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Rearrangement of Cyclic Silanes with Aluminum Trichloride

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The $\text{Al}(\text{Fe})\text{Cl}_3$ -catalyzed rearrangement of monocyclic permethylated oligosilanes was investigated for different isomers in the range of $\text{Me}_{14}\text{Si}_7$ to $\text{Me}_{28}\text{Si}_{14}$. The reactions of the smaller isomers ($\text{Me}_{14}\text{Si}_7$ to $\text{Me}_{20}\text{Si}_{10}$) resulted in the selective formation of single compounds. In contrast to this, the rearrangements of isomers $\text{Me}_{22}\text{Si}_{11}$, $\text{Me}_{24}\text{Si}_{12}$, $\text{Me}_{26}\text{Si}_{13}$, and $\text{Me}_{28}\text{Si}_{14}$ yielded mixtures of isomers. Several of the obtained compounds could be characterized unambiguously by single crystal structure analysis. On the basis of these data and careful analysis of ^{29}Si NMR data we conclude that in all cases cyclopentasilanes were formed as the final products.

Introduction

The rearrangement chemistry of carbocations, which proceeds via 1,2 alkyl shifts, can be considered as one of the most important chapters of organic chemistry.¹ A striking example of the usefulness of this chemistry was provided by Schleyer's famous adamantane synthesis.² In 1969 Ishikawa and Kumada reported that related Lewis-acid-catalyzed rearrangement chemistry also exists for polysilanes.³ In subsequent full papers they⁴ and Blinka and West⁵ have investigated this reaction to some degree and found that linear and cyclic permethylated polysilanes rearrange to highly branched molecules. As for alkanes, the driving force of the reaction is thermodynamic. When the energies of the products are close, mixtures of compounds with similar energy may be formed. The AlCl_3 -catalyzed reaction of linear octadecamethyloctasilane for example leads to a mixture of 2,2,4-tris(trimethylsilyl)nonamethylpentasilane and hexakis(trimethylsilyl)disilane in a ratio of 4 to 1 (Scheme 1).^{4a} Subjecting pure hexakis(trimethylsilyl)disilane to the same conditions leads to the same mixture which corresponds to the thermodynamic equilibrium of isomers (Scheme 1).^{4a}

Recently, we were able to utilize this chemistry for the synthesis of an all-sila analogue of adamantane.⁶ Encouraged by this success we decided to use this chemistry for the synthesis of some crucial starting materials for our polysilyl anion

chemistry.⁷ Especially, the contribution by Blinka and West convinced us of the potential of this chemistry.⁵ In their account they reported the strikingly selective conversions of the homocyclic permethylcyclosilanes $\text{Si}_6\text{Me}_{12}$ – $\text{Si}_{12}\text{Me}_{24}$ to single isomeric branched compounds in each case. The same products were also obtained from the rearrangement of isomeric starting materials. The $(\text{Me}_2\text{Si})_n$ rings up to $n = 9$ were found to rearrange to branched cyclopentasilanes, whereas the larger rings ($n = 10$ – 12) were reported to yield branched cyclohexasilanes (Scheme 2). In all cases, the rearrangement reaction favored geminal bis(trimethylsilyl) substitution.

The rearrangement products of isomers $(\text{Me}_2\text{Si})_{10}$ – $(\text{Me}_2\text{Si})_{12}$ were reported to be branched cyclohexasilanes (Scheme 2). We were especially interested to utilize the rearrangement chemistry to obtain compounds such as 1,1,3,3,5,5-hexakis(trimethylsilyl)cyclohexasilane (Scheme 2), which would be a very interesting substrate with respect to some of our recent chemistry.⁸

Results and Discussion

The homocyclic starting materials $(\text{Me}_2\text{Si})_n$ used by Blinka and West were obtained from a modified Wurtz-type coupling synthesis of cyclopolyasilanes. The larger isomers ($n > 9$) were formed only in yields below 0.2%, and isolation was achieved employing preparative HPLC techniques.⁹ As this approach is not practical for larger scale synthesis, we wanted to evaluate the utility of the AlCl_3 -catalyzed rearrangement chemistry of cyclic polysilanes using already branched cyclopolyasilanes $(\text{Me}_2\text{Si})_7$ – $(\text{Me}_2\text{Si})_{14}$. These compounds are readily available utilizing oligosilylpotassium chemistry.

Synthesis of Starting Materials. A series of branched monocyclic methylated polysilanes covering isomers from $(\text{Me}_2\text{Si})_7$ to $(\text{Me}_2\text{Si})_{14}$ was synthesized.

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(1) Consequently every advanced organic chemistry textbook provides some insight into its basics.

(2) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, 79, 3292.

(3) (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1969**, 567–568. (b) Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 157.

(4) (a) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, 103, 4845–4850. (b) Ishikawa, M.; Watanabe, M.; Iyoda, J.; Ikeda, H.; Kumada, M. *Organometallics* **1982**, 1, 317–322.

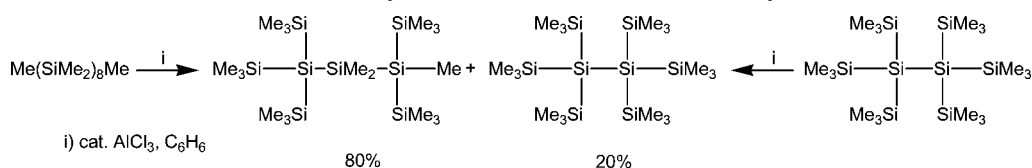
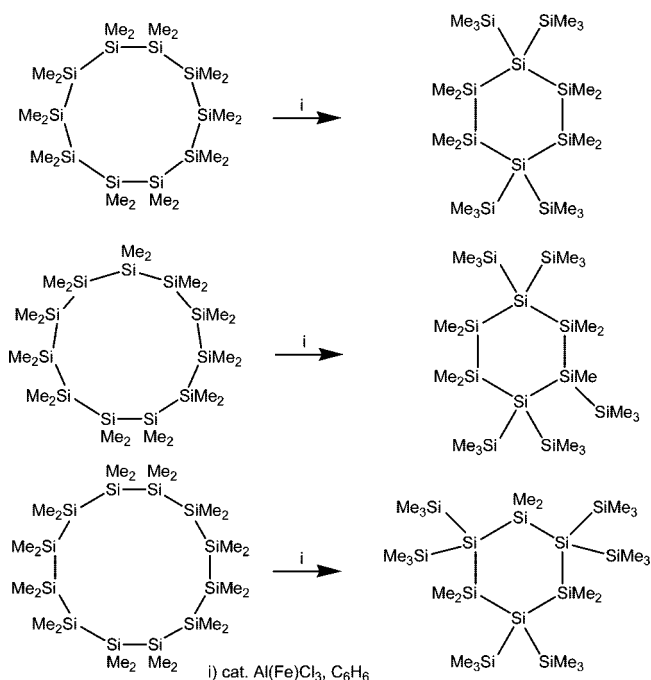
(5) Blinka, T. A.; West, R. *Organometallics* **1986**, 5, 128–133.

(6) Fischer, J.; Baumgartner, J.; Marschner, C. *Science* **2005**, 310, 825.

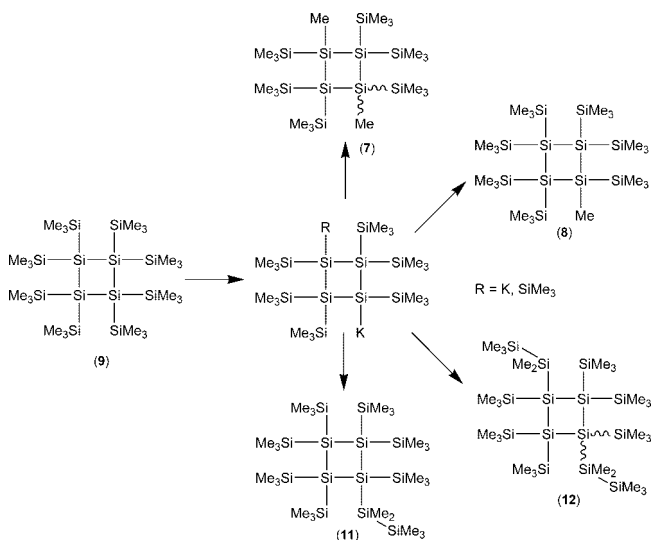
(7) Marschner, C. *Organometallics* **2006**, 25, 2110–2125.

(8) (a) Fischer, J.; Konopa, T.; Ullrich, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, 685, 79–92. (b) Wallner, A.; Hölbling, M.; Baumgartner, J.; Marschner, C. *Silicon Chem.* **2005**, 3, 175–185.

(9) Brough, L. F.; Matsumura, K.; West, R. *Angew. Chem.* **1979**, 91, 1022–1023.

Scheme 1. AlCl_3 -Catalyzed Isomerization of OctadecamethyloctasilaneScheme 2. Rearrangement of the Permethylated Homocyclosilanes $(\text{Me}_2\text{Si})_{10}$ – $(\text{Me}_2\text{Si})_{12}$ to Branched Cyclohexasilanes as Reported by Blinka and West⁵

The $\text{Si}_7\text{Me}_{14}$ isomer trimethylsilylundecamethylcyclohexasilane (**1**) was obtained by the known reaction of undecamethylcyclohexasilanylpotassium with trimethylchlorosilane.¹⁰ Two isomers $\text{Si}_8\text{Me}_{16}$ were obtained. 1,1,2,2-Tetrakis(trimethylsilyl)tetramethylcyclotetrasilane (**2**) was easily available from the intramolecular coupling of 1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyl-1,4-dipotassiotetrasilane with 1,2-dibromoethane.¹¹ A mixture of the *cis*- and *trans*-isomers of 1,4-bis(trimethylsilyl)decamethylcyclohexasilane (**3**) was obtained from the methylation of 1,4-bis(trimethylsilyl)octamethyl-1,4-dipotassiocyclohexasilane.^{8a} In a similar way also the $\text{Si}_9\text{Me}_{18}$ isomer 1,1,4-tris(trimethylsilyl)nonamethylcyclohexasilane (**4**) was obtained from the methylation of 1,4,4-tris(trimethylsilyl)octamethyl-1-potassiocyclohexasilane.^{8a} For reasons outlined above $\text{Si}_{10}\text{Me}_{20}$ isomers were especially interesting to us so that we were preparing three different isomers for the rearrangement reaction. Tris(trimethylsilyl)silylundecamethylcyclohexasilane (**5**) was obtained from the reaction of bromoundecamethylcyclohexasilane with tris(trimethylsilyl)silylpotassium.^{8a} The presumed product of the isomerization, 1,1,4,4-tetrakis(trimethylsilyl)cyclohexasilane (**6**), was prepared by reaction of 1,1,4,4-tetrakis(trimethylsilyl)tetramethyl-1,4-dipotassiotetrasilane with 1,2-dichlorotetramethyldisilane.^{8a} Octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) obtained as a byproduct from the synthesis of tetrakis(trimethylsilyl)silane²² served as a $\text{Si}_{12}\text{Me}_{24}$ isomer. The same compound could also be used to achieve syntheses

Scheme 3. Synthesis of $(\text{Me}_2\text{Si})_n$ Isomers with $n = 10$ –14 Starting from **9**

of $\text{Si}_{10}\text{Me}_{20}$ (**7**), $\text{Si}_{11}\text{Me}_{22}$ (**8**), $\text{Si}_{13}\text{Me}_{26}$ (**11**), and $\text{Si}_{14}\text{Me}_{28}$ (**12**) isomers by the reactions of its mono- or dianion with 1 or 2 equiv of dimethylsulfate or chloropentamethyldisilane, respectively (Scheme 3).

A mixture of the *cis*- and *trans*-isomers of 1,4-bis(pentamethyldisilanyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (**10**), also $\text{Me}_{24}\text{Si}_{10}$ isomers, was obtained from the reaction of 1,4-bis(trimethylsilyl)octamethyl-1,4-dipotassiocyclohexasilane^{8a} with 2 equiv of chloropentamethyldisilane.

Isomerization Reactions: $(\text{Me}_2\text{Si})_7$ – $(\text{Me}_2\text{Si})_9$. Isomerization experiments were carried out as described by Blinka and West⁵ with a cosublimates of AlCl_3 and FeCl_3 (1%) as the catalyst in refluxing cyclohexane. Alternatively the reactions also could be carried out in dichloromethane at ambient temperature. Sometimes this protocol provided a higher degree of chlorinated products.

