, and H7 (ca. 0.05 ppm difference between 230 and 375 K), whereas H3, H9, and H10 undergo the largest changes: the shift difference between the 230 and 375 K spectra is 0.15 ppm for H3 and H9 and 0.10 ppm for H10. Since the H3, H9, and H10 atoms are the ones closest to the silicon ring, it is likely that their  $\delta$ -values shift as a result of local through-bond or through-space effects induced by silicon ring geometry changes. In the case of dipyrenyl compounds, one should not overlook the possibility that ring current effects are a factor of importance for the magnetic shielding.<sup>39,40</sup>

(37) Smith, Z.; Almenningen, A.; Hengge, E.; Kovar, D. *J. Am. Chem. Soc.* **1982**, *104*, 4362.

(38) The pyrenyl chemical shifts were assigned with the aid of NMR spectra of linear 1-pyrenyl-substituted oligosilanes: Gelan, J.; Adriaensens, P.; Vanderzande, D.; Declercq, D.; Hermans, E.; De Schryver, F. C. *J. Am. Chem. Soc.* **1994**, *116*, 7877.

(39) Reyniers, P.; Kühnle, W.; Zachariasse, K. *J. Phys. Chem.* **1990**, *94*, 4073.

(40) Declercq, D.; Delbeke, P.; De Schryver, F. C.; Van Meervelt, L.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 5702.

(36) Due to experimental conditions the signals of the toluene solvent and the pyrenyl groups were subject to line broadening at 230 K, which was however not as strong as that observed for the Si-Me signals. For instance, the widths at half-height of the 0.9 ppm signal were 1.1 and 2.7 Hz at 280 and 230 K, respectively, while those of the pyrenyl H10 signal amounted to 1.1 and 1.7 Hz at these temperatures. The width of the central toluene line near 2.1 ppm was 0.6 Hz at 280 K and 1.0 Hz at 230 K.

However, the spatial separation between the pyrenyl groups, as measured by the C101–C102 distance, amounts to 7.6 Å in structure **2A** and 5.8 Å in structure **2B**. This suggests that for the pyrenyl signals ring current effects imposed by the other pyrenyl unit can be neglected. This is supported by the observation of a relatively large effect for H3, which is situated at a large distance from the other pyrenyl moiety.

Another NMR related point is that in order to describe the stereochemistry of reactions c and e in Scheme 1 correctly, the long-standing question<sup>41</sup> of the assignment of the <sup>1</sup>H NMR spectra of the *trans*- and *cis*-substituted dichlorides **4a** and **4b** had to be solved. In the <sup>1</sup>H NMR spectrum of the mixture obtained from the reaction of **5a** with chloroform, two sets of signals appear. In benzene-*d*<sub>6</sub>, the methyl singlets of the isomer formed in the largest amount are situated at 0.58 (SiClMe), 0.27 (SiMe<sub>2</sub>), and 0.24 (SiMe<sub>2</sub>) ppm, while the resonances of the other isomer are found at 0.54, 0.39, and 0.13 ppm. In a NOESY experiment, a distinct cross correlation was found between the signal at 0.58 ppm and the signals at 0.27 and 0.24 ppm. The resolution was not sufficient to establish whether the correlation with either of these signals was the stronger. In contrast, no clear correlation between the 0.54 ppm signal and any of the 0.39 and 0.13 ppm signals was detected. Because of the short distance, the strongest NOEs are expected for axial methyl groups at the same face of the silicon ring. Assuming that the *trans*- and *cis*-isomers **4a** and **4b** adopt a chair conformation with two equatorial chlorine substituents and one equatorial and one axial substituent, respectively (which is the situation observed for *trans*- and *cis*-Cl<sub>2</sub>Si<sub>6</sub>-*i*-Pr<sub>10</sub> in the solid state<sup>18</sup>), the NOE must be present in the *trans*-isomer. Hence, the signals at 0.58, 0.27, and 0.24 ppm originate from **4a**, while the peaks at 0.54, 0.39, and 0.13 ppm belong to the spectrum of **4b**. Note that in the spectrum of **4a** the separation between the SiMe<sub>2</sub> singlets is much smaller than in the spectrum of **4b**. This lends support to the NOESY-based assignment, since also for *trans*-Cl<sub>2</sub>Si<sub>6</sub>-*i*-Pr<sub>10</sub> the Si-*i*-Pr<sub>2</sub> proton shifts are situated at a smaller separation than for *cis*-Cl<sub>2</sub>Si<sub>6</sub>-*i*-Pr<sub>10</sub>.<sup>18</sup>

