Route Si$_6$ revisited

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Abstract

Starting from 1,4-dipotassiotetrasilane 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane can easily be obtained. This can be used to generate *trans*-1,4-dipotassiocyclohexasilane. Transmetallation with magnesium leads to a formal inversion of configuration at one of the anionic silicon atoms. Depending on the stereochemical configuration of the starting material hydrolyses give either the *trans*- or *cis*-1,4-dihydrocyclohexasilanes. The 1,4-dipotassiocyclohexasilane also provides a convenient precursor for the synthesis of [2.2.0], [2.2.1] and [2.2.2] bicyclo oligosilane systems. The principal possibility of further functionalization of the cage molecules is demonstrated by the synthesis and derivatization of 1,4-dipotassio-[2.2.2]-bicycloocta-silane. The extraordinary selectivity for the cleavage of trimethylsilyl groups is demonstrated for the case of bis(trimethylsilyl)bis-(undecamethylcyclohexasilanyl)silane, where in a molecule which contains 16 silicon–silicon bonds, a trimethylsilyl group is selectively attacked.
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1. Introduction

Polysilanes are an important class of compounds which has received considerable attention over the last decades. They comprise linear and branched polymers [1] as well as cyclic and cage-like structures [2]. Cyclosilanes are among the oldest known compounds with silicon–silicon bonds. Their origins date back directly to Kipping [3].

Cyclosilanes have been studied in our laboratories in Graz over the last decades. Especially, Hengge and his group have contributed tremendously to the advancement of cyclosilane chemistry [2b,2d]. Our recent development of α,ω-oligosilyldianions [4] provided us with the opportunity to address a number of so far sparsely approached problems of cyclosilane chemistry. We could synthesize a number of functionalized cyclosilanes and study certain aspects of stereoselective reactions. Some of the compounds which served as starting

materials for us were already known from studies by West et al. from the investigations of Lewis acid-catalyzed rearrangements of linear permethylated si-lanes [5].

2. Results and discussion

The reaction of 1,4-dipotassiumtetrasilane [4] (**1**) with 1,2-dibromotetramethyldisilane leads to the clean formation of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcy-clohexasilane (**2**) (Scheme 1) [5,6]. Reaction of **2** with one equivalent of potassium *tert*-butoxide generates cyclohexasilanylpotassium **3**. The reactivity of **3** is quite comparable to that of other oligosilyl potassium compounds [7]. It can easily be derivatized with sulfuric acid or dimethyl sulfate to give the corresponding hydro (**4**) or methyl (**5**) compound (Scheme 2). Reaction of **2** with two equivalents of potassium *tert*-butoxide in the presence of 18-crown-6 gives rise to the formation of the *trans*-1,4-dipotassium-1,4-bis(trimethylsilyl)octa-methylcyclohexasilane crown ether adduct **6** (Scheme 1). Compound **6** is to the best of our knowledge the first

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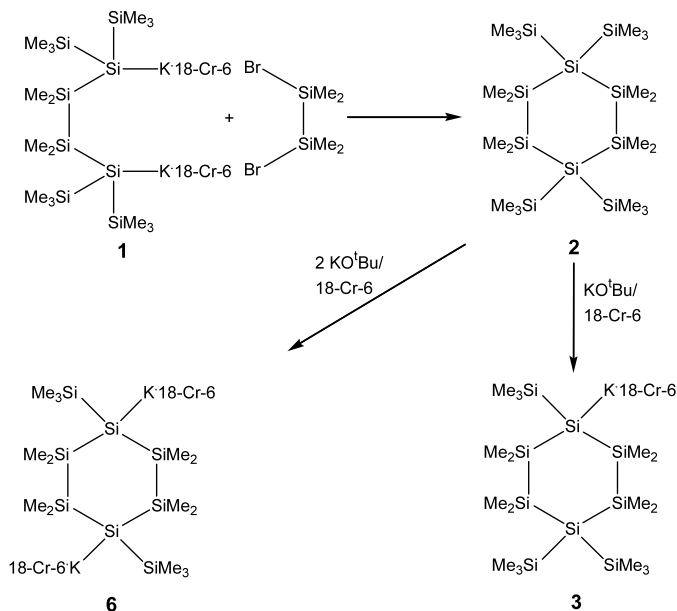
Scheme 1. Synthesis of 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane (2) and the respective 1-potassio (3) and 1,4-dipotassio (6) derivatives.

Fig. 1. The molecular structure and numbering of 6 with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations: K(1)–Si(1) 3.4404(13); K(2)–Si(4) 3.4717(14); Si(4)–Si(8) 2.3364(11); Si(4)–Si(5) 2.3407(11); Si(4)–Si(3) 2.3496(18); Si(6)–Si(1) 2.3438(18); Si(6)–Si(5) 2.3484(11); Si(1)–Si(7) 2.3402(11); Si(1)–Si(2) 2.3535(11); Si(2)–Si(3) 2.3554(11); Si(8)–Si(4)–Si(5) 102.36(4); Si(8)–Si(4)–Si(3) 102.06(4); Si(5)–Si(4)–Si(3) 101.59(4); Si(8)–Si(4)–K(2) 114.20(4); Si(5)–Si(4)–K(2) 100.93(4); Si(3)–Si(4)–K(2) 131.46(4); Si(1)–Si(6)–Si(5) 111.07(4); Si(7)–Si(1)–Si(6) 102.38(4); Si(7)–Si(1)–Si(2) 102.02(4); Si(6)–Si(1)–Si(2) 100.73(4); Si(6)–Si(1)–K(1) 115.41(4); Si(2)–Si(1)–K(1) 117.13(4); Si(1)–Si(2)–Si(3) 112.67(4); Si(4)–Si(3)–Si(2) 109.46(4); Si(4)–Si(5)–Si(6) 110.92(4).

example of a cyclic polysilane dianion. The compound was characterized by X-ray single crystal crystallography (Fig. 1). It exhibits the potassium substituents in the axial positions and the large trimethylsilyl groups in the equatorial positions. Although the potassium atoms are coordinated by the bulky crown-ethers the distance to the negatively charged silicon atoms is too large to influence the conformation of the ring.

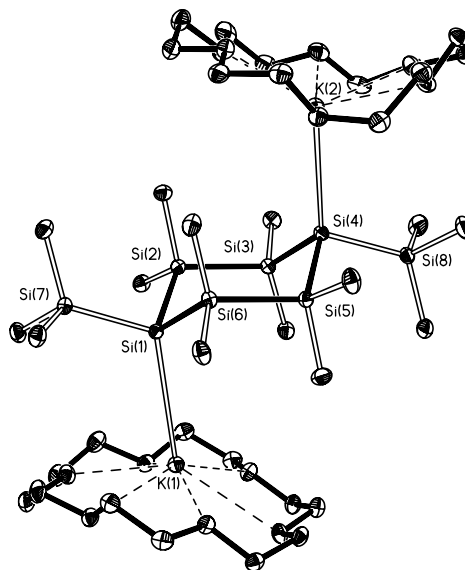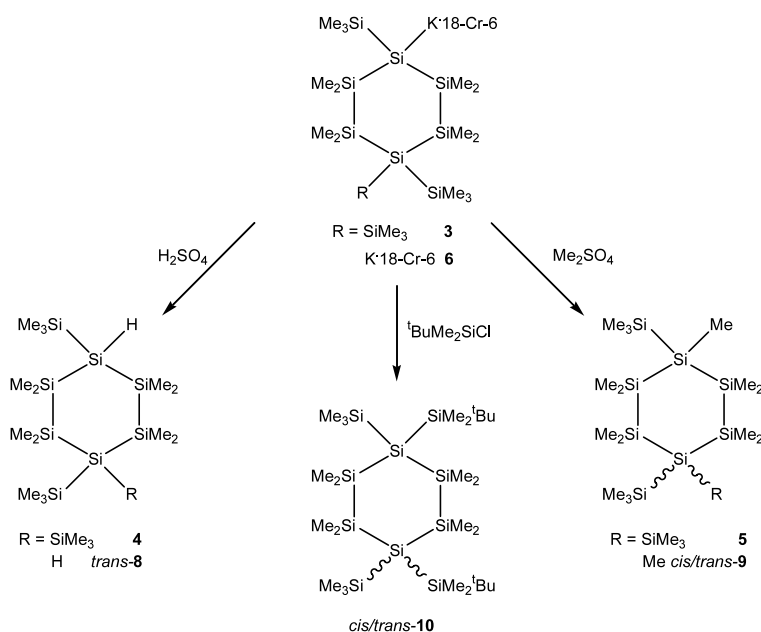The reaction of 6 with one equivalent of magnesium bromide gives a bicyclic compound where the 1- and 4- positions are bridged by a magnesium atom (7) (Scheme 4) [8]. The configurational flexibility of triple silyl

Scheme 2. Derivatization reactions of the mono- and dipotassio compounds 3 and 6 respectively.

substituted silylanions [9] facilitates the formation of **7** which can be considered to be an oligosilyldianion isomeric to **6** with inverted configuration at position 1.

The availability of these stereoisomers allows the syntheses of the *cis*- and *trans*-dihydrocyclohexasilanes (**8**). As has been found by Sommer et al., silylanions can be hydrolyzed with retention of configuration [10]. Therefore, preferentially *trans*-1,4-bis(trimethylsilyl)-1,4-dihydrooctamethylcyclohexasilane (*trans*-**8**) is obtained by hydrolysis of **6** and the corresponding *cis*-isomer (*cis*-**8**) from **7** (Scheme 3). From our earlier investigations the silyl potassium compounds are known to have a far lower configurational stability than their magnesium congeners [11]. The hydrolysis of the dipotassium compound **6** resulted in a 6:1 mixture of *trans*- and *cis*-**8** as could be quantified by means of both GCMS and ¹H NMR analysis. The reaction was carried out with several solvent systems but the product distribution proved to remain essentially the same. Repeating the experiment at −75 °C reproduced the same results.

We assume that the formation of the dihydro derivative **8** is a two-step reaction. Starting from **6** the first protonation step proceeds and yields the 4-hydro-1-potassiumcyclohexasilanes **8a** and **8b**. As the configurational stability is low, rapid inversion occurs and a thermodynamically controlled mixture of *cis*- and *trans*-isomers is formed. The product distribution is governed by the large trimethylsilyl groups which prefer the equatorial over axial positions as can be deduced from X-ray structure analysis. From the product distribution we find the *trans*-configuration of the reaction intermediate **8a** to be 4.2 kJ mol⁻¹ more stable than the *cis*-

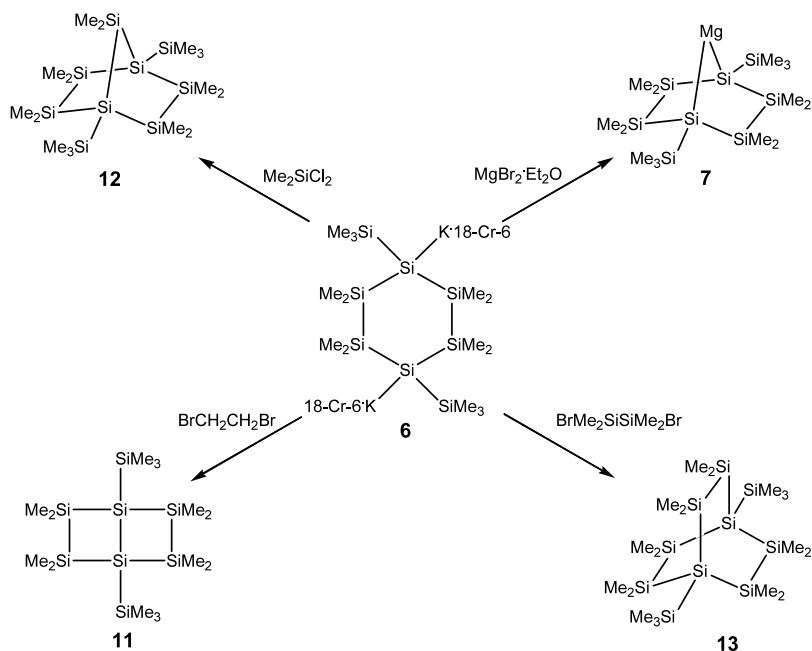isomer. A second protonation step finally affords *trans*-**8** as the major product (Scheme 3).