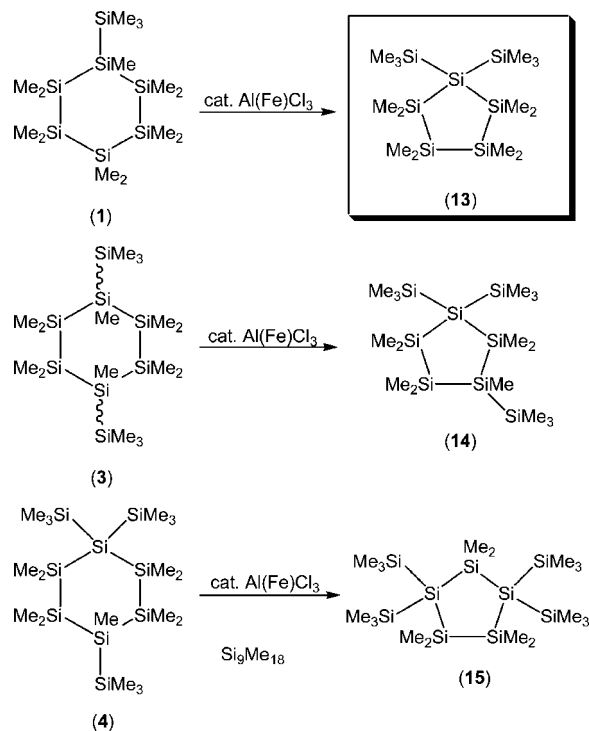
In accordance with the results of the Blinka and West report we obtained only single isomers from the reactions of the isomers of $(\text{Me}_2\text{Si})_7$ – $(\text{Me}_2\text{Si})_{10}$. As already known from the studies of Ishikawa et al., the reaction of trimethylsilylundecamethylcyclohexasilane (**1**) under rearrangement conditions gave 1,1-bis(trimethylsilyl)decamethylcyclopentasilane (**13**) (Scheme 4).^{4b} The *cis/trans* mixture of 1,4-bis(trimethylsilyl)decamethylcyclohexasilane (**3**) led to 1,1,3-tris(trimethylsilyl)nonamethylcyclopentasilane (**14**) exclusively (Scheme 4), and also the conversion of 1,1,4-tris(trimethylsilyl)nonamethylcyclohexasilane (**4**) gave the expected 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane (**15**)¹² (Scheme 4). Spectral data, in particular the ²⁹Si NMR resonances obtained for products **13**, **14**, and **15**, were in accordance with the data reported by Ishikawa et al.^{4b} and Blinka and West.^{5,13}

The attempted isomerization of the $\text{Si}_8\text{Me}_{16}$ isomer **2** followed a different course. Likely as a result of ring strain accompanied

(10) Uhlig, F.; Gspaltl, P.; Trabi, M.; Hengge, E. *J. Organomet. Chem.* **1995**, 493, 33–40.

(11) Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. *Organometallics* **2004**, 23, 1899–1907.

(12) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, 22, 3723–3731.

Scheme 4. Isomerization Reactions of (Me₂Si)_n Isomers with *n* = 7–9

Scheme 5. Ring Opening of (Me₂Si)₈ Isomer 2 under Isomerization Conditions


by no steric protection of the dimethylsilylene units only ring cleavage to 1,2-bis(chlorodimethylsilyl)tetrakis(trimethylsilyl)disilane (**16**) was observed (Scheme 5).

Isomerization Reactions: (Me₂Si)₁₀–(Me₂Si)₁₄. It was of interest whether 1,1,4,4-tetrakis(trimethylsilyl)cyclohexasilane (**6**), which we had obtained employing oligosilylpotassium chemistry,^{8a} could also be obtained from isomerization reactions. Therefore, we attempted the rearrangement reaction of its easily available isomer tris(trimethylsilyl)(undecamethylcyclohexasilanyl)silane (**5**). While we did obtain a single isomer from the reaction, it was not the expected cyclohexasilane but 1,1,3,3,4-pentakis(trimethylsilyl)pentamethylcyclopentasilane (**17**) (Scheme 6). Changing to cycloctasilane **7** as starting material again gave compound **17** exclusively.

At this stage we also realized that the ²⁹Si NMR values for 1,1,4,4-tetrakis(trimethylsilyl)cyclohexasilane (**6**) reported by Blinka and West (−7.1, −24.1, −129.0 ppm) do not correspond to the values reported by us for the same compound (−8.2, −40.0, −131.7 ppm) that was prepared by a different route.^{8a} Especially, the resonance for the SiMe₂ unit is considerably different and suggests the existence of different compounds. The ²⁹Si NMR spectrum for the obtained compound **17** is very characteristic, as the compound lacks all symmetry in the silicon framework so that all 10 silicon atoms appear as discrete resonances. However, no resonance close to −24.1 ppm was

observed. Our own structural characterization of **6** included ¹H, ¹³C, ²⁹Si NMR, MS, elemental analysis, and a single-crystal structure.^{8a,14} In order to check the possibility that the non-branched 10-membered ring Si₁₀Me₂₀ rearranges to **6** while compound **5** under the same conditions leads to the formation of **17**, we subjected compound **6**, obtained by the alternative protocol, to rearrangement conditions. The result of this experiment was that again cyclopentasilane **17** was obtained as the sole isomer (Scheme 6). It seems that the ring contraction of **6** from a six- to a five-membered ring, which is accompanied by the generation of another branching point, provides substantial additional stability.

The rearrangement reaction of the Si₁₁Me₂₂ isomer heptakis(trimethylsilyl)methylcycloctasilane (**8**) gave a mixture of several isomers, of which 1,1-bis(trimethylsilyl)-3-tris(trimethylsilyl)silylheptamethylcyclopentasilane (**18**) could be crystallized and was subjected to structure analysis (Scheme 7). From the ²⁹Si NMR spectra we were not able to verify the predicted formation of 1,1,2,4,4-pentakis(trimethylsilyl)heptamethylcyclohexasilane,⁵ as no resonances corresponding to the reported signal set were found. The fact that a tris(trimethylsilyl)silyl group was formed for at least the major isomer indicates that steric strain due to the high degree of substitution becomes important. From the ²⁹Si NMR spectra we assume that the other compounds formed are isomeric hexakis(trimethylsilyl)tetramethylcyclopentasilanes (Scheme 7).

Rearrangement of (SiMe₂)₁₂ was reported to give 1,1,3,3,5,5-hexakis(trimethylsilyl)hexamethylcyclohexasilane (Scheme 2).¹⁵ The rearrangement of octakis(trimethylsilyl)cycloctasilane (**9**) gave a mixture of at least four different diastereomers. Three of these proved to possess the cyclopentasilane unit according to crystal structure analysis (Scheme 8). The rather unusual reported ²⁹Si NMR shift of the proposed 1,1,3,3,5,5-hexakis(trimethylsilyl)hexamethylcyclohexasilane of −153.2 ppm⁵ could not be observed in the obtained reaction mixture.

Two of the crystal structures (**19/20**) obtained for this isomer were similar to **18** but had an additional trimethylsilyl group in the 5-position. The other characterized isomer (**21**) was also similar to **18** but had a dimethylsilylene group inserted between the tris(trimethylsilyl)silyl group and the cyclopentasilane ring. We suppose that the fourth compound (**22**) is an isomer of **19/20** with the additional trimethylsilyl group in the 4-position (Scheme 8). Reaction with the alternative starting material **10** led to the same product distribution (Scheme 8).

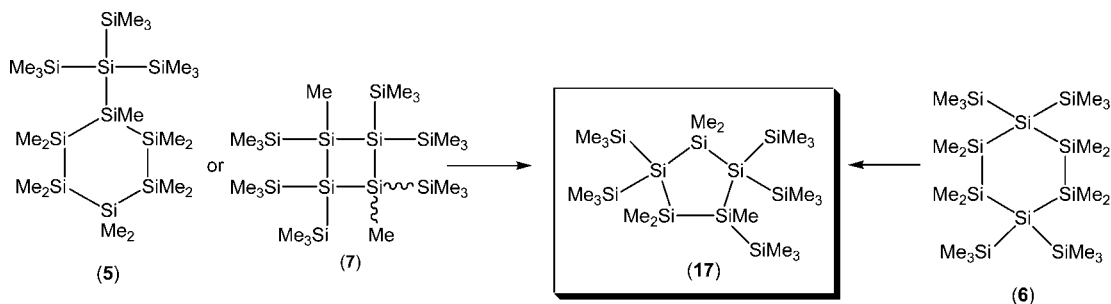
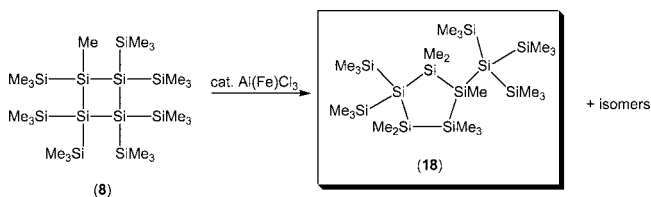
Rearrangement reactions of Si₁₃Me₂₆ and Si₁₄Me₂₈ isomers have not been reported so far. We were able to obtain crystals from the main product (**23**) of the rearrangement of the four-membered ring Si₁₃Me₂₆ isomer (**11**) for structure analysis (Scheme 9). Again the 1,1-bis(trimethylsilyl)cyclopentasilane unit was found with a dimethyl[tris(trimethylsilyl)silyl]silyl group in the 3-position and another trimethylsilyl group *trans* to this in the 4-position. There are two other minor products. On the basis of the ²⁹Si NMR data we conclude that these are 1,1-bis(trimethylsilyl)-3-[2'-tris(trimethylsilyl)silyl]tetramethyldisilanyl]heptamethylcyclopentasilane (**24**) and *cis*-1,1,2-tris(trimethylsilyl)-4-dimethyl[tris(trimethylsilyl)silyl]silylhexamethylcyclopentasilane (**25**) (Scheme 9).

The isomerization of the Si₁₄Me₂₈ (**12**) isomers gave three isomers in approximately the same ratio (Scheme 10). One

(13) In the course of the comparison of the ²⁹Si NMR resonances of **15** with the data provided by Blinka and West⁵ we noticed a typing error for the resonance at −19.4 ppm, which was reported to be at −1.94 ppm.

(14) Fischer, R.; Konopa, T.; Ullly, S.; Wallner, A.; Baumgartner, J.; Marschner, C. *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, 2005; pp 355–360.

(15) Stanislawski, D. A.; West, R. J. *Organomet. Chem.* **1980**, 204, 295–305.

Scheme 6. Isomerization of $(\text{Me}_2\text{Si})_{10}$ Isomers 5, 6, and 7 to the Same Product (17)Scheme 7. Isomerization Reaction of $(\text{Me}_2\text{Si})_{11}$ Isomer 8^a

^aThe configuration of products in frames has been determined by crystal structure analyses, while the configurations of other products are tentatively based on ^{29}Si and ^1H NMR spectroscopy.

isomer could be separated by crystallization from the initial mixture. From its ^{29}Si NMR data, which lack resonances corresponding to a tris(silyl)methylsilyl unit, we conclude that it is **26**. A second product could also be crystallized and was characterized by crystal structure analysis as 1,1,3,3-tetrakis(trimethylsilyl)-5-dimethyl[tris(trimethylsilyl)silyl]silylpentamethylcyclopentasilane (**27**). On the basis of the remaining ^{29}Si NMR resonances and some consideration on conformation we conclude that the third isomer is *cis*-1-tris(trimethylsilyl)silyl]-3-dimethyl[tris(trimethylsilyl)silyl]silyloctamethylcyclopentasilane (**28**) (Scheme 10).

