

Rearrangement/Fragmentation Reactions of Oligosilanes with Aluminum Chloride

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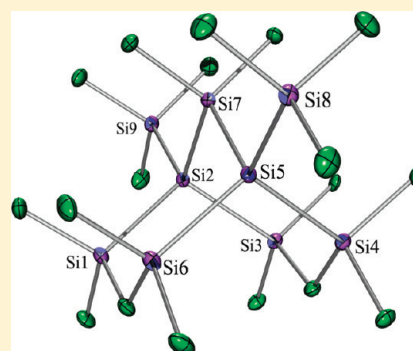
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 Supporting Information

ABSTRACT: Reinvestigation of the Lewis acid catalyzed rearrangement of some open-chain permethyloligosilanes with the $\text{Al}(\text{Fe})\text{Cl}_3$ catalyst system exhibited several cases of additional reactivity: namely, a fragmentation/cyclization reaction. Introduction of (trimethylsilyl)methyl substituents into the oligosilane substrates strongly facilitated this reaction, yielding cyclic or bicyclic carbacyclosilanes. Investigations concerning the composition of the catalyst system indicated that the incorporation of about 0.1% FeCl_3 into the AlCl_3 lattice provided an effective catalyst.



INTRODUCTION

Over the last few years our group has been strongly involved in the study of the chemistry of oligosilanes.^{1,2} In particular, the development of a convenient synthetic access to structurally diverse oligosilanyl anions^{3–6} allowed the preparation of a huge variety of previously unknown small polysilanes.^{1,2}

Some 40 years ago Ishikawa and Kumada discovered the AlCl_3 -catalyzed rearrangement of linear methylated oligosilanes to branched isomers.^{7,8} This chemistry can be considered to be complementary to our oligosilanyl anion chemistry, as it produces the strongly branched oligosilanes^{9,10} that are required as precursors for effectively stabilized oligosilanyl anions.

We became aware of this potential during the synthesis of an all-silicon analogue of the adamantane structure.¹¹ In a subsequent study we investigated AlCl_3 -catalyzed rearrangement reactions of already branched cyclosilanes.¹² One of the main conclusions we could draw from this work was that these rearrangement reactions always lead to substituted cyclopentasilanes.¹²

More recently, we showed that the introduction of trimethylgermyl groups into oligosilanes followed by AlCl_3 -catalyzed rearrangement exclusively led to the formation of isomers with germanium atoms possessing the highest possible silylation degree.¹³ In the course of this study a computational investigation of the reaction mechanism demonstrated its similarity to the well-known Wagner–Meerwein reaction: starting with the abstraction of a methyl group from the oligosilane, a silylium ion forms, which undergoes a series of 1,2-methyl and -silyl shifts

until the most stable ion is obtained. Eventually remethylation of the ion concludes the rearrangement process.¹³

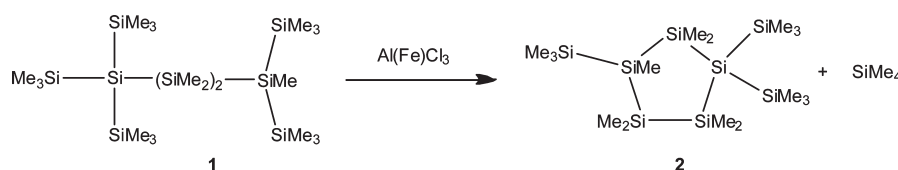
RESULTS AND DISCUSSION

The rearrangement processes of methylated oligosilanes can conveniently be monitored by NMR spectroscopy. ^1H NMR gives a good impression of the degree of conversion and in addition can be used to judge the molecular symmetry of the formed products from the number and integration of methyl resonances. ^{29}Si NMR spectroscopy provides even more insight. Not only is the direct methylation degree of silicon atoms reflected by their chemical shift but also to a lesser extent some information about the neighboring silicon atoms can be obtained. In general the rearrangement process leads to highly branched structures, and by analysis of the corresponding ^{29}Si NMR spectra we can distinguish between nonmethylated ($\delta(\text{SiSi}_4)$: ca. -110 to -140 ppm), monomethylated ($\delta(\text{MeSiSi}_3)$: ca. -70 to -100 ppm), dimethylated ($\delta(\text{Me}_2\text{SiSi}_2)$: ca. -25 to -60 ppm), and trimethylated silicon atoms ($\delta(\text{Me}_3\text{SiSi})$: ca. -5 to -20 ppm). In addition, tetraalkylated silicon atoms resonate close to a chemical shift value of 0 ppm. A high degree of branching of a neighboring silicon atom usually results in an additional downfield shift. How general this assignment scheme is can be estimated by studying Schemes 5, 6, and 8–13 of this report. ^{29}Si NMR shifts of

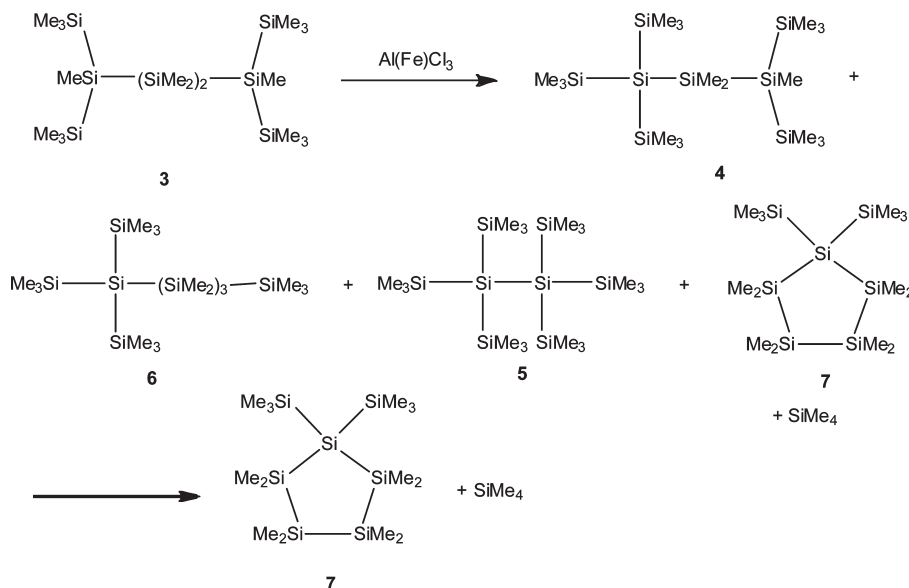
Received: November 29, 2010

Published: July 11, 2011

Scheme 1. Cyclization Reaction of a Branched Methylated Nonasilane To Give 1,1,3-Tris(trimethylsilyl)heptamethylcyclopentasilane



Scheme 2. Rearrangement/Cyclization Reaction of a Branched Methylated Octasilane To Give Branched Isomers and Further To Give 1,1-Bis(trimethylsilyl)octamethylcyclopentasilane



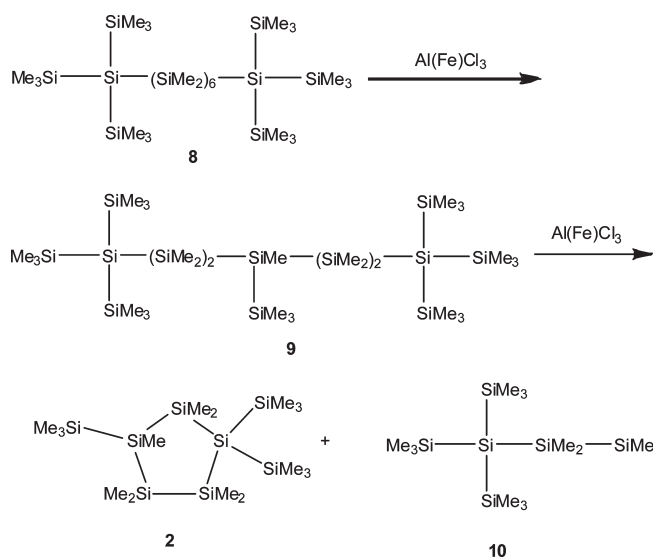
the involved oligosilanes are shown with the compounds. In addition, a short discussion of the chemical shift behavior of silicon atoms connected to methylene groups is given after the synthetic part.

Although much of the relevant analytical data required to describe the course of reaction can be obtained from NMR spectroscopy, reactions can also be followed by GC/MS analysis. While MS fragmentation patterns of rearranged oligosilanes are usually indistinguishable from the starting material, the retention behavior often changes and the method is suitable to detect fragmentation/cyclization reactions. Isolated products are finally subjected to standard characterization techniques such as NMR and UV spectroscopy, elemental analysis or HRMS, and (if possible) X-ray single-crystal diffraction analysis.

For our studies concerning the rearrangement of branched cyclosilanes¹² we used a cosublimates of AlCl_3 and FeCl_3 as described by Blinka and West¹⁴ as the catalyst. Attempts to use plain AlCl_3 proved to give less reproducible results in comparison to those for the cosublimates. However, the fact that in the original papers by Ishikawa, Kumada, and co-workers^{7–10} only the use of AlCl_3 was reported prompted us to study the rearrangement of some materials isomeric with their noncyclic oligosilane substrates with the Al(Fe)Cl_3 cosublimates catalyst.

Acyclic Methylated Oligosilanes. In the course of our studies we found that in general Al(Fe)Cl_3 -catalyzed reactions of branched oligosilanes which are isomeric with materials already studied by the Kumada group^{7–10} led to the same results. However, a few reactions showed an additional twist.

Scheme 3. Cyclization/Fragmentation Reaction of a Branched Methylated Tetradecasiline To Give 1,1,3-Tris(trimethylsilyl)Heptamethylcyclopentasilane and 2,2-Bis(trimethylsilyl)octamethyltetrasilane

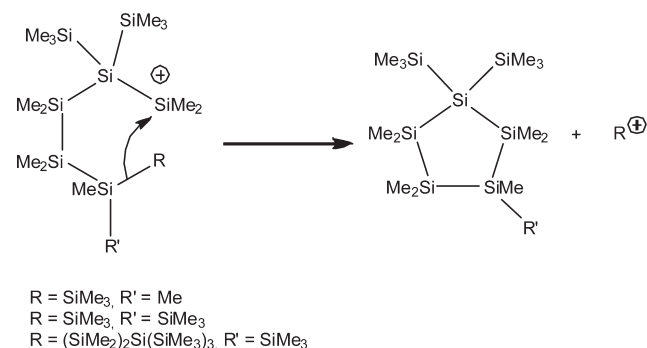


For example, the AlCl_3 -mediated rearrangement of *n*-eicosa-methylnonasilane was reported to yield 2,2,5-tris(trimethylsilyl)

undecamethylhexasilane (**1**) and 2,2,4,4-tetrakis(trimethylsilyl)-octamethylpentasilane in a ratio of 4:1 in high yield.⁹ Explicitly it was noted that no other isomers were detected by spectroscopic analysis.⁹ In contrast to that, the rearrangement of 2,2,5-tris(trimethylsilyl)undecamethylhexasilane (**1**) with Al(Fe)Cl₃ led to the almost quantitative formation of 1,1,3-tris(trimethylsilyl)heptamethylcyclopentasilane (**2**)^{10,12} and tetramethylsilane (Scheme 1).

Similarly Ishikawa et al. reported that the rearrangement of *n*-octadecamethyloctasilane gave a mixture of 2,2,4-tris(trimethylsilyl)nonamethylpentasilane (**4**) and 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetrasilane (**5**) in a ratio of 81:19.⁹ Our attempts to rearrange the isomeric compound 2,5-bis(trimethylsilyl)dodecamethylhexasilane (**3**) with Al(Fe)Cl₃ revealed initial formation of the two aforementioned compounds **4** and **5** in addition to 2,2-bis(trimethylsilyl)dodecamethylhexasilane (**6**) and 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (**7**).^{10,12} However, after a prolonged reaction time the cyclic compound **7** and tetramethylsilane became the major reaction products (Scheme 2).