Contrary to the potassium compound **6** the magnesium derivative **7** exhibits a configurational stability large enough to overrule the directing effect of the trimethylsilyl groups and affords *cis*-**8** as the only product upon hydrolysis (Scheme 3).

The reactions of **6** with dimethyl sulfate and *tert*-butyldimethylsilylchloride do not exhibit the same selectivity in the formation of the derivatives. The alkylation reaction gives the *trans*- and *cis* isomers (**9**) in a ratio of 3:1. It can be assumed that after the first methylation step the second one is not as fast as the protonation reaction. After mono-alkylation is achieved the difference in conformational stability of the ring conformers seems to decrease. Since, the configuration at the anionic silicon atom is not stable the second methyl group can approach not only in a *trans*- (*trans*-**9**) but also in a *cis*-fashion (*cis*-**9**). This effect is even more pronounced for the case of the reaction with *tert*-butyldimethylsilylchloride. Here after the first substitution the trimethylsilyl group has to compete with a larger group for the equatorial position. This effects a flip of conformation and as a result a 1:1 mixture of *cis*- and *trans*-isomers (**10**) (Scheme 2).

Starting from **6** it is also very easy to access a number of bicyclic oligosilanes (Scheme 4). The reaction with 1,2-dibromoethane [12] is especially interesting for it allows the formation of the bicyclo [2.2.0] system **11**. While this is a well known structural unit its synthesis so far was rather tedious. It required the use of rather bulky isopropyl substituents at the silicon atom to ensure the formation of the desired ring size and gave
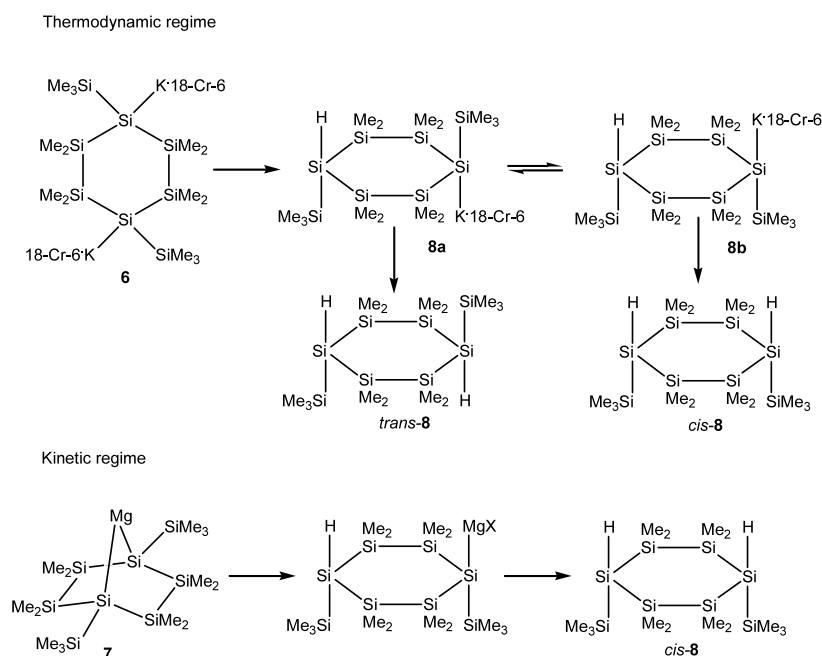
Scheme 3. Formation of *cis*- and *trans*-**8** can be directed by using the dipotassio compound **6** or the magnesium compound **7**.

Me₂Si Si SiMe₃
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
Me₃Si SiMe₂
12

Mg Si SiMe₃
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
Me₃Si SiMe₂
7

Me₂SiCl₂   MgBr₂·Et₂O

Me₃Si Si
Me₂Si Si SiMe₂
Me₂Si SiMe₂
Si SiMe₃
K·18-Cr-6
6
18-Cr-6·K

BrCH₂CH₂Br   BrMe₂SiSiMe₂Br

SiMe₃
Me₂Si—Si—SiMe₂
Me₂Si—Si—SiMe₂
SiMe₃
11

Me₂Si SiMe₃
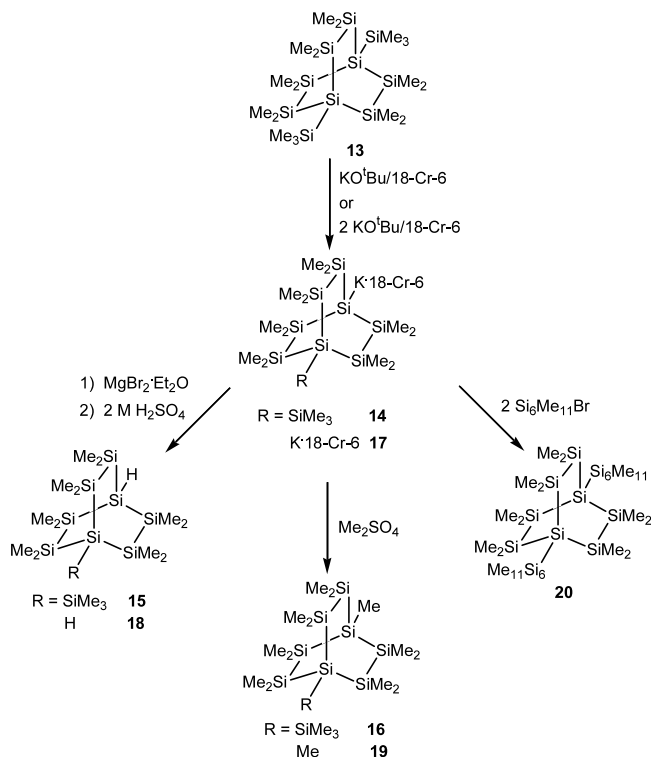Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
Me₃Si SiMe₂
13

Scheme 4. 1,4-Dipotassium compound **6** as starting material for the syntheses of bicyclic compounds.

the fused hexasilane in rather low yield [13]. The *trans*-annular ring closure reaction applied in our case renders this requirement obsolete as the ring size is determined by the regiochemistry of the anionic silicon atoms. A similar Wurtz-type reaction which utilizes 1,4-dichloro-cyclohexasilane and sodium was reported to give an intramolecular reaction also only with isopropyl substituents [13c].

The reaction of **6** with dimethyldichlorosilane leads to the sole formation of a [2.2.1] bicyclo heptasilane skeleton **12** (Scheme 4). Analogously the reaction of **6** with 1,2-dibromo-1,1,2,2-tetramethyldisilane also gave a single compound with [2.2.2] bicyclooctasilane structure and two trimethylsilyl groups attached to the bridge-head atoms (**13**) (Scheme 4). Both types of bicyclic compounds have been prepared by West and others before in Wurtz-type reactions [14]. Since these are not very selective reactions yields of specific compounds are rather poor. From this point of view our syntheses can be considered to be major improvements both in terms of yield and selectivity.

13 was subjected to reaction with one or two equivalents potassium *tert*-butoxide to yield the respective mono- (**14**) or dipotassium compounds (**17**) (Scheme 5).

17 is an interesting compound as it can be retro-synthetically composed starting from two molecules of tetrakis(trimethylsilyl)silane. Gradually trimethylsilyl groups are replaced by potassium atoms and subsequently by disilylydene bridges. Eventually only the central silicon atoms of the original tetrakis(trimethylsilyl)silane molecules are remaining in the [2.2.2] bicyclooctasilane unit. This nicely demonstrates the role of

Me₂Si SiMe₃
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
Me₃Si SiMe₂
13

KOᵗBu/18-Cr-6
or
2 KOᵗBu/18-Cr-6

Me₂Si K·18-Cr-6
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
R SiMe₂
R = SiMe₃ **14**
K·18-Cr-6 **17**

1) MgBr₂·Et₂O
2) 2 M H₂SO₄

Me₂Si H
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
R SiMe₂
R = SiMe₃ **15**
H **18**

Me₂SO₄

Me₂Si Me
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
R SiMe₂
R = SiMe₃ **16**
Me **19**

2 Si₆Me₁₁Br

Me₂Si Si₆Me₁₁
Me₂Si Si SiMe₂
Me₂Si Si SiMe₂
Me₁₁Si₆ SiMe₂
20

Scheme 5. Derivatization reaction of the bicyclo[2.2.2]octasilane mono- and dianions **14** and **17**.

trimethylsilyl substituents as masked functional groups (Scheme 6).

Complex **17** can be derivatized to give the respective hydrosilane (**18**) and permethylated [2.2.2] bicyclooctasilane (**19**). Hydrolysis, however, can only be effected cleanly after previous transmetallation of **17** with
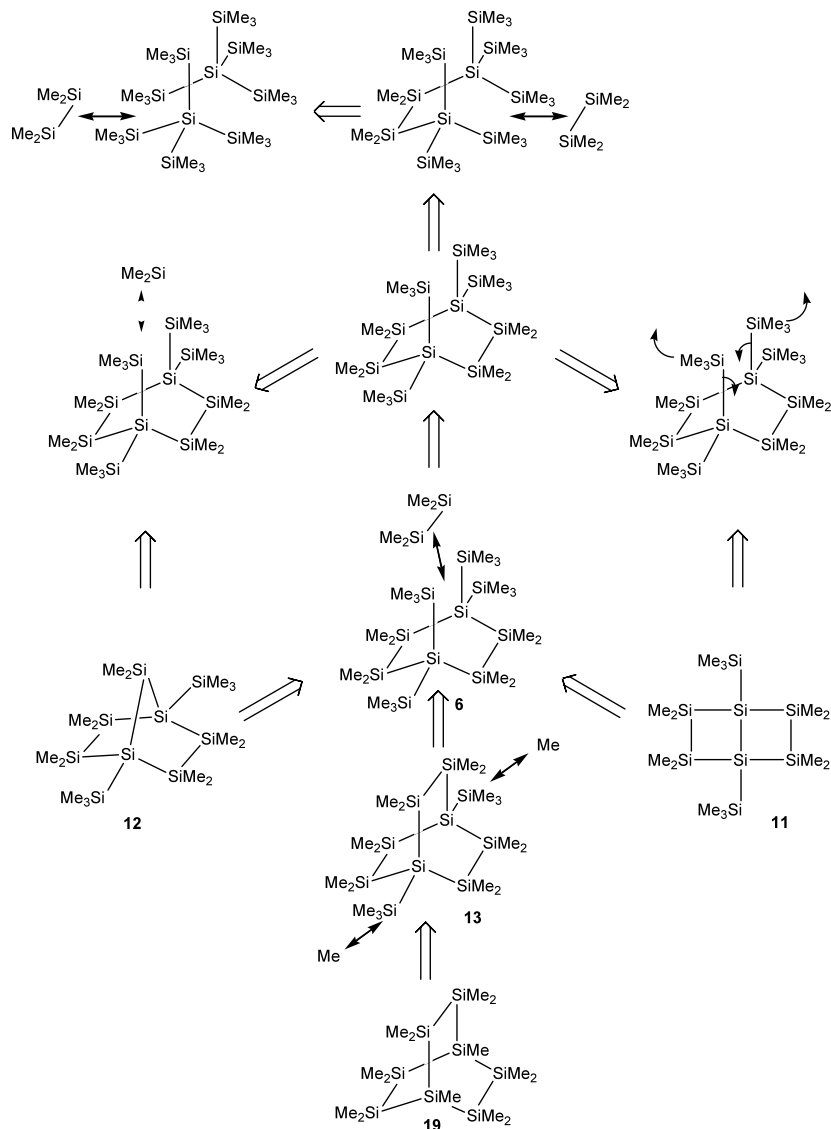
Scheme 6. Retrosynthetic analysis of the synthesis of permethylated bicyclosilanes **11**, **12**, **13**, and **19**.

magnesium bromide. Reaction with two equivalents of bromoundecamethylcyclohexasilane gives a bicyclic compound with two attached rings (**20**) (Scheme 5).