^{29}Si NMR Spectroscopy. The individual structural elements of the cyclopentasilanes can be obtained simply from ^{29}Si NMR spectra. 1,1-Bis(trimethylsilyl)octamethylcyclopentasilane (**13**) exhibits the resonance for the quaternary Si atom at -132.0 ppm and two resonances for the dimethylsilylene groups at -31.6 and -40.2 ppm. For 1,1,3-tris(trimethylsilyl)heptamethylcyclopentasilane (**14**) one resonance at -130.8 ppm (SiSi_4), one at -80.5 ppm (MeSiSi_3), and three resonances for dimethylsilylene groups (-24.7 , -27.2 , -31.1 ppm) were observed. The higher symmetric 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane (**15**) exhibits -129.6 (SiSi_4), -24.8 , and -19.9 (Me_2SiSi_2). The ^{29}Si NMR spectrum of compound **17** is most illustrative, as it shows clearly how a higher degree of steric interaction causes a downfield shift of the resonances. The SiSi_4 shift of -129.4 for the 1,1-bis(trimethylsilyl)silyl unit, which is accompanied by two dimethylsilylenes, compares well to **15**. The resonance of the second 1,1-bis(trimethylsilyl)silyl unit, which has a trimethylsilylmethylsilylene neighbor now, was found at -120.8 ppm. Also the MeSiSi_3 resonance (-66.8 ppm) is shifted some 14 ppm to lower field compared to compound **14**. Finally the same was found for the dimethylsilylene units, whose shifts are unusually low-field (-16.7 and -14.8 ppm), almost in the area of typical trimethylsilyl resonances. These are highly unusual shifts compared to dodecamethylcyclopentasilane (-42.1 ppm) and dodecamethylcyclohexasilane (-41.9 ppm).¹⁵

The resonances for compound **18**, an Si_{11} isomer with a tris(trimethylsilyl) group, show that the transfer of steric bulk

out of the ring causes a back shift to higher field. In general the resonance pattern very much resembles that of compound **14** with the exception that the bulkier tris(trimethylsilyl)silyl groups effect a downfield shift of about 7 ppm at the SiMe_2 unit. Compounds **19** and **20** resemble **18** but have an additional trimethylsilyl group. This again causes significant low-field shifts of the SiMe_2 resonances.

Also for the $\text{Me}_{26}\text{Si}_{13}$ and $\text{Me}_{28}\text{Si}_{14}$ isomers the same pattern can be observed. The additional silicon atoms are subsequently attached to side-chains of the ring. It is interesting to compare **27** with **17**. The former has a [tris(trimethylsilyl)silyl]dimethylsilyl group instead of the trimethylsilyl group in **17**. While most of the values are very close, the resonance for the silicon atom where the side-chain is attached experiences a strong low-field shift to -47.9 ppm into a region that is otherwise more typical for SiMe_2 groups.

In conclusion the behavior of the ^{29}Si NMR resonances is similar to what has been found for polysilane dendrimers.¹⁶ Increased steric crowding in the neighborhood causes a shift to lower field. Table 2 gives an overview of ^{29}Si resonances of a selection of cyclopentasilanes. As the assignments are not based on ^{29}Si INADEQUATE experiments¹⁷ but on comparison of data, some ambiguities could not be avoided. Nevertheless, it can be seen that the typical ranges of shifts of SiMe_3 , SiMe_2 , and SiMe units are extended into the low-field area. For the SiMe_2 and SiMe groups values between -14.8 and -40.2 ppm and -49.7 to -80.5 ppm, respectively, were observed (Table 2).

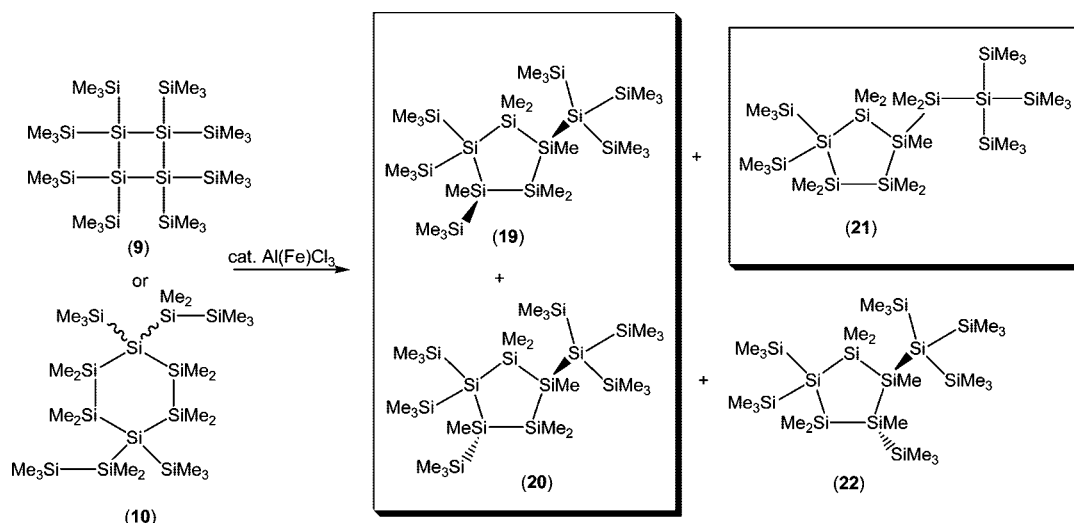
Crystal Structures. During this study we were able to characterize several of the starting materials and a substantial number of the rearrangement products by crystal structure analysis. The starting materials and some of the isomerization products of the smaller isomers have been obtained selectively. The crystals of these compounds were usually of good quality, and thus also the quality of the structure determination was satisfactory. The rearrangement products of some of the higher isomers ($\text{Si}_{11}\text{Me}_{22}$ to $\text{Si}_{14}\text{Me}_{18}$) were more problematic, as several isomers were formed in these reactions. Frequently these isomers (which are energetically very close) are very hard to separate. Of course this is not surprising considering that they have very similar properties. Because of similar space demand of close isomers, we also obtained crystals with two different isomers being present.

From the obtained mixture of the *cis*- and *trans*-isomers of **3** the *trans*-isomers could be isolated by crystallization. The structure analysis showed it to exhibit the expected *chair* conformation with the two trimethylsilyl groups occupying the

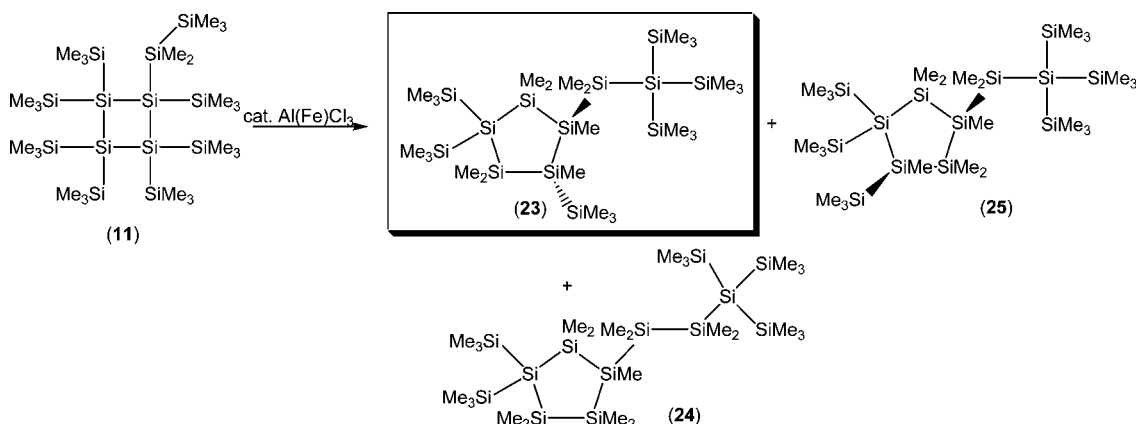
(16) Lambert, J. B.; Pflug, J. L.; Wu, H.; Liu, X. *J. Organomet. Chem.* **2003**, 685, 113–121.

(17) Kuroda, M.; Kabe, Y.; Hashimoto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1727–1730.

(18) Chen, Y. S.; Gaspar, P. P. *Organometallics* **1982**, 1, 1410–1412.

Scheme 8. Isomerization Reactions of $(\text{Me}_2\text{Si})_{12}$ Isomers **9** and **10**^a

^aThe configuration of products in frames has been determined by crystal structure analyses, while the configurations of other products are tentatively based on ^{29}Si and ^1H NMR spectroscopy.

Scheme 9. Isomerization Reaction of $(\text{Me}_2\text{Si})_{13}$ Isomer **11**^a

^aThe configuration of products in frames has been determined by crystal structure analyses, while the configurations of other products are tentatively based on ^{29}Si and ^1H NMR spectroscopy.

equatorial positions (Figure 1).¹⁴ This structural behavior is quite common and was observed before for several other 1,4-disubstituted permethylcyclohexasilanes.¹⁴ All Si–Si bond lengths are close to the typical 2.35 Å, and the bent angle between the planes (Si4–Si3–Si4A–Si3A) and (Si3–Si2–Si4A) of 128.1° is nearly identical with the value for cyclohexane. This indicates a very nonstrained molecule.

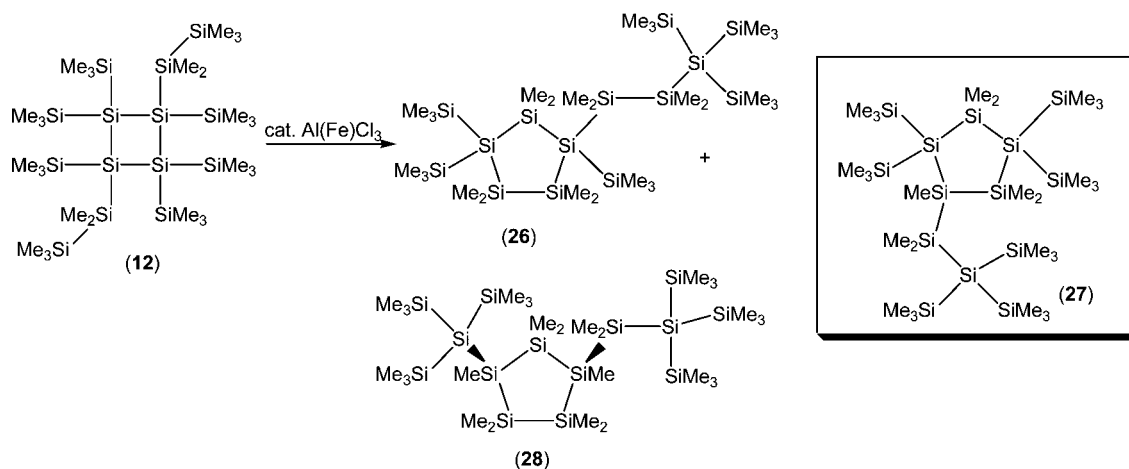
Compound **4** differs from **3** by an additional trimethylsilyl group in the 1-position. As a result of this, the spatial orientation changes to a *twist* conformer (Figure 2). The same conformation was found previously for **6**.¹⁴ We attributed the preferential *twist* conformation of **6** to the fact that it provided an opportunity for the trimethylsilyl groups to avoid the sterically nonfavorable axial positions. It is interesting to note that as shown in the case of **4** only one 1,1-bis(trimethylsilyl)silyl unit seems to be sufficient for the cyclohexasilane molecule to engage in this conformation. Again Si–Si bonds with values around 2.35 Å are fairly typical in the molecule.

As we are using cyclotetrasilane **9** as a starting material in this study we also want to comment on its crystal structure. According to Gaspar in his initial report on the synthesis of **9**,

the structure has already been studied by Clardy, Leftow, and Arnold.¹⁸ Nevertheless, the only evidence for this is an ORTEP picture in Gaspar's report. For this reason we decided to disclose the results of our own structural study of **9**. The molecule crystallizes in the monoclinic space group $C2/m$ and consists of a planar four-membered ring (Figure 3). Due to the high degree of steric overcrowding in the molecule, most of the Si–Si bonds are noticeably elongated. The endocyclic bond lengths were found to be 2.3979(11) Å. Interestingly, there are two different exocyclic Si–Si bond lengths. While Si(1)–Si(3) and Si(2)–Si(5) are at 2.38 Å, the distance between Si(1) and Si(4) is only 2.3649(15) Å.

For the rearrangement products for which crystal structures were obtained the assignment of conformations unfortunately is less clear-cut than for the cyclohexasilanes **3** and **4**. All of these compounds are cyclopentasilanes. While there are the two conformational extremes of envelope (C_s) and half-chair (C_2) known for five-membered rings, frequently conformations in between can be observed.¹⁹

(19) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience; New York, 1994.

