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On some reactions of undecamethylcyclohexasilanyl-substituted silanes

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Dedicated to Professor Gerhard Roewer on the occasion of his 60th birthday.

Abstract

A number of undecamethylcyclohexasilanyl-substituted silanes have been prepared employing a salt elimination reaction between undecamethylcyclohexasilanyl potassium and several silyl halides or triflates. This method provides access to compounds with one or two undecamethylcyclohexasilanyl units attached to one silicon atom. Several attempts to introduce a third ring failed, resulting in formation of bis(undecamethylcyclohexasilanyl). An alternative approach to the substance class using silyl anions and undecamethylcyclohexasilanyl bromide was also developed. The molecular structure of bis(undecamethylcyclohexasilanyl)methylsilane was determined by X-ray crystallography. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclosilanes; NMR; X-ray structure

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1. Introduction

Since the first synthesis of bis(undecamethylcyclohexasilanyl)dimethylsilane in our laboratory we have been interested in the chemistry of cyclosilanyl-substituted silanes [1].

The first synthetic attempts focused on the restricted availability of defined monosubstituted cyclohexasilanes in reasonable quantities. Initially, treatment of dodecamethylcyclohexasilane with HCl–$AlCl_3$, which is not a very selective process, was employed. Good results were obtained only if the crude product of this reaction was derivatized as phenylundecamethylcyclohexasilane, which was converted in a second step into the chlorosilane by means of reaction with hydrogen chloride [1]. Later, we reported on an improved synthesis of chloroundecamethylcyclohexasilane by treatment of dodecamethylcyclohexasilane with antimony pentachloride [2]. Recently, we also found an easy access to alkali cyclosilanyl derivatives, which were previously only accessible by a difficult and low-yielding route involving mercury silanyl compounds [3].

2. Results and discussion

Undecamethylcyclohexasilanyl potassium (Si_6Me_{11}-K), a highly suitable precursor for monosubstituted cyclohexasilanes, can now be prepared by an effective and high-yielding one-step procedure [3]. Treatment with aqueous sulfuric acid gives the respective hydrosilane ($Si_6Me_{11}H$) in almost quantitative yield [4]. This compound can be converted into the corresponding chloride or bromide by treatment with carbon tetrachloride or bromoform, avoiding the inconvenient use of gaseous hydrogen halides. In addition, $Si_6Me_{11}H$ also provides access to the bis(cyclohexasilanyl)mercury derivative, a versatile starting material for the forma-

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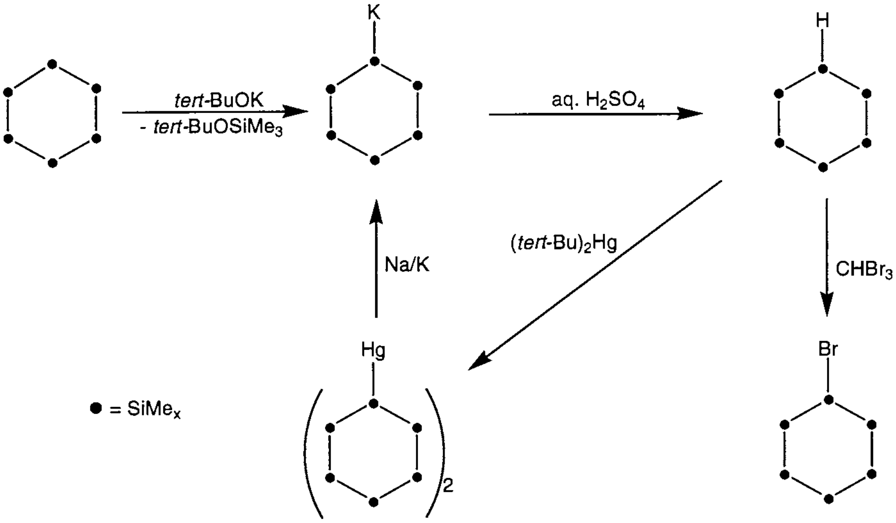
tion of the base-free undecamethylcyclohexasilanyl potassium salt (Scheme 1).