Compound **20** demonstrated the utility of the cyclohexasilanyl group to function as a bulky ligand. We have recently communicated a number of compounds where one or two cyclohexasilanyl groups are attached to Group 4 element atoms [15]. Most of these compounds have been prepared utilizing undecamethylcyclohexasilanyl potassium [16].

The outlined silyl potassium chemistry can also be used to obtain similar compounds. Starting from tris(trimethylsilyl)silyl potassium [7] the reaction with bromoundecamethylcyclohexasilane gives tris(trimethylsilyl)silylundecamethylcyclohexasilane (**21**) (Scheme 7) [15a]. The compound can be converted into the corresponding potassium derivative (**22**). Subsequent reaction with another equivalent bromoundecamethylcyclohexa-

silane yields tris(trimethylsilyl)silylundecamethylcyclohexasilane (**23**). The extraordinary selectivity of potassium *tert*-butoxide is demonstrated by the exclusive attack at one of the two trimethylsilyl groups in the presence of 14 other Si–Si bonds. The resulting compound (**24**) can be treated with dimethyl sulfate to give the methylated compound (**25**) (Scheme 7).

2.1. X-ray crystallography

1,1,4,4-Tetrasubstituted cyclohexasilane compounds **6**, *trans*-**8** and *trans*-**10** were subjected to X-ray crystal structure analyses (Table 1, Figs. 1–3). All molecules show the Si$_6$ ring in a chair conformation without too much difference between the endo- and exocyclic Si–Si bonds lengths, which all lie in a range between 2.33 and 2.36 Å.
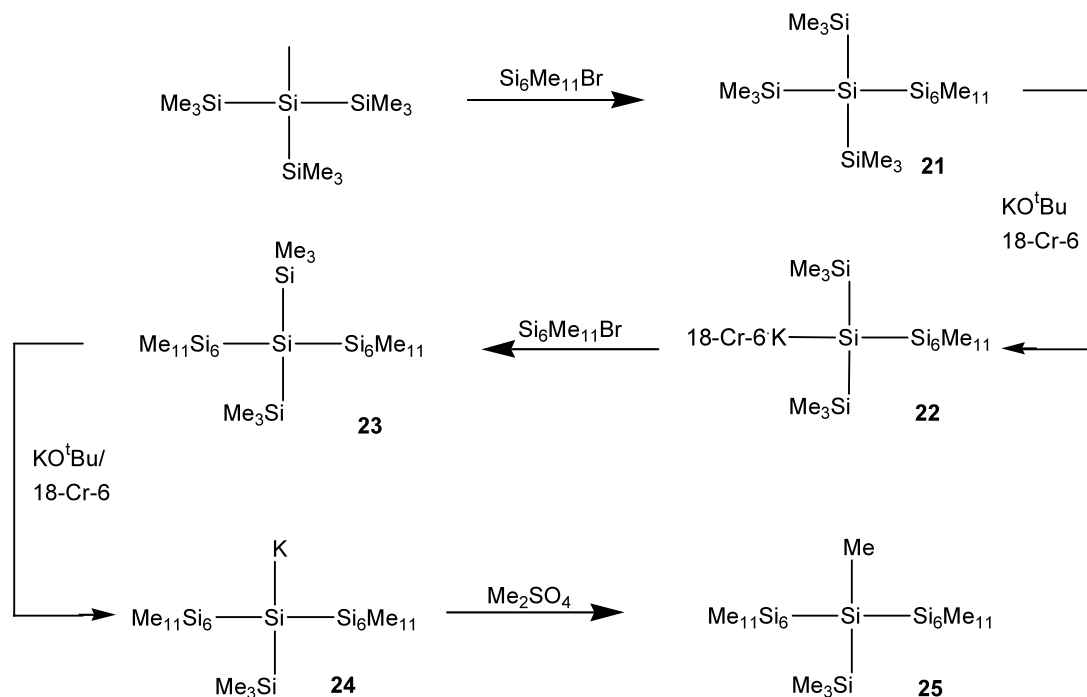
Scheme 7. Synthesis of undecamethylcyclohexasilanyl substituted silanes and silyl potassium compounds.

Table 1
Crystallographic data

|	6	*trans*-8	*trans*-10	21	23
Empirical formula	$K_2Si_8O_{12}C_{38}H_{90}$	$Si_8C_{14}H_{44}$	$Si_{10}C_{26}H_{72}$	$Si_{10}C_{20}H_{60}$	$Si_{15}C_{28}H_{84}$
M_w	1042.02	437.19	665.74	581.58	842.30
Temperature (K)	100(2)	100(2)	150(2)	100(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Size (mm)	$0.48 \times 0.33 \times 0.30$	$0.50 \times 0.25 \times 0.18$	$0.65 \times 0.48 \times 0.20$	$0.54 \times 0.32 \times 0.05$	$0.40 \times 0.22 \times 0.18$
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$Pnma$	$P\bar{1}$	$C2/c$	$P2(1)/n$
a (Å)	12.825(3)	27.968(6)	9.2975(19)	38.0763(8)	10.175(2)
b (Å)	14.520(3)	15.301(3)	9.4333(19)	9.906(2)	40.013(8)
c (Å)	18.547(4)	6.6643(13)	13.604(3)	24.549(5)	13.582(3)
α (°)	104.52(3)	90	87.90(3)	90	90
β (°)	102.86(3)	90	73.66(3)	125.60(3)	95.79(3)
γ (°)	109.17(3)	90	68.78(3)	90	90
V (Å^3)	2977.1(10)	2851.9(10)	1064.5(4)	7529(3)	5501.5(19)
Z	2	4	1	8	4
ρ_{calc} (g cm^{-3})	1.162	1.018	1.038	1.026	1.017
Absorption coefficient (mm^{-1})	0.367	0.374	0.324	0.358	0.365
$F(000)$	1128	960	368	2560	1848
θ range	$1.62 < \theta < 24.71$	$1.46 < \theta < 26.30$	$2.32 < \theta < 24.71$	$1.66 < \theta < 24.71$	$1.82 < \theta < 26.37$
Reflections collected/unique	20603/9957	21248/3011	7130/3526	25108/6402	43172/11171
Completeness to θ (%)	98.2	99.9	97.4	99.6	99.4
Absorption correction	Empirical	Empirical	Empirical	Empirical	Empirical
Data/restraints/parameters	9957/0/555	3011/0/179	3526/0/175	6402/0/291	11171/0/416
Goodness-of-fit on F^2	1.017	1.025	1.046	1.122	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$, $wR_2 = 0.1004$	$R_1 = 0.0533$, $wR_2 = 0.1035$	$R_1 = 0.0714$, $wR_2 = 0.1822$	$R_1 = 0.0955$, $wR_2 = 0.2308$	$R_1 = 0.0644$, $wR_2 = 0.1201$
R indices (all data)	$R_1 = 0.0561$, $wR_2 = 0.1071$	$R_1 = 0.0891$, $wR_2 = 0.1162$	$R_1 = 0.0810$, $wR_2 = 0.1904$	$R_1 = 0.1205$, $wR_2 = 0.2462$	$R_1 = 0.0909$, $wR_2 = 0.1297$
Extinction coefficient	None	None	None	None	None
Largest difference peak/hole (e Å^{-3})	0.438/−0.316	0.486/−0.239	0.063/−0.585	1.298/−0.695	0.389/−0.297
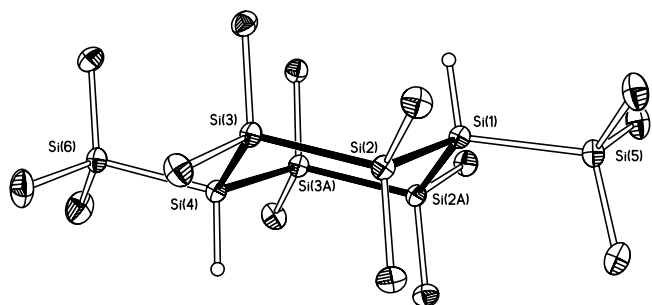
Fig. 2. The molecular structure and numbering of *trans*-**8** with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations: Si(1)–Si(2) 2.3531(13); Si(1)–Si(5) 2.3537(19); Si(3)–Si(2) 2.3462(13); Si(3)–Si(4) 2.3475(12); Si(4)–Si(6) 2.3542(19); Si(2)–Si(1)–Si(5) 113.15(4); Si(2)–Si(3)–Si(4) 112.20(5); Si(3)–Si(2)–Si(1) 110.10(5).

For *trans*-**8** all the hydrogen atoms except for the Me$_3$Si groups were located successfully. The compound represents an almost regular cyclohexasilane chair with ring bond angles between 110.1° and 112.2°. The distances of the Si(1)–H(1) and Si(4)–H(2) bonds are about 1.40 Å and they occupy a *trans*-diaxial conformation.

The structures of **6** and *trans*-**10** also show this *trans*-diaxial arrangement. In **6** we find that the four ring bond angles except for those around silicon atoms 1 and 4 are in approximately the same range as found in *trans*-**8** (109.5°–112.7°). The remaining two angles around the anionic silicon atoms are only 100.7° and 101.6°. They reflect the increased spatial requirement of the negative charge. For *trans*-**10** as expected the larger substituents (i.e. the ^{t}BuMe$_2$Si groups) occupy the equatorial positions. Presumably via an 1,3-interaction the large ^{t}BuMe$_2$Si group exhibits a strong flattening influence

on the six-membered ring. This results in ring bond angles of around 119° about all dimethyl substituted silicon atoms. At the quarternary silicon atoms, however, only a value of 107.8° is found. The ring bond angles sum up to 646.44° for **6**, 668.9° for *trans*-**8**, and 692.3° for *trans*-**10**.