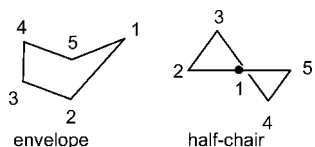
Scheme 10. Isomerization Reaction of (Me₂Si)₁₄ Isomer 12^a

^aThe configuration of products in frames has been determined by crystal structure analyses, while the configurations of other products are tentatively based on ²⁹Si and ¹H NMR spectroscopy.

Table 1. Absolute (in Hartree) and Relative (corrected for the zero-point vibrational energies, in kJ/mol) Energies of 17, 6, and 5

17	6	5
E -3692.741877	-3692.739578	-3692.728363
E _{rel} 0.0	6.0	35.5

1,1-Bis(trimethylsilyl)octamethylcyclopentasilane (**13**) as the simplest member of this class of compounds possesses a remarkable similarity to **4** and **6**. To avoid an axial position for one of the trimethylsilyl groups, the ring adopts a half-chair conformation. This way the Si–Si bonds in the molecule are between 2.34 and 2.36 Å and the angle between the two trimethylsilyl groups is close to ideal tetrahedral (109.8°), while the angles within the ring are comparably small, ranging from 101.8° to 105.5°.



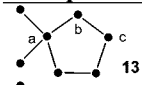
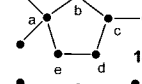
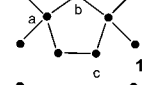
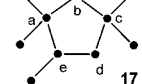
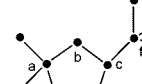
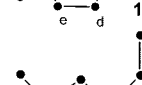
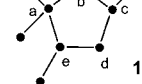
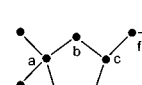
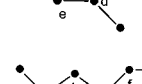
The conformation of compound **17** is displaying again the same features (Figure 5). The two bis(trimethylsilyl)silyl units are twisted in a way that all trimethylsilyl groups can avoid an axial position. The trimethylsilyl unit with the geminal methyl group on Si(2) is able to adopt an explicitly equatorial orientation. Due to the higher degree of steric crowding the Si–Si bond lengths within the ring are elongated to values between 2.36 and 2.38 Å, while the exocyclic distances are still around 2.36 Å.

The quality of the structure of compound **18** (Figure 6) is relatively poor, as indicated by high *R* values. Nevertheless, the scaffold of the molecule represents another cyclopentasilane containing the 1,1-bis(trimethylsilyl)silyl unit, which is again twisted. The additional four silicon atoms are assembled into a tris(trimethylsilyl)silyl moiety that adopts an equatorial orientation on Si(1), which is the flap of the envelope conformation.

The situation for the structures of compounds **19** and **20** is difficult. The two compounds are isomers and crystallize together. The structure analysis reveals they have a very close space demand. According to the refinement the ratio of the two isomers is about 2:1, with **19** as the major component. The conformation of compound **19** (Figure 7) is very similar to that of **18** but features an additional trimethylsilyl group on Si(3). In contrast to this compound **20**, which is the isomer of **19** with the configuration at Si(3) inverted, has to adopt a different conformation. This is again required to avoid the axial position of the trimethylsilyl group at Si(3). In order to achieve this, the two SiMe₂ units of the ring flip.

The structure of compound **21** (Figure 8) resembles again that of **18**, but the tris(trimethylsilyl)silyl group is now separated from the ring by a dimethylsilylene unit. This structure must be fairly nonstrained, as we find the same features also for the structures of compounds **23** and **27** (Figures 9 and 10). The additional trimethylsilyl groups of the latter compounds are successively added to the ring. For **23** the extra trimethylsilyl

Table 2. ^{29}Si NMR Shifts (δ) of Selected Cyclopentasilanes (assignments of resonances within the range of a few ppm may be ambiguous)

Compound	Me_3Si	a	b	c	d	e	f	g	h
 13	-7.6	-132.0	-31.6	-40.2					
 14	-7.2, -7.8, -9.6	-130.8	-24.7	-80.5	-31.1	-27.2			
 15	-7.6	-129.6	-19.9	-24.8					
 17	-6.8, -7.3, -8.3, -9.3, -10.4	-120.8	-14.8	-129.4	-16.7	-66.8			
 18	-7.6, -8.0, -9.6	-128.8	-22.4	-73.4	-30.9/-31.8		-133.6		
 19	-7.9, -8.7, -9.5	-126.9	-21.7	-74.5	-23.8	-71.8	-128.0		
 23	-7.9, -8.0, -9.8, -9.9	-130.0	-17.1	-60.0/-68.7	-22.4	-26.5	-125.1		
 26	-7.3, -7.6, -8.9, -9.7	-129.2	-17.8	-128.6	-25.0/-25.2	-21.9	-30.9	-122.1	
 27	-6.0, -7.5, -8.0, -9.8, -9.9	-116.8	-17.6	-128.2	-17.2	-49.7	-27.2	-124.7	

groups can adopt an equatorial orientation. For **27**, which contains two 1,1-bis(trimethylsilyl)silyl units, the situation is

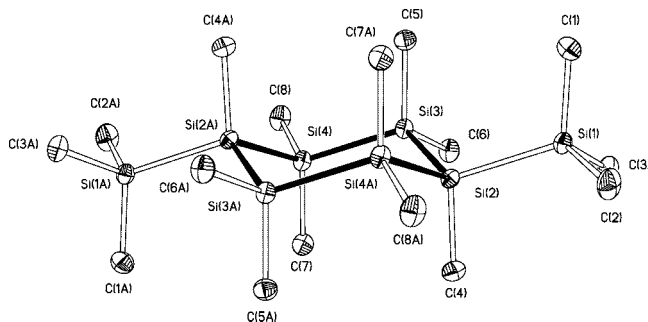


Figure 1. Molecular structure and numbering of *trans*-**3**. (One molecule and half of another one that resides at the center of inversion are in the unit cell. Only one molecule is drawn. Thermal ellipsoids at the 30% probability level.) Selected bond lengths [Å] and bond angles [deg]: Si(1)–C(1) 1.871(2); Si(1)–Si(2) 2.348(1); Si(2)–Si(3) 2.345(1); Si(2)–Si(4A) 2.346(9); Si(3)–Si(4) 2.347(1); Si(4)–Si(2A) 2.346(9); Si(3)–Si(2)–Si(4A) 108.72(3); Si(3)–Si(2)–Si(1) 111.15(3); Si(4A)–Si(2)–Si(1) 111.90(3); Si(2)–Si(3)–Si(4) 111.93(3); Si(3)–Si(4)–Si(2A) 111.45(3).

again reminiscent of **17**. The additional silicon atoms of **27** are packed into the remote tris(trimethylsilyl)silyl group.

Figure 11, which is a compilation of the polysilane cores of structures of substituted cyclopentasilanes, gives a good impression of the conformational efforts of the systems to acquire nonstrained conformations and the avoiding of axial arrangements of silyl substituents.

Theoretical Considerations. To understand the outcome of the rearrangement reactions, it is important to know about the energies of the product. There are two components contributing to these. One is caused by steric interactions and ring strain. The second contribution involves the degree of branching of the silicon framework. While we can assess the first contribution using a simple force-field calculation approach, the second part requires a more realistic model. In order to compare energies of the three $\text{Si}_{10}\text{Me}_{20}$ isomers **5**, **6**, and **17** we have carried out DFT calculations at the B3LYP/6-31G* level with the optimization starting from crystal structure geometries (see Table 1). The outcome of these calculations shows the five-membered ring as the lowest energy isomer and is thus in complete accordance with the observed situation.

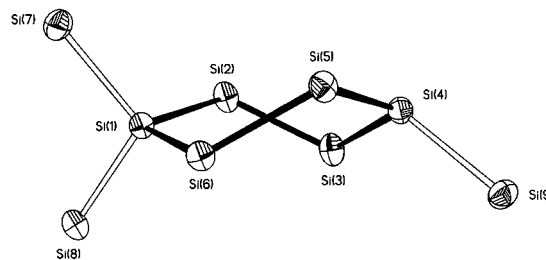
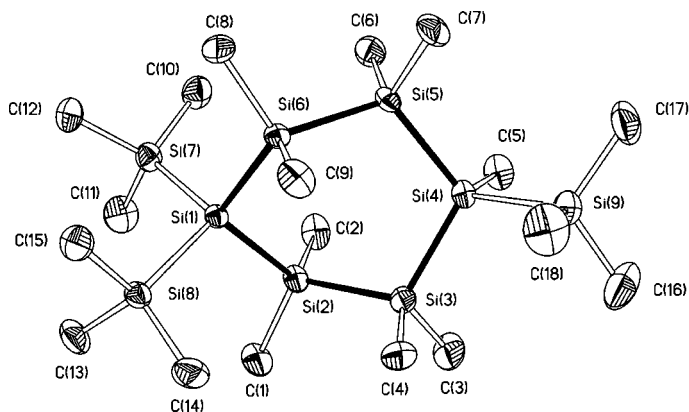


Figure 2. Left: Molecular structure and numbering of **4**. Right: Ring conformation of **4** with all methyl groups omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–Si(2) 2.348(2); Si(2)–Si(3) 2.336(2); Si(3)–Si(4) 2.348(2); Si(4)–Si(5) 2.355(2); Si(5)–Si(6) 2.337(2); Si(1)–Si(6) 2.355(2); Si(1)–Si(7) 2.349(2); Si(1)–Si(8) 2.352(2); Si(4)–Si(9) 2.345(2); Si(2)–Si(1)–Si(7) 108.13(6); Si(2)–Si(1)–Si(8) 110.77(6); Si(7)–Si(1)–Si(8) 107.18(6); Si(7)–Si(1)–Si(6) 111.52(6); Si(8)–Si(1)–Si(6) 108.81(6); Si(3)–Si(2)–Si(1) 113.55(6); Si(9)–Si(4)–Si(5) 112.63(6); Si(6)–Si(5)–Si(4) 113.60(6); Si(5)–Si(6)–Si(1) 114.07(5).

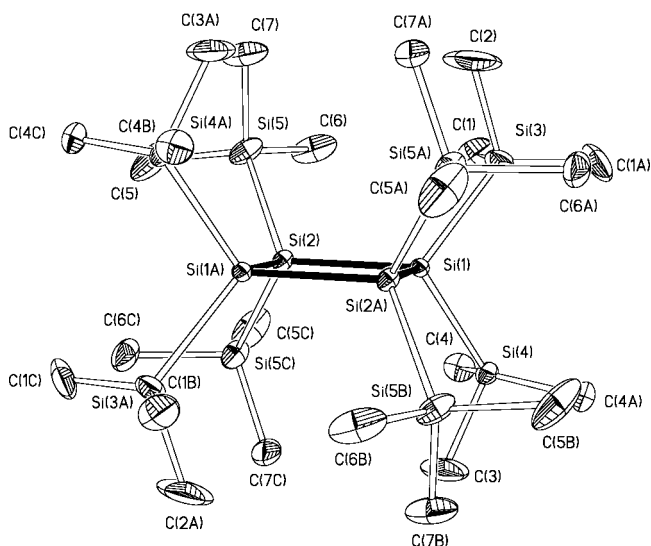


Figure 3. Molecular structure and numbering of **9**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: C(1)–Si(3) 1.919(11); Si(1)–Si(4) 2.365(2); Si(1)–Si(3) 2.382(2); Si(1)–Si(2) 2.398(1); Si(2)–Si(5) 2.382(1); Si(1)–Si(2A) 2.398(1); Si(4)–Si(1)–Si(3) 100.89(6); Si(4)–Si(1)–Si(2) 115.82(4); Si(3)–Si(1)–Si(2) 117.68(4); Si(4)–Si(1)–Si(2A) 115.82(4); Si(3)–Si(1)–Si(2A) 117.68(4); Si(2)–Si(1)–Si(2A) 90.02(5).

Conclusion

Our study on the aluminum chloride-catalyzed rearrangements of cyclic polysilanes has confirmed parts of the older studies.^{4,5} It was found that the permethylated monocyclic polysilanes Me₁₂Si₆, Me₁₄Si₇, Me₁₆Si₈, and Me₁₈Si₉ rearrange to cyclopentasilanes with trimethylsilyl substituents. The formation of a maximum number of 4-fold silylated silicon atoms and the minimization of steric interactions were observed as guiding motifs.

The result of the rearrangement of two Me₂₀Si₁₀ isomers was different from the outcome reported by Blinka and West⁵ in that sense that not 1,1,4,4-tetrakis(trimethylsilyl)cyclohexasilane but another example of a substituted cyclopentasilane was formed.