With this convenient route to undecamethylcyclohexasilanyl potassium at hand, we decided to revisit the chemistry of the bis(undecamethylcyclohexasilanyl)silyl compounds. Analogously to the synthesis of bis(undecamethylcyclohexasilanyl)dimethylsilane, we employed a salt elimination strategy involving substituted monosilyl electrophiles and the undecamethylcyclohexasilanyl potassium derivative.

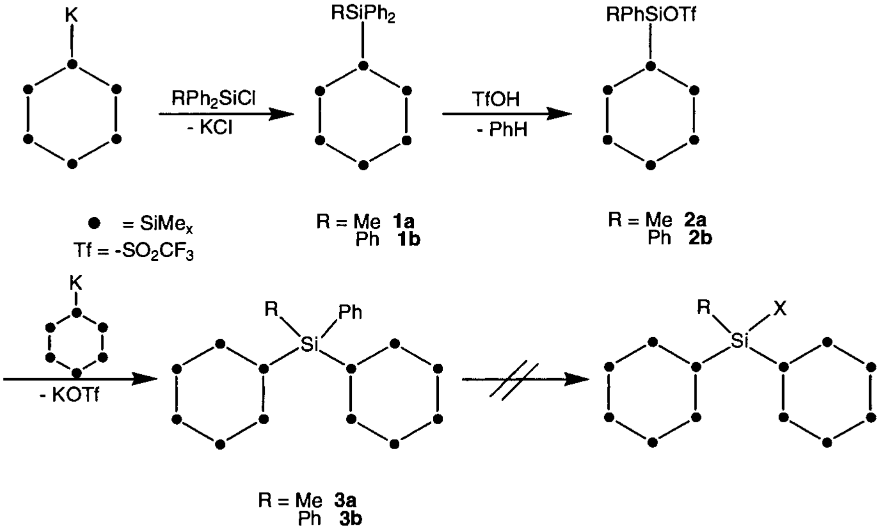
Treatment of undecamethylcyclohexasilanyl potassium with phenylated chlorosilanes yielding the cyclohexasilanylsilanes (**1**) was followed by a protodesilylation reaction with triflic acid [5], which proceeded smoothly as described recently [6]. Subsequent conversion with a second equivalent of undecamethylcyclohexasilanyl potassium resulted in the formation of the desired bis(undecamethylcyclohexasilanyl)silanes **3** (Scheme 2).

At this point it was planned to utilize the remaining phenyl groups of **3a** and **3b** in order to introduce additional functionality by replacing the phenyl substituents with trifluoromethanesulfonyl groups. However, treatment of both the methyl phenyl-substituted **3a** and the diphenyl derivative **3b** with triflic acid did not result in a reaction even when excess triflic acid or heating was applied. An alternative route utilizing HCl–$AlCl_3$ instead of triflic acid was also not successful. It is assumed that the steric shielding of the central silicon atom prevents a reaction.

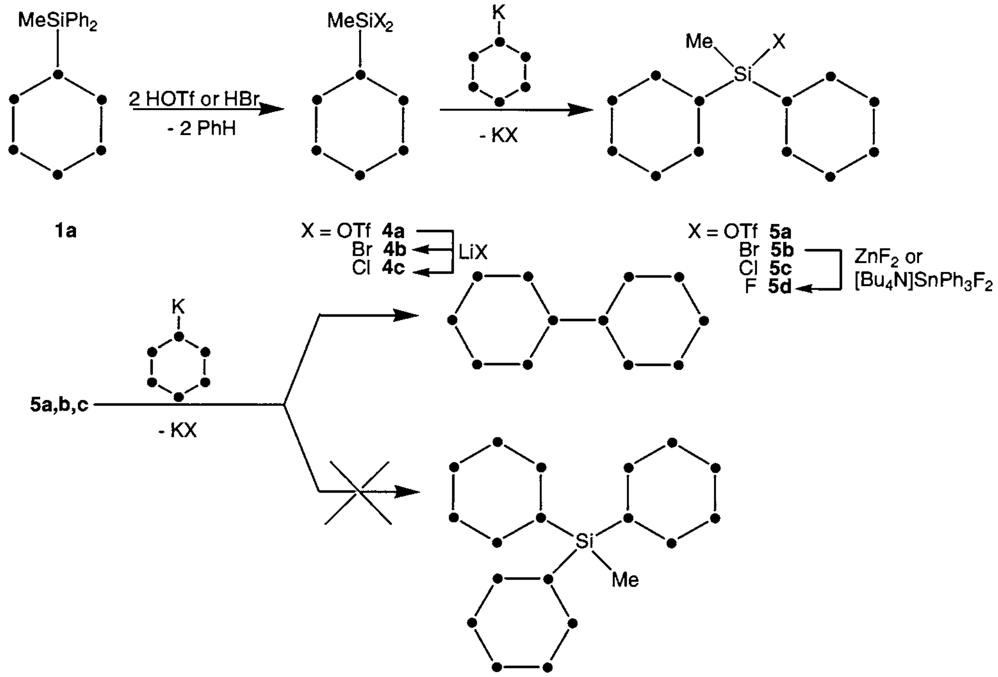
As an alternative route we decided to substitute the phenyl with triflate groups before reacting the undecamethylcyclohexasilanylsilane compound with a second equivalent of the potassium salt. This can easily be accomplished by treatment of compound **1a** with two equivalents of triflic acid (**4a**, Scheme 3). Reaction of