For **6** we find silicon–potassium bond lengths of 3.4404(13) and 3.4717(14) Å. These distances are in between those for (Me$_3$Si)$_5$Si$_2$K·C$_7$H$_8$ (3.315 Å) [7b], ^{t}Bu$_3$SiK·3C$_6$D$_6$ (3.378 Å) [17], (Me$_3$Si)$_3$SiK·3C$_6$H$_6$ (3.352 Å) [18], and Ph(Me$_3$Si)$_4$Si$_2$K·18-Cr-6 (3.599 Å) [7b].

Compound **21** (Fig. 4) is a good example to compare the steric demands of the cyclohexasilanyl and tri-methylsilyl groups. The silicon–silicon bond between the quarternary silicon atom and the ring moiety is significantly longer (2.401(2) Å) compared to those of the trimethylsilyl groups (2.358(2)–2.364(2) Å). Also the dihedral angles between the cyclohexasilanyl and the trimethylsilyl groups of 109.76(8)°, 112.52(8)°, and 114.67(9)° are larger compared to those between the trimethylsilyl groups (103.90(8)°, 107.25(9)°, 108.10(9)°). The situation with **23** (Fig. 5) is quite similar as the longest silicon–silicon bonds are those between the central silicon atom and the rings (2.4071(14) Å and 2.4133(14) Å). The angles between the two ring bridge atoms and the central silicon is only slightly larger than an ideal tetrahedral angle (110.57(5)°) whereas the two trimethylsilyl groups only span an angle of 103.54(5)°.
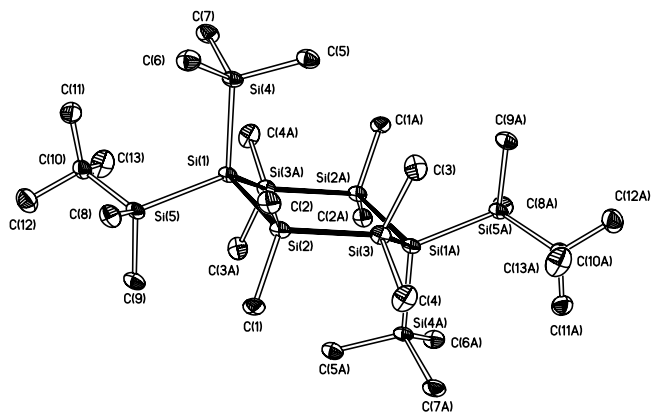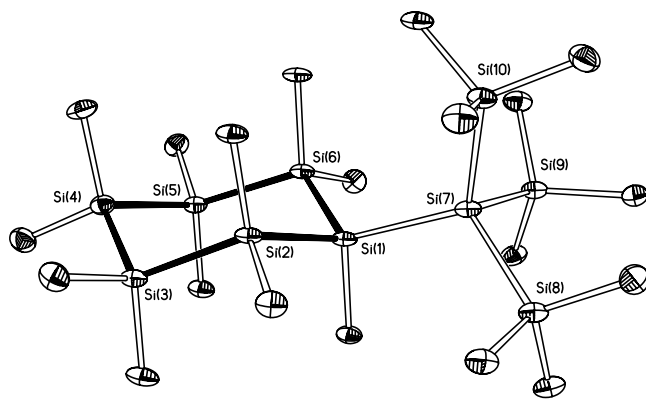

Fig. 3. The molecular structure and numbering of *trans*-**10** with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations: Si(2)–Si(3) 2.3735(16); Si(2)–Si(1) 2.3840(15); Si(1)–Si(4) 2.3733(15); Si(1)–Si(5) 2.3930(16); Si(3)–Si(2)–Si(1) 119.79(5); Si(4)–Si(1)–Si(2) 107.95(5); Si(4)–Si(1)–Si(5) 112.21(6); Si(2)–Si(1)–Si(5) 103.57(5).

Fig. 4. The molecular structure and numbering of **21** with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations: Si(1)–Si(2) 2.354(2); Si(1)–Si(6) 2.363(2); Si(1)–Si(7) 2.401(2); Si(2)–Si(3) 2.342(2); Si(3)–Si(4) 2.335(2); Si(4)–Si(5) 2.331(2); Si(5)–Si(6) 2.339(2); Si(7)–Si(10) 2.358(2); Si(7)–Si(8) 2.364(2); Si(2)–Si(1)–Si(6) 106.24(8); Si(2)–Si(1)–Si(7) 115.31(8); Si(6)–Si(1)–Si(7) 115.32(8); Si(3)–Si(2)–Si(1) 113.44(8); Si(4)–Si(3)–Si(2) 110.61(9); Si(5)–Si(4)–Si(3) 108.11(8); Si(4)–Si(5)–Si(6) 114.45(9); Si(5)–Si(6)–Si(1) 113.05(8); Si(10)–Si(7)–Si(9) 108.10(9); Si(10)–Si(7)–Si(8) 107.25(9); Si(9)–Si(7)–Si(8) 103.90(8); Si(10)–Si(7)–Si(1) 114.67(9); Si(9)–Si(7)–Si(1) 109.76(8); Si(8)–Si(7)–Si(1) 112.52(8).
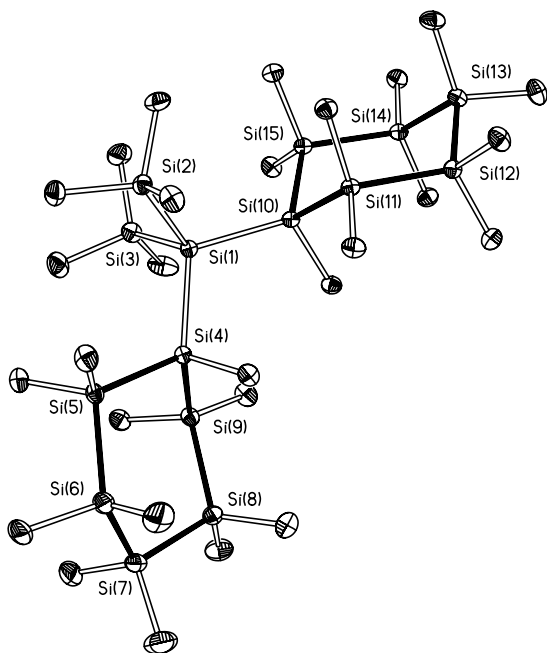
Fig. 5. The molecular structure and numbering of **23** with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations: Si(1)–Si(3) 2.3599(14); Si(1)–Si(2) 2.3661(15); Si(1)–Si(4) 2.4071(14); Si(1)–Si(10) 2.4133(14); Si(4)–Si(5) 2.3735(14); Si(4)–Si(9) 2.3777(15); Si(5)–Si(6) 2.3650(16); Si(6)–Si(7) 2.3397(18); Si(7)–Si(8) 2.3377(16); Si(8)–Si(9) 2.3527(15); Si(10)–Si(15) 2.3757(14); Si(10)–Si(11) 2.3799(13); Si(11)–Si(12) 2.3536(14); Si(12)–Si(13) 2.3389(15); Si(13)–Si(14) 2.3364(14); Si(3)–Si(1)–Si(2) 103.54(5); Si(3)–Si(1)–Si(4) 108.15(5); Si(2)–Si(1)–Si(4) 112.23(5); Si(3)–Si(1)–Si(10) 112.58(5); Si(2)–Si(1)–Si(10) 109.63(5); Si(4)–Si(1)–Si(10) 110.57(5); Si(5)–Si(4)–Si(9) 103.91(5); Si(5)–Si(4)–Si(1) 118.18(5); Si(9)–Si(4)–Si(1) 116.32(5); Si(6)–Si(5)–Si(4) 111.91(5); Si(7)–Si(6)–Si(5) 118.08(6); Si(8)–Si(7)–Si(6) 110.67(6); Si(7)–Si(8)–Si(9) 110.66(6); Si(8)–Si(9)–Si(4) 112.41(6); Si(15)–Si(10)–Si(11) 105.54(5); Si(15)–Si(10)–Si(1) 116.02(5); Si(11)–Si(10)–Si(1) 116.14(5); Si(12)–Si(11)–Si(10) 112.28(5); Si(13)–Si(12)–Si(11) 112.58(5); Si(14)–Si(13)–Si(12) 107.47(5); Si(13)–Si(14)–Si(15) 111.03(5); Si(14)–Si(15)–Si(10) 112.72(5).

3. Experimental

All manipulations involving air-sensitive compounds were performed either under a nitrogen or Ar atmosphere using standard Schlenk techniques or were carried out in a nitrogen filled glove box. All solvents besides CDCl$_3$ were dried over sodium–potassium alloy under nitrogen and were freshly distilled prior to use. Commercially available reagents were purchased and used as received. 1,4-Dipotassium-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane (**1**) [4], 1,2-dibromo-1,1,2,2-tetramethyldisilane [19], and bromoundecamethylcyclohexasilane [20] were prepared following published procedures.

Aqueous work-up was performed by pouring the reaction mixture on 2 M H$_2$SO$_4$, separation of the layers and subsequently the aqueous layer was extracted twice with the solvent given in the text. The combined

organic layers were stirred with a saturated aqueous sodium hydrogen carbonate solution. The organic layer was dried over sodium sulfate which was filtered off afterwards.

NMR spectra were recorded on a Varian UNITY INOVA 300 (^{1}H 299.948 MHz, ^{13}C 75.428 MHz, ^{29}Si 59.587 MHz) spectrometer. The spectra were referenced to the deuterated solvent and shifts are reported in ppm downfield from Me$_4$Si.

GC analyses were carried out on a HP 5890 series II equipped with capillary column DB-1HT (25 m × 0.251 mm; 0.1 μm) and a HP 5971 mass spectrometer. The MS fragmentation pattern is given for every substance, and relative intensities are given in brackets.

GCMS samples of the derivatized silyl anions were obtained by adding a solution of the nucleophile to a mixture of 10% ethyl bromide in Et$_2$O or to the organic layer of a mixture of Et$_2$O–2 M H$_2$SO$_4$ to give the corresponding ethylated respectively hydrosilane species in very rapid, clean and quantitative reactions.

Elementary analysis was carried using a Heraeus VARIO ELEMENTAR EL apparatus.

X-ray structure analysis data were collected on a Bruker SMART APEX diffractometer with Mo–K$_\alpha$ radiation. Structures were determined and refined by using direct methods as implemented in SHELXTL-5.1 [21]. Crystal and refinement data are listed in Table 1.

3.1. 1,1,4,4-Tetrakis(trimethylsilyl)octamethylcyclohexasilane (2)

At room temperature (r.t.) a solution of 1.13 g (4.09 mmol) 1,2-dibromo-1,1,2,2-tetramethyldisilane in toluene is added dropwise to a solution of 4.40 g (4.09 mmol) 1,4-dipotassium-1,1,4,4-tetrakis(trimethylsilyl)-2,2,3,3-tetramethyltetrasilane [4] in 40 ml toluene. After complete addition the yellow color of the silyl anion vanishes and a white precipitate appears. The reaction mixture is stirred at r.t. for 4 h and is then subjected to an aqueous workup with toluene–2 M H$_2$SO$_4$. After removal of the solvent 2.28 g (96%) of off-white crystalline, clean **2** is obtained. The crude product is further purified by recrystallization from acetone.