Scheme 4. Mechanistic Rationale for the Cyclization Behavior Involving a 1,5-Silyl Migration

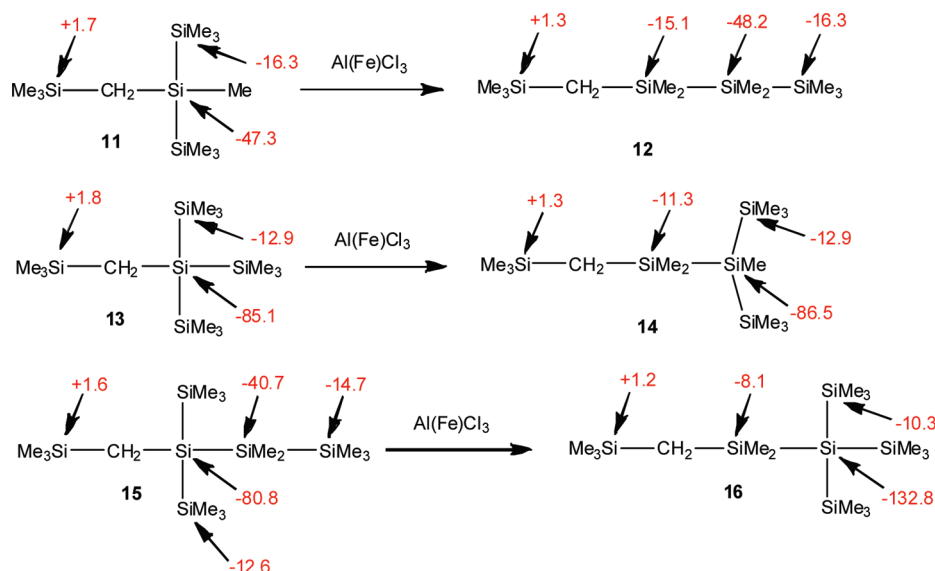


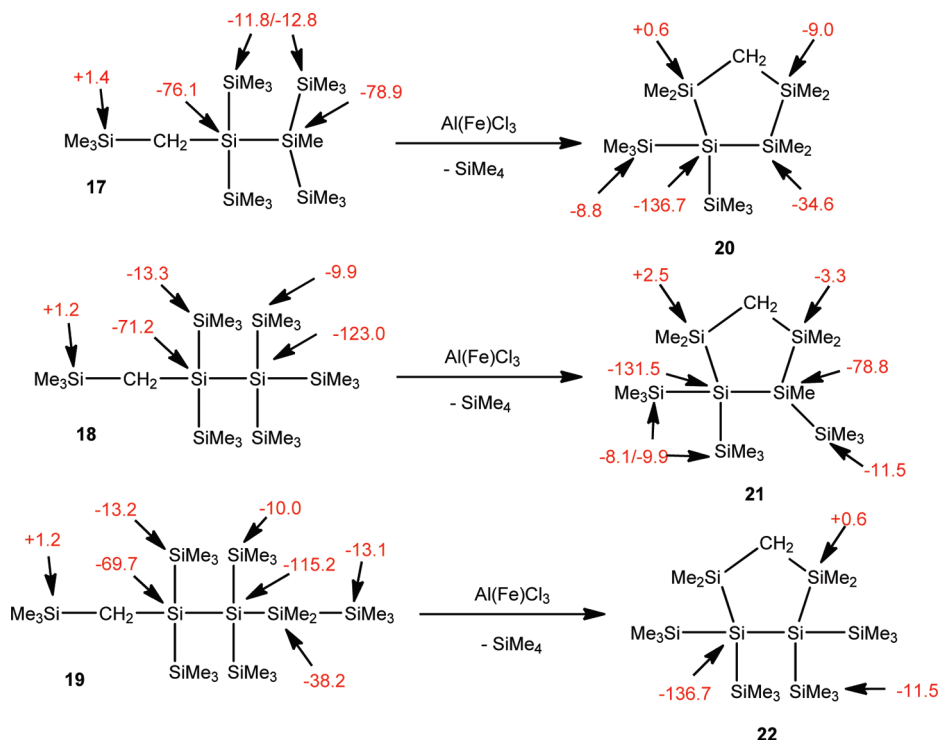
A related result was obtained when 2,2,9,9-tetrakis(trimethylsilyl)octadecamethyldecasilane (**8**) was subjected to the rearrangement conditions with Al(Fe)Cl₃. After initial formation of 2,2,5,8,8-pentakis(trimethylsilyl)pentadecamethylnonasilane (**9**) again the occurrence of 1,1,3-tris(trimethylsilyl)pentamethylcyclopentasilane (**2**) was observed, this time accompanied by 2,2-bis(trimethylsilyl)octamethyltetrasilane⁹ (**10**) as an elimination product (Scheme 3).

As this desilylative cyclization behavior was never mentioned in the Ishikawa/Kumada group reports,^{7–10} we attribute it to the enhanced reactivity of Al(Fe)Cl₃ compared to that of commercially available AlCl₃. Mechanistically the reaction can be interpreted as a migration/fragmentation reaction. We assume that the cyclization occurs via a 1,5-silyl shift. In the course of this shift the cationic charge is not retained in the molecule, as in the usual rearrangement reaction, but is eliminated as a trimethylsilylium ion which upon methylation with [MeAlCl₃][–] is converted to tetramethylsilane. There seems to be a steric component of this reaction, as it was not possible to cyclize 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane, which is likely sterically too hindered at the 5-position to undergo a nucleophilic attack at the silylium ion (Scheme 4).

Acyclic Methylated Oligosilanes Containing One Me₃SiCH₂ Group. In a recent study we investigated the conformational behavior of acyclic methylated oligosilanes containing (trimethylsilyl)methyl groups.¹⁵ These compounds provided us with the opportunity to study their rearrangement behavior. Initial expectations to obtain homogeneous product distributions were not too high, as it was demonstrated by Blinka and West that the introduction of an ethyl group into an otherwise methylated oligosilane led to a scrambling of ethyl groups upon rearrangement to give non-, mono-, di-, tri-, and higher ethylated products.¹⁴ We found the same behavior after introducing single phenyl groups into methylated oligosilanes. However, after preliminary results showed a clean rearrangement course, it was decided to study the reactions of a series of branched

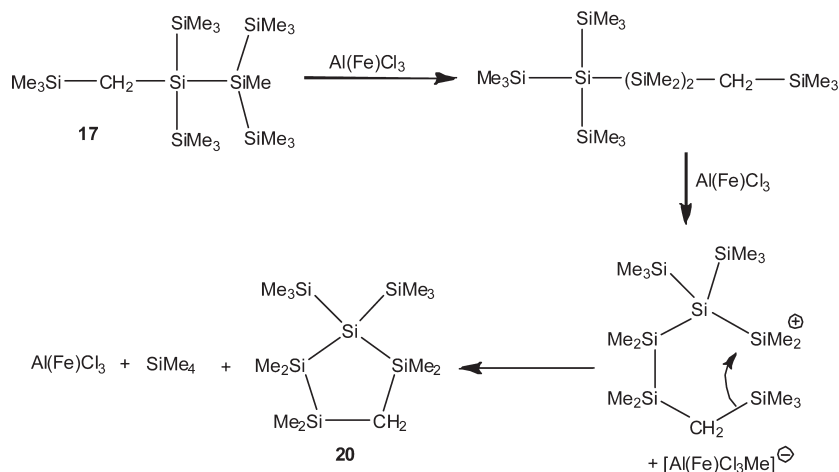
Scheme 5. Rearrangement Reactions of (Trimethylsilyl)methyl-Substituted Tri-, Tetra-, and Pentasilanes^a



Scheme 6. Cyclization Reactions of (Trimethylsilyl)methyl-Substituted Hexa-, Hepta-, and Octasilanes^a

^a ²⁹Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

Scheme 7. Mechanistic Rationale for the Cyclization Behavior of a (Trimethylsilyl)methyl-Substituted Hexasilane Involving a 1,5-Methylene Shift

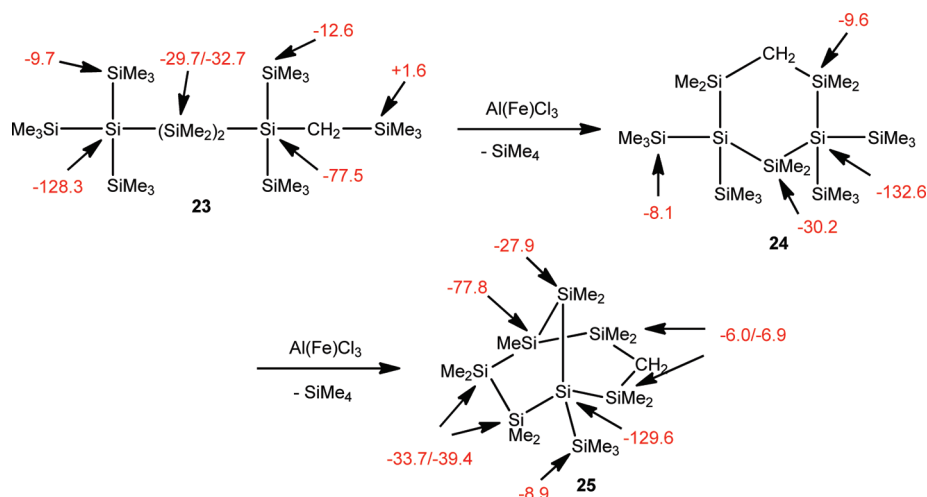


compounds of the general composition Me₃SiCH₂(SiMe₂)_nSiMe₃, with *n* ranging from 2 to 8.

The series starts with the linear trisilane **11**, where the (trimethylsilyl)methyl substituent is located in the 2-position. The rearrangement involved a 1,2-shift of this group to a terminal silicon atom, thus minimizing steric interaction and affording 1-[(trimethylsilyl)methyl]heptamethyltrisilane (**12**) as the product (Scheme 5). The rearrangement of the next higher homologue, 2-(trimethylsilyl)-2-[(trimethylsilyl)methyl]hexamethyltrisilane (**13**), proceeded to

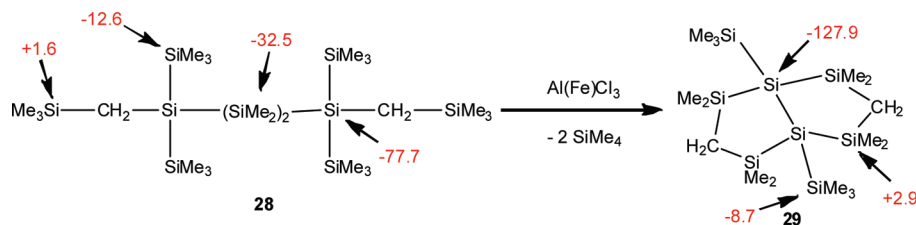
2-(trimethylsilyl)-1-[(trimethylsilyl)methyl]hexamethyltrisilane (**14**) (Scheme 5). Starting material **13** and product **14** both contain isotetrasilane structures. Again a 1,2-shift of the (trimethylsilyl)methyl group moved the more bulky substituent from the branching point of the silane to a terminal position. Steric interaction at the branching point is thus diminished. In a similar way the next member of the series, 2-(trimethylsilyl)-2-[(trimethylsilyl)methyl]octamethyltetrasilane (**15**), was converted to 2,2-bis(trimethylsilyl)-3-[(trimethylsilyl)methyl]pentamethyltrisilane (**16**) (Scheme 5). The driving force behind this

Scheme 8. Cyclization Reaction of a (Trimethylsilyl)methyl-Substituted Branched Nonasilane To Give an Intermediate Monocyclic Molecule and Further To Give a Bicyclic Molecule^a



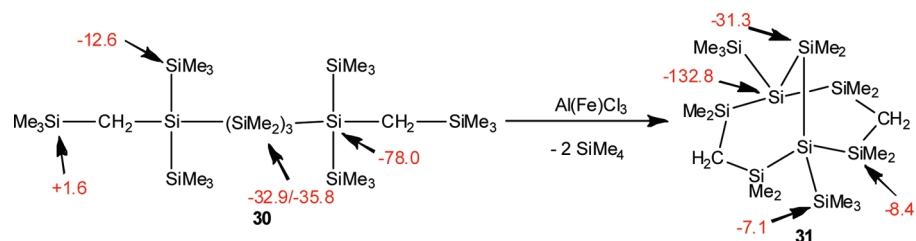
^a ²⁹Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

Scheme 9. Cyclization Reaction of a Bis[(trimethylsilyl)methyl]-Substituted Branched Octasilane To Give a Bicyclic Molecule^a



^a ²⁹Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

Scheme 10. Cyclization Reaction of a Bis[(trimethylsilyl)methyl]-Substituted Branched Nonasilane To Give a Bicyclic Molecule^a



^a ²⁹Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

transformation is the typical branching mechanism which favors the formation of neopentasilanyl units such as in 16.

All reactions depicted in Scheme 5 show the expected rearrangement behavior, featuring a series of 1,2-shifts to the most stable silylium ion, yielding the most stable branched oligosilane isomers.

The next higher homologues 17–19 possess enough formal dimethylsilylene units to exhibit a cyclization reaction behavior (Scheme 6) similar to what was already outlined above for compounds 1, 3, and 8. It is interesting to see that in compounds 21 and 22 the branching points are located in 1,2-relationships. While a 1,3-disilyl substitution pattern would be sterically less hindered, it would also be associated with a lower silylation degree at the branching points.

For cyclooligosilane rearrangement reactions a general trend favoring the formation of five-membered rings was observed.¹² This trend was also found for the reactions of 17–19 (Scheme 6). In all cases carbacyclopentasilanes were formed. The incorporated methylene group was always connected to dimethylsilylene units and was never attached to a branching point of the oligosilane backbone (Scheme 6).

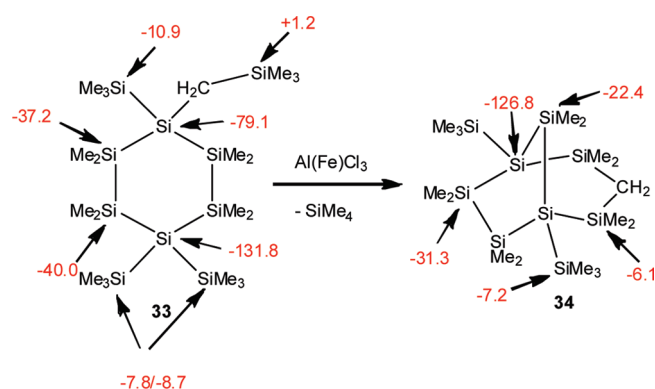
It seems that the first step of these cyclization processes is a rearrangement similar to what was observed for 11, 13, and 15. The preferentially formed acyclic intermediate would feature the (trimethylsilyl)methyl group at a terminal position. Such a structure can then undergo a cyclization reaction in a way similar to that pointed out above. The feasibility of this can be judged from the fact that in none of the rearrangement reactions of

17–19 could any intermediate be detected by NMR spectroscopy, indicating that once the reaction started, it would invariably lead to the desilylative cyclization. Scheme 7 depicts the assumed cyclization path for compound 17.

The next higher homologue, 23, was expected to follow a similar path. Spectroscopic evidence suggested initially a related cyclization. Supposedly a carbacyclohexasilane was formed to avoid attachment of the methylene group to a disilylated silicon atom. In addition to this product the formation of another compound was detected right from the beginning of the reaction, which eventually became the only product. After isolation, structural and spectroscopic characterization this product was found to be 3-carba-1-(trimethylsilyl)undecamethylbicyclo[3.2.1]nonasilane (25), which was formed by elimination of another 1 equiv of tetramethylsilane (Scheme 8). It was surprising to find 25 as the final product, as we previously recognized the formation of tetrasilylated silicon atoms to be a major driving force. Whereas compound 24 possesses two of these structural elements, only one of them is found in the structure of 25. An explanation for this apparent problem would be that, while the outcome of most of the rearrangements is governed by the thermodynamic stability of the formed cations, the elimination of tetramethylsilane would introduce a nonreversible kinetic component to the reaction.