For *trans*-dihydride **5a** the two SiMe<sub>2</sub> signals are also positioned closely together, viz., at 0.29 and 0.26 ppm. However, for the aryl-substituted cyclohexasilanes the smaller chemical shift difference is observed for the *cis*-isomers. In CDCl<sub>3</sub> signals of *cis*-Ph<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub> are situated at 0.28 and 0.25 ppm, while for the *trans*-isomer they are found at 0.36 and 0.23 ppm. For **2** in benzene-*d*<sub>6</sub>, the signals even coincide at room temperature. At present, it is not clear which factors determine the difference between the <sup>1</sup>H NMR spectra of *cis*- and *trans*-isomers.

## Conclusions

In this contribution the synthesis of the *cis*-1,4-disubstituted cyclohexasilane **2** is reported. The synthesis and isolation of this compound are possible because of the selective crystallization of *trans*-1,4-dihydride **5a** from a mixture of isomers and the stereochemistry of the reaction of **4a,b** with aryllithium compounds, which favors the formation of *cis*-product

from starting material that consists mostly of the *trans*-isomer.

From two different solvents *cis*-dipyrenyl compound **2** crystallizes in a structure in which the cyclohexasilane ring adopts a unique boatlike conformation. According to NMR data, a boatlike conformation also is present in solution. The preference for **2** for a boatlike ring structure is probably caused by the tendency of the pyrenyl substituents to occupy an equatorial or bisectonal position and the floppiness of the silicon ring.

## Experimental Section

**General Procedures.** Reactions involving organolithium reagents and/or silyl chlorides were conducted in a nitrogen or argon atmosphere using standard Schlenk techniques. Starting materials and reagents were obtained from commercial sources and used as received unless stated otherwise. Solvents generally were distilled before use; diethyl ether and THF were distilled from sodium-benzophenone, while chloroform was distilled from calcium chloride. Column chromatography was performed on Biobeads SX1 (Biorad) using methylene chloride as eluent.

NMR spectra were obtained on Bruker AC 300 or Varian Unity Inova spectrometers, both of them operating at 300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C, and 60 MHz for <sup>29</sup>Si NMR. <sup>29</sup>Si NMR spectra were recorded with a proton decoupled inverse gated pulse sequence or via a DEPT sequence. DEPT spectra were obtained with a pulse angle of 27° for the final proton pulse, and the <sup>3</sup>J<sub>Si-H</sub> was set at 7 Hz. The NOESY experiment was performed with a relaxation delay of 6 s and a mixing time of 0.75 s. All NMR shifts are given in ppm relative to TMS; coupling constants are given in Hz. Infrared spectra were recorded using a Mattson Galaxy Series FTIR 5000 or a Perkin-Elmer 283 instrument using KBr pellets. GC–MS spectra were collected on a ATI Unicam Automass System 2 quadrupole mass spectrometer. For gas chromatography a Varian 3400 chromatograph equipped with a DB5 capillary column and a FID detector was used. Elemental analysis was carried out at Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

**Synthesis. Dichlorodecamethylcyclohexasilanes (4a–d).** This mixture of compounds was synthesized from dodecamethylcyclohexasilane **3**<sup>42</sup> and antimony pentachloride following the procedure described by Hengge and Eibl.<sup>22</sup> Antimony compounds were removed by Kugelrohr distillation. The fraction boiling at 90 °C at 0.05 mmHg was collected as the product. Yield: 90% of a mixture of predominantly 1,3- and 1,4-disubstituted isomers **4a–d**. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.66 (s, ClSiMe, **4c/4d**), 0.62 (s, ClSiMe, **4a**), 0.60 (s, ClSiMe, **4b**), 0.59 (s, ClSiMe, **4c/4d**), 0.34 (s, SiMe<sub>2</sub>, **4b**), 0.28 (2 × s, SiMe<sub>2</sub>, **4a**), 0.22 (s, SiMe<sub>2</sub>, **4b**). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ +0.31, –0.35 (both ClSiMe), –5.96, –6.22, –6.53, –6.68, –6.78, –7.21 (all SiMe<sub>2</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ +16.7, +16.4, +16.2, +15.9 (all SiCl), –38.9, –39.3, –39.6, –39.9 (all SiMe<sub>2</sub>). In the description of the NMR spectra only main peaks are given.