NMR ^{1}H (CDCl$_3$, δ ppm) 0.32 (s, 24H, *Me*$_2$Si), 0.27 (s, 36H, *Me*$_3$Si); ^{13}C (CDCl$_3$, δ ppm) 4.0 (*Me*$_3$Si), −0.9 (*Me*$_2$Si); ^{29}Si (CDCl$_3$, δ ppm) −8.2 (Me$_3$*Si*), −40.0 (Me$_2$*Si*), −131.7 ((Me$_3$Si)$_2$*Si*).

MS (70 eV) *m/z* (%): 580 (14) [M$^+$], 507 (2) [M$^+$ − SiMe$_3$], 359 (30) [Si$_8$Me$_9^+$], 301 (13) [Si$_7$Me$_7^+$], 259 (14) [Si$_5$Me$_5^+$ − H], 131 (15) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{20}$H$_{60}$Si$_{10}$ (581.55 g mol^{-1}) Calc.: C, 41.31; H, 10.40. Found: C, 41.09; H, 10.35%.

3.2. 1,4,4-Tris(trimethylsilyl)-octamethylcyclohexasilanylpotassium·18-Cr-6 (3)

200 mg (0.345 mmol) **2**, 39 mg (0.345 mmol) potassium *tert*-butoxide and 91 mg (0.345 mmol) 18-crown-6 are dissolved in 2 ml toluene. The cleavage reaction proceeds within 4 h to selectively yield **3** as a yellow solution from which the pure product is obtained as a crown ether adduct upon addition of 5 ml *n*-pentane and cooling to −35 °C.

NMR ^{1}H (C$_6$D$_6$, δ ppm) 3.43 (s, 24H, CH_2O), 0.66 (s, 12H, *Me*$_2$SiSiK), 0.62 (s, 9H, *Me*$_3$SiSiK), 0.59 (s, 12H, *Me*$_2$SiMe$_2$SiSiK), 0.50 (2, 18H, (*Me*$_3$Si)$_2$Si); ^{13}C (C$_6$D$_6$, δ ppm) 70.1 (CH_2O), 8.6 (*Me*$_3$SiSiK), 4.5 ((*Me*$_3$Si)$_2$Si), 4.1 (*Me*$_2$SiSiK), 0.1 (*Me*$_2$SiMe$_2$SiSiK); ^{29}Si (C$_6$D$_6$, δ ppm) −2.3 ((Me$_3$*Si*)SiK), −8.5 ((Me$_3$*Si*)$_2$Si), −30.4 (Me$_2$*Si*SiK), −37.9 (Me$_2$*Si*Me$_2$SiSiK), −130.7 ((Me$_3$Si)$_2$*Si*), −186.3 (*Si*K).

3.3. 1,1,4-Tris(trimethylsilyl)-4-hydro-octamethylcyclohexasilane (4)

At r.t. a solution of 60 mg (0.075 mmol) **3** in 5 ml THF is added to a stirred two phase mixture of 10 ml Et$_2$O and 10 ml 2 M H$_2$SO$_4$. After stirring the reaction mixture for 15 min an aqueous work up with 2 M H$_2$SO$_4$–Et$_2$O yields 37 mg (97% yield) of **4** as a colorless solid.

NMR ^{1}H (C$_6$D$_6$, δ ppm) 2.69 (s, 1H, *H*-Si, $^1J_{Si-H} = 156$ Hz), 0.41 (s, 6H, *Me*$_2$Si), 0.38 (s, 6H, *Me*$_2$Si), 0.36 (s, 6H, *Me*$_2$Si), 0.33 (s, 9H, *Me*$_3$Si), 0.31 (s, 9H, *Me*$_3$Si), 0.29 (s, 6H, *Me*$_2$Si), 0.28 (s, 9H, *Me*$_3$Si); ^{13}C (C$_6$D$_6$, δ ppm) 3.9 (*Me*$_3$Si), 3.8 (*Me*$_3$Si), 2.5 (*Me*$_3$Si), −1.1 (*Me*$_2$Si), −1.5 (*Me*$_2$Si), −1.7 (*Me*$_2$Si), −2.6 (*Me*$_2$Si); ^{29}Si (C$_6$D$_6$, δ ppm) −7.6 (Me$_3$*Si*), −8.5 (Me$_3$*Si*), −9.0 (Me$_3$*Si*), −37.0 (Me$_2$*Si*), −38.4 (Me$_2$*Si*), −112.9 (*Si*H), −131.0 ((SiMe$_3$)$_2$*Si*).

MS (70 eV) *m*/*z* (%): 508 (7) [M$^+$], 434 (67) [M$^+$ − SiMe$_3$H], 419 (10) [M$^+$ − SiMe$_4$H], 361 (90) [M$^+$ − Si$_2$Me$_6$H], 303 (8) [M$^+$ − Si$_3$Me$_8$H], 287 (23) [M$^+$ − Si$_3$Me$_9$H$_2$], 131 (10) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{17}$H$_{52}$Si$_9$ (509.37 g mol^{-1}) Calc.: C, 40.09; H, 10.29. Found: C, 39.87; H, 10.32%.

3.4. 1,1,4-Tris(trimethylsilyl)nonamethylcyclohexasilane (5)

At 0 °C a solution of 60 mg (0.075 mmol) **3** in 5 ml THF is added to a mixture of 10 ml Et$_2$O and 0.25 ml dimethylsulfate. The reaction mixture is allowed to warm up to r.t. and after stirring for 1 h the reaction mixture is subjected to an aqueous workup with 2 M H$_2$SO$_4$–Et$_2$O to give 35 mg (91%) of **5** as a colorless solid.

NMR ^{1}H (C$_6$D$_6$, δ ppm) 0.38 (s, 6H, *Me*$_2$Si), 0.36 (s, 6H, *Me*$_2$Si), 0.35 (s, 6H, *Me*$_2$Si), 0.33 (s, 9H, *Me*$_3$Si), 0.31 (s, 9H, *Me*$_3$Si), 0.29 (s, 6H, *Me*$_2$Si), 0.23 (s, 9H, *Me*$_3$Si), 0.22 (s, 3H, *Me*Si); ^{13}C (C$_6$D$_6$, δ ppm) 3.9 (*Me*$_3$Si), 3.8 (*Me*$_3$Si), 0.9 (*Me*$_3$Si), −0.5 (*Me*$_2$Si), −1.3 (*Me*$_2$Si), −2.7 (*Me*$_2$Si), −4.4 (*Me*$_2$Si), −11.0 (*Me*Si); ^{29}Si (C$_6$D$_6$, δ ppm) −7.3 (Me$_3$*Si*), −9.0 (Me$_3$*Si*), −9.9 (Me$_3$*Si*), −37.2 (Me$_2$*Si*), −40.2 (Me$_2$*Si*), −83.4 (Me*Si*), −131.3 ((SiMe$_3$)$_2$*Si*).

MS (70 eV) *m*/*z* (%): 522 (26) [M$^+$], 449 (1) [M$^+$ − SiMe$_3$], 434 (1) [M$^+$ − SiMe$_4$], 375 (10) [M$^+$ − Si$_2$Me$_6$H], 361 (8) [M$^+$ − Si$_2$Me$_7$], 301 (41) [M$^+$ − Si$_3$Me$_9$H$_2$], 131 (13) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{18}$H$_{54}$Si$_9$ (523.39 g mol^{-1}) Calc.: C, 41.30; H, 10.40. Found: C, 40.97; H, 10.32%.

3.5. 1,4-Bis(trimethylsilyl)octamethylcyclohexasilanyl-1,4-dipotassium·2 × 18-Cr-6 (6)

At r.t. 1.00 g (1.72 mmol) of **2**, 387 mg (3.45 mmol) of potassium *tert*-butoxide and 910 mg (3.45 mmol) of 18-crown-6 are reacted in 5 ml toluene to give a yellow solution from which 1.65 g (92% yield) of **6** precipitates as yellow crystals. As **6** is hardly soluble in benzene NMR samples were prepared in a mixture of 600 μl THF-*d*$_8$ and 100 μl benzene-*d*$_6$.

NMR ^{1}H (C$_6$D$_6$–THF-*d*$_8$, δ ppm) 3.43 (s, 48H, CH_2O), 0.28 (s, 24H, *Me*$_2$Si), 0.00 (s, 18H, *Me*$_3$Si); ^{13}C (C$_6$D$_6$–THF-*d*$_8$, δ ppm) 70.2 (CH_2O), 8.4 (*Me*$_3$Si), 2.1 (*Me*$_2$Si); ^{29}Si (C$_6$D$_6$–THF-*d*$_8$, δ ppm) −1.2 (Me$_3$*Si*), −28.2 (Me$_2$*Si*), −189.2 (*Si*K).

3.6. 7-Magnesa-1,4-bis(trimethylsilyl)octamethylbicyclo[2.2.1]-1,2,3,4,5,6-hexasilaheptane·2THF (7)

250 mg (0.240 mmol) of **6** are dissolved in THF. Upon addition of 62 mg (0.240 mmol) MgBr$_2$·Et$_2$O the yellow color vanishes and a white precipitate of KBr·18-Cr-6 appears which is removed by filtration. Upon addition of *n*-pentane and cooling to −35 °C 107 mg (74%) of **7** are obtained as colorless crystals.

NMR ^{1}H (C$_6$D$_6$, δ ppm) 3.58 (m, 8H, CH_2O), 1.39 (m, 8H, CH_2CH$_2$O), 0.38 (s, 12H, *Me*$_2$Si), 0.37 (s, 12H, *Me*$_2$Si), 0.30 (s, 18H, *Me*$_3$Si); ^{13}C (C$_6$D$_6$, δ ppm) 67.4 (CH_2O), 25.5 (CH_2CH$_2$O) 6.48 (*Me*$_3$Si), 2.53 (*Me*$_2$Si), 2.51 (*Me*$_2$Si); ^{29}Si (C$_6$D$_6$, δ ppm) −4.02 (Me$_3$*Si*), −31.95 (Me$_2$*Si*), −168.29 (*Si*K).

Anal. C$_{22}$H$_{58}$MgO$_2$Si$_8$ (603.69 g mol^{-1}) Calc.: C, 43.77; H, 9.68. Found: C, 43.02; H, 9.93%.

3.7. 1,4-Bis(trimethylsilyl)-1,4-dihydro-octamethylcyclohexasilane (8)

3.7.1. Preparation of trans-8

At r.t. a solution of 100 mg **6** in 4 ml THF is added via a syringe to a stirred two phase mixture of 10 ml Et$_2$O and 2 M H$_2$SO$_4$. After complete addition the reaction

mixture is stirred for another 15 min followed by an aqueous work up with 2 M H_2SO_4–Et_2O. Removal of the solvent yields 39 mg (94%) of *trans*-**8** as colorless crystals.

NMR ^{1}H (C_6D_6, δ ppm): 2.68 (s, 2H, *H*-Si, $^1J_{Si–H}$ = 156Hz), 0.37 (2 signals, s, 24H, Me_2Si), 0.29 (s, 18H, Me_3Si); ^{13}C (C_6D_6, δ ppm) 2.7 (Me_3Si), -2.9 (Me_2Si), -3.6 (Me_2Si); ^{29}Si (C_6D_6, δ ppm) -8.6 (Me_3Si), -36.4 (Me_2Si), -117.2 (SiH).