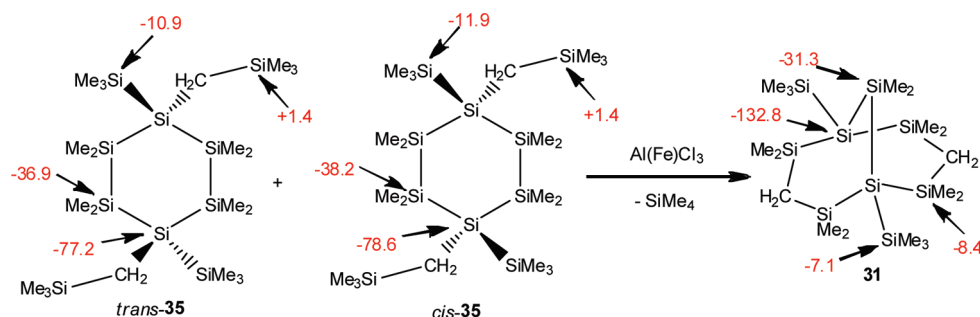
Acyclic Methylated Oligosilanes with Two Me_3SiCH_2 Groups. After the investigation of the rearrangement behavior of oligosilanes containing one (trimethylsilyl)methyl group a

Scheme 11. Cyclization Reaction of a (Trimethylsilyl)methyl-Substituted Tris(trimethylsilyl)cyclohexasilane To Give a Bicyclic Molecule^a



^a ^{29}Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

Scheme 12. Cyclization Reaction of an Isomeric Mixture of 1,4-Bis[(trimethylsilyl)methyl]-Substituted 1,4-Bis(trimethylsilyl)-cyclohexasilanes To Give a Bicyclic Molecule with Two Methylene Bridges^a



^a ^{29}Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

second series of substrates containing two of these substituents was investigated. Rearrangement of the first two compounds of this series, $(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2\text{SiMe}_3)_2$ (26) and $[(\text{Me}_3\text{Si})_2\text{Si}(\text{CH}_2\text{SiMe}_3)]_2$ (27), did not give clean reactions. In contrast to this, the next higher homologue, 28, gave a single product. Elimination of 2 equiv of tetramethylsilane led to the bicyclic compound 3,7-dicarba-1,5-bis(trimethylsilyl)octamethylbicyclo[3.3.0]octasilane (29) (Scheme 9).

Increasing the number of dimethylsilylene units by one unit led to a reaction which was less clean but still formed one major product that could be isolated and characterized. The structure of the resulting compound is related to 29 with the additional SiMe_2 unit inserted into the central Si–Si bond, thus representing 3,7-dicarba-1,5-bis(trimethylsilyl)decamethylbicyclo[3.3.1]nonasilane (31) (Scheme 10).

Rearrangement of 2,9-bis(trimethylsilyl)-2,9-bis[(trimethylsilyl)methyl]octadecamethyldecasilane (32), where in comparison to 30 the number of dimethylsilylene units was increased by another three units, was also not clean.

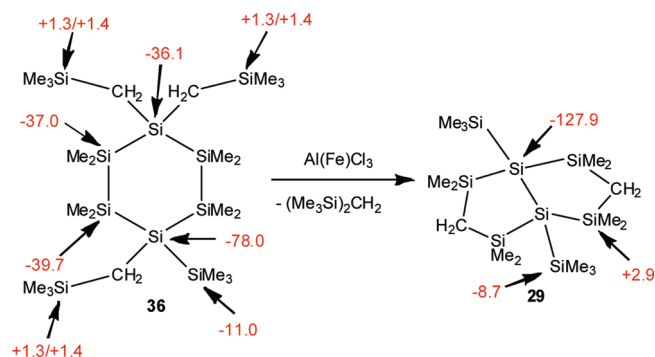
Cyclic Methylated Oligosilanes Containing Me_3SiCH_2 Substituents. Considering the enhanced cyclization potential of compounds containing (trimethylsilyl)methyl groups, we assumed that cyclic oligosilanes with this substituent should exhibit a pronounced tendency to form bicyclic compounds under rearrangement conditions. The reaction of the easily available cyclohexasilane 33 confirmed this assumption, and 3-carba-1,5-bis(trimethylsilyl)decamethylbicyclo[3.2.1]octasilane (34) was obtained (Scheme 11).

Also, the rearrangement of a mixture of *cis*- and *trans*-35 followed a selective pathway leading to the already known bicyclic compound 31 (see above) (Scheme 12).

The rearrangement of 36, which contains three (trimethylsilyl)methyl substituents, led cleanly to the formation of 29 (Scheme 13). This was unexpected, for it was assumed that the product would contain three methylene units corresponding to the three (trimethylsilyl)methyl groups of the starting material. However, different from most of the reactions described so far, the elimination of tetramethylsilane was not observed but rather that of bis(trimethylsilyl)methane. The course of reaction is therefore similar to what was observed with compound 8, where also a more complex silylium ion was eliminated.

Finally, the reactions of 1,1,4,4-tetrakis[(trimethylsilyl)methyl]octamethylcyclohexasilane (37) and the bicyclic compound 1-(trimethylsilyl)-4-[(trimethylsilyl)methyl]dodecamethylbicyclo[2.2.2]octasilane (38) did not give clean conversions to single products.

Scheme 13. Cyclization Reaction of a Tris[(trimethylsilyl)-methyl]-Substituted (Trimethylsilyl)cyclohexasilane To Give a Bicyclic Molecule with Two Methylene Bridges^a



^a ²⁹Si NMR chemical shifts (ppm) of substrates and cyclized products have been added to the structures.

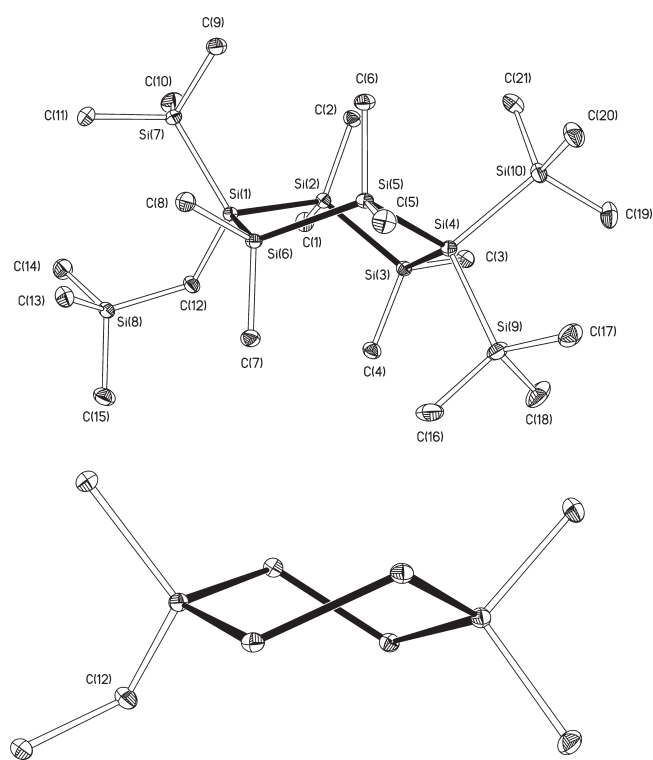


Figure 1. Molecular structure and numbering of **33**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–C(12) = 1.913(2), Si(1)–Si(7) = 2.3572(9), Si(1)–Si(6) = 2.3640(10), Si(1)–Si(2) = 2.3683(9), Si(2)–Si(3) = 2.3443(10), Si(8)–C(12) = 1.877(2); Si(6)–Si(1)–Si(2) = 110.83(3), Si(3)–Si(2)–Si(1) = 111.29(3), Si(2)–Si(3)–Si(4) = 112.29(3), Si(3)–Si(4)–Si(5) = 110.95(3), Si(6)–Si(5)–Si(4) = 112.68(3), Si(5)–Si(6)–Si(1) = 112.94(3).

X-ray Crystallography. The cyclohexasilanes **33**, **35-trans**, and **37** as well as the bicyclic compounds **25**, **29**, **31**, **34**, and **38** could be subjected to crystal structure analyses.

The molecular structure of **33** (Figure 1), which crystallizes in the monoclinic space group $C2/c$, resembles that obtained for 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane.¹⁶ Both structures are rare cases of six-membered rings in a stable

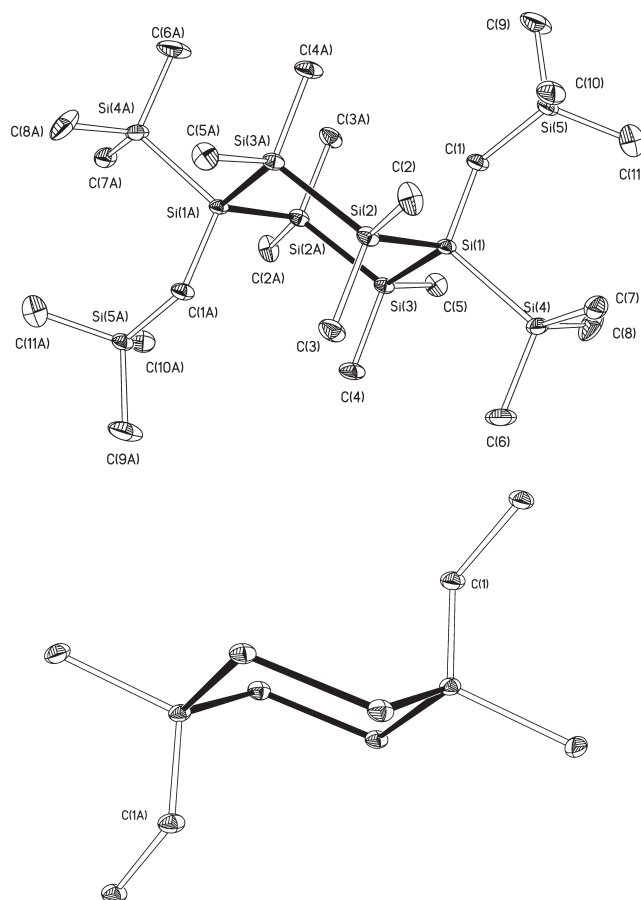


Figure 2. Molecular structure and numbering of **35-trans**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–Si(2) = 2.3484(18), Si(1)–Si(3) = 2.3658(13), Si(2)–Si(3A) = 2.3541(15), Si(3)–Si(2A) = 2.3541(15), Si(5)–C(1) = 1.860(3); Si(2)–Si(1)–Si(3) = 107.03(6), Si(1)–Si(2)–Si(3A) = 111.58(6), Si(2A)–Si(3)–Si(1) = 111.45(5).

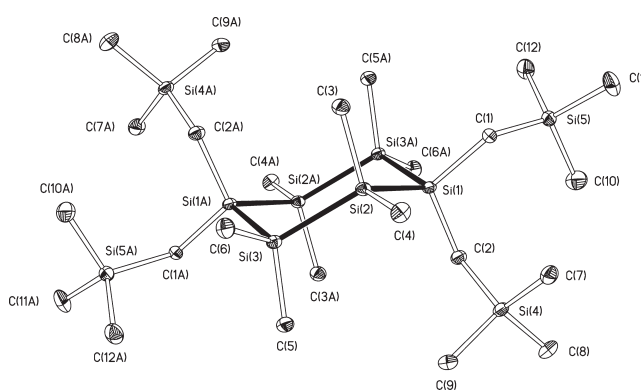


Figure 3. Molecular structure and numbering of **37**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–C(2) = 1.889(3), Si(1)–C(1) = 1.897(3), Si(1)–Si(3A) = 2.3570(11), Si(1)–Si(2) = 2.3592(12), Si(2)–Si(3) = 2.3495(11), Si(3)–Si(1A) = 2.3571(11); Si(3A)–Si(1)–Si(2) = 105.83(4), Si(3)–Si(2)–Si(1) = 119.18(4), Si(2)–Si(3)–Si(1A) = 109.49(5).

twist conformation. Both **35-trans** (Figure 2) and **37** (Figure 3) crystallize in the monoclinic space group $P2_1/c$, and their six-membered rings show the expected chair conformation. Si–Si

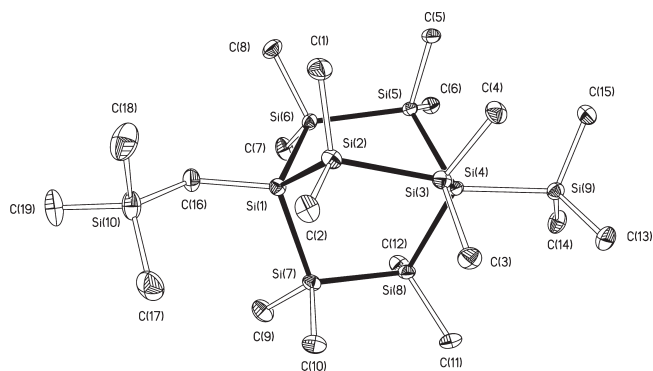


Figure 4. Molecular structure and numbering of **38**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–C(16) = 1.909(3), Si(1)–Si(7) = 2.3537(10), Si(1)–Si(6) = 2.3583(11), Si(1)–Si(2) = 2.3599(10), Si(2)–Si(3) = 2.3767(10), Si(3)–Si(4) = 2.3373(10), Si(4)–Si(5) = 2.3367(10), Si(4)–Si(8) = 2.3422(9), Si(10)–C(16) = 1.855(3); Si(7)–Si(1)–Si(6) = 107.89(4), Si(7)–Si(1)–Si(2) = 106.26(3), Si(6)–Si(1)–Si(2) = 106.75(3), Si(1)–Si(2)–Si(3) = 108.17(4), Si(4)–Si(3)–Si(2) = 111.87(4), Si(5)–Si(4)–Si(3) = 106.81(4), Si(5)–Si(4)–Si(8) = 108.03(4), Si(3)–Si(4)–Si(8) = 107.59(4), Si(4)–Si(5)–Si(6) = 107.12(4), Si(5)–Si(6)–Si(1) = 113.13(3), Si(1)–Si(7)–Si(8) = 108.45(4), Si(4)–Si(8)–Si(7) = 110.81(4).