Scheme 1. A general entry into the chemistry of monofunctionalized undecamethylcyclohexasilanes.



Scheme 2. Synthesis of phenylated bis(cyclohexasilanyl)silanes.



Scheme 3. Synthesis of functional bis(cyclohexasilanyl)silanes.

the ditriflate derivative with one equivalent of undecamethylcyclohexasilanyl potassium yielded the methylbis(undecamethylcyclohexasilanyl)silyl triflate **5a** (Scheme 3). The addition of a third equivalent of the potassium salt to form the tris(undecamethylcyclohexasilanyl)silyl compound mainly results in the formation of bis(undecamethylcyclohexasilanyl), possibly caused by transmetallation with an undecamethylcyclohexasilanyl triflate intermediate accepting another equivalent of undecamethylcyclohexasilanyl potassium.

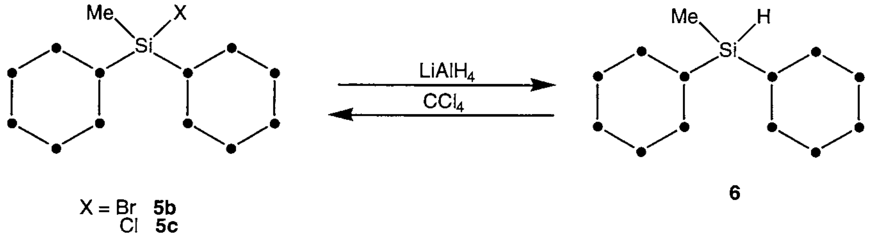
The formation of methylbis(undecamethylcyclohexasilanyl)silyl triflate **5a** was confirmed by ^{29}Si- and ^{1}H-NMR spectroscopy, although we were unable to isolate a clean compound or to purify the crude mixture by crystallization. Accordingly, we decided to investigate the use of halide instead of triflate derivatives. Both the (cyclohexasilanyl)methylsilyldibromide **4b** and the corresponding dichloride **4c** are easily accessible by reaction of ditriflate **4a** with the respective lithium halide in diethyl ether. Alternatively, the dibromide **4b** can be obtained in a very clean reaction by treatment of the diphenyl compound **1a** with neat liquid hydrogen bromide at − 78°C (Scheme 3).

Reaction of the dihalides **4b**,**c** with one equivalent of undecamethylcyclohexasilanyl potassium resulted in substitution and formation of the respective monohalides, which were purified by crystallization from pentane (Scheme 3). Again, attempts to treat the monohalides **5b**,**c** with another equivalent of undecamethylcyclohexasilanyl potassium led mainly to the formation of bis(undecamethylcyclohexasilanyl).