MS (70 eV) *m/z* (%): 362 (65) $[M^+ - SiMe_3H]$, 288 (100) $[M^+ - 2 \times SiMe_3H]$, 273 (30) $[M^+ - Si_2Me_7H_2]$, 227 (9) $[M^+ - Si_2Me_{10}H_3]$, 131 (4) $[Si_2Me_5^+]$, 73 (93) $[SiMe_3^+]$.

Anal. $C_{14}H_{44}Si_8$ (437.19 g mol^{-1}) Calc.: C, 38.46; H, 10.14. Found: C, 38.13; H, 10.21%.

3.7.2. Preparation of cis-**8**

A solution of 280 mg (0.46 mmol) of **7** in THF is added to a solution of 100 µl (1.96 mmol) H_2SO_4 in 20 ml MeOH cooled to $-75\,^\circ$C. After complete addition the reaction mixture is stirred for 5 min at $-75\,^\circ$C and is then allowed to warm up to r.t. 250 mg (2.98 mmol) $NaHCO_3$ are added to neutralize the excess of H_2SO_4. The solid is filtered off and the solvent is removed in vacuum. The colorless residue is dissolved in Et_2O and is subjected to an aqueous workup with Et_2O–2 M H_2SO_4. Crystallization from diethyl ether at $-80\,^\circ$C affords *cis*-**8** as colorless crystals.

^{1}H (C_6D_6, δ ppm): 2.78 (s, 2H, *H*-Si, $^1J_{Si–H}$ = 156Hz), 0.40 (s, 12H, Me_2Si), 0.33 (s, 12H, Me_2Si), 0.29 (s, 18H, Me_3Si); ^{13}C (C_6D_6, δ ppm) 2.4 (Me_3Si), -2.0 (Me_2Si), -3.0 (Me_2Si); ^{29}Si (C_6D_6, δ ppm) -9.5 (Me_3Si), -37.9 (Me_2Si), -112.4 (SiH).

MS (70 eV) *m/z* (%): 362 (63) $[M^+ - SiMe_3H]$, 288 (97) $[M^+ - 2 \times SiMe_3H]$, 273 (28) $[M^+ - Si_2Me_7H_2]$, 227 (8) $[M^+ - Si_2Me_{10}H_3]$, 131 (2) $[Si_2Me_5^+]$, 73 (100) $[SiMe_3^+]$.

Anal. $C_{14}H_{44}Si_8$ (437.19 g mol^{-1}) Calc.: C, 38.46; H, 10.14. Found: C, 38.22; H, 10.02%.

3.8. 1,4-Bis(trimethylsilyl)decamethylcyclohexasilane (**9**)

At 0 $^\circ$C a solution of 250 mg (0.24 mmol) of **6** in 10 ml THF is added to a mixture of 10 ml Et_2O and 0.50 ml dimethyl sulfate. During the addition a white precipitate is formed. After complete addition the reaction mixture is allowed to warm up to r.t. and stirring is continued for 1 h. Afterwards the reaction mixture is subjected to an aqueous workup with 2 M H_2SO_4–Et_2O to give 109 mg (94%) of a 3:1 mixture of *trans*- and *cis*-**9** as a colorless solid. The neat *trans*-isomer is obtained upon crystallization from diethyl ether at $-80\,^\circ$C as colorless crystals. The *cis*-isomer is obtained upon fractional crystallization from the mother liquor.

trans-**9**: ^{1}H (C_6D_6, δ ppm): 0.32 (s, 12H, Me_2Si), 0.31 (s, 12H, Me_2Si), 0.24 (s, 18H, Me_3Si), 0.23 (s, 6H, MeSi); ^{13}C (C_6D_6, δ ppm) 1.2 (Me_3Si), -2.8 (Me_2Si), -4.8 (Me_2Si), -11.1 (MeSi); ^{29}Si (C_6D_6, δ ppm) -9.5 (Me_3Si), -37.8 (Me_2Si), -82.0 ($SiMe$).

MS (70 eV) *m/z* (%):464 (43) $[M^+]$, 317 (15) $[M^+ - Si_2Me_6H]$, 259 (22) $[M^+ - Si_3Me_8H]$, 243 (36) $[M^+ - Si_3Me_9H_2]$, 157 (5) $[M^+ - Si_4Me_{13}]$, 131 (4) $[Si_2Me_5^+]$, 73 (100) $[SiMe_3^+]$.

Anal. $C_{16}H_{48}Si_8$ (465.24 g mol^{-1}) Calc.: C, 41.31; H, 10.40. Found: C, 41.02; H, 10.33%.

cis-**9**: ^{1}H (C_6D_6, δ ppm): 0.29 (2 signals, s, 24H, Me_2Si), 0.24 (s, 18H, Me_3Si), 0.23 (s, 6H, MeSi); ^{13}C (C_6D_6, δ ppm) 1.3 (Me_3Si), -3.2 (Me_2Si), -4.1 (Me_2Si), -11.5 (MeSi); ^{29}Si (C_6D_6, δ ppm) -10.3 (Me_3Si), -39.4 (Me_2Si), -83.2 ($SiMe$).

MS (70 eV) *m/z* (%): 464 (41) $[M^+]$, 317 (18) $[M^+ - Si_2Me_6H]$, 259 (27) $[M^+ - Si_3Me_8H]$, 243 (48) $[M^+ - Si_3Me_9H_2]$, 157 (11) $[M^+ - Si_4Me_{13}]$, 131 (12) $[Si_2Me_5^+]$, 73 (100) $[SiMe_3^+]$.

Anal. $C_{16}H_{48}Si_8$ (465.24 g mol^{-1}) Calc.: C, 41.31; H, 10.40. Found: C, 40.89; H, 10.44%.

3.9. 1,4-Bis(tert-butyldimethylsilyl)-1,4-bis(trimethylsilyl)octamethylcyclohexasilane (**10**)

At r.t. to a solution of 29 mg (0.19 mmol) *tert*-butyldimethylchlorosilane in 5 ml toluene a suspension of 100 mg (0.096 mmol) **6** in ml toluene is added. Within 12 h the yellow color vanishes and a white precipitate drops out. The reaction mixture is subjected to an aqueous workup with toluene–2 M H_2SO_4. After removal of the solvent a 1:1 mixture of both isomers is obtained as white crystals. *trans*-**10** can be isolated upon crystallization from diethyl ether at $-80\,^\circ$C. From the mother liquor *cis*-**10** is obtained upon concentration.

trans-**10**: ^{1}H (CDCl$_3$): 0.92 (s, 18H, Me_3C), 0.29 (s, 12H, Me_2Si), 0.24 (s, 12H, Me_2Si), 0.22 (s, 18H, Me_3Si); 0.16 (s, 12H, ^{t}Bu Me_2Si) ^{13}C (CDCl$_3$) 28.7 (Me_3C), 19.2 (Me_3C), 4.9 (Me_3Si), 0.9 (Me_2Si), 0.4 (Me_2Si), -0.1 (^{t}BuMe_2Si) ^{29}Si (CDCl$_3$) 5.0 (^{t}BuMe$_2Si$), -11.7 (Me_3Si), -39.2 (Me_2Si), -132.6 (Me_3SiSi).

Anal. $C_{26}H_{72}Si_{10}$ (665.71 g mol^{-1}) Calc.: C, 46.91; H, 10.90. Found: C, 45.91; H, 10.78%.

cis-**10**: ^{1}H (CDCl$_3$): 0.91 (s, 18H, Me_3C), 0.27 (s, 12H, Me_2Si), 0.26 (s, 12H, Me_2Si), 0.23 (s, 18H, Me_3Si), 0.15 (s, 12H, ^{t}BuMe_2Si) ^{13}C (CDCl$_3$) 28.6 (Me_3C), 19.2 (Me_3C), 4.8 (Me_3Si), 0.7 (Me_2Si), 0.4 (Me_2Si), -0.1 (^{t}BuMe_2Si), ^{29}Si (CDCl$_3$) 3.7 (^{t}BuMe$_2Si$), -10.7 (Me_3Si), -39.6 (Me_2Si), -132.2 (Me_3SiSi).

Anal. $C_{26}H_{72}Si_{10}$ (665.71 g mol^{-1}) Calc.: C, 46.91; H, 10.90. Found: C, 46.01; H, 10.97%.

3.10. 1,4-Bis(trimethylsilyl)octamethylbicyclo[2.2.0]hexasilane (11)

At r.t. a suspension of 250 mg (0.24 mmol) **6** in 5 ml toluene is added very slowly to a solution of 20 µl (0.24 mmol) 1,2-dibromoethane in 15 ml toluene. The reaction mixture remains colorless during the whole addition process and a white precipitate forms. After complete addition the reaction mixture is stirred for 2 more hours. Afterwards the solvents is removed in vacuum and the crown ether is removed by sublimation at 45 °C and 0.003 mbar. The remaining residue is extracted twice with 5 ml portions of *n*-pentane. After removal of the solvent 98 mg (94%) of **11** are obtained as a colorless solid.

NMR ^{1}H (C_6D_6, δ in ppm) 0.56 (s, 12H, Me_2Si), 0.50 (s, 12H, Me_2Si), 0.33 (s, 18H, Me_3Si); ^{13}C (C_6D_6, δ in ppm) 2.9 (Me_3Si), 0.5 (Me_2Si), −1.2 (Me_2Si); ^{29}Si (C_6D_6, δ in ppm) −7.2 (Me_3Si), −8.2 (Me_2Si), −101.0 (Me_3SiSi).

MS (70 eV) *m/z* (%): 434 (67) [M$^+$], 361 (31) [M$^+$ − SiMe$_3$], 303 (4) [M$^+$ − Si$_2$Me$_5$], 287 (45) [M$^+$ − Si$_2$Me$_6$H], 213 (13) [M$^+$ − Si$_3$Me$_9$H$_2$], 155 (14) [M$^+$ − Si$_4$Me$_{11}$H$_2$], 131 (8) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. $C_{14}H_{42}Si_8$ (435.17 g mol^{-1}) Calc.: C, 38.64; H, 9.73. Found: C, 37.94; H, 9.58%.

3.11. 1,4-Bis(trimethylsilyl)decamethylbicyclo[2.2.1]heptasilane (12)

At r.t. a solution of 250 mg (0.24 mmol) of **6** in 10 ml toluene is added to a solution of 30 µl (0.24 mmol) dimethyldichlorosilane in 5 ml toluene at a rate that the color vanishes immediately. After complete addition the reaction mixture is stirred for 2 more hours. Then the reaction mixture is subjected to an aqueous workup with toluene–2 M H$_2$SO$_4$. After removal of the solvent 112 mg (95%) of colorless crystalline **12** is obtained.

NMR ^{1}H (C_6D_6, δ in ppm) 0.49 (s, 6H, Me_2Si), 0.37 (s, 12H, Me_2Si), 0.36 (s, 12H, Me_2Si), 0.30 (s, 18H, Me_3Si); ^{13}C (C_6D_6, δ in ppm) 3.3 (Me_3Si), 0.7 (Me_2Si), −0.7 (Me_2Si) −1.7 (Me_2Si); ^{29}Si (C_6D_6, δ in ppm) −5.8 (Me_3Si), −17.3 (Me_2Si), −31.7 (Me_2Si), −122.0 (Me_3SiSi).