In contrast to the reactions of the smaller isomers, rearrangements of isomers Me₂₂Si₁₁, Me₂₄Si₁₂, Me₂₆Si₁₃, and Me₂₈Si₁₄

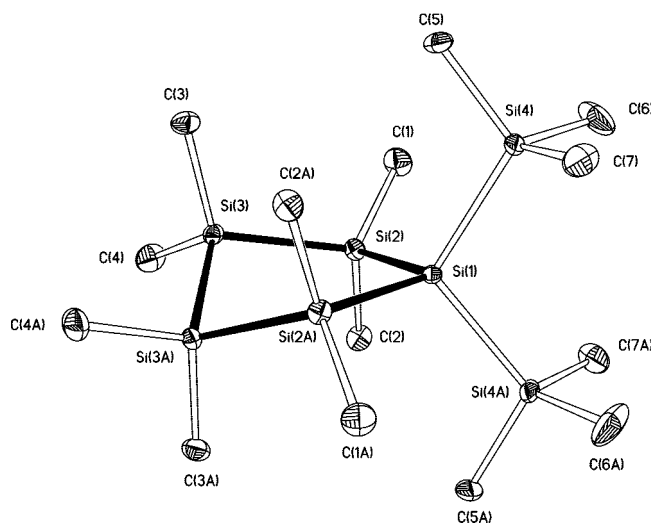


Figure 4. Molecular structure and numbering of **13** (two crystallographically independent molecules in the unit cell, only one shown). Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–Si(2) 2.362(2); Si(2)–Si(3) 2.344(2); Si(3)–Si(3A) 2.345(2); Si(1)–Si(4) 2.351(2); Si(4A)–Si(1)–Si(4) 109.82(9); Si(4A)–Si(1)–Si(2A) 111.71(5); Si(4)–Si(1)–Si(2A) 109.03(5); Si(2A)–Si(1)–Si(2) 105.49(8); Si(3)–Si(2)–Si(1) 104.87(6); Si(2)–Si(3)–Si(3A) 101.80(5).

yielded mixtures of isomers. Several of the compounds could be characterized unambiguously by single-crystal structure analysis. On the basis of these data and careful analysis of ²⁹Si NMR data we conclude that in all cases only cyclopentasilanes were formed. This is in contrast to what was reported for Me₂₀Si₁₀, Me₂₂Si₁₁, and Me₂₄Si₁₂.⁵

DFT calculations of the energies of the three Si₁₀Me₂₀ isomers showed that the isomerization of a six-membered ring to a five-membered one with an additional branching point is accompanied by an energy gain of about 6 kcal/mol.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents were dried over sodium/potassium alloy under nitrogen and were

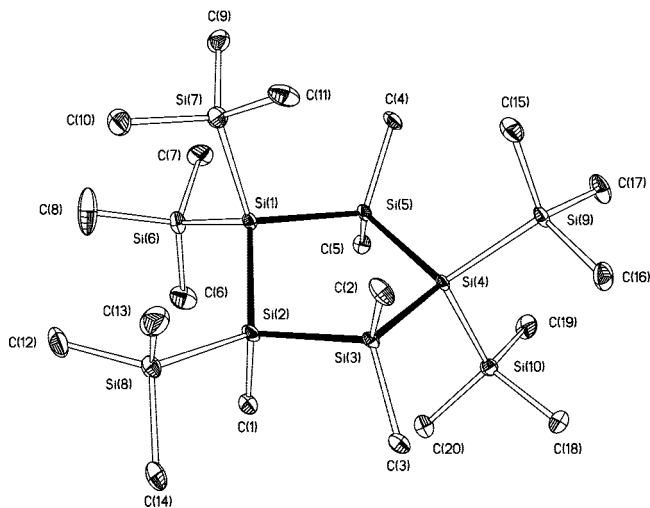


Figure 5. Molecular structure and numbering of **17**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–Si(2) 2.376(3); Si(2)–Si(3) 2.363(3); Si(3)–Si(4) 2.362(3); Si(4)–Si(5) 2.369(3); Si(1)–Si(5) 2.379(3); Si(1)–Si(6) 2.365(3); Si(1)–Si(7) 2.354(3); Si(2)–Si(8) 2.351(3); Si(4)–Si(9) 2.382(1); Si(4)–Si(10) 2.356(3); Si(2)–C(1) 1.919(9); Si(7)–Si(1)–Si(6) 106.25(11); Si(7)–Si(1)–Si(2) 115.50(11); Si(7)–Si(1)–Si(5) 110.66(11); Si(6)–Si(1)–Si(5) 108.92(11); Si(2)–Si(1)–Si(5) 102.45(10); Si(8)–Si(2)–Si(3) 112.39(12); Si(8)–Si(2)–Si(1) 119.64(12); Si(3)–Si(2)–Si(1) 104.28(11); Si(10)–Si(4)–Si(9) 107.77(11); Si(10)–Si(4)–Si(5) 111.17(11); Si(9)–Si(4)–Si(5) 113.49(11).

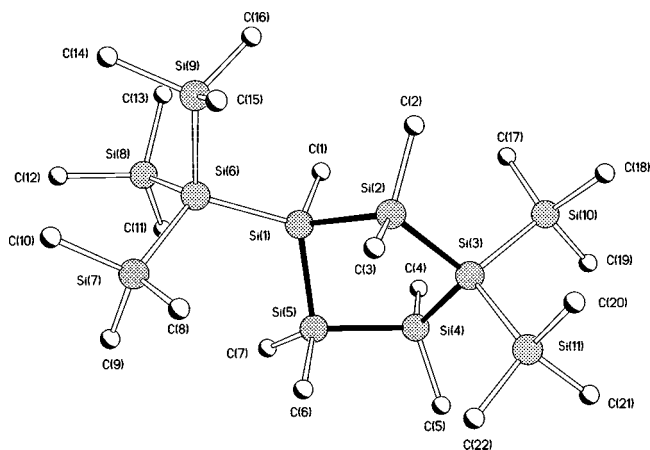


Figure 6. Molecular structure and numbering of **18**. Selected bond lengths [Å] and bond angles [deg]: Si(1)–C(1) 1.957(2); Si(1)–Si(2) 2.366(7); Si(2)–Si(3) 2.380(7); Si(3)–Si(4) 2.342(7); Si(4)–Si(5) 2.2330(7); Si(1)–Si(5) 2.412(8); Si(1)–Si(6) 2.369(7); Si(3)–Si(10) 2.2358(7); Si(3)–Si(11) 2.380(7); Si(6)–Si(7) 2.338(7); Si(6)–Si(8) 2.360(7); Si(6)–Si(9) 2.358(7); Si(2)–Si(1)–Si(6) 121.0(3); Si(2)–Si(1)–Si(5) 99.0(3); Si(6)–Si(1)–Si(5) 116.6(3); Si(1)–Si(2)–Si(3) 105.8(3); Si(4)–Si(3)–Si(10) 109.5(3); Si(10)–Si(3)–Si(2) 113.4(3); Si(4)–Si(3)–Si(11) 111.4(3); Si(10)–Si(3)–Si(11) 107.3(3); Si(2)–Si(3)–Si(11) 109.7(3); Si(5)–Si(4)–Si(3) 104.0(3); Si(4)–Si(5)–Si(1) 101.8(3); Si(7)–Si(6)–Si(9) 107.0(3); Si(7)–Si(6)–Si(1) 115.8(3); Si(9)–Si(6)–Si(1) 110.1(3).

freshly distilled prior to use. Potassium *tert*-butanolate was purchased from Merck. All other chemicals were bought from different suppliers and were used without further purification. The Al(Fe)Cl₃ catalyst for the rearrangement reactions was prepared by cosublimation of AlCl₃ and 1% FeCl₃.⁵ The following compounds were prepared following reported procedures: dodecam-

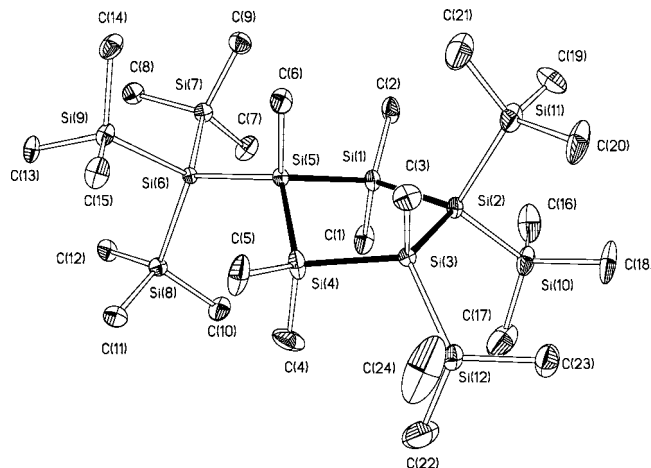


Figure 7. Molecular structure and numbering of **19**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–Si(2) 2.358(3); Si(2)–Si(3) 2.369(4); Si(3)–Si(4) 2.325(4); Si(4)–Si(5) 2.356(3); Si(1)–Si(5) 2.353(3); Si(2)–Si(10) 2.340(3); Si(2)–Si(11) 2.335(4); Si(3)–Si(12) 2.315(4); Si(5)–Si(6) 2.364(3); Si(6)–Si(7) 2.346(3); Si(6)–Si(8) 2.344(3); Si(6)–Si(9) 2.353(3); C(4)–Si(4) 1.870(9); Si(12)–Si(3)–Si(4) 113.94(15); Si(12)–Si(3)–Si(2) 120.08(15); Si(4)–Si(3)–Si(2) 104.71(13).

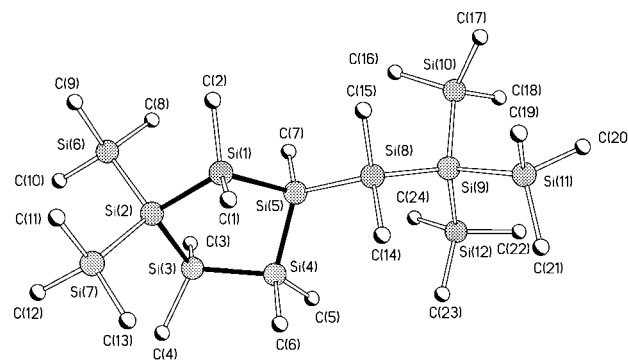


Figure 8. Molecular structure and numbering of **21**. Selected bond lengths [Å] and bond angles [deg]: Si(1)–Si(2) 2.361(6); Si(2)–Si(3) 2.346(6); Si(3)–Si(4) 2.322(7); Si(4)–Si(5) 2.320(6); Si(1)–Si(5) 2.357(6); Si(2)–Si(6) 2.345(6); Si(2)–Si(7) 2.343(6); Si(5)–Si(8) 2.349(7); Si(8)–Si(9) 2.337(6); Si(9)–Si(10) 2.347(6); Si(9)–Si(11) 2.338(7); Si(9)–Si(12) 2.333(6); Si(5)–Si(1)–Si(2) 105.8(2); Si(7)–Si(2)–Si(6) 110.1(2); Si(3)–Si(2)–Si(6) 111.4(2); Si(3)–Si(2)–Si(1) 105.1(2); Si(6)–Si(2)–Si(1) 109.5(2); Si(5)–Si(4)–Si(3) 104.2(2); Si(4)–Si(5)–Si(8) 120.3(3); Si(4)–Si(5)–Si(1) 99.5(2); Si(8)–Si(5)–Si(1) 108.0(2); Si(9)–Si(8)–Si(5) 119.4(2); Si(12)–Si(9)–Si(8) 113.3(2); Si(12)–Si(9)–Si(11) 106.3(2); Si(8)–Si(9)–Si(11) 107.7(2); Si(11)–Si(9)–Si(10) 106.5(2).

ethylcyclohexasilane,²⁰ trimethylsilylundecamethylcyclohexasilane (**1**),²¹ 1,1,2,2-tetrakis(trimethylsilyl)tetramethylcyclotetrasilane (**2**),^{8b} *cis/trans*-1,4-bis(trimethylsilyl)decamethylcyclohexasilane (**3**),^{8a} 1,1,4-tris(trimethylsilyl)nonamethylcyclohexasilane (**4**),^{8a} tris(trimethylsilyl)silylundecamethylcyclohexasilane (**5**),^{8a} and 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (**6**).^{8a} Octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) was obtained as a byproduct of the synthesis of tetrakis(trimethylsilyl)silane.²²

(20) West, R.; Brough, L.; Wojnowski, W. *Inorg. Synth.* **1979**, *19*, 265–268.