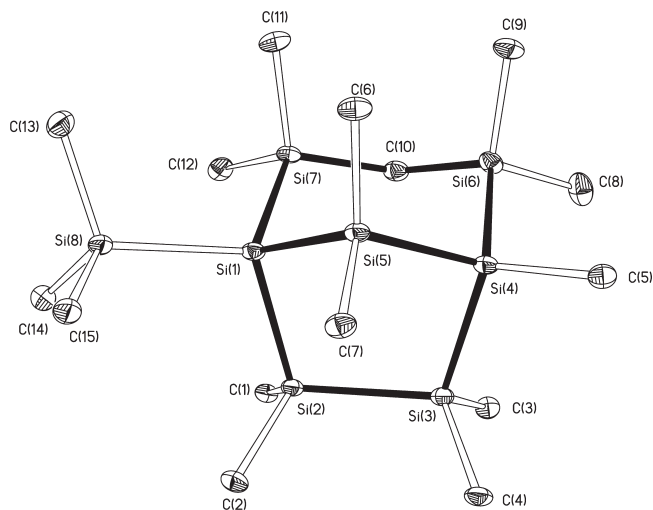


Figure 5. Molecular structure and numbering of **25**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–Si(5) = 2.344(3), Si(1)–Si(7) = 2.346(3), Si(1)–Si(2) = 2.354(3), Si(2)–Si(3) = 2.356(3), Si(3)–Si(4) = 2.355(3), Si(4)–Si(5) = 2.336(3), Si(4)–Si(6) = 2.346(3), Si(6)–C(10) = 1.865(6), Si(7)–C(10) = 1.892(6); Si(5)–Si(1)–Si(7) = 107.91(10), Si(5)–Si(1)–Si(2) = 101.05(10), Si(7)–Si(1)–Si(2) = 108.35(10), Si(1)–Si(2)–Si(3) = 103.96(10), Si(4)–Si(3)–Si(2) = 105.08(10), Si(5)–Si(4)–Si(6) = 108.70(10), Si(5)–Si(4)–Si(3) = 100.94(10), Si(6)–Si(4)–Si(3) = 108.54(10), Si(4)–Si(5)–Si(1) = 98.18(10), Si(6)–C(10)–Si(7) = 121.0(3).

bond distances in all three cyclohexasilanes are in the normal range between 2.35 and 2.37 Å, and the same is true for the Si–C distances, except for that between the ring silicon atoms and the attached CH₂ groups in **33** and **35-trans**. These distances are somewhat elongated to a value of 1.91 Å, whereas they are around 1.89 Å for **37**. The two CH₂–SiMe₃ groups of **35-trans** do not adopt the expected equatorial but rather axial positions, as was reported for similar compounds in the literature.¹⁷

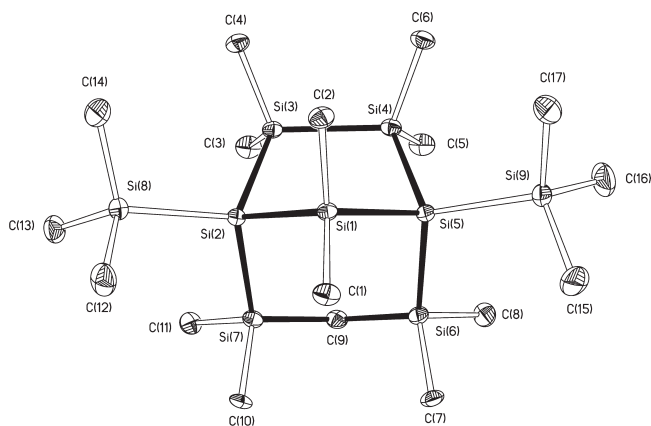


Figure 6. Molecular structure and numbering of **34**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–Si(5) = 2.3372(10), Si(1)–Si(2) = 2.3389(11), Si(2)–Si(7) = 2.3459(12), Si(2)–Si(3) = 2.3538(11), Si(3)–Si(4) = 2.3722(11), Si(4)–Si(5) = 2.3498(10), Si(5)–Si(6) = 2.3455(12), Si(6)–C(9) = 1.882(2), Si(7)–C(9) = 1.877(2); Si(5)–Si(1)–Si(2) = 100.51(4), Si(1)–Si(2)–Si(7) = 106.82(4), Si(1)–Si(2)–Si(3) = 100.35(4), Si(7)–Si(2)–Si(3) = 108.11(4), Si(2)–Si(3)–Si(4) = 104.73(4), Si(5)–Si(4)–Si(3) = 105.42(4), Si(1)–Si(5)–Si(9) = 114.10(4), Si(1)–Si(5)–Si(6) = 107.20(4), Si(1)–Si(5)–Si(4) = 100.21(4), Si(6)–Si(5)–Si(4) = 107.28(4), Si(7)–C(9)–Si(6) = 121.32(13).

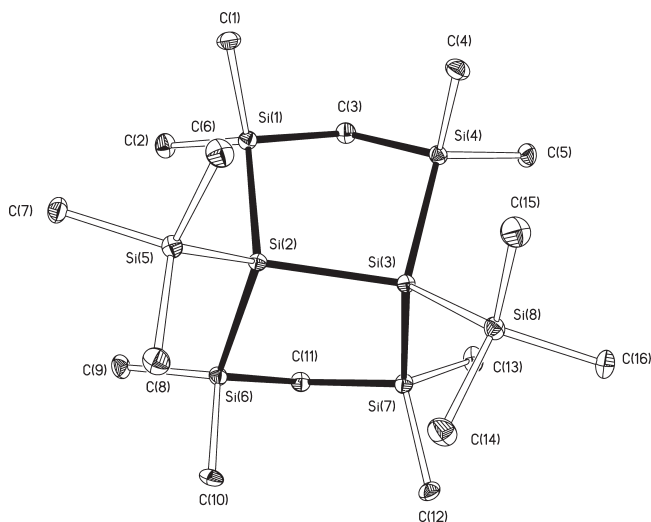


Figure 7. Molecular structure and numbering of **29**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–C(3) = 1.876(3), Si(1)–Si(2) = 2.3625(10), Si(2)–Si(6) = 2.3508(12), Si(2)–Si(3) = 2.3719(11), Si(3)–Si(4) = 2.3573(11), Si(3)–Si(7) = 2.3653(11), Si(4)–C(3) = 1.884(3), Si(6)–C(11) = 1.881(3); C(3)–Si(1)–C(2) = 111.55(12), C(3)–Si(1)–C(1) = 109.04(12), C(3)–Si(1)–Si(2) = 105.22(9), Si(6)–Si(2)–Si(1) = 111.95(5), Si(6)–Si(2)–Si(3) = 98.03(4), Si(1)–Si(2)–Si(3) = 99.89(4), Si(4)–Si(3)–Si(7) = 111.32(4), Si(4)–Si(3)–Si(2) = 98.11(4), Si(7)–Si(3)–Si(2) = 100.02(4), Si(1)–C(3)–Si(4) = 113.21(13), Si(6)–C(11)–Si(7) = 113.09(13).

Compound **38** (Figure 4) crystallizes in the monoclinic space group $P2_1/c$, whereas the parent compound without the CH₂ spacer was found to crystallize in a tetragonal space group due to the high degree of symmetry.¹⁸ The molecule consists of a regular [2.2.2]cyclooctasilane framework with all Si–Si bond

lengths within a range of 2.34–2.36 Å and all Si–Si–Si bond angles close to the ideal tetrahedral angle (106–113°). The distance between the silicon atoms and the CH₂ spacer is again at 1.91 Å longer than all the other Si–C distances (1.89 Å).

The [3.2.1]-3-*carba*-cyclooctasilane compounds **25** (Figure 5) and **34** (Figure 6) both crystallize in the triclinic space group *P* $\bar{1}$. For both structures no elongation of the bonds between the Si atoms and the CH₂ spacer was observed, but in the case of **34** the *exo*-methyl groups next to the spacer are somewhat longer

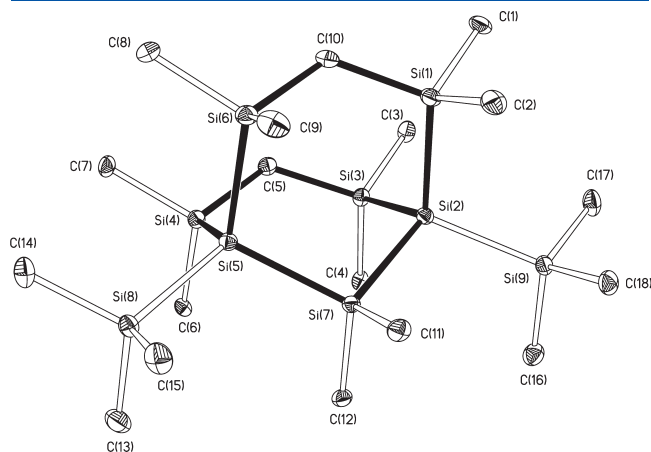


Figure 8. Molecular structure and numbering of **31**. Selected bond lengths (Å) and bond angles (deg) with esd's: Si(1)–C(10) = 1.884(3), Si(1)–Si(2) = 2.3552(11), Si(2)–Si(7) = 2.3404(12), Si(2)–Si(3) = 2.3534(11), Si(3)–C(5) = 1.882(3), Si(4)–Si(5) = 2.3522(11), Si(5)–Si(7) = 2.3382(13), Si(5)–Si(6) = 2.3556(11), Si(6)–C(10) = 1.877(3); Si(7)–Si(2)–Si(3) = 106.86(5), Si(7)–Si(2)–Si(1) = 106.22(4), Si(3)–Si(2)–Si(1) = 109.43(5), Si(7)–Si(5)–Si(4) = 106.51(4), Si(8)–Si(5)–Si(4) = 111.15(5), Si(7)–Si(5)–Si(6) = 106.79(5), Si(4)–Si(5)–Si(6) = 109.75(4), Si(5)–Si(7)–Si(2) = 104.12(5), Si(4)–C(5)–Si(3) = 122.29(14), Si(6)–C(10)–Si(1) = 123.51(14).

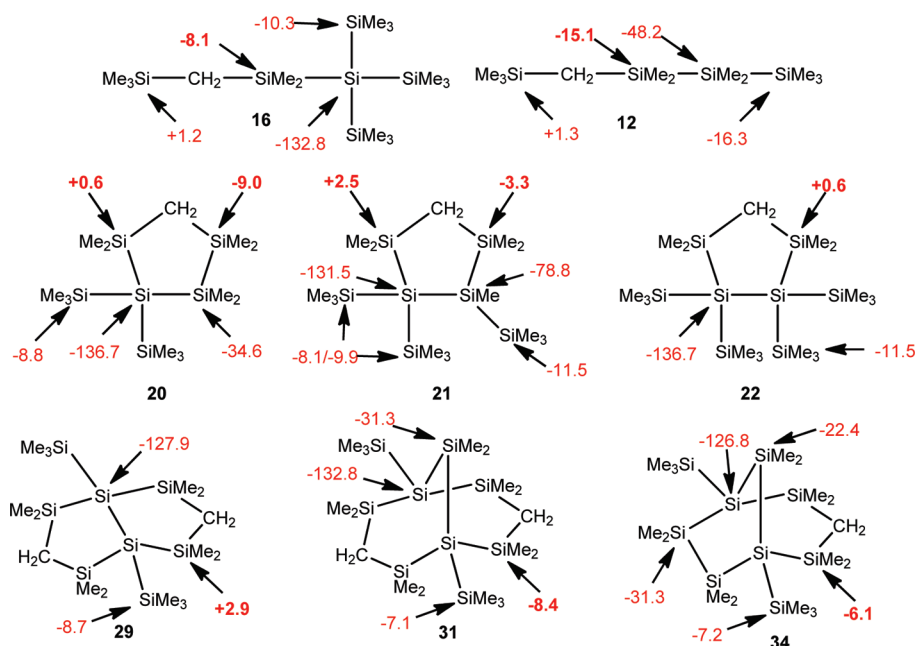
(Si(6)–C(7) and Si(7)–C(10) both 1.90 Å). In contrast to this, Si–Si bond lengths are all fairly short, in the ranges of 2.34–2.37 Å for **34** and 2.34–2.35 Å for **25**.

Compound **29** (Figure 7) also crystallizes in the triclinic space group *P* $\bar{1}$. All Si–Si bonds, even the central one, Si(2)–Si(3), are in the range of regular bond lengths (2.34–2.37 Å). The previously studied all-silicon compound 1,5-bis(trimethylsilyl)dodecamethylbicyclo[3.3.0]octasilane¹⁹ exhibited a cisoid configuration of the two rings with a torsion angle of the two SiMe₃ substituents along the bridge of 40.3°. In **29** the replacement of two SiMe₂ units by CH₂ led to diminished strain, resulting in a torsion angle of 14.5°.

The parent all-silicon compound of **31** (Figure 8), hexadecamethylbicyclo[3.3.1]nonasilane, was found to crystallize in the monoclinic space group *P*₂₁/*c* with two molecules in the asymmetric unit,²⁰ while **31** crystallized in the triclinic space group *P* $\bar{1}$. In the all-silicon compound the two six-membered rings featured a chair and a twist conformation. The replacement of two SiMe₂ units by CH₂ also changed this system, in which both rings have perfect chair conformations.