MS (70 eV) *m/z* (%): 492 (53) [M$^+$], 419 (24) [M$^+$ − SiMe$_3$], 361 (10) [M$^+$ − Si$_2$Me$_5$], 345 (38) [M$^+$ − Si$_2$Me$_6$H], 213 (12) [M$^+$ − Si$_4$Me$_{11}$H$_2$], 155 (9) [M$^+$ − Si$_5$Me$_{13}$H$_2$], 131 (11) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. $C_{16}H_{48}Si_9$ (493.32 g mol^{-1}) Calc.: C, 38.96; H, 9.81. Found: C, 38.23; H, 9.62%.

3.12. 1,4-Bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane (13)

At r.t. 1.35 g (1.29 mmol) of **6** in 10 ml THF are added to a solution of 360 mg (1.29 mmol) 1,2-dibromo-1,1,2,2-tetramethyldisilane in 40 ml toluene within 15 min in a way that the reaction mixture remains colorless. After complete addition and the precipitation of KBr· 18-Cr-6 the reaction mixture is stirred for another 2 h and then subjected to an aqueous workup with toluene– 2 M H$_2$SO$_4$. After drying with sodium sulfate and evaporation of the solvent 670 mg (96% yield) of colorless, crystalline **13** are obtained.

NMR ^{1}H (CDCl$_3$, δ in ppm) 0.32 (s, 36H, Me_2Si), 0.27 (s, 18H, Me_3Si); ^{13}C (CDCl$_3$, δ in ppm) 3.9 (Me_3Si), −0.9 (Me_2Si); ^{29}Si (CDCl$_3$, δ in ppm) −6.1 (Me_3Si), −38.3 (Me_2Si), −130.2 (Me_3SiSi).

MS (70 eV) *m/z* (%): 550 (28) [M$^+$], 477 (10) [M$^+$ − SiMe$_3$], 403 (36) [M$^+$ − Si$_2$Me$_6$H], 345 (12) [M$^+$ − Si$_3$Me$_8$H], 213 (11) [Si$_6$Me$_3^+$], 131 (16) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. $C_{18}H_{54}Si_{10}$ (551.48 g mol^{-1}) Calc.: C, 39.20; H, 9.87. Found: C, 38.57; H, 10.03%.

3.13. 4-Trimethylsilyldodecamethylbicyclo[2.2.2]octasilanyl potassium·18-Cr-6 (14)

A mixture of 50 mg (0.091 mmol) **13**, 10 mg (0.091 mmol) potassium *tert*-butoxide and 24 mg (0.091 mmol) 18-crown-6 is dissolved in 3 ml toluene to give an orange reaction mixture. Within 3 h the cleavage proceeds to completeness. Upon addition of 5 ml *n*-pentane and cooling to −35 °C 52 mg (73%) of **14** are obtained as yellow crystals.

NMR ^{1}H (C_6D_6, δ in ppm) 3.22 (s, 24H, CH_2O), 0.71 (s, 18H, Me_2SiSiK), 0.57 (s, 18H, Me_2SiSi(SiMe$_3$)), 0.52 (s, 9H, Me_3Si); ^{13}C (C_6D_6, δ in ppm), 70.0 (CH_2O), 4.3 (Me_3Si), 3.8 (Me_2SiSiK), 0.8 (Me_2SiSi(SiMe$_3$)); ^{29}Si (C_6D_6, δ in ppm) −6.9 (Me$_3$Si), −33.5 (Me$_2Si$SiK), −39.5 (Me$_2Si$Si(SiMe$_3$)), −129.3 (Me$_3$SiSi), −176.0 (SiK).

3.14. 4-Trimethylsilyl-1-hydrododecamethylbicyclo[2.2.2]octasilane (15)

To a solution of 50 mg (0.19 mmol) MgBr$_2$·Et$_2$O in THF a solution of 100 mg (0.13 mmol) **14** in toluene is added at r.t. The yellow color of the silyl potassium compound fades upon addition and a white precipitate forms. The reaction mixture is added via a syringe to a heavily stirred two phase mixture of Et$_2$O–2 M H$_2$SO$_4$ cooled to 0 °C. After complete addition the reaction mixture is allowed to warm up to r.t. Aqueous work up yields 60 mg (98%) of **15** as a colorless solid.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 3.04 (s, 1H, *H*-Si, $^1J_{Si-H} = 158$Hz), 0.38 (s, 18H, *Me$_2$*Si), 0.36 (s, 18H, *Me$_2$*Si), 0.30 (s, 9H, *Me$_3$*Si); ^{13}C (C$_6$D$_6$, δ in ppm), 3.7 (*Me$_3$*Si), -1.1 (*Me$_2$*Si), -1.6 (*Me$_2$*Si); ^{29}Si (C$_6$D$_6$, δ in ppm) -5.9 (Me$_3$Si), -37.9 (Me$_2$*Si*), -40.0 (Me$_2$*Si*), -109.6 (*Si*H), -129.9 (Me$_3$Si*Si*).

MS (70 eV) *m/z* (%): 478 (27) [M$^+$], 404 (35) [M$^+$ $-$ SiMe$_3$H], 389 (27) [M$^+$ $-$ SiMe$_4$H], 331 (77) [M$^+$ $-$ Si$_2$Me$_6$H], 257 (14) [M$^+$ $-$ Si$_3$Me$_9$H$_2$], 213 (14) [Si$_6$Me$_3^+$], 131 (12) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{15}$H$_{46}$Si$_9$ (479.30 g mol^{-1}) Calc.: C, 37.59; H, 9.67. Found: C, 37.12; H, 9.78%.

3.15. 4-Trimethylsilyltridecamethylbicyclo[2.2.2]octasilane (16)

At 0 °C a solution of 100 mg (0.13 mmol) **14** in 5 ml toluene is added to a solution of 0.25 ml dimethyl sulfate in 5 ml Et$_2$O. During the addition a white precipitate forms. After complete addition the reaction mixture is stirred at 0 °C for 30 min and is then allowed to warm up to r.t. followed by an aqueous work up with toluene–2 M H$_2$SO$_4$ to yield 61 mg (95%) **16** as colorless crystals.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.31 (s, 18H, *Me$_2$*Si), 0.30 (s, 9H, *Me$_3$*Si), 0.29 (s, 18H, *Me$_2$*Si), 0.23 (s, 3H, *Me*Si); ^{13}C (C$_6$D$_6$, δ in ppm) 3.6 (*Me$_3$*Si), -1.1 (*Me$_2$*Si), -3.5 (*Me$_2$*Si), -14.6 (*Me*Si); ^{29}Si (C$_6$D$_6$, δ in ppm) -6.0 (Me$_3$Si), -38.1 (Me$_2$*Si*), -40.5 (Me$_2$*Si*), -81.2 (Me*Si*), -130.3 (Me$_3$Si*Si*).

MS (70 eV) *m/z* (%): 492 (37) [M$^+$], 419 (20) [M$^+$ $-$ SiMe$_3$], 361 (7) [M$^+$ $-$ Si$_2$Me$_5$], 345 (34) [M$^+$ $-$ Si$_2$Me$_6$H], 213 (11) [M$^+$ $-$ Si$_4$Me$_{11}$H$_2$], 155 (8) [M$^+$ $-$ Si$_5$Me$_{13}$H$_2$], 131 (11) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{16}$H$_{48}$Si$_9$ (493.32 g mol^{-1}) Calc.: C, 38.96; H, 9.81. Found: C, 38. 37; H, 10.07%.

3.16. Dodecamethylbicyclo[2.2.2]octasilanyl-1,4-dipotassium·2 × 18-Cr-6 (17)

To a mixture of 250 mg (0.45 mmol) **13**, 101 mg (0.91 mmol) potassium *tert*-butoxide and 240 mg (0.91 mmol) 18-crown-6 5 ml toluene are added to yield a red solution from which 423 mg (92%) **17** precipitate out as orange crystals upon standing for 12 h.

NMR ^{1}H (100 μl C$_6$D$_6$–600 μl THF-*d$_8$*, δ in ppm) 3.47 (s, 48H, *CH$_2$*O), 0.06 (s, 36H, *Me$_2$*Si); ^{13}C (100 μl C$_6$D$_6$–600 μl THF-*d$_8$*, δ in ppm) 70.3 (*CH$_2$*O), 4.8 (*Me$_2$*Si); ^{29}Si (100 μl C$_6$D$_6$–600 μl THF-*d$_8$*, δ in ppm) -33.2 (Me$_2$*Si*), -179.6 (*Si*K).

3.17. 1,4-Dihydrododecamethylbicyclo[2.2.2]octasilane (18)

At r.t. a solution of 100 mg (0.099 mmol) **17** in toluene is added to a solution of 52 mg (0.20 mmol) MgBr$_2$·Et$_2$O in THF and is then subjected to hydrolysis

analogously to the preparation of **15** in order to obtain 39 mg (98%) of **18** as colorless crystals.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 3.40 (s, 2H, Si-*H*, $^1J_{Si-H} = 158$Hz), 0.37 (s, 36H, *Me$_2$*Si); ^{13}C (C$_6$D$_6$, δ in ppm) -1.7 (*Me$_2$*Si); ^{29}Si (C$_6$D$_6$, δ in ppm) -39.8 (Me$_2$*Si*), -109.1 (*Si*H).

MS (70 eV) *m/z* (%): 406 (30) [M$^+$], 346 (6) [M$^+$ $-$ SiMe$_2$H$_2$], 332 (30) [M$^+$ $-$ SiMe$_3$H], 273 (12) [M$^+$ $-$ Si$_2$Me$_5$H$_2$], 258 (30) [M$^+$ $-$ Si$_2$Me$_6$H$_2$], 73 (100) [SiMe$_3^+$], 59 (14) [SiMe$_2$H].

Anal. C$_{12}$H$_{38}$Si$_8$ (407.12 g mol^{-1}) Calc.: C, 35.40; H, 9.41. Found: C, 34.79; H, 9.33%.

3.18. Tetradecamethylbicyclo[2.2.2]octasilane (19)

At 0 °C a solution of 100 mg (0.099 mmol) **17** in 5 ml toluene is added to a solution of 0.25 ml dimethyl sulfate in 5 ml Et$_2$O analogously to the preparation of **16** to yield 61 mg (95%) of **19** as colorless crystals.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.30 (s, 36H, *Me$_2$*Si), 0.22 (s, 6H, *Me*Si); ^{13}C (C$_6$D$_6$, δ in ppm) -3.5 (*Me$_2$*Si), -14.5 (*Me*Si); ^{29}Si (C$_6$D$_6$, δ in ppm) -40.2 (Me$_2$*Si*), -81.2 (Me*Si*).

MS (70 eV) *m/z* (%): 434 (68) [M$^+$], 361 (31) [M$^+$ $-$ SiMe$_3$], 303 (6) [M$^+$ $-$ Si$_2$Me$_5$], 287 (41) [M$^+$ $-$ Si$_2$Me$_6$H], 213 (15) [M$^+$ $-$ Si$_3$Me$_9$H$_2$], 155 (16) [M$^+$ $-$ Si$_4$Me$_{11}$H$_2$], 131 (10) [Si$_2$Me$_5^+$], 73 (100) [SiMe$_3^+$].

Anal. C$_{14}$H$_{42}$Si$_8$ (435.17 g mol^{-1}) Calc.: C, 33.12; H, 9.73. Found: C, 32.89; H, 9.68%.