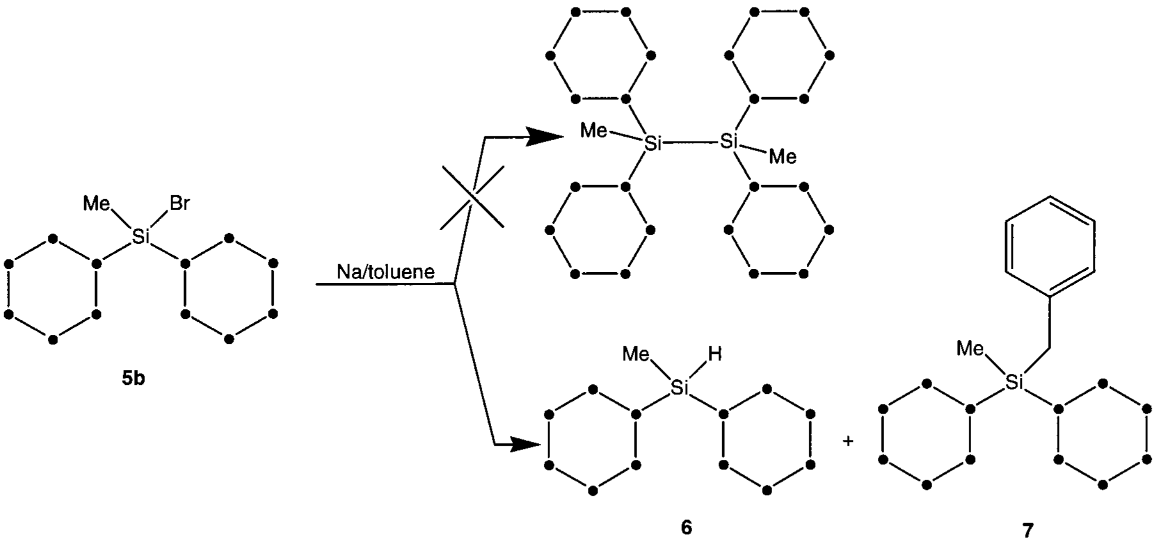
In order to obtain the corresponding monofluoride **5d**, we reacted bromide **5b** with zinc fluoride in ether. The reaction proceeded as hoped, but required 30 days in refluxing diethyl ether to proceed to completion. An improvement of this time-consuming route is the use of tetrabutylammonium triphenyldifluorostannate [7] as the fluorinating agent, resulting in the complete conversion of the bromide precursor after 2 days at room temperature (Scheme 3).

Reaction of the monohalides **5b** and **5c** with lithium aluminum hydride gave the expected hydrosilane **6** in an almost quantitative reaction. Chlorination of hydrosilane **6** was attempted to obtain additional information with respect to the steric accessibility of the bis(undecamethylcyclohexasilanyl)silyl fragment. The chlorination of the secondary hydrosilane, a usually quite feasible reaction, required several days in refluxing CCl_4 (Scheme 4) and was accompanied by the formation of undecamethylcyclohexasilanyl chloride and (undecamethylcyclohexasilanyl)methylsilyl dichloride, indicating Si–Si bond cleavage.

Since we were unable to attach a third undecamethylcyclohexasilanyl unit to the central silicon atom, we decided to attempt a Wurtz-type coupling reaction of bromide **5b** to see whether we could obtain a disilane with four undecamethylcyclohexasilanyl substituents. However, treatment of **5b** with sodium in refluxing toluene did not yield the expected disilane, but a mixture of two products in an approximate ratio of 1:1. One of the compounds was the already mentioned hydrosilane **6**, the other being the benzyl-substituted derivative **7** (Scheme 5).



Scheme 4. Hydrogenation and halogenation of the bis(undecamethylcyclohexasilanyl) fragment.



Scheme 5. Attempted Wurtz-type coupling of bromosilane **5b**.

We assume that this reaction involves the formation of the expected silyl sodium species in a first step. However, the bulky silyl sodium derivative does not react with the sterically hindered silyl bromide **5b** at all, but rather effects the deprotonation of toluene, resulting in the formation of hydrosilane **6** and benzyl sodium. The latter, being sterically less encumbered than the silyl sodium compound, reacts with **5b** to form benzylsilane **7**.

Compound **6** was investigated by single-crystal X-ray analysis (Fig. 1). Comparison with bis(undecamethylcyclohexasilanyl)dimethylsilane [1b] showed the structures to be quite similar (Table 1). As expected, the dihedral angle between the bridgehead and the central silicon atom is slightly larger for the case of the hydrosilane (**6**). (116 vs. 113°). All other dihedral angles around the central silicon atom indicate an almost perfect tetrahedral environment.