NMR Spectroscopy. ¹H, ¹³C, and ²⁹Si NMR spectra of the compounds described in this study were measured. To some extent the spectroscopic characteristics of oligosilanes with attached (trimethylsilyl)methyl units have already been discussed recently.¹⁵ As ²⁹Si NMR spectra are the most significant for structural assignments of oligosilanes, a short discussion seems appropriate. Especially cyclosilanes with endocyclic methylene groups were found to exhibit some interesting behavior. For compound **20** (Chart 1), with two SiMe₂ groups attached to the CH₂ unit, we would expect their ²⁹Si resonances around –9.0 ppm, which is typical for a trimethylsilyl group attached to a silicon atom. In fact, we find indeed one resonance (–9.0 ppm) (for the SiMe₂ group attached to another SiMe₂) in the expected region, whereas the other resonance (which is connected to a quaternary silicon atom) is shifted downfield to +0.6 ppm (Chart 1). For compound **21** the situation is similar,

Chart 1. ²⁹Si NMR Chemical Shifts (ppm) of Selected Compounds^a



^aData used in the discussion are shown in boldface type.

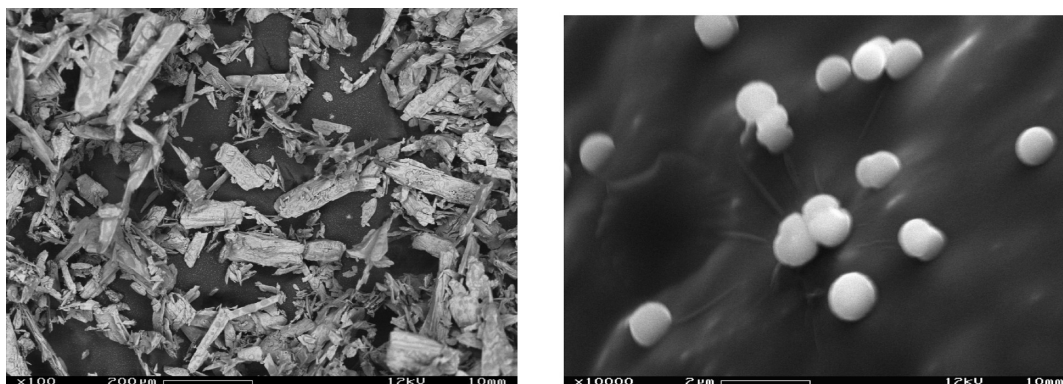


Figure 9. SEM images of the catalyst particles: (left) backscattered electron image, image width 1.2 mm; (right) secondary electron image, image width 11.5 μm .

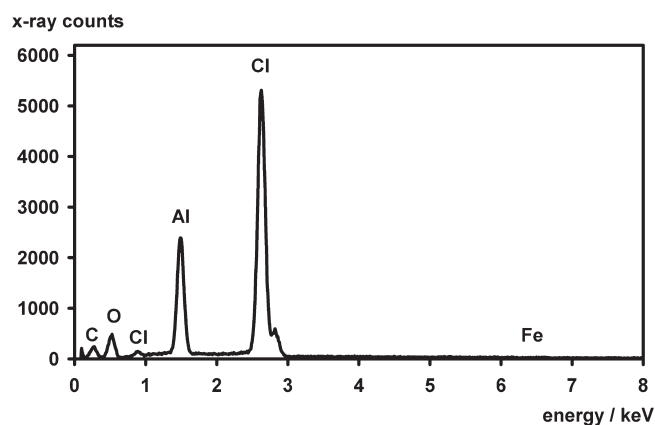


Figure 10. EDX spectrum for the left-hand image in Figure 9.

but in this case the first SiMe_2 (now attached to a tertiary Si atom) resonance is now observed at -3.3 ppm while the second resonance is further shifted to $+2.5$ ppm. For the symmetrical compound **22** both SiMe_2 groups (attached to quaternary Si atoms) were found to resonate at $+0.6$ ppm.

Analysis of the SiMe_2CH_2 resonances of acyclic compounds **12** (-15.1 ppm) and **16** (-8.1 ppm) showed also that a higher silylation degree of the attached silicon atom causes a downfield shift (Chart 1). However, the extent of this shift seems also to be connected to some type of steric strain, which is particularly effective in the cyclopentasilanyl unit. This is seen by a comparison of the bicyclic compounds **29**, **31**, and **34**. While the last two (**31**, **34**) exhibit SiMe_2CH_2 resonances in the expected range around -8.0 ppm, for **29**, which has structural features resembling those of **20–22**, again a marked downfield shift to $+2.9$ ppm was observed (Chart 1).

The influence of ring strain on SiMe_2 groups of homocyclic polysilanes can be seen also from a comparison of 1,1,3,3-tetrakis(trimethylsilyl)hexamethylcyclopentasilane^{14,21} ($\text{SiMe}_2\text{SiMe}_2$ -24.8 ppm) and 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane⁶ ($\text{SiMe}_2\text{SiMe}_2$ -40.0 ppm).

Catalyst. It is somewhat peculiar that some of our results are different from the findings of Ishikawa, Kumada, and co-workers.^{7–10} The additional cyclization reactivity observed by us is most likely caused by the modified catalyst. While Ishikawa et al. reported the use of commercially available AlCl_3 , they also noticed that on use of larger amounts of the catalyst chlorination

of the products was a frequently occurring side reaction. For this reason they recommended treatment of the reaction mixture with methyl Grignard reagent in order to obtain permethylated products. Large catalyst amounts, which are common if the reaction does not start properly, were also reported to lead to polymerization or decomposition. Blinka and West¹⁴ pointed out two types of catalysts that worked in their hands: either sublimed technical AlCl_3 (with a specified FeCl_3 content of 0.1%) or a cosublimed of pure AlCl_3 and 1% FeCl_3 . They further noticed that pure sublimed AlCl_3 , nonsublimed technical AlCl_3 , and a mixture of pure AlCl_3 and 1% FeCl_3 (without prior cosublimation) did not show catalytic activity.¹⁴

For these reasons it seemed a worthwhile goal to establish conditions which allow a reliable start of the reaction with reasonably small amounts of catalyst. To find these optimized conditions, we used the known rearrangement reaction of dodecamethylcyclohexasilane to (trimethylsilyl)nonamethylcyclopentasilane^{10,14} as a test system. Cosublimates of AlCl_3 and FeCl_3 were prepared with 1%, 3%, 5%, and 10% FeCl_3 content. The 1% FeCl_3 product had a pale yellow color, whereas the other products were bright yellow. The almost identical colors and the fact that the 5% and 10% batches led to a larger sublimation residue (of FeCl_3) seemed to indicate that these samples have a similar stoichiometry. This was supported by the fact that there was no marked difference in the reactivity of these two samples. The minimum catalyst amount to achieve complete conversion was for all samples between 0.03 and 0.09 mol equiv. Experiments to study the activity of the catalyst were conducted in dichloromethane at room temperature. This solvent was found useful for an easy rearrangement of substrates but occasionally led to chlorination side reactions at longer reaction times. For difficult cases, therefore, cyclohexane was the preferred solvent, even though it requires elevated temperatures.

As additional alternative catalysts a cosublimed of AlBr_3 and FeBr_3 and samples of technical AlBr_3 and $\text{Al}(\text{OTf})_3$ were studied. The $\text{AlBr}_3/\text{FeBr}_3$ cosublimed was of equal value to the $\text{AlCl}_3/\text{FeCl}_3$ system in dichloromethane with respect to both minimum catalyst amount and reaction time, whereas technical AlBr_3 required the use of at least 0.15 mol equiv for complete conversion. However, the visible inhomogeneity of this material made conclusive statements difficult. Finally, $\text{Al}(\text{OTf})_3$ did not show any activity as a catalyst at all. In conclusion, the system reported by Blinka and West¹⁴ was found to be the best one.

To find a mechanistic rationale for the requirement of the FeCl_3 cosublimation procedure, we were interested in the type of

incorporation of the FeCl_3 into the AlCl_3 lattice. As it is not clear in what way this incorporation occurs, we decided to study the material by X-ray powder diffraction, electron microscopy (SEM, EDXS), and atomic emission spectroscopy (ICP-OES). The powder diffraction measurement of a sample prepared by cosublimation of AlCl_3 and 1% FeCl_3 did not indicate any presence of FeCl_3 at all and gave a pattern indistinguishable from that of pure AlCl_3 . The virtually identical cell constants thus suggested a very low concentration of FeCl_3 , which likely is incorporated in a very regular way into the lattice.

For the SEM measurements two samples were chosen. The first one was a cosublimation of AlCl_3 and 3% FeCl_3 , which was heated in refluxing cyclohexane for several hours in order to mimic the rearrangement conditions. As the EDXS measurements of this sample did not indicate the presence of any iron (see the Supporting Information for details), we tried to increase the FeCl_3 content by preparing a sample by cosublimation of AlCl_3 and 10% FeCl_3 . The SEM images of Figure 9 show the size and shape of the particles of this sample. Rod-shaped particles with a length of up to several 100 μm and spherical particles with diameters of approximately 1 μm can be seen. EDXS was again used for the chemical analysis of the particles and to detect whether any strong accumulation of iron somewhere at the particles or at specific particles could be found. The detection limit of EDXS is around 0.1 wt %, the lateral resolution is around 1 μm , and the analysis depth is also around 1 μm . Thus, in the case of the big particles the EDXS analysis definitely corresponds to a surface analysis. No iron could be detected, either in an overall analysis or in the analysis of individual particles (see Figure 10). Thus, the iron concentration in the catalyst particles was, despite the high initial concentration of 10% FeCl_3 , below the detection limit of EDXS. ICP-OES analysis eventually proved that the iron concentration in the sample was close to 0.1 wt %. When the results from EDXS and ICP-OES are combined, it follows that the iron is homogeneously distributed both across the individual particles and also across the whole sample. No local accumulation of iron could be detected. This was also confirmed by the backscattered electron images (see Figure 10 left), where the contrast increases with increasing mean atomic number and therefore iron-enriched areas should appear much brighter than the rest of the surface. The small contrast variations observed in the images proved to be only due to variations in the particle topography. Quantitative evaluation of the spectra showed that in case of the large particles the atom ratio $\text{Al}:\text{Cl}$ corresponds within measurement accuracy to AlCl_3 . Additionally some oxygen could be detected. Much higher oxygen concentrations were found in the small spherical particles. Possibly, despite great care during the transfer of the samples, air admission could not be completely avoided.

CONCLUSION

On investigation of some rearrangement reactions of branched oligosilanes with catalytic amounts of $\text{Al}(\text{Fe})\text{Cl}_3$, a novel cyclization reaction was found in addition to the already known rearrangement behavior.^{7–12,14} The introduction of (trimethylsilyl)methyl substituents into oligosilanes strongly facilitates the rearrangement/cyclization behavior leading to rearranged branched oligosilanes and in the case of a sufficient number of silicon atoms to carbacyclosilanes with endocyclic methylene units. Depending on the number of (trimethylsilyl)methyl groups and the structure of the starting material, either mono- or bicyclic compounds were obtained. The bicyclic

nature of these compounds restricts the conformational flexibility of the polysilane skeleton, making them interesting building blocks for the construction of longer chains with all-transoid conformation.^{22–27}

Investigations concerning the composition of the catalyst system indicated that the cosublimation of AlCl_3 even with 10% FeCl_3 leads to the incorporation of only about 0.1% FeCl_3 into the AlCl_3 lattice.

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. Solvents were dried using a column solvent purification system. All chemicals bought from different suppliers were used without further purification.

^1H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise, C_6D_6 was used for all samples or, in the case of reaction samples, they were 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.^{28,29} Elementary analysis was carried out using a Heraeus Vario Elementar instrument. EI high-resolution mass spectra (HRMS) were obtained using a Waters GCT premier instrument.

2,5-Bis(trimethylsilyl)dodecamethylhexasilane (**3**),³⁰ 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetrasilane (**5**),^{3,31} 2,2,9,9-tetrakis(trimethylsilyl)octadecamethyldecasilane (**8**),³² 2-(trimethylsilyl)-2-[(trimethylsilyl)methyl]hexamethyltrisilane (**13**),¹⁵ 2-trimethylsilyl-2-[(trimethylsilyl)methyl]octamethyltetrasilane (**15**),¹⁵ 2,2,3-tetrakis(trimethylsilyl)-3-[(trimethylsilyl)methyl]hexamethyltetrasilane (**18**),¹⁵ 2,2,5,5-tris(trimethylsilyl)-5-[(trimethylsilyl)methyl]decamethylhexasilane (**23**),¹⁵ 2,2-bis[(trimethylsilyl)methyl]hexamethyltrisilane (**26**),¹⁵ 2,3-bis(trimethylsilyl)-2,3-bis[(trimethylsilyl)methyl]hexamethyltetrasilane (**27**),¹⁵ 2,5-bis(trimethylsilyl)-2,5-bis[(trimethylsilyl)methyl]decamethylhexasilane (**28**),¹⁵ 2,6-bis(trimethylsilyl)-2,6-bis[(trimethylsilyl)methyl]dodecamethylheptasilane (**30**),¹⁵ 2,9-bis(trimethylsilyl)-2,9-bis[(trimethylsilyl)methyl]octadecamethyldecasilane (**32**),¹⁵ 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane,^{21,33,34} 2,2,3-tris(trimethylsilyl)heptamethyltetrasilane,³⁵ 2,2,4,4-tetrakis(trimethylsilyl)octamethylpentasilanes,³ pentamethylchlorodisilane,³⁶ 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane,⁶ and 1,4-bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane⁶ were prepared by employing published procedures.

X-ray Structure Determinations. 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 K α radiation (0.710 73 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT³⁷ and SADABS,³⁸ respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).³⁹ 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. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Unfortunately, the obtained crystal quality of some substances was poor. This fact is reflected by quite high R and low θ values. Crystallographic data for compounds **25**, **29**, **31**, and **33** are given in Table 1 and for compounds **34**, **35-trans**, **37**, and **38** in Table 2.