(21) Uhlig, F.; Gspaltl, P.; Trabi, M.; Hengge, E. *J. Organomet. Chem.* **1995**, *493*, 33–40.

(22) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1967**, *8*, 245–253.

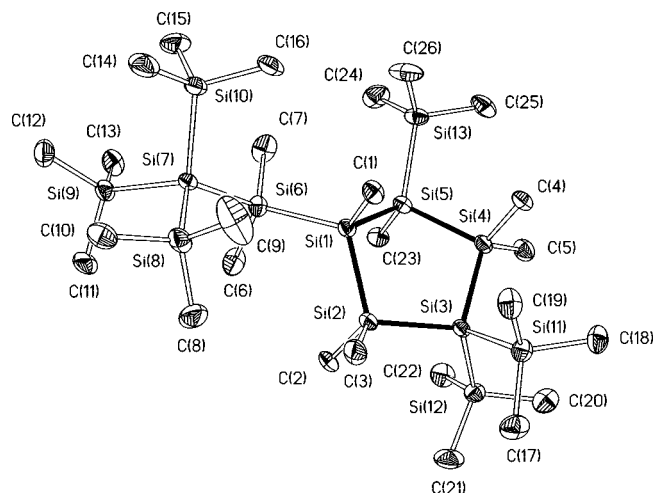


Figure 9. Molecular structure and numbering of **23**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–C(1) 1.913(6); Si(1)–Si(2) 2.367(3); Si(2)–Si(3) 2.365(3); Si(3)–Si(4) 2.356(3); Si(4)–Si(5) 2.351(3); Si(1)–Si(5) 2.367(3); Si(1)–Si(6) 2.367(3); Si(3)–Si(11) 2.359(3); Si(3)–Si(12) 2.352(3); Si(6)–Si(7) 2.366(3); Si(7)–Si(8) 2.330(3); Si(7)–Si(9) 2.364(3); Si(7)–Si(10) 2.341(3); Si(5)–Si(1)–Si(6) 108.65(10); Si(5)–Si(1)–Si(2) 101.27(10); Si(6)–Si(1)–Si(2) 117.38(10); Si(3)–Si(2)–Si(1) 105.95(10).

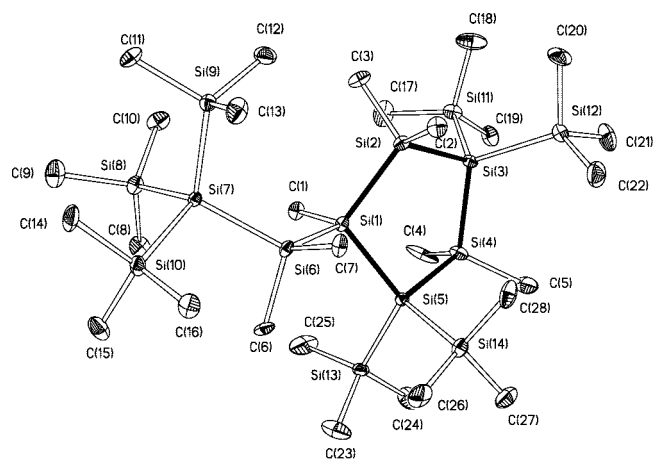


Figure 10. Molecular structure and numbering of **27**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and bond angles [deg]: Si(1)–C(1) 1.902(6); Si(1)–Si(2) 2.371(3); Si(2)–Si(3) 2.371(3); Si(3)–Si(4) 2.362(3); Si(4)–Si(5) 2.373(3); Si(1)–Si(5) 2.384(2); Si(1)–Si(6) 2.375(2); Si(3)–Si(11) 2.369(3); Si(3)–Si(12) 2.367(3); Si(5)–Si(13) 2.376(3); Si(5)–Si(14) 2.364(3); Si(6)–Si(7) 2.371(2); Si(7)–Si(8) 2.351(2); Si(7)–Si(9) 2.363(3); Si(7)–Si(10) 2.369(3); Si(2)–Si(1)–Si(6) 117.41(9); Si(2)–Si(1)–Si(5) 105.27(9); Si(6)–Si(1)–Si(5) 109.70(9); Si(4)–Si(3)–Si(12) 116.75(10).

^1H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si NMR spectra were either dissolved in a deuterated solvent or measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si , the INEPT pulse sequence was used for the amplification of the signal.²³ Elementary analysis was carried out using a Heraeus Vario Elemental.

(23) (a) Morris, G. A.; Freeman, R. J. *Am. Chem. Soc.* **1979**, *101*, 760–762. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877–879.

X-Ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT²⁴ and SADABS,²⁵ respectively. The structures were solved by direct methods and refined by the full-matrix least-squares method (SHELXL97).²⁶ If not noted otherwise all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Unfortunately the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low θ values.

Crystallographic data (excluding structure factors) for the structures of compounds *trans*-**3**, **4**, **13**, **17**, **18**, **19**, **21**, **23**, and **27** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-631358 (*trans*-**3**), 631357 (**4**), 650909 (**9**), 631352 (**13**), 631356 (**17**), 631355 (**18**), 631353 (**19**), 631354 (**21**), 649627 (**23**), and 649626 (**27**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk] or from the Internet: <http://www.ccdc.cam.ac.uk>.

Synthesis of Starting Materials. **1,1,2,3,3,4-Hexakis(trimethylsilyl)dimethylcyclotetrasilane (Si₁₀Me₂₀) (7).** A mixture of octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) (818 mg, 1.17 mmol), KO^tBu (289 mg, 2.57 mmol, 2.2 equiv), and 18-crown-6 (682 mg, 2.58 mmol, 2.2 equiv) was dissolved in benzene (15 mL). Shortly after, a red suspension formed. After 16 h the flask was cooled in an ice-bath and a solution of Me₂SO₄ (223 μL , 2.34 mmol, 2.0 equiv) in benzene (5 mL) was added over 5 min. At the end of addition a greenish turbid solution was observed.

The solution was subjected to an aqueous workup (washing with 0.5 M H₂SO₄ and saturated NaHCO₃ solution). All aqueous phases were extracted with two portions of Et₂O. The combined organic layers were dried over Na₂SO₄. After removal of the solvent a white residue was obtained that consisted of a mixture of *cis*- and *trans*-isomers of **7** in a ratio of 1:1.24. Repeated recrystallizations from Et₂O/2-propanol mixtures led to a marked enrichment of the *trans*-isomer.

trans-**7** isomer: NMR data (δ in ppm, C₆D₆): ^1H 0.69 (s, 6H); 0.37 (s, 36H); 0.30 (s, 18H); ^{13}C 3.9; 0.1; –1.6; ^{29}Si –8.7; –12.0; –55.3; –93.7.

cis-**7** isomer: NMR data (δ in ppm, C₆D₆): ^1H 0.79 (s, 6H); 0.40 (s, 18H); 0.34 (s, 18H); 0.29 (s, 18H); ^{13}C 4.1; 3.7; 0.1; –1.0; ^{29}Si –6.7; –10.0; –12.3; –51.5; –95.2.

Anal. Calcd for C₂₀H₆₀Si₁₀ (581.55): C 41.31, H 10.40. Found: C 40.82, H 10.47.

Heptakis(trimethylsilyl)methylcyclotetrasilane (Si₁₁Me₂₂) (8). In an analogous way to the synthesis of **7** using octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) (320 mg, 0.459 mmol), KO^tBu (52 mg, 0.46 mmol, 1.0 equiv), 18-crown-6 (121 mg, 0.458 mmol, 1.0 equiv), and Me₂SO₄ (44 μL , 0.46 mmol, 1.0 equiv) **10** (270 mg, 0.422 mmol, 92%) was obtained as a white

(24) SAINTPLUS: Software Reference Manual, Version 6.45; Bruker-AXS: Madison, WI, 1997–2003.

(25) Blessing, R. H. *Acta Crystallogr. A* **1995**, *51*, 33–38; SADABS, Version 2.1; Bruker AXS, 1998.

(26) Sheldrick, G. M. SHELXL97, Programs for Crystal Structure Analysis (Release 97-2); Universität Göttingen: Göttingen, Germany, 1998.

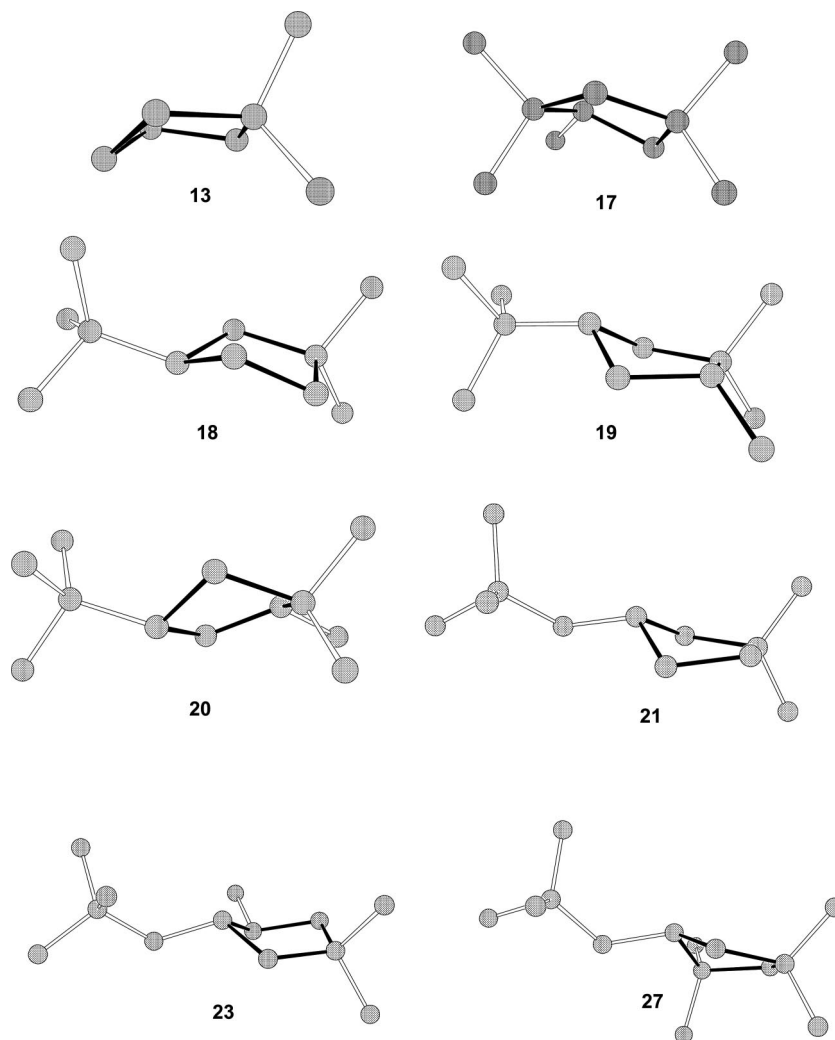


Figure 11. Schematic representation of crystal structures of substituted cyclopentasilanes. Only the polysilane skeleton is drawn for clarity.

solid that was contaminated with ca. 5% of **9**, which could not be removed by recrystallization from Et₂O/acetone.

NMR data (δ in ppm, C₆D₆): ¹H 0.74 (s, 3H); 0.47 (s, 9H); 0.44 (s, 18H); 0.42 (s, 9H); 0.37 (s, 18H); 0.29 (s, 9H); ¹³C 4.4 (2 \times); 4.2; 4.1; 0.2; ²⁹Si -8.1; -9.4; -12.5; -46.0; -93.4; -97.3.

Anal. Calcd for C₂₂H₆₆Si₁₁ (639.70): C 41.31, H 10.40. Found: C 41.19, H 10.73.

1,4-Bis(pentamethyldisilanyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (Si₁₂Me₂₄) (10). A mixture of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane^{8a} (**6**) (422 mg, 0.727 mmol), KO^tBu (167 mg, 1.49 mmol, 2.05 equiv), and 18-crown-6 (394 mg, 1.49 mmol, 2.05 equiv) was dissolved in benzene (5 mL). After 24 h the yellow suspension was added to a solution of chloropentamethyldisilane (249 mg, 1.49 mmol, 2.05 equiv) in benzene (2 mL). After 5 h the yellowish solution was subjected to an aqueous workup. After removal of the solvent a white residue (477 mg, 0.683 mmol, 94%) was obtained that consisted of a mixture of *cis*- and *trans*-isomers of **10** in a ratio of 1:1.4.