An alternative attempt to the bis(undecamethylcyclohexasilanyl)silyl moiety involved some other recently developed silyl potassium chemistry from our laboratories [8]. In this case we decided to use the undecamethylcyclohexasilanyl moiety not as a nucleophile but as an electrophile. In the first step we reacted undecamethylcyclohexasilanyl bromide with tris(trimethylsilyl)silyl potassium. The reaction proceeded cleanly yielding tris(trimethylsilyl)(undecamethylcyclohexasilanyl)silane **8**, which was transformed by treatment with one equivalent of potassium *tert*-butoxide into bis(trimethylsilyl)(undecamethylcyclohexasilanyl)silyl potassium **9**. Reaction with a second equivalent of undecamethylcyclohexasilanyl bromide resulted into the formation of bis(trimethylsilyl)bis(undecamethylcyclohexasilanyl)silane **10** (Scheme 6).

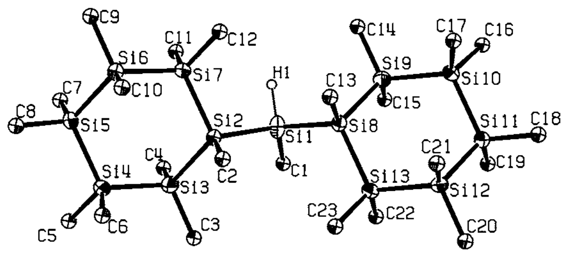


Fig. 1. Crystal structure of methylbis(undecamethylcyclohexasilanyl)silane (**6**).

Table 1
Selected bond lengths (pm) and bond angles (°) of methylbis(undecamethylcyclohexasilanyl)silane (**6**) and dimethylbis(undecamethylcyclohexasilanyl)silane [1b]

	$(Si_6Me_{11})_2Si(H)Me$ (**6**)	$(Si_6Me_{11})_2SiMe_2$
Bond lengths		
Si(1)–Si(2), Si(1)–Si(8)	235.4(2), 234.9(2)	236.8, 235.6
Bond angles		
Si(1)–C(1), Si(1)–C(1′)	186.3(7)	190.3, 189.7
Si(2)–Si(1)–Si(8)	116.08(9)	112.89
Si(2)–Si(1)–C(1)	112.4(2)	110.22
Si(8)–Si(1)–C(1)	111.2(2)	107.55
Si(2)–Si(1)–C(1′)		109.23
Si(8)–Si(1)–C(1′)		111.17

3. Conclusions

The substitution chemistry of the bis(undecamethylcyclohexasilanyl)silyl fragment was only partially successful. Neither was protodesilylation of the phenylated compounds possible nor was the nucleophilic substitution of the corresponding halides a facile process. We believe that steric arguments are mainly responsible for this, since small nucleophiles such as the benzyl anion or reagents such as lithium aluminum hydride undergo the desired reaction, while the sterically demanding undecamethylcyclohexasilanyl potassium fails. Another hint leading to this conclusion was the ease of the metal–halogen exchange reaction.

Currently we are studying the chemistry of the (trimethylsilyl)bis(undecamethylcyclohexasilanyl)silyl potassium, which may be a useful precursor for the introduction of a variety of other substituents into the bis(undecamethylcyclohexasilanyl)silyl system.