Crystallographic data (excluding structure factors) for the structures of compounds **25**, **29**, **31**, **33**, **34**, **35-trans**, **37**, and **38** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-720006 (**33**),

Table 1. Crystallographic Data for Compounds 25, 29, 31, and 33

	25	29	31	33
empirical formula	Si ₈ C ₁₅ H ₄₄	Si ₈ C ₁₆ H ₄₆	Si ₉ C ₁₈ H ₅₂	Si ₁₀ C ₂₁ H ₆₂
<i>M_w</i>	449.22	463.25	541.40	595.61
temp (K)	100(2)	100(2)	100(2)	100(2)
size (mm)	0.30 × 0.22 × 0.20	0.34 × 0.28 × 0.20	0.32 × 0.22 × 0.18	0.35 × 0.30 × 0.10
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.793(2)	9.6431(19)	9.3855(19)	16.278(3)
<i>b</i> (Å)	9.793(2)	10.100(2)	11.547(2)	10.248(2)
<i>c</i> (Å)	15.025(3)	15.544(3)	16.262(3)	46.368(9)
α (deg)	89.15(3)	75.42(3)	71.75(3)	90
β (deg)	80.67(3)	87.67(3)	80.80(3)	94.92(3)
γ (deg)	88.36(3)	78.90(3)	73.88(3)	90
<i>V</i> (Å ³)	1421(2)	1438(2)	1603(2)	7706(3)
<i>Z</i>	2	2	2	8
ρ_{calcd} (g cm ^{−3})	1.050	1.070	1.080	1.027
abs coeff (mm ^{−1})	0.377	0.375	0.378	0.351
<i>F</i> (000)	492	508	572	2624
θ range (deg)	2.08 < θ < 25.00	1.17 < θ < 24.00	1.32 < θ < 26.36	1.76 < θ < 26.37
no. of collected/unique rflns	10 251/4975	11 183/5711	12 830/6442	30 040/7837
completeness to θ (%)	99.2	97.3	98.5	99.7
no. of data/restraints/params	4975/0/222	5711/0/231	6442/0/260	7837/0/300
goodness of fit on <i>F</i> ²	0.97	1.09	1.10	1.16
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.080, <i>wR</i> 2 = 0.133	<i>R</i> 1 = 0.049, <i>wR</i> 2 = 0.132	<i>R</i> 1 = 0.054, <i>wR</i> 2 = 0.131	<i>R</i> 1 = 0.043, <i>wR</i> 2 = 0.098
<i>R</i> indices (all data)	<i>R</i> 1 = 0.170, <i>wR</i> 2 = 0.166	<i>R</i> 1 = 0.052, <i>wR</i> 2 = 0.135	<i>R</i> 1 = 0.061, <i>wR</i> 2 = 0.136	<i>R</i> 1 = 0.050, <i>wR</i> 2 = 0.100
largest diff peak/hole (e/Å ³)	0.57/−0.42	0.73/−0.43	0.59/−0.35	0.60/−0.22

720005 (35-*trans*), 720009 (37), 720007 (38), 720003 (34), 720002 (31), 720004 (29), and 720008 (25). Copies of the data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/products/csd/request/>.

SEM/EDXS: Analysis of the Catalyst. The catalyst particles from the cosublimates of AlCl₃ and FeCl₃ with 5% FeCl₃ were investigated by energy dispersive X-ray spectrometry (EDXS: Noran Voyager, Thermo Fisher Scientific Inc., Waltham, MA, USA) in the scanning electron microscope (SEM: Leo DSM 982 Gemini, Carl Zeiss SMT Inc., Oberkochen, Germany). The samples were mounted in the glovebox, where they had also been synthesized, on an adhesive attached to a copper plate. Subsequently they were transferred in an airtight specimen holder to a carbon coater, where they were coated with a thin carbon layer (thickness ~20 nm) and finally transferred again in the airtight specimen holder to the SEM. Both the carbon coater and the SEM are equipped with purpose-built airlocks to avoid contact between sample and air as far as possible. The coating of the samples with a thin conductive carbon layer is necessary to avoid charging of the electrically insulating specimens during electron irradiation in the SEM.

General Procedures for the Preparation of Silyl Anions.
Method A for Monoanions in THF. The corresponding oligosilane together with KO^tBu (1–1.05 equiv) was dissolved in a minimum amount of THF. The completeness of the conversion could be confirmed by ²⁹Si NMR spectroscopy and was usually achieved within a few hours.

Method B for Dianions in THF. The corresponding oligosilane together with KO^tBu (2–2.05 equiv) was dissolved in a minimum amount of THF. The completeness of the conversion could be confirmed by ²⁹Si NMR spectroscopy and could require, depending on the starting material, some days. Heating to 60 °C allows to increase the reaction rate.

Method C for Monoanions in Benzene. The corresponding oligosilane together with KO^tBu (1–1.05 equiv) and 18-crown-6 (1–1.05

equiv) was dissolved in a minimum amount of benzene. The completeness of the conversion could be confirmed by ²⁹Si NMR spectroscopy and should be achieved within 1 h.

Method D for Dianions in Benzene. The corresponding oligosilane together with KO^tBu (2 to 2.05 equiv) and 18-crown-6 (2–2.05 equiv) was dissolved in a minimum amount of benzene. The completeness of the conversion could be confirmed by ²⁹Si NMR spectroscopy and was usually complete within 18 h.

For the derivatization of the obtained anions, the obtained solutions were treated with an electrophile and after complete conversion subjected to an aqueous workup, which included washing with dilute H₂SO₄ and saturated NaHCO₃ solution. Extraction of the product with pentane was followed by drying over Na₂SO₄ and removal of the solvents.

Synthesis of Starting Materials. 2,2,5-Tris(trimethylsilyl)undecamethylhexasilane (**1**). Compound **1** was obtained from 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (395 mg, 0.65 mmol) and KO^tBu (72 mg, 0.64 mmol) using method A and dimethyl sulfate (61 μ L, 0.64 mmol). Colorless crystals (350 mg, 98%) were obtained from pentane (mp 68–71 °C). NMR data (δ in ppm): ²⁹Si, −9.8, −12.1, −31.9, −33.4, −81.3, −129.1; ¹H, 0.47 (s, 6H), 0.42 (s, 6H), 0.31 (s, 27H), 0.24 (s, 18H), 0.23 (s, 3H); ¹³C, 3.5, 1.1, 1.0, −1.1, −11.1. Anal. Calcd for C₂₀H₆₀Si₉ (553.46): C, 43.40; H, 10.93. Found: C, 43.26; H, 10.91.

2-[(Trimethylsilyl)methyl]heptamethyltrisilane (**11**). Compound **11** was obtained from tris(trimethylsilyl)methylsilane (465 mg, 1.77 mmol) and KO^tBu (219 mg, 1.95 mmol) using method A and (trimethylsilyl)methyl chloride (224 mg, 1.82 mmol), yielding a colorless oil (468 mg, 96%). NMR data (δ in ppm): ²⁹Si, 1.7, −16.3, −47.3; ¹H, 0.21 (s, 3H), 0.15 (s, 18H), 0.09 (s, 9H), −0.17 (s, 2H); ¹³C, 1.7, −1.0, −3.8, −6.0. Anal. Calcd for C₁₁H₃₂Si₄ (276.72): C, 47.75; H, 11.66. Found: 46.67; H, 10.96. HRMS for C₁₁H₃₂Si₄: *m/z* calcd 276.1581, found 276.1595.

Table 2. Crystallographic Data for Compounds 34, 35-*trans*, 37, and 38

	34	35- <i>trans</i>	37	38
empirical formula	Si ₉ C ₁₇ H ₅₀	Si ₁₀ C ₂₂ H ₆₄	Si ₁₀ C ₂₄ H ₆₈	Si ₁₀ C ₁₉ H ₅₆
<i>M_w</i>	507.38	609.63	637.68	565.54
temp (K)	150(2)	100(2)	100(2)	100(2)
size (mm)	0.38 × 0.25 × 0.20	0.33 × 0.28 × 0.16	0.30 × 0.28 × 0.20	0.30 × 0.30 × 0.15
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.866(2)	9.7457(19)	9.7384(19)	19.710(4)
<i>b</i> (Å)	12.667(3)	17.373(4)	23.464(5)	10.492(2)
<i>c</i> (Å)	13.420(3)	11.849(2)	9.820(2)	18.068(4)
α (deg)	72.56(3)	90	90	90
β (deg)	89.26(3)	97.06(3)	114.63(3)	101.12(3)
γ (deg)	86.28(3)	90	90	90
<i>V</i> (Å ³)	1597(2)	1991(2)	2040(2)	3667(2)
<i>Z</i>	2	2	2	4
ρ_{calcd} (g cm ^{−3})	1.055	1.017	1.038	1.025
abs coeff (mm ^{−1})	0.378	0.341	0.335	0.366
<i>F</i> (000)	556	672	704	1260
θ range (deg)	1.59 < θ < 26.37	2.09 < θ < 25.00	1.74 < θ < 26.37	2.11 < θ < 26.38
no. of collected/unique rflns	12 807/6436	13 146/3466	16 073/4171	28 568/7477
completeness to θ (%)	98.4	98.8	100	99.8
no. of data/restraints/params	6436/0/251	3466/0/155	4171/0/164	7477/0/280
goodness of fit on <i>F</i> ²	1.14	1.05	1.09	1.05
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.045, <i>wR</i> 2 = 0.103	<i>R</i> 1 = 0.060, <i>wR</i> 2 = 0.152	<i>R</i> 1 = 0.053, <i>wR</i> 2 = 0.112	<i>R</i> 1 = 0.047, <i>wR</i> 2 = 0.116
<i>R</i> indices (all data)	<i>R</i> 1 = 0.050, <i>wR</i> 2 = 0.105	<i>R</i> 1 = 0.089, <i>wR</i> 2 = 0.173	<i>R</i> 1 = 0.073, <i>wR</i> 2 = 0.120	<i>R</i> 1 = 0.053, <i>wR</i> 2 = 0.120
largest diff peak/hole (e/Å ³)	0.55/−0.22	0.88/−0.44	0.63/−0.26	1.45/−0.38

2,3-Bis(trimethylsilyl)-2-[(trimethylsilyl)methyl]heptamethyltetrasilane (**17**). Compound **17** was obtained from 2,2,3-tetrakis(trimethylsilyl)-3-[(trimethylsilyl)methyl]hexamethyltetrasilane (**18**; 406 mg, 0.80 mmol) and KO^tBu (89 mg, 0.79 mmol) using method A and dimethyl sulfate (101 mg, 0.80 mmol). After aqueous workup **17** was obtained as a colorless oil (315 mg, 88%). NMR data (δ in ppm): ²⁹Si, 1.4, −11.8, −12.8, −76.1, −78.9; ¹H, 0.32 (s, 3H), 0.30 (s, 18H), 0.27 (s, 18H), 0.19 (s, 2H), 0.14 (s, 9H); ¹³C, 2.3, 1.9, 1.7, 0.4, −8.5. UV absorption (pentane, λ_{max} in nm (ϵ in M^{−1} cm^{−1})): 216 (1.4 × 10⁴). Anal. Calcd for C₁₇H₅₀Si₇ (451.18): C, 45.26; H, 11.17. Found: C, 45.26; H, 10.75.

2,3,3-Tris(trimethylsilyl)-2-[(trimethylsilyl)methyl]octamethylpentasilane (**19**). Compound **19** was obtained from 2,2,3-tetrakis(trimethylsilyl)-3-[(trimethylsilyl)methyl]hexamethyltetrasilane (**18**; 696 mg, 1.37 mmol) and KO^tBu (158 mg, 1.38 mmol) using method A and chloropentamethyldisilane (228 mg, 1.37 mmol). After aqueous workup colorless crystals (720 mg, 93%) of **19** were obtained after removing the solvent (mp 138–140 °C). NMR data (δ in ppm): ²⁹Si, 1.2, −10.0, 13.1, −13.2, −38.2, −69.7, −115.2; ¹H, 0.39 (s, 6H), 0.35 (s, 18H), 0.33 (s, 18H), 0.20 (s, 9H), 0.14 (s, 9H), 0.09 (s, 2H); ¹³C, 4.6, 3.3, 2.1, 1.3, 0.8, 0.1. UV absorption (pentane, λ_{max} in nm (ϵ in M^{−1} cm^{−1})): 216 (1.9 × 10⁴). Anal. Calcd for C₂₁H₆₂Si₉ (567.49): C, 44.45; H, 11.01. Found: C, 44.46; H, 10.83.

1,1,4-Tris(trimethylsilyl)-4-[(trimethylsilyl)methyl]octamethylcyclohexasilane (**33**). To an ice-cold solution of (chloromethyl)trimethylsilane (116 mg, 0.94 mmol, 1.0 equiv) in THF (5 mL) were added the monoanion of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (550 mg, 0.94 mmol) and KO^tBu (106 mg, 0.94 mmol) (Method A) dropwise over a period of 10 min. After it was stirred for 16 h at room temperature, the reaction mixture was subjected to an aqueous workup. Recrystallization from Et₂O/acetone yielded colorless **33** (230 mg, 41%;

mp 131–137 °C). NMR data (δ in ppm): ²⁹Si, 1.2, −7.8, −8.7, −11.9, −37.2, −40.0, −79.0, −131.8; ¹H, 0.41 (s, 6H), 0.39 (s, 6H), 0.38 (s, 6H), 0.37 (s, 6H), 0.33 (s, 9H), 0.32 (s, 9H), 0.31 (s, 9H), 0.16 (s, 9H), 0.06 (s, 2H); ¹³C, 4.0, 3.9, 2.5, 1.9, −0.2, −1.0, −2.0, −3.3, −6.1. UV absorption (pentane, λ_{max} in nm (ϵ in M^{−1} cm^{−1})): 206 (4.8 × 10⁴), 249 (s, 6 × 7 × 10³), 267 (s, 2.7 × 10²). Anal. Calcd for C₂₁H₆₂Si₁₀ (595.57): C, 42.35; H, 10.49. Found: C, 41.11; H, 10.49. HRMS for C₂₁H₆₂Si₁₀: *m/z* calcd 594.2545, found 594.2549.

cis-/*trans*-1,4-Bis(trimethylsilyl)-1,4-bis[(trimethylsilyl)methyl]octamethylcyclohexasilane (**35**). The reaction was carried out analogously to the preparation of **33** using the dianion prepared from 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (424 mg, 0.73 mmol) and KO^tBu (164 mg, 1.46 mmol) (Method B) and chloromethyltrimethylsilane (179 mg, 2 equiv). The mixture of *cis*- and *trans*-**35** (430 mg, 97%) was obtained as a colorless solid. By recrystallization with Et₂O/acetone the *trans* isomer was separated (mp 157–164 °C). Data for the *trans*-**35** isomer are as follows. NMR data (δ in ppm): ²⁹Si, 1.4, −10.9, −36.9, −77.2; ¹H, 0.41 (s, 12H), 0.39 (s, 12H), 0.32 (s, 18H), 0.16 (s, 18H), 0.09 (s, 4H); ¹³C, 2.7, 2.0, −1.1, −3.2, −5.7. UV absorption (pentane, λ_{max} in nm (ϵ in M^{−1} cm^{−1})): 211 (3.8 × 10⁴), 269 (s, 4.5 × 10³). Data for the *cis*-**2** isomer are as follows. NMR data (δ in ppm): ²⁹Si, 1.3, −11.9, −38.2, −78.6; ¹H, 0.37 (s, 12H), 0.35 (s, 12H), 0.30 (s, 18H), 0.15 (s, 18H), 0.06 (s, 4H); ¹³C, 2.5, 1.3, −2.2, −2.7, −6.1. Anal. Calcd for C₂₂H₆₄Si₁₀ (609.60): C, 43.35; H, 10.58. Found: C, 43.92; H, 10.55.