NMR data of the isomeric mixture (δ in ppm, C₆D₆): ¹H 0.42 (s, 12H); 0.41 (s, 12H); 0.39 (s, 12H); 0.33 (s, 9H); 0.33 (s, 9H); 0.22 (s, 18H); ¹³C 4.2 (2 \times); 0.1 (2 \times); -0.1; -0.2; -0.4 (4 \times); ²⁹Si -8.8/-9.0; -14.7/-14.7; -37.4/-37.1; -37.9/-37.7; -126.0/-126.0.

Heptakis(trimethylsilyl)pentamethyldisilanyl cyclotetrasilane (Si₁₃Me₂₆) (11). In a similar way to the synthesis of **10** the silylpotassium compound generated from octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) (625 mg, 0.896 mmol), KO^tBu (101 mg, 0.900 mmol, 1.0 equiv), and 18-crown-6 (237 mg, 0.897 mmol, 1.0 equiv) was reacted with pentamethylchlorodisilane (149 mg, 0.893 mmol, 1.0 equiv). After aqueous workup and removal of the solvent the remaining white residue was recrystallized from Et₂O/acetone to give **11** (465 mg, 0.615 mmol, 69%) contaminated with about 5% of **9**.

NMR data (δ in ppm, C₆D₆): ¹H 0.54 (s, 6H); 0.47 (s, 18 H); 0.47 (s, 9H); 0.46 (s, 36H); 0.25 (s, 9H); ¹³C 5.0; 4.8; 4.7; 4.7 (2 \times); 1.9; 0.9; ²⁹Si -9.1; -9.3; -9.4; -9.5; -9.8; -11.4; -35.0; -79.5; -88.3; -92.1.

Anal. Calcd for C₂₆H₇₈Si₁₃ (756.01): C 41.31, H 10.40. Found: C 41.11, H 10.36.

1,1,2,3,3,4-Hexakis(trimethylsilyl)bis(pentamethyldisilanyl)cyclotetrasilane (Si₁₄Me₂₈) (12). In a similar way to the synthesis of **10** the silyldipotassium compound generated from octakis(trimethylsilyl)cyclotetrasilane¹⁸ (**9**) (408 mg, 0.585 mmol), KO^tBu (135 mg, 1.20 mmol, 2.05 equiv), and 18-crown-6 (317 mg, 1.20 mmol, 2.05 equiv) was reacted with pentamethylchlorodisilane (195 mg, 1.17 mmol, 2.0 equiv). After aqueous workup and removal of the solvent the remaining white residue was found to be a 1:1 mixture of the *cis*- and

Table 3. Crystallographic Data for Compounds *trans*-3, 4, 9, 13, and 17

	<i>trans</i> -3	4	9	13	17
empirical formula	Si ₁₆ C ₃₂ H ₉₆	Si ₉ C ₁₈ H ₅₄	Si ₁₂ C ₂₄ H ₆₆	Si ₁₄ C ₂₈ H ₈₄	Si ₁₀ C ₂₀ H ₆₀
<i>M_w</i>	930.53	523.42	691.85	814.21	581.58
temperature [K]	100(2)	200(2)	100(2)	100(2)	100(2)
size [mm]	0.46 × 0.33 × 0.24	0.32 × 0.22 × 0.16	0.34 × 0.22 × 0.16	0.40 × 0.20 × 0.15	0.33 × 0.22 × 0.18
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>C2/m</i>	<i>C2</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.417(2)	10.106(2)	19.235(4)	16.458(3)	9.476(2)
<i>b</i> [Å]	10.430(2)	22.497(5)	12.713(3)	10.881(2)	12.848(2)
<i>c</i> [Å]	14.391(3)	30.430(6)	10.285(2)	16.485(3)	16.166(3)
α [deg]	76.58(3)	90	90	90	85.29(3)
β [deg]	88.85(3)	90	118.53(3)	117.18(3)	88.57(3)
γ [deg]	88.39(3)	90	90	90	74.54(3)
<i>V</i> [Å ³]	1520.1(5)	6918(2)	2209(5)	2626.0(9)	1890.5(7)
<i>Z</i>	1	8	2	2	2
ρ_{calc} [g cm ⁻³]	1.016	1.005	1.040	1.030	1.022
absorp coeff [mm ⁻¹]	0.354	0.350	0.365	0.359	0.356
<i>F</i> (000)	512	2304	756	896	640
θ range	1.96 < θ < 25.00	1.81 < θ < 25.00	2.00 < θ < 26.40	1.39 < θ < 25.00	1.26 < θ < 24.00
no. of reflns collected/unique	10 821/5292	46 747/6077	5959/2309	9410/4571	12 461/5898
completeness to θ [%]	98.6	100	97.4	99.9	99.1
no. of data/restraints/params	5292/0/233	6077/0/262	2309/30/136	4571/1/206	5898/0/291
goodness of fit on <i>F</i> ²	0.99	1.30	1.13	1.04	1.22
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.038, w <i>R</i> 2 = 0.100	<i>R</i> 1 = 0.076, w <i>R</i> 2 = 0.160	<i>R</i> 1 = 0.059, w <i>R</i> 2 = 0.166	<i>R</i> 1 = 0.052, w <i>R</i> 2 = 0.107	<i>R</i> 1 = 0.108, w <i>R</i> 2 = 0.240
<i>R</i> indices (all data)	<i>R</i> 1 = 0.042, w <i>R</i> 2 = 0.105	<i>R</i> 1 = 0.091, w <i>R</i> 2 = 0.166	<i>R</i> 1 = 0.065, w <i>R</i> 2 = 0.170	<i>R</i> 1 = 0.063, w <i>R</i> 2 = 0.112	<i>R</i> 1 = 0.134, w <i>R</i> 2 = 0.258
largest diff peak/hole [e ⁻ /Å ³]	0.63/−0.23	0.53/−0.27	0.77/−0.40	0.63/−0.32	1.01/−0.48

trans-isomers of **12**. Recrystallization from Et₂O/acetone did not afford enrichment of an isomer.

NMR data of the isomeric mixture (δ in ppm, C₆D₆): ¹H 0.55 (s, 24H); 0.48 (m, 108H); 0.25 (s, 36H); ¹³C 5.4; 5.2; 5.0; 4.9 (2×); 2.1; 2.0; 0.9 (2×); ²⁹Si −9.2; −9.3; −9.6; −9.7; −11.1; −11.2; −34.5; −34.7; −79.8; −80.0; −84.7; −84.7.

Anal. Calcd for C₂₈H₈₄Si₁₄ (814.16): C 41.31, H 10.40. Found: C 40.92, H 10.33.

General Procedure for the Rearrangement Reactions. Solutions of the starting material oligosilane (50–1000 mg) and approximately 0.15 equiv of Al(Fe)Cl₃ in cyclohexane (5–10 mL) in a Schlenk tube with a Teflon screw-cap were heated to 80 °C. Alternatively, solutions in dichloromethane did not require heating.

After 16–24 h the rate of conversion was checked by ²⁹Si NMR spectroscopy. If no or insufficient conversion was observed, additional Al(Fe)Cl₃ was added. After completion of the reaction acetone (10–20 mL) was added to the cold solution. The formed white precipitate was removed by either filtration or centrifugation. After removal of the solvent the residue was subjected to crystallization conditions. In the case of air-sensitive compounds the workup procedure was carried out under a nitrogen atmosphere.

Rearrangement of the Si₇Me₁₄ Isomer 1 to 13. The reaction was carried out following the general procedure using trimethylsilylundecamethylcyclohexasilane²¹ (**1**) (5.00 g, 12.3 mmol) and Al(Fe)Cl₃ (200 mg, 1.50 mmol, 0.12 equiv) in cyclohexane. Completion was reached after 10 h. **13** was obtained as a white crystalline product (3.00 g, 7.37 mmol, 60%) after recrystallization from acetone at −80 °C.

NMR data (δ in ppm, C₆D₆): ¹H 0.36 (s, 12H); 0.29 (s, 18H); 0.24 (s, 12H); ¹³C 3.6; −1.6; −6.4; ²⁹Si −7.9; −32.0; −40.5; −132.9.

Rearrangement of the Si₈Me₁₆ Isomer 3 to 14. The reaction was carried out following the general procedure using **3** (265 mg, 0.570 mmol) and Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.40 equiv) in cyclohexane. After 16 h another portion of Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.40 equiv) was added. Completion was reached

after an additional 24 h. White crystalline **14** was obtained after recrystallization from acetone at rt. Spectral and physical data were essentially identical to the reported data.⁵

Rearrangement of the Si₉Me₁₈ Isomer 4 to 15. The reaction was carried out following the general procedure using **4** (360 mg, 0.688 mmol) and Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.33 equiv) in cyclohexane. After 24 h no conversion was detected and an additional portion of Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.33 equiv) was added. After a further 24 h complete conversion occurred and **15** was obtained as a white crystalline solid. Spectral and physical data were identical to the data reported for independent syntheses.^{5,12,13}

Ring-Opening Reaction of Compound 2. The reaction was carried out following the general procedure using **2** (60 mg, 0.13 mmol) and Al(Fe)Cl₃ (3 mg, 0.02 mmol, 0.2 equiv) in dichloromethane at rt. After 8 h the complete formation of dichlorosilane **16** was detected. An alternative reaction in cyclohexane at 80 °C with **2** (487 mg, 1.05 mmol) and Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.22 equiv) led to the same result.

NMR data (δ in ppm, CH₂Cl₂, D₂O capillary): ¹H 0.20 (s, 12H); 0.14 (s, 36 H); ¹³C 5.7; 3.4; ²⁹Si 21.2; −9.4; −132.4.

Rearrangement of the Si₁₀Me₂₀ Isomers 5, 6, and 7 to 17. The general procedure was followed using **5** (190 mg, 0.332 mmol) and Al(Fe)Cl₃ (25 mg, 0.19 mmol, 0.57 equiv) in heptane (5 mL). After 2 days the conversion was complete and **17** was obtained as the sole product as a colorless liquid (0.095 g, 0.17 mmol, 51%), which could be crystallized from acetone.

NMR data (δ in ppm, C₆D₆): ¹H 0.61 (s, 3H, Me₂Si); 0.60 (s, 3H, Me₂Si); 0.50 (s, 3H, Me₂Si); 0.49 (s, 3H, Me₂Si); 0.34 (s, 9H, Me₃Si); 0.33 (s, 9H, Me₃Si); 0.32 (s, 9H, Me₃Si); 0.31 (s, 9H, Me₃Si); 0.29 (s, 9H, Me₃Si); 0.26 (s, 3H, MeSi); ¹³C 4.7 (Me₂Si); 4.3 (Me₃Si); 4.1 (Me₂Si); 4.0 (Me₃Si); 4.0 (Me₃Si); 3.9 (Me₃Si); 1.1 (Me₃Si); 0.84 (Me₂Si); −0.49 (Me₂Si); −6.8 (MeSi); ²⁹Si −6.8 (Me₃Si); −7.2 (Me₃Si); −8.3 (Me₃Si); −9.3 (Me₃Si); −10.4 (Me₃Si); −14.8 (Me₂Si); −16.7 (Me₂Si); −66.8 (MeSiMe₃Si); −120.8 (Me₃SiSiMe₃Si); −129.4 (Me₃SiSiMe₃Si).