***trans*-1,4-Dihydrodecamethylcyclohexasilane (5a).** In a dry argon atmosphere, lithium aluminum hydride (1.50 g, 39.5 mmol) was added in small portions to an ice-cooled solution of **4a–d** (12.71 g, 32.62 mmol) in 250 mL of diethyl ether.<sup>22</sup> After stirring overnight at room temperature GC revealed the absence of the starting compounds. The reaction mixture was poured into 1 M sulfuric acid kept at 0 °C. Subsequently, the layers were separated and the aqueous phase was extracted twice with hexane. The combined organic fractions were washed three times with 50 mL of water, dried on magnesium sulfate, filtered, and evaporated.

(41) Mitter, F. K.; Hengge, E. *J. Organomet. Chem.* **1987**, 332, 47.

(42) Chen, S. M.; Katti, A.; Blinka, A.; West, R. *Synthesis* **1985**, 684.



This gave 9.89 g (30.8 mmol, 94%) of a mixture of **5a–d**. Pure **5a** was isolated upon four recrystallizations from ethyl acetate at  $-20\text{ }^{\circ}\text{C}$ . Yield: 2.62 g (8.18 mmol, 25%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.61 (q, 2H,  $J = 5.1$ , SiH), 0.29 (s, 12H, SiMe<sub>2</sub>), 0.26 (s, 12H, SiMe<sub>2</sub>), 0.24 (d, 6H,  $J = 5.1$ , HSiMe).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-4.7$  (SiMe<sub>2</sub>),  $-5.3$  (SiMe<sub>2</sub>),  $-12.5$  (HSiMe).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-40.5$  (SiMe<sub>2</sub>),  $-68.1$  (HSiMe). GC-MS:  $m/z$  320 ( $\text{M}^+$ ). IR (KBr): 2944, 2889 (Me), 2076 (Si–H), 1247, 798 (Si–Me)  $\text{cm}^{-1}$ .

**1,4-Dichlorodecamethylcyclohexasilane (4a,b)**. Dihydrate **5a** was dissolved in chloroform from which water and ethanol had been removed by passing it over a basic alumina column. After standing for 3 days at room temperature GC indicated that conversion of **5a** was complete. Evaporation of the solvent afforded a mixture of *trans*-dichloride **4a** and *cis*-dichloride **4b** (molar ratio 1.2:1 as indicated by  $^1\text{H}$  NMR spectroscopy) in quantitative yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ppm: **4a**  $\delta$  0.62 (s, 6H, ClSiMe), 0.27 (s, 24H, SiMe<sub>2</sub>); **4b**  $\delta$  0.60 (s, 6H, ClSiMe), 0.33 (s, 12H, SiMe<sub>2</sub>), 0.22 (s, 12H, SiMe<sub>2</sub>).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): **4a**  $\delta$  0.58 (s, 6H, ClSiMe), 0.27 (s, 12H, SiMe<sub>2</sub>), 0.24 (s, 12H, SiMe<sub>2</sub>); **4b**  $\delta$  0.54 (s, 6H, ClSiMe), 0.39 (s, 12H, SiMe<sub>2</sub>), 0.13 (s, 12H, SiMe<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ): **4a**  $\delta$   $-0.23$  (ClSiMe),  $-6.48$ ,  $-6.73$  (SiMe<sub>2</sub>); **4b**  $\delta$   $-0.25$  (ClSiMe),  $-6.53$ ,  $-6.80$  (SiMe<sub>2</sub>).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ): **4a**  $\delta$   $+16.1$  (SiCl),  $-40.0$  (SiMe<sub>2</sub>); **4b**  $\delta$   $+15.6$  (SiCl),  $-39.7$  (SiMe<sub>2</sub>). GC-MS:  $2 \times m/z$  388 ( $\text{M}^+$ ).