1-(Trimethylsilyl)-1,4,4-tris[(trimethylsilyl)methyl]octamethylcyclohexasilane (**36**). The reaction was carried out analogously to the preparation of **33** using the monoanion obtained from **35** (334 mg, 0.54 mmol), KO^tBu (62 mg, 1.0 equiv), and 18-crown-6 (145 mg, 1.0 equiv) (Method C) and chloromethyltrimethylsilane (68 mg, 1 equiv). Compound **36** (285 mg, 83%) was obtained as a colorless

solid after recrystallization with Et₂O/acetone (mp 103–107 °C). NMR data (δ in ppm): ²⁹Si, 1.4, 1.3, –11.0, –36.1, –37.1, –40.0, –78.0; ¹H, 0.40 (s, 6H), 0.37 (s, 6H), 0.36 (s, 6H), 0.35 (s, 6H), 0.32 (s, 9H), 0.32 (s, 9H), 0.22 (s, 2H), 0.19 (s, 9H), 0.18 (s, 9H), 0.16 (s, 9H), 0.13 (s, 2H), 0.09 (s, 2H); ¹³C, 2.6, 2.4, 2.3, 2.0, –0.1, –0.7, –1.5, –2.9, –3.2, –4.3, –5.7. UV absorption (pentane, λ_{max} in nm (ϵ in M^{–1} cm^{–1})): 233 (s, 1.2×10^4), 255 (s, 5.8×10^3). Anal. Calcd for C₂₃H₆₆Si₁₀ (623.63): C, 44.30; H, 10.67. Found: C, 44.81; H, 10.76.

1,1,4,4-Tetrakis[(trimethylsilyl)methyl]octamethylcyclohexasilane (37). The reaction was carried out analogously to the preparation of **35** using the dianion obtained from **35** (493 mg, 0.79 mmol), KO^tBu (183 mg, 1.63 mmol), and 18-crown-6 (432 mg, 1.63 mmol) (Method D) and chloromethyltrimethylsilane (203 mg, 1.65 mmol). Compound **37** (461 mg, 89%) was obtained as a colorless solid after recrystallization with Et₂O (mp 173–179 °C). NMR data (δ in ppm): ²⁹Si, 1.4, –36.6, –40.5; ¹H, 0.36 (s, 24H), 0.19 (s, 36H), 0.16 (s, 8H); ¹³C, 2.3, –1.2, –3.8. UV absorption (pentane, λ_{max} in nm (ϵ in M^{–1} cm^{–1})): 231 (s, 8.7×10^3), 261 (s, 1.2×10^3). Anal. Calcd for C₂₄H₆₈Si₁₀ (637.66): C, 45.21; H, 10.75. Found: C, 45.23; H, 10.74.

1-(Trimethylsilyl)-4-[(trimethylsilyl)methyl]dodecamethylbicyclo[2.2.2]octasilane (38). The reaction was carried out analogously to the preparation of **33** using the monoanion of 1,4-bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane (641 mg, 1.16 mmol) and KO^tBu (131 mg, 1.17 mmol) (Method A) and chloromethyltrimethylsilane (147 mg, 1.20 mmol, 1.03 equiv). Compound **38** (630 mg, 96%) was obtained as a colorless solid (mp 168–175 °C). NMR data (δ in ppm): ²⁹Si, 1.0, –6.1, –37.8, –39.9, –79.2, –131.5; ¹H, 0.38 (s, 18H), 0.36 (s, 18H), 0.31 (s, 9H), 0.15 (s, 9H), 0.05 (s, 2H); ¹³C, 3.7, 1.5, –0.9, –2.4, –2.4. Anal. Calcd for C₁₉H₅₆Si₁₀ (565.50): C, 40.35; H, 9.98. Found: C, 39.99; H, 9.97.

General Procedure for the Rearrangement Reactions. Solutions of the corresponding oligosilanes (50–1000 mg) and approximately 0.15 equiv of Al(Fe)Cl₃ in cyclohexane in a Schlenk tube with a Teflon screw cap were heated to 80 °C. After 16 or 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 and the white precipitate that formed 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 and simple filtration through a path of Celite. Especially when higher catalyst loads were used, chlorinated byproducts were detected by mass spectroscopy. Treatment of these mixtures with methylmagnesium bromide or methylolithium could be used to obtain homogeneous product distributions.

Synthesis of the Catalysts. A mixture of AlCl₃ and FeCl₃ (3%) was sublimed at a temperature of 100 °C and a pressure of 0.3–0.5 mbar for 3–4 h. A bright yellow powder was obtained, which was stored under nitrogen. For the characterization experiments a sample of the sublimate was refluxed for 12 h in cyclohexane in order to mimic the reaction conditions (see Figures S2 and S3 in the Supporting Information). ICP analysis of this sample indicated a value of 0.36 mg of Fe/g (0.104%). For all other measurements a sublimate (AlCl₃ 2.441 g, FeCl₃ 297 mg (10%)) was used which according to ICP contained 1.30 mg of Fe/g (0.37%).

Rearrangement of 2,2,5-Tris(trimethylsilyl)undecamethylhexasilane (1) to 1,1,3-Tris(trimethylsilyl)heptamethylcyclopentasilane (2). Following the general procedure, the reaction of **1** (386 mg, 0.70 mmol) was carried out with Al(Fe)Cl₃ (25 mg, 0.27 equiv) for 12 h in cyclohexane. After 16 h complete conversion was detected and compound **2**^{10,12} (303 mg, 93%) was isolated.

Rearrangements of 2,5-Bis(trimethylsilyl)dodecamethylhexasilane (3) and 2,2,3,3-Tetrakis(trimethylsilyl)hexamethyltetrasilane (5). Following the general procedure, the reaction of **3** (332 mg, 0.63 mmol) was started with Al(Fe)Cl₃ (25 mg, 0.30 equiv) at 80 °C in cyclohexane.

After 16 h a mixture of **4** (48%), **5** (12%), **6** (34%), and **7** (6%) was detected. Another batch of Al(Fe)Cl₃ (25 mg, 0.30 equiv) was added, and almost no change of composition was detected after an additional 24 h. After 6 days a mixture of compounds, with **6** (30%) and **7** (30%) being the main products, was observed. Additional Al(Fe)Cl₃ (25 mg, 0.30 equiv) was added. After another 6 days compound **7** and tetramethylsilane were found to be the main products along with numerous smaller signals in the NMR spectrum. An increasingly worse signal/noise ratio indicates some decomposition process. Assignment of the structure of compound **6** was based on the ²⁹Si NMR data (δ in ppm, cyclohexane, D₂O capillary): ²⁹Si, –9.5, –14.8, –32.8, –37.8, –42.0, –129.1.^{10,12}

Repeating the reaction with **5** gave essentially the same result.

Rearrangement of 2,9,9-Tetrakis(trimethylsilyl)octadecamethyldecasilane (8) to 2,2,5,9,9-Pentakis(trimethylsilyl)pentadecamethylnonasilane (9) and Further to 1,1,3-Tris(trimethylsilyl)pentamethylcyclopentasilane (2) and 2,2-Bis(trimethylsilyl)octamethyltetrasilane (10). Following the general procedure, the reaction of **8** (379 mg, 0.45 mmol) was started with Al(Fe)Cl₃ (20 mg, 0.33 equiv) at 80 °C in cyclohexane. Two additional batches of Al(Fe)Cl₃ (2 × 25 mg, 0.83 equiv) were required before extensive conversion of **8** to **9** was observed. Addition of another batch of Al(Fe)Cl₃ (25 mg, 0.42 equiv) led to further conversion of **8** but was also accompanied by the formation of additional products. Workup allowed the isolation of **9** (46 mg, 13%) still contaminated with some 17% of **8**. Purification was achieved by recrystallization from acetone/isopropyl alcohol and further from diethyl ether at –30 °C (mp 89–92 °C). NMR data of **9** (δ in ppm): ²⁹Si, –9.8, –11.7, –30.6, –32.7, –72.6, –128.5; ¹H, 0.56 (s, 6H), 0.55 (s, 6H), 0.55 (s, 6H), 0.51 (s, 6H), 0.34 (s, 54H), 0.31 (s, 9H), 0.29 (s, 3H); ¹³C, 3.5, 1.6, 1.4, 1.3, –0.1, –0.2, –8.6. UV absorption (pentane, λ_{max} in nm (ϵ in M^{–1} cm^{–1})): 216 (6.1×10^4); 258 (4.8×10^4); 270 (2.4×10^4). Anal. Calcd for C₃₀H₉₀Si₁₄ (844.24): C, 42.68; H, 10.74. Found: C, 41.90; H, 10.11.

If the reaction was not stopped, complete conversion of **8** and **9** was observed. In addition to a small amount of side products compounds **2** and **10** in approximately equal quantities were the major reaction products.

Rearrangement of 2-[(Trimethylsilyl)methyl]heptamethyltrisilane (11) to 1-[(Trimethylsilyl)methyl]heptamethyltrisilane (12). The reaction was carried out by following the general procedure, using **11** (186 mg, 0.672 mmol) and Al(Fe)Cl₃ (2 × 25 mg, 0.56 equiv) in cyclohexane at 80 °C. After 48 h no conversion was detected and a second batch of Al(Fe)Cl₃ was added. Clean and complete conversion to **12** was detected after 120 h. After workup and removal of solvent **12** (173 mg, 93%) was obtained as a colorless oil. NMR data (δ in ppm): ²⁹Si, 1.3, –15.1, –16.3, –48.2; ¹H, 0.21 (s, 6H), 0.15 (s, 9H), 0.15 (s, 6H), 0.09 (s, 9H), –0.19 (s, 2H); ¹³C, 1.8, 1.7, –0.5, –1.2, –6.8. Anal. Calcd for C₁₁H₃₂Si₄ (276.72): C, 47.75; H, 11.66. Found: C, 44.04; H, 10.26.

Rearrangement of 2-(Trimethylsilyl)-2-[(trimethylsilyl)methyl]hexamethyltrisilane (13) to 2-(Trimethylsilyl)-1-[(trimethylsilyl)methyl]hexamethyltrisilane (14). The reaction was carried out by following the general procedure, using **13** (421 mg, 1.26 mmol) and Al(Fe)Cl₃ (120 mg, 0.72 equiv) in cyclohexane. Completion was reached after 24 h. **14** (380 mg, 90%) could be obtained as a colorless oil. NMR data (δ in ppm): ²⁹Si, 1.3, –11.3, –12.9, –86.5; ¹H, 0.29 (s, 6H), 0.21 (s, 18H), 0.13 (s, 3H), 0.10 (s, 9H), –0.08 (s, 2H); ¹³C, 3.7, 1.7, 1.2, 0.6, –13.1. Anal. Calcd for C₁₃H₃₈Si₅ (334.87): C, 46.63; H, 11.44. Found: C, 44.66; H, 10.86.

Rearrangement of 2-(Trimethylsilyl)-2-[(Trimethylsilyl)methyl]octamethyltetrasilane (15) to 2-(Trimethylsilyl)-2-[(Trimethylsilyl)methyl]dimethylsilyl]hexamethyltrisilane (16). The reaction was carried out by following the general procedure using **15** (240 mg, 0.611 mmol) and Al(Fe)Cl₃ (20 mg, 0.25 equiv) in cyclohexane. Completion was reached after 16 h. **16** (227 mg, 95%) could be obtained as a colorless oil. NMR data (δ in ppm): ²⁹Si, 1.2, –8.1, –10.3, –132.8; ¹H, 0.36 (s, 6H),

0.27 (s, 27H), 0.09 (s, 9H), 0.02 (s, 2H); ^{13}C , 6.4, 3.5, 2.9, 1.8. Anal. Calcd for $\text{C}_{15}\text{H}_{44}\text{Si}_6$ (393.03): C, 45.84; H, 11.28. Found: C, 46.28; H, 11.21.