3.19. 1,4-Bis(undecamethylcyclohexasilanyl)-dodecamethylbicyclo[2.2.2]octasilane (20)

At r.t. 123 mg (0.298 mmol) bromoundecamethylcyclohexasilane are added to a suspension of 150 mg (0.149 mmol) **17** in 5 ml toluene. Within 30 min the yellow color vanishes and a white precipitate forms. Aqueous work up with toluene–2 M H$_2$SO$_4$ and recrystallization from acetone at -80 °C affords 137 mg (86%) of **20** as colorless needles.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.31 (s, 6H, *Me*Si), 0.29 (s, 36H, *Me$_2$*Si), 0.28 (s, 12H, *Me$_2$*Si), 0.19 (s, 12H, *Me$_2$*Si), 0.12 (s, 6H, *Me*Si), 0.11 (2 signals, 2 × 12H, *Me$_2$*Si), 0.10 (s, 6H, *Me*Si); ^{13}C (C$_6$D$_6$, δ in ppm) -0.4 (*Me$_2$*Si), -2.4 (*Me$_2$*Si), -2.8 (*Me$_2$*Si), -3.9 (*Me*Si), -4.4 (*Me$_2$*Si), -5.2 (*Me*Si), -6.3 (*Me$_2$*Si), -6.8 (*Me*Si); ^{29}Si (C$_6$D$_6$, δ in ppm) -35.8 (Me$_2$*Si*), -36.5 (Me$_2$*Si*), -38.9 (Me$_2$*Si*), -43.1 (Me$_2$*Si*), -65.5 (Me*Si*), -123.4 ((SiMe$_2$)$_3$*Si*).

Anal. C$_{34}$H$_{102}$Si$_{20}$ (1072.89 g mol^{-1}) Calc.: C, 38.06; H, 9.58. Found: C, 37. 68; H, 9.72%.

3.20. Tris(trimethylsilyl)-(undecamethylcyclohexasilanyl)silane (21)

2.00 g (6.25 mmol) of tetrakis(trimethylsilyl)silane, 700 mg (6.25 mmol) potassium tert-butoxide and 1.65 g (6.25 mmol) 18-crown-6 are dissolved in 10 ml toluene to yield a deeply yellow solution of tris(trimethylsilyl)silyl potassium·18-Cr-6. When the reaction has completed 2.58 g (6.25 mmol) of bromoundecamethylcyclohexasilane are added with stirring at r.t. The yellow color fades and a white precipitate can be observed. The reaction mixture is stirred at r.t. for 6 h and is then subjected to an aqueous work up which yields 3.55 g (98%) of crude 21 which is purified by recrystallization from acetone at -80 °C.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.45 (s, 3H, MeSi), 0.44 (s, 6H, Me$_2$Si), 0.39 (s, 6H, Me$_2$Si), 0.36 (s, 27H, Me$_3$Si), 0.25 (2 signals, s, 6H+3H, Me$_2$Si+MeSi), 0.23 (s, 3H, MeSi), 0.22 (s, 6H, Me$_2$Si), ^{13}C (C$_6$D$_6$, δ in ppm) 4.1 (Me$_3$Si), -1.9 (Me$_2$Si), -2.5 (Me$_2$Si), -4.1 (MeSi), -4.3 (Me$_2$Si), -5.4 (MeSi), -6.2 (Me$_2$Si), -6.7 (MeSi), ^{29}Si (C$_6$D$_6$, δ in ppm) -9.6 (Me$_3$Si), -35.9 (Me$_2$Si), -39.2 (Me$_2$Si), -43.3 (Me$_2$Si), -70.2 (MeSi), -126.5 (Me$_3$SiSi).

MS (70 eV) m/z (%): 580 (1) [M$^+$], 333 (44) [Si$_6$Me$_{11}^+$], 259 (71) [M$^+-$Si$_5$Me$_{12}$H], 232 (100) [Si$_4$Me$_8^+$], 131 (12) [Si$_2$Me$_5^+$], 73 (95) [SiMe$_3^+$].

Anal. C$_{20}$H$_{60}$Si$_{10}$ (581.55 g mol^{-1}) Calc.: C, 41.31; H, 10.40. Found: C, 41.07; H, 10.52%.

3.21. Bis(trimethylsilyl)-(undecamethylcyclohexasilanyl)silylpotassium·18-Cr-6 (22)

1.00 g (1.72 mmol) of 21, 193 mg (1.72 mmol) potassium tert-butoxide and 0.455 g (1.72 mmol) 18-crown-6 are reacted in 10 ml toluene to yield a deeply yellow solution of 22. Upon removal of the solvent and addition of n-pentane 1.33 g (95%) of 22 are obtained as yellow crystals.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 3.22 (s, 24H, CH$_2$O), 0.67 (s, 3H, MeSi), 0.64 (s, 18H, Me$_3$Si), 0.63 (s, 6H, Me$_2$Si), 0.62 (s, 6H, Me$_2$Si), 0.48 (s, 6H, Me$_2$Si), 0.41 (s, 6H, Me$_2$Si), 0.40 (s, 3H, MeSi), 0.39 (s, 3H, MeSi) ^{13}C (C$_6$D$_6$, δ in ppm) 70.0 (H$_2$CO), 8.5 (Me$_3$Si), 0.2 (Me$_2$Si), -1.6 (Me$_2$Si), -3.3 (MeSi), -3.9 (Me$_2$Si), -4.7 (MeSi), -5.6 (Me$_2$Si), -6.3 (MeSi), ^{29}Si (C$_6$D$_6$, δ in ppm) -7.9 (Me$_3$Si), -40.4 (Me$_2$Si), -43.1 (Me$_2$Si), -45.1 (Me$_2$Si), -67.9 (MeSi), -182.4 (SiK).

3.22. 1,1,1,3,3,3-Hexamethyl-2,2-bis(undecamethylcyclohexasilanyl)trisilane (23)

At r.t. to a deeply yellow solution of 1.00 g (1.23 mmol) 22 in 10 ml toluene 509 mg (1.23 mmol) bromoundecamethylcyclohexasilane are added with stirring. The reaction mixture acquires a brownish taint and is stirred for 12 h followed by an aqueous work up with toluene–2 M H$_2$SO$_4$ to yield 997 mg (96%) of crude 23 which is further purified by crystallization from acetone at -80 °C to yield 820 mg (79%) of clean 23 as colorless needles. Crystals suitable for X-ray analysis were obtained by recrystallization from n-pentane.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.63 (s, 6H, MeSi), 0.50 (s, 12H, Me$_2$Si), 0.47 (s, 18H, Me$_3$Si), 0.45 (s, 12H, Me$_2$Si), 0.26 (s, 12H, Me$_2$Si), 0.25 (s, 6H, MeSi), 0.24 (s, 6H, MeSi), 0.23 (s, 12H, Me$_2$Si), ^{13}C (C$_6$D$_6$, δ in ppm) 4.9 (Me$_3$Si), -1.3 (Me$_2$Si), -1.8 (MeSi), -1.9 (Me$_2$Si), -4.2 (Me$_2$Si), -5.1 (MeSi), -6.0 (Me$_2$Si), -6.7 (MeSi), ^{29}Si (C$_6$D$_6$, δ in ppm) -10.1 (Me$_3$Si), -33.4 (Me$_2$Si), -38.1 (Me$_2$Si), -43.6 (Me$_2$Si), -67.8 (MeSi), -110.4 (Me$_3$SiSi).

Anal. C$_{28}$H$_{84}$Si$_{15}$ (842.25 g mol^{-1}) Calc.: C, 39.93; H, 10.05. Found: C, 39.37; H, 10.28%.

3.23. 1,1,1-Trimethyl-2,2-bis(undecamethylcyclohexasilanyl)disilanylpotassium·18-Cr-6 (24)

500 mg (0.594 mmol) of 23, 67 mg (0.594 mmol) potassium tert-butoxide and 0.157 g (0.594 mmol) 18-crown-6 are reacted in 10 ml toluene to yield a deeply red solution of 24. After removal of the solvent 630 mg (99%) of a red oil are obtained from which no crystalline product could be isolated.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 3.21 (s, 24H, CH$_2$O), 0.76 (s, 6H, MeSi), 0.70 (s, 9H, Me$_3$Si), 0.63 (s, 12H, Me$_2$Si), 0.45 (s, 12H, Me$_2$Si), 0.41 (s, 12H, Me$_2$Si), 0.40 (s, 6H, MeSi), 0.39 (s, 6H, MeSi) 0.20 (s, 12H, Me$_2$Si), ^{13}C (C$_6$D$_6$, δ in ppm) 70.0 (H$_2$CO), 9.6 (Me$_3$Si), 2.0 (Me$_2$Si), -1.1 (Me$_2$Si), -3.5 (MeSi), -4.4 (MeSi), -5.2 (Me$_2$Si), -6.0 (Me$_2$Si), -6.0 (MeSi), ^{29}Si (C$_6$D$_6$, δ in ppm) -6.5 (Me$_3$Si), -38.0 (Me$_2$Si), -40.5 (Me$_2$Si), -42.6 (Me$_2$Si), -63.6 (MeSi), -182.5 (SiK).

3.24. 1,1,1,2-Tetramethyl-2,2-bis(undecamethylcyclohexasilanyl)disilane (25)

The product obtained from the formation of 24 is dissolved in 5 ml toluene and is at r.t. added dropwise to a solution of 0.25 ml dimethylsulfate in 5 ml toluene. The reaction mixture decolorizes immediately after addition and a white precipitate is formed. The suspension is stirred for 4 h at r.t. and is then subjected to an aqueous work up with toluene–2 M H$_2$SO$_4$ to yield 450 mg (97%) of 25 as a white solid.

NMR ^{1}H (C$_6$D$_6$, δ in ppm) 0.53 (s, 6H, MeSi), 0.46 (s, 6H, Me$_2$Si), 0.43 (s, 6H, Me$_2$Si), 0.41 (s, 6H, Me$_2$Si), 0.39 (s, 6H, Me$_2$Si), 0.37 (s, 6H, Me$_2$Si), 0.34 (2 signals, s, 6H+6H, Me$_2$Si+MeSi), 0.26 (2 signals, s, 12H,

Me_2Si), 0.24 (s, 6H, Me_2Si), 0.23 (s, 9H, Me_3Si), 0.21 (s, 3H, MeSi) ^{13}C (C$_6$D$_6$, δ in ppm) 1.7 (Me_3Si), -1.9 (2 signals, Me_2Si), -3.2 (2 signals, Me_2Si), -4.3 (Me_2Si), -4.4 (Me_2Si), -5.0 (Me_2Si), -5.2 (Me_2Si), -6.0 (MeSi), -6.2 (Me_2Si), -6.3 (Me_2Si), -6.5 (Me_2Si, δ in ppm) ^{29}Si (C$_6$D$_6$) -12.3 (Me$_3$$Si$), -34.8 (Me$_2$$Si$), -36.0 (Me$_2$$Si$), -39.9 (Me$_2$$Si$), -40.0 (Me$_2$$Si$), -43.2 (Me$_2$$Si$), -62.6 (MeSi), -70.6 (Me$_3$SiSi).

Anal. C$_{26}$H$_{78}$Si$_{14}$ (784.10 g mol^{-1}) Calc.: C, 39.83; H, 10.03. Found: C, 40.01; H, 9.84%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169637 for **6**, 169633 for *trans*-**8**, 169635 for *trans*-**10**, 169636 for **21** and 169634 for **23**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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