**(1-Pyrenyl)undecamethylcyclohexasilane (1)**. 1-Bromopyrene (0.47 g, 1.67 mmol) was dissolved in 0.5 mL of THF. The mixture was diluted with ca. 20 mL of diethyl ether, after which a solution of 1.6 M *n*-butyllithium in hexane (1.3 mL, 2.1 mmol) was added slowly. A white precipitate formed. After 3 h stirring the solvent was decanted and the remaining precipitate was washed three times with diethyl ether and suspended in 50 mL of diethyl ether. This suspension was added dropwise to a solution of dichlorosilanes **4a,b** (0.72 g, 1.85 mmol) in 5 mL of diethyl ether. After stirring overnight the reaction mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and 1.6 M methyllithium in diethyl ether (1.3 mL, 2.1 mmol) was added. After stirring at room temperature during 2 h the reaction mixture was poured into water. The water layer was extracted three times with ether, upon which the ethereal solution was washed with water, dried on sodium sulfate, and evaporated to dryness. Hot acetone was added, after which the mother liquor was decanted and the solvent evaporated. The resulting solid was purified by three recrystallizations from acetone. Yield: 30 mg (0.056 mmol, 3%) of a colorless solid. Mp:  $162\text{--}164\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.53 (AB, 1H,  $J = 9.2$ , H10), 8.34 (AB, 1H,  $J = 7.6$ , H2), 8.07 ( $2 \times$  AB,  $J = 9.2$  and  $J = 7.6$ , 2H, H9 + H3), 8.05 (ABC, 2H, H6 + H8), 7.94 (AB, 2H, H4 + H5), 7.89 (ABC, 1H, H7), 0.94 (s, 3H, C1 Me), 0.46 (s, 3H, C4 Me), 0.44 ( $3 \times$  s, 18H, SiMe<sub>2</sub>), 0.44 (s, 3H, C4 Me), 0.37 (s, 6H, SiMe<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  136.5 (C141), 134.4 (C11), 133.5 (C21), 132.2 (C121), 131.9 (C111), 131.4 (C131), 129.5 (C101), 128.0 (C41/51), 127.9 (C41/51), 126.8 (C91), 126.0 (C71), 125.5 (C151), 125.4 (C81), 125.4 (C161), 125.3 (C61), 124.7 (C31),  $-3.2$  (C1),  $-4.3$ ,  $-5.2$ ,  $-5.2$ ,  $-5.8$ ,  $-5.9$  (SiMe<sub>2</sub>).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-39.1$ ,  $-40.8$ ,  $-41.5$ ,  $-42.4$ . IR (KBr): 3043 (Ar–H), 2942, 2880 (Me), 1246, 843 (Si–Me), 789  $\text{cm}^{-1}$ . There was not enough material available to perform an elemental analysis. See the Supporting Information for NMR spectra of **1**.

**cis-1,4-Di(1-pyrenyl)decamethylcyclohexasilane (2)**. A suspension of 1-pyrenyllithium in 50 mL of diethyl ether was prepared from 1-bromopyrene (1.20 g, 4.27 mmol) as described above. A solution of **4a,b** (0.57 g, 1.46 mmol) in 20 mL of diethyl ether was added, after which the mixture was stirred overnight. Upon the addition of 50 mL of water, the organic layer was separated and the water layer was extracted twice with diethyl ether. Drying of the ethereal phases over magnesium sulfate, filtering, and evaporation gave 0.60 g of an off-white solid, which was purified by column chromatography.

This yielded 0.40 g (0.55 mmol, 37%) of **2**. After the extraction with diethyl ether, the aqueous layer was once more extracted, this time with 20 mL of dichloromethane. Drying, filtering, and evaporation of the dichloromethane yielded another crop of solid, which proved to be pure **2** (0.20 g, 0.28 mmol, 19%). Mp:  $249\text{ }^{\circ}\text{C}$  (decomp).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.52 (AB, 2H,  $J = 9.0$ , H10), 8.27 (AB, 2H,  $J = 7.7$ , H2), 8.05 (AB, 2H,  $J = 9.0$ , H9), 8.01 (AB, 2H,  $J = 7.7$ , H3), 7.96 (ABC, 2H,  $J = 7.4$ , H6/H8), 7.95 (ABC, 2H,  $J = 7.7$ , H6/H8), 7.85 (AB, 4H, H4 + H5), 7.77 (ABC, 2H,  $J = 7.4$  and  $J = 7.7$ , H7), 0.92 (s, 6H, C1 Me + C4 Me), 0.36 (s, 24H, SiMe<sub>2</sub>, this signal splits into two singlets upon raising or lowering the temperature).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.46 (AB, 2H,  $J = 9.1$ , H10), 8.32 (AB, 2H,  $J = 7.7$ , H2), 8.28–8.19 (m, 8H, H9 + H3 + H6 + H8), 8.14 (AB, 4H, H4 + H5), 8.08 (ABC, 2H,  $J = 7.4$  and  $J = 7.7$ , H7), 1.01 (s, 6H, C1 Me + C4 Me), 0.44 (s, 12H, SiMe<sub>2</sub>), 0.37 (s, 12H, SiMe<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  136.0 (C141), 134.4 (C11), 133.3 (C21), 131.7 (C121), 131.6 (C111), 131.1 (C131), 129.2 (C101), 127.7 (C41/51), 127.6 (C41/51), 126.6 (C91), 125.9 (C71), 125.2 (C81), 125.1 (C61), 125.0 (C161), 124.8 (C151), 124.4 (C31),  $-3.4$  (SiMe<sub>2</sub>),  $-4.4$  (C1 + C4),  $-4.5$  (SiMe<sub>2</sub>).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-39.6$  (SiMe<sub>2</sub>),  $-42.0$  (Si1 + Si4). IR (KBr): 3034 (Ar–H), 2944, 2886 (Me), 1242, 841 (Si–Me), 804, 777  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{48}\text{Si}_6\text{C}_6\text{H}_6$ : C, 72.11; H, 6.81. Found: C, 71.96; H, 6.88.