Rearrangement of Tetrakis(trimethylsilyl)-1-[(trimethylsilyl)methyl]-2-methyldisilane (17) to 1,1-Bis(trimethylsilyl)-3-carba-2,2,4,4,5,5-hexamethylcyclopentasilane (20). The reaction was carried out by following the general procedure using **17** (253 mg, 0.561 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (60 mg, 0.80 equiv) in cyclohexane. Completion was reached after 36 h. **20** (186 mg, 91%) could be obtained as a colorless liquid. NMR data (δ in ppm): ^{29}Si , 0.6, -8.8, -9.0, -34.6, -136.7; ^1H , 0.35 (s, 6H), 0.30 (s, 6H), 0.27 (s, 18H), 0.20 (s, 6H), -0.08 (s, 2H); ^{13}C , 7.1, 3.2, 1.6, 0.4, -2.2. Anal. Calcd for $\text{C}_{13}\text{H}_{38}\text{Si}_6$ (362.96): C, 43.02; H, 10.55. Found: C, 37.67; H, 8.71.

Rearrangement of Pentakis(trimethylsilyl)[(trimethylsilyl)methyl]disilane (18) to 1,1,5-Tris(trimethylsilyl)-3-carba-2,2,4,4,5-pentamethylcyclopentasilane (21). The reaction was carried out by following the general procedure using **18** (227 mg, 0.446 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (20 mg, 0.34 equiv) in cyclohexane. Completion was reached after 16 h. White crystalline **21** (68 mg, 36%) could be obtained after recrystallization from pentane/2-propanol at 0 °C (oil at room temperature). NMR data (δ in ppm): ^{29}Si , 2.5, -3.3, -8.1, -9.9, -11.5, -78.8, -131.5; ^1H , 0.34 (s, 3H), 0.31 (s, 3H), 0.29 (s, 3H), 0.28 (s, 9H), 0.27 (s, 9H), 0.26 (s, 3H), 0.25 (s, 9H), 0.24 (s, 3H), -0.02 (d, 1H, $J = 13$ Hz), -0.11 (d, 1H, $J = 13$ Hz); ^{13}C , 7.5, 4.3, 3.6, 3.4, 3.3, 1.8, 0.5, 0.2, -7.4. Anal. Calcd for $\text{C}_{15}\text{H}_{44}\text{Si}_7$ (421.11): C, 42.78; H, 10.53. Found: C, 42.00; H, 10.24.

Rearrangement of 1-Pentamethyldisilanyl-tetrakis(trimethylsilyl)-2-[(trimethylsilyl)methyl]disilane (19) to 1,1,5,5-tetrakis(trimethylsilyl)-3-carba-2,2,4,4-cyclopentasilane (22). The reaction was carried out by following the general procedure using **19** (252 mg, 0.444 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (50 mg, 0.84 equiv) in cyclohexane. Completion was reached after 24 h. White crystalline **22** (110 mg, 52%) could be obtained after recrystallization from methanol/2-propanol at -30 °C (oil at room temperature). NMR data (δ in ppm): ^{29}Si , 1.6, -9.1, -128.7; ^1H , 0.31 (s, 36H), 0.31 (s, 12H), -0.05 (s, 2H); ^{13}C , 8.7, 4.0, 3.5. Anal. Calcd for $\text{C}_{17}\text{H}_{50}\text{Si}_8$ (479.27): C, 42.60; H, 10.52. Found: C, 39.95; H, 9.61. HRMS for $\text{C}_{17}\text{H}_{50}\text{Si}_8$: m/z calcd 478.2067, found 478.2099.

Rearrangement of Pentakis(trimethylsilyl)[(trimethylsilyl)methyl]-2,2,3,3-tetramethyltetrasilane (23) to 1-(Trimethylsilyl)-3-carbaundecamethylbicyclo[3.2.1]octasilane (25). The reaction was carried out by following the general procedure using **23** (291 mg, 0.465 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (60 mg, 0.97 equiv) in cyclohexane. After 24 h a 1:1 mixture of **25** and 1,1,5,5-tetrakis(trimethylsilyl)-3-carbahexamethylcyclohexasilane (**24**) (NMR data (δ in ppm, D_2O capillary): ^{29}Si -8.1, -9.6, -30.2, -132.6.) could be observed. Complete conversion was reached after 48 h. White crystalline **25** (110 mg, 53%) could be obtained after recrystallization from pentane/2-propanol (mp 100–110 °C). NMR data (δ in ppm): ^{29}Si , -6.0, -6.9, -8.9, -27.9, -33.7, -39.4, -77.8, -129.6; ^1H , 0.54 (s, 3H), 0.39 (s, 3H), 0.37 (s, 3H), 0.36 (s, 3H), 0.33 (s, 3H), 0.31 (s, 3H), 0.30 (s, 3H), 0.29 (s, 9H), 0.28 (s, 3H), 0.26 (s, 3H), 0.24 (s, 3H), 0.05 (d, 1H, $J = 13$ Hz), -0.16 (d, 1H, $J = 13$ Hz); ^{13}C , 8.6, 5.3, 3.6, 3.4, 2.5, 1.0, 0.1, -1.1, -1.1, -1.8, -3.7, -4.0, -14.1. Anal. Calcd for $\text{C}_{15}\text{H}_{44}\text{Si}_6$ (449.20): C, 40.11; H, 9.87. Found: C, 38.52; H, 9.65.

Rearrangement of 33 to 3-Carba-1,5-bis(trimethylsilyl)decamethylbicyclo[3.2.1]octasilane (34). The reaction was carried out by following the general procedure using **33** (202 mg, 0.339 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (20 mg, 0.44 equiv) in cyclohexane. Completion was reached after 16 h, and white crystalline **34** (117 mg, 68%) could be obtained after recrystallization from dichloromethane at room temperature (mp 162–169 °C). NMR data (δ in ppm): ^{29}Si , -6.2, -7.3, -22.5, -31.4, -126.8; ^1H , 0.63 (s, 3H), 0.43 (s, 3H), 0.37 (s, 6H), 0.36 (s, 6H), 0.32 (s, 6H), 0.30 (s, 6H), 0.29 (s, 18H), 0.02 (d, 1H, $J = 13$ Hz), -0.14 (d, 1H, $J = 13$ Hz); ^{13}C , 9.7, 5.4, 3.6, 3.4, 2.6, 0.8, -1.0, -2.1. UV absorption (pentane, λ_{max} in nm (ϵ in $\text{M}^{-1} \text{cm}^{-1}$)): 218 (4.9×10^4),

243 (1.8×10^4). Anal. Calcd for $\text{C}_{17}\text{H}_{50}\text{Si}_9$ (507.35): C, 40.25; H, 9.93. Found: C, 39.67; H, 9.71. HRMS for $\text{C}_{17}\text{H}_{50}\text{Si}_9$: m/z calcd 506.1836, found 506.1824.

Rearrangement of 35 or 1,1,5,5-Tetrakis(trimethylsilyl)-1,5-bis-[(trimethylsilyl)methyl]hexamethylpentasilane (30) to 3,7-Dicarba-1,5-bis(trimethylsilyl)decamethylbicyclo[3.3.1]nonasilane (31). The reaction was carried out by following the general procedure using **35** (425 mg, 0.697 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (60 mg, 0.65 equiv) in cyclohexane. Completion was reached after 24 h. White crystalline **31** (280 mg, 77%) could be obtained after recrystallization from benzene at room temperature (mp 189–195 °C). NMR data (δ in ppm): ^{29}Si , -7.2, -8.4, -31.3, -132.8; ^1H , 0.59 (s, 6H), 0.33 (s, 12H), 0.32 (s, 12H), 0.29 (s, 18H), -0.04 (d, 2H, $J = 13$ Hz), -0.10 (d, 2H, $J = 13$ Hz); ^{13}C , 11.0, 5.9, 3.9, 3.6, 3.3. UV absorption (pentane, λ_{max} in nm (ϵ in $\text{M}^{-1} \text{cm}^{-1}$)): 216 (3.1×10^4), 244 (2.1×10^4). Anal. Calcd for $\text{C}_{18}\text{H}_{52}\text{Si}_9$ (521.38): C, 41.47; H, 10.05. Found: C, 41.47; H, 10.00.

Starting from **30** (362 mg, 0.519 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (125 mg, 1.81 equiv), complete conversion was reached after 4 days but some unidentified byproducts were detected in this case.

Rearrangement of 36 or 1,1,4,4-Tetrakis(trimethylsilyl)-1,4-bis-[(trimethylsilyl)methyl]tetramethyltetrasilane (28) to 3,7-Dicarba-1,5-bis(trimethylsilyl)decamethylbicyclo[3.3.0]octasilane (29). The reaction was carried out by following the general procedure using **36** (153 mg, 0.251 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (15 mg, 0.45 equiv) in cyclohexane. Completion was reached after 16 h, and white crystalline **29** (65 mg, 56%) was obtained after recrystallization from dichloromethane at -30 °C (sublimation from 280 °C). NMR data (δ in ppm): ^{29}Si , 2.9, -8.7, -127.9; ^1H , 0.36 (s, 12H), 0.33 (s, 18H), 0.31 (s, 12H), -0.04 (d, 2H, $J = 13$ Hz), -0.26 (d, 2H, $J = 13$ Hz); ^{13}C , 9.3, 3.5, 3.2, 3.1. UV absorption (pentane, λ_{max} in nm (ϵ in $\text{M}^{-1} \text{cm}^{-1}$)): 224 (2.1×10^4). Anal. Calcd for $\text{C}_{16}\text{H}_{46}\text{Si}_8$ (463.22): C, 41.49; H, 10.01. Found: C, 39.65; H, 9.81.

Starting from **28** (130 mg, 0.203 mmol) and $\text{Al}(\text{Fe})\text{Cl}_3$ (30 mg, 1.11 equiv), **29** (44 mg, 47%) was obtained after 48 h.

■ ASSOCIATED CONTENT

S Supporting Information. CIF files giving X-ray crystallographic data for **25**, **29**, **31**, **33**, **34**, **35-trans**, **37**, and **38** and figures giving additional experimental details of catalyst characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This study was supported by the Austrian *Fonds zur Förderung der wissenschaftlichen Forschung* (FWF) via the projects P-18538 and I-669. We wish to thank Prof. Dr. Christian L. Lengauer (Institut für Mineralogie und Kristallographie, Universität Wien – Geozentrum) for powder XRD measurements of $\text{Al}(\text{Fe})\text{Cl}_3$ samples.

■ REFERENCES

- (1) Marschner, C. *Organometallics* **2006**, *25*, 2110–2125.
- (2) Marschner, C.; Baumgartner, J.; Wallner, A. *Dalton Trans.* **2006**, 5667–5674.
- (3) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 1998, 221–226.
- (4) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023–1030.

- (5) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723–3731.
- (6) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, *685*, 79–92.
- (7) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1969**, 567b.
- (8) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1970**, 157a.
- (9) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845–4850.
- (10) Ishikawa, M.; Watanabe, M.; Iyoda, J.; Ikeda, H.; Kumada, M. *Organometallics* **1982**, *1*, 317–322.
- (11) Fischer, J.; Baumgartner, J.; Marschner, C. *Science* **2005**, *310*, 825.
- (12) Wagner, H.; Wallner, A.; Fischer, J.; Flock, M.; Baumgartner, J.; Marschner, C. *Organometallics* **2007**, *26*, 6704–6717.
- (13) Wagner, H.; Baumgartner, J.; Müller, T.; Marschner, C. *J. Am. Chem. Soc.* **2009**, *131*, 5022–5023.
- (14) Blinka, T. A.; West, R. *Organometallics* **1986**, *5*, 128–133.
- (15) Wallner, A.; Hlina, J.; Wagner, H.; Baumgartner, J.; Marschner, C. *Organometallics* **2011**, 10.1021/om1011159.
- (16) Fischer, R.; Konopa, T.; Ully, S.; Wallner, A.; Baumgartner, J.; Marschner, C. In *Organosilicon Chemistry VI: From Molecules to Materials*; Auner, N., Weis, J., Eds. Wiley-VCH: Weinheim, Germany, 2005; pp 355–360.
- (17) Stueger, H.; Fuerpass, G.; Renger, K.; Baumgartner, J. *Organometallics* **2005**, *24*, 6374–6381.
- (18) Wallner, A.; Hölbling, M.; Baumgartner, J.; Marschner, C. *Silicon Chem.* **2006**, *3*, 175–185.
- (19) Zirngast, M.; Baumgartner, J.; Marschner, C. *Organometallics* **2008**, *27*, 6472–6478.
- (20) Stallings, W.; Donohue, J. *Inorg. Chem.* **1976**, *15*, 524–529.
- (21) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723–3731.
- (22) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287–3290.
- (23) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 7486–7487.
- (24) Tsuji, H.; Michl, J.; Tamao, K. *J. Organomet. Chem.* **2003**, *685*, 9–14.
- (25) Tsuji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **2004**, *23*, 3375–3377.
- (26) Fukazawa, A.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2006**, *128*, 6800–6801.
- (27) Mallesha, H.; Tsuji, H.; Tamao, K. *Organometallics* **2004**, *23*, 1639–1642.
- (28) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762.
- (29) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877–879.
- (30) Kayser, C.; KICKELBICK, G.; Marschner, C. *Angew. Chem.* **2002**, *114*, 1031–1034.
- (31) Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67–76.
- (32) Wallner, A.; Wagner, H.; Baumgartner, J.; Marschner, C.; Rohm, H. W.; Köckerling, M.; Krempner, C. *Organometallics* **2008**, *27*, 5221–5229.
- (33) Whittaker, S. M.; Brun, M.-C.; Cervantes-Lee, F.; Pannell, K. H. *J. Organomet. Chem.* **1995**, *499*, 247–252.
- (34) Lambert, J. B.; Pflug, J. L.; Allgeier, A. M.; Campbell, D. J.; Higgins, T. B.; Singewald, E. T.; Stern, C. L. *Acta Crystallogr., Sect. C* **1995**, *51*, 713–715.
- (35) Apeloig, Y.; Yuzefovich, M.; Bendikov, M.; Bravo-Zhivotovskii, D.; Klinkhammer, K. *Organometallics* **1997**, *16*, 1265–1269.
- (36) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63–69.
- (37) SAINTPLUS: *Software Reference Manual, Version 6.45*; Bruker-AXS: Madison, WI, 1997–2003.
- (38) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
- (39) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2007**, *64*, 112–122.