Table 4. Crystallographic Data for Compounds 18, 19, 21, 23, and 27

	18	19	21	23	27
empirical formula	Si ₁₁ C ₂₂ H ₆₆	Si ₁₂ C ₂₄ H ₇₂	Si ₁₂ C ₂₄ H ₇₂	Si ₁₃ C ₂₆ H ₇₈	Si ₈ C ₁₆ H ₄₈
<i>M_w</i>	639.74	697.90	697.90	756.05	465.26
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.34 × 0.22 × 0.18	0.35 × 0.25 × 0.22	0.33 × 0.20 × 0.14	0.46 × 0.40 × 0.20	0.28 × 0.20 × 0.18
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	<i>Cc</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> [Å]	9.426(2)	9.214(2)	9.620(2)	9.910(2)	38.585(8)
<i>b</i> [Å]	17.381(6)	14.738(3)	31.999(6)	15.866(3)	9.6279(2)
<i>c</i> [Å]	25.200(5)	16.797(3)	14.645(3)	17.130(3)	29.840(6)
α [deg]	90	88.72(3)	90	76.20(3)	90
β [deg]	92.44(3)	84.71(3)	98.75(3)	78.64(3)	107.39(3)
γ [deg]	90	76.88(3)	90	72.26(3)	90
<i>V</i> [Å ³]	4124.9(2)	2212.0(7)	4455.8(2)	2468(7)	10579(4)
<i>Z</i>	4	2	4	2	14
ρ_{calc} [g cm ⁻³]	1.030	1.048	1.040	1.017	1.022
absorp coeff [mm ⁻¹]	0.359	0.365	0.363	0.355	0.357
<i>F</i> (000)	1408	768	1536	832	3584
θ range	1.62 < θ < 22.49	1.22 < θ < 24.00	1.27 < θ < 22.50	1.66 < θ < 25.27	1.11 < θ < 25.00
no. of reflns collected/unique	11 388/5336	14 078/6878	25345/5822	17 984/8819	37 092/9319
completeness to θ [%]	99.9	99.1	100	98.4	100
no. of data/restraints/params	5336/8/321	6878/30/384	5822/0/349	8819/0/378	9319/0/407
goodness of fit on <i>F</i> ²	1.12	1.31	1.27	0.97	1.27
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.139, w <i>R</i> 2 = 0.308	<i>R</i> 1 = 0.117, w <i>R</i> 2 = 0.244	<i>R</i> 1 = 0.191, w <i>R</i> 2 = 0.403	<i>R</i> 1 = 0.088, w <i>R</i> 2 = 0.165	<i>R</i> 1 = 0.106, w <i>R</i> 2 = 0.185
<i>R</i> indices (all data)	<i>R</i> 1 = 0.160, w <i>R</i> 2 = 0.325	<i>R</i> 1 = 0.128, w <i>R</i> 2 = 0.249	<i>R</i> 1 = 0.201, w <i>R</i> 2 = 0.409	<i>R</i> 1 = 0.185, w <i>R</i> 2 = 0.203	<i>R</i> 1 = 0.140, w <i>R</i> 2 = 0.198
largest diff peak/hole [e ⁻ /Å ³]	1.25/−0.73	0.97/−0.71	1.50/−0.95	0.55/−0.35	0.62/−0.41

MS (70 eV) *m/z* (%): 580 (3.9) [*M*⁺], 507 (2.7) [*M*⁺ − SiMe₃], 419 (0.8) [*M*⁺ − Si₂Me₇], 361 (14.2) [Si₇Me₁₁⁺], 131 (27.8) [Si₂Me₅⁺], 73 (100) [SiMe₃⁺].

Rearrangement reactions of compounds **6** and **7** under similar conditions also led to the exclusive formation of compound **17**.

Rearrangement of the Si₁₁Me₂₂ Isomer 8 to 18. The general procedure was followed using **8** (270 mg, 0.422 mmol) and Al(Fe)Cl₃ (20 mg, 0.15 mmol, 0.36 equiv) in cyclohexane. After 24 h complete conversion of the starting material was observed to a mixture of several compounds. After a further 24 h a slight change in the isomeric ratio of the compounds was observed. Addition of Al(Fe)Cl₃ (20 mg, 0.15 mmol, 0.36 equiv) and reaction for 24 h caused a strong change in the isomeric ratio of the products. A final addition of Al(Fe)Cl₃ (20 mg, 0.15 mmol, 0.36 equiv) was without effect. Judging from the ²⁹Si NMR spectra four isomeric products were formed, with two compounds being major isomers. Crystallization attempts from acetone/2-propanol mixtures allowed the isolation of one isomer, which could be characterized as 3,3-bis(trimethylsilyl)-1-tris(trimethylsilyl)silylhexamethylcyclopentasilane (**18**).

NMR data (δ in ppm, C₆D₆): ¹H 0.57 (s, 3H); 0.56 (s, 3H); 0.42 (s, 3H); 0.41 (s, 3H); 0.37 (s, 3H); 0.37 (s, 3H); 0.37 (s, 3H); 0.34 (s, 27H); 0.32 (s, 9H); 0.32 (s, 9H); ¹³C 3.9; 3.6; 3.5; 2.6; 0.5; −0.5; −2.2; −3.1; −4.7; −5.2. ²⁹Si: −7.6; −8.0; −9.6; −22.4; −30.9; −31.8; −73.4; −128.8; −133.6.

Anal. Calcd for C₂₂H₆₆Si₁₁ (639.70): C 41.31, H 10.40. Found: C 40.80, H 10.67.

Rearrangement Reactions of the Si₁₂Me₂₄ Isomers 9 and 10. The general procedure was followed using **9** (310 mg, 0.444 mmol) and Al(Fe)Cl₃ (6 mg, 0.05 mmol, 0.1 equiv) in dichloromethane at 40 °C. After 4 h complete conversion of the starting material was observed. In an alternative experiment cyclohexane **9** (390 mg, 0.559 mmol) and Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.41 equiv) were reacted at 80 °C. Complete conversion in this case required 24 h. Both experiments gave essentially identical ²⁹Si NMR spectra.

On the basis of analysis of these spectra four isomeric products were formed. Crystallization attempts from acetone/

2-propanol mixtures allowed the separation of a mixture of two isomers, which could be characterized by single-crystal structure analysis as *cis*-1,1,2-tris(trimethylsilyl)-4-[tris(trimethylsilyl)silyl]hexamethylcyclopentasilane (**19**) and *trans*-1,1,2-tris(trimethylsilyl)-4-[tris(trimethylsilyl)silyl]hexamethylcyclopentasilane (**20**). Further crystallization of the mother liquor provided crystals of 1,1-bis(trimethylsilyl)-3-dimethyl[tris(trimethylsilyl)silyl]silylheptamethylcyclopentasilane (**21**), which was also subjected to single-crystal structure analysis. On the basis of ²⁹Si NMR shifts, which are similar to those of **19** and **20**, we assume the fourth isomer to be *trans*-1,1,3-tris(trimethylsilyl)-4-[tris(trimethylsilyl)silyl]hexamethylcyclopentasilane (**22**).

To prove that the same rearrangement reaction products form also from a starting material with larger ring size, we also subjected **10** (300 mg, 0.430 mmol) to the conditions of the general procedure with Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.53 equiv) in cyclohexane at 80 °C. After 24 h no conversion was observed and additional Al(Fe)Cl₃ (30 mg, 0.23 mmol, 0.53 equiv) was added. After a further 24 h ²⁹Si NMR spectra indicated an identical isomeric mixture to that observed for the rearrangement of **9**.

19: NMR data (δ in ppm, C₆D₆): ¹H 0.59 (s, 3H); 0.55 (s, 3H); 0.52 (s, 3H); 0.41 (s, 3H); 0.40 (s, 3H); 0.38 (s, 3H); 0.35 (s, 9H); 0.34 (s, 27H); 0.33 (s, 9H); 0.29 (s, 9H); ²⁹Si −7.9; −8.7; −9.5 (3 × SiMe₃); −9.6; −21.9; −24.0; −71.9; −74.6; −127.2; −128.3.

20: NMR data (δ in ppm, C₆D₆): ¹H 0.58 (s, 3H); 0.57 (s, 3H); 0.48 (s, 3H); 0.41 (s, 3H); 0.40 (s, 3H); 0.38 (s, 9H); 0.35 (s, 27H); 0.34 (s, 3H); 0.33 (s, 9H); 0.28 (s, 9H); ²⁹Si −6.1; −9.5 (3 × SiMe₃); −9.6; −10.4; −17.2; −24.9; −72.3; −73.0; −126.6; −127.9.

Mixture of **21** and **22:** ²⁹Si NMR data (δ in ppm, C₆D₆) −7.6; −7.8; −7.9; −8.1; −8.8; −9.5 (3 × SiMe₃); −9.6 (3 × SiMe₃); −17.0; −20.6; −22.4; −25.9; −28.9; −29.9; −69.1; −71.9; −72.4; −126.0; −126.7; −132.2; −134.9.

Rearrangement Reactions of the Si₁₃Me₂₆ Isomer 11. The general procedure was followed using **11** (250 mg, 0.331 mmol) and Al(Fe)Cl₃ (15 mg, 0.11 mmol, 0.33 equiv) in cyclohexane

at 80 °C. Complete conversion was achieved after 16 h. One major and two isomeric side products were observed. By crystallization from pentane/2-propanol the main product can be separated.

23: NMR data (δ in ppm, C_6D_6): 1H 0.70 (s, 3H); 0.65 (s, 3H); 0.61 (s, 3H); 0.54 (s, 3H); 0.52 (s, 3H); 0.52 (s, 3H); 0.42 (s, 3H); 0.35 (s, 27H); 0.34 (s, 9H); 0.33 (s, 9H); 0.33 (s, 9H); 0.29 (s, 3H); ^{13}C 5.5; 3.8; 3.8; 3.6; 3.4; 2.5; 1.7; 1.5; 0.6; -0.5; -6.4; -9.5. ^{29}Si : -7.9; -8.0; -9.8; -9.9; -17.2; -22.6; -26.6; -60.3; -68.8; -125.5; -130.4. Anal. Calcd for $C_{26}H_{78}Si_{13}$ (756.01): C 41.31, H 10.40. Found: C 40.52, H 10.09.

Mixture of **24** and **25**: ^{29}Si NMR data (δ in ppm, C_6D_6) -8.1; -9.4; -9.5; -9.7; -9.8; -9.9; -9.9; -19.6; -21.4; -22.6; -25.8; -28.5; -29.6; -30.1; -32.6; -72.4; -72.7; -75.0; -125.0; -125.3; -129.4; -131.4.

Rearrangement Reaction of $Si_{14}Me_{28}$ Isomer 12. The general procedure was followed using **12** (264 mg, 0.324 mmol) and $Al(Fe)Cl_3$ (20 mg, 0.15 mmol, 0.46 equiv) in cyclohexane at 80 °C. No conversion was observed after 16 h, and additional $Al(Fe)Cl_3$ (20 mg, 0.15 mmol, 0.46 equiv) was added. Complete conversion as indicated by ^{29}Si NMR spectroscopy on the next day led to the formation of three major products. One of these products (**27**) can be separated by crystallization from either diethyl ether or acetone at 0 °C.

26: NMR data (δ in ppm, C_6D_6): 1H 0.66 (s, 3H); 0.66 (s, 3H); 0.62 (s, 3H); 0.60 (s, 3H); 0.60 (s, 3H); 0.58 (s, 3H); 0.48

(s, 3H); 0.48 (s, 3H); 0.45 (s, 3H); 0.40 (s, 3H); 0.38 (s, 9H); 0.34 (s, 27 + 9H); 0.31 (s, 9H); ^{29}Si -7.3; -7.6; -8.9; -9.7; -17.8; -21.9; -25.0; -25.2; -30.9; -122.1; -128.6; -129.2.

27: NMR data (δ in ppm, C_6D_6): 1H 0.75 (s, 3H); 0.66 (s, 3H); 0.64 (s, 6H); 0.63 (s, 3H); 0.59 (s, 3H); 0.58 (s, 3H); 0.41 (s, 9H); 0.39 (s, 9H); 0.35 (s, 9H); 0.34 (s, 27H); 0.34 (s, 9H). ^{13}C : 6.2; 5.4; 4.8; 4.2; 3.6; 2.9; 1.0; 0.8; -3.1; ^{29}Si -6.0; -7.5; -8.0; -9.8; -9.9; -17.2; -17.6; -27.2; -49.7; -116.8; -124.7; -128.2. Anal. Calcd for $C_{28}H_{84}Si_{14}$ (814.16): C 41.31, H 10.40.

28: ^{29}Si NMR data (δ in ppm, C_6D_6) -9.8; -9.8; -18.3; -20.7; -30.1; -32.0; -64.8; -70.4; -129.0; -131.7.

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Note Added after ASAP Publication. In the version of this paper that was published on the Web on November 22, 2007, the artwork and title for Scheme 3 were incorrect, due to a production error. The artwork and title that now appear for Scheme 3 are correct.

Supporting Information Available: CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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