**Reaction of cis- and trans-1,4-Dichlorodecamethylcyclohexasilane with Phenyllithium**. Bromobenzene (0.32 g, 2.04 mmol) was dissolved in 3 mL of diethyl ether. Butyllithium (1.45 mL of a 1.41 M solution in hexane, 2.05 mmol) was added slowly, and another 3 mL of diethyl ether was added. After 2.5 h GC indicated that all the bromobenzene had reacted. Subsequently a mixture of **4a** and **4b** (0.14 g, 0.36 mmol, composition 1.4:1 by GC and 1.3:1 by  $^1\text{H}$  NMR) was dissolved in ether and cooled to  $0\text{ }^{\circ}\text{C}$ . The phenyllithium solution (2.6 mL, 0.71 mmol) was added, and the homogeneous mixture was stirred overnight. A GC of a sample directly taken from the reaction mixture (i.e., no working up of the sample had been performed) showed that **4a,b** were not present anymore and that two products had been formed in a 2.3:1 ratio. Water (2 mL) was added and the organic layer separated. The water layer was extracted five times with 5 mL of diethyl ether, and the combined ethereal layers were dried on magnesium sulfate, filtered, and evaporated to dryness. A  $^1\text{H}$  NMR of a solution of the whole yield (0.17 g, 0.36 mmol, quantitative yield) revealed a *cis*–*trans* ratio of 2.3:1 for the 1,4- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$  product. No attempt was made to separate the two isomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): *cis*- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$   $\delta$  7.51 (m, 2H, Ar–H), 7.34 (m, 3H, Ar–H), 0.57 (s, 6H, PhSiMe), 0.28 (s, 12H, SiMe<sub>2</sub>), 0.25 (s, 12H, SiMe<sub>2</sub>); *trans*- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$   $\delta$  7.51 (m, 2H, Ar–H), 7.34 (m, 3H, Ar–H), 0.56 (s, 6H, PhSiMe), 0.36 (s, 12H, SiMe<sub>2</sub>), 0.23 (s, 12H, SiMe<sub>2</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): *cis*- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$   $\delta$  137.6 (C *ipso*), 134.9 (C *ortho*), 127.9 (C *para*), 127.6 (C *meta*),  $-5.2$ ,  $-5.7$ ,  $-7.1$  (SiMe); *trans*- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$   $\delta$  137.6 (C *ipso*), 134.7 (C *ortho*), 127.8 (C *para*), 127.7 (C *meta*),  $-4.3$ ,  $-6.5$ ,  $-6.7$  (SiMe). The reported position of 146.98 ppm for the *ipso* carbon atom<sup>16</sup> of *trans*-1,4- $\text{Ph}_2\text{Si}_6\text{Me}_{10}$  is in our opinion erroneous.

**Crystal Structure Determinations**. Crystals were obtained by careful crystallization from ethyl acetate (**5a**), benzene (**2A**), or dioxane (**2B**). X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode ( $\lambda = 0.71073\text{ \AA}$ ). The structures were solved with direct methods (SIR97)<sup>43</sup> and refined with SHELXL97<sup>44</sup> against  $F^2$  of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. In **2A** and **2B** hydrogen atoms were introduced at calculated positions and refined as

(43) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(44) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.

rigid groups, methyl hydrogens as rotating groups. In **5a**, hydrogen atoms were located in the difference Fourier map and refined freely with isotropic displacement parameters. Molecular illustration, structure checking, and calculations were performed with the PLATON package.<sup>45</sup> Further details are given in Table 1.

**Acknowledgment.** This work was supported in part (M.L., A.L.S.) by the Council for Chemical Sciences of

---

(45) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: The Netherlands, 2001.

The Netherlands Organization for Scientific Research (CW-NWO).

**Supporting Information Available:** Details of the three structure determinations, including atomic coordinates, bond lengths and angles, thermal parameters, least-squares planes, and interatomic contacts and <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020980R