4. Experimental

4.1. General data

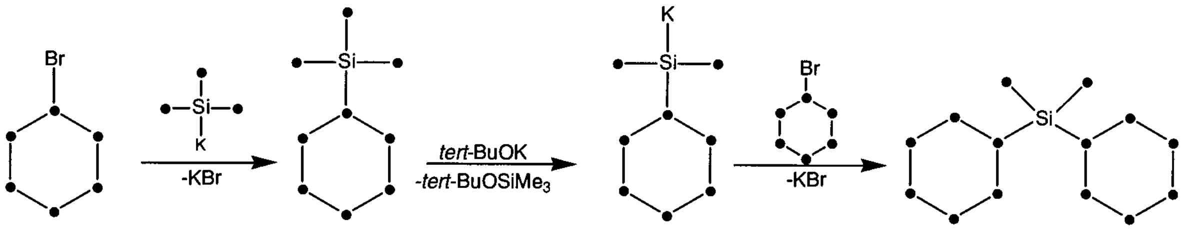
All manipulations involving air-sensitive materials were performed under nitrogen or argon using standard Schlenk techniques. All solvents were dried over a sodium–potassium alloy under nitrogen and distilled prior to use. Undecamethylcyclohexasilanyl potassium [3], undecamethylcyclohexasilanyl-dimethylsilylbromide [6] and tris(trimethylsilyl)silyl potassium [8] were prepared according to published procedures. All NMR spectra were recorded on a Bruker MSL 300 spectrometer (^1H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.627 MHz, ^{19}F, 282.23 MHz). Samples were dissolved in $CDCl_3$, C_6D_6, or toluene using a capillary filled with D_2O as external standard. Shifts are reported in ppm downfield from TMS (tetramethylsilane). GC analyses were carried out on an HP 5890 series II (capillary column DB-1HT; 15 m × 0.251 mm, 0.1 μm; flame ionization detector). Mass spectra were obtained either with a HP 5971 or a Kratos profile spectrometer.

4.2. Synthesis of undecamethylcyclohexasilane

A solution of undecamethylcyclohexasilanyl potassium (22.9 mmol) in dimethoxyethane (DME) was added dropwise to a diethyl ether–aqueous H_2SO_4 mixture. After complete addition the aqueous layer was saturated with sodium chloride and extracted twice with ether. The combined etheral solutions were dried over sodium sulfate and the solvent was removed in vacuo. The remaining residue (7.13 g, 21.3 mmol, 93%) was found to be undecamethylcyclohexasilane contaminated with approximately 4% nonamethylcyclopentasilane as judged by GC and ^1H-NMR.

4.3. Synthesis of bromoundecamethylcyclohexasilane

Undecamethylcyclohexasilane (2.0 g, 5.97 mmol) was dissolved in bromoform (15 ml) and stirred for 4 days at room temperature (r.t.) After complete conversion the solvent was removed in vacuo and the remaining orange residue was dissolved in pentane and crystallized at −78°C. Colourless crystals (2.21 g, 5.34 mmol, 89%) were obtained. Spectral properties of the compound were in agreement with literature data [1].



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Scheme 6. The 'inverse' approach to the bis(undecamethylcyclohexasilanyl)silyl fragment.

4.4. Synthesis of methyldiphenyl(undecamethylcyclohexasilanyl)silane (1a)

Undecamethylcyclohexasilanyl potassium (54.4 mmol) dissolved in DME (200 ml) was added dropwise to a stirred solution of chloromethyldiphenylsilane (12.7 g, 54.4 mmol) in toluene (120 ml) at 0°C. After stirring the mixture for an additional hour, the solution was poured onto ice-cooled hydrochloric acid (1 M, 200 ml). The aqueous layer was extracted with toluene and the combined organic layers were dried over Na_2SO_4. After evaporation of the solvents a brownish residue was obtained, which was recrystallized from isopropanol yielding colourless crystals (15.3 g, 28.8 mmol, 53%) of **1b**. M.p.: 187–190°C. ^{1}H-NMR (TMS): δ 7.58 (5H), 7.37 (5H), 0.33 (s, 3H) 0.19–0.00 (m, 33H). ^{13}C-NMR (TMS): δ 138.81, 135.09, 128.61, 127.96, −1.53, −3.14, −4.70, −5.16, −6.55, −9.53. ^{29}Si-NMR (TMS): δ −15.41, −38.12, −40.44, −42.40, −81.35. MS (70 eV): m/z (%): 530 [M$^+$, 25%], 333 (Si_6Me_{11}, 2%), 318 (Si_6Me_{10}, 23%), 73 ($SiMe_3$, 100%). Anal. Found: C, 54.26; H, 8.73. Calc.: C, 54.44; H, 8.82%.

4.5. Synthesis of methylphenyl(trifluoromethanesulfonyloxy)(undecamethylcyclohexasilanyl)silane (2a)

Methyldiphenyl(undecamethylcyclohexasilanyl)silane (**1a**) (14.3 g, 26.9 mmol) was dissolved in toluene (150 ml) and cooled to −20°C. After the dropwise addition of triflic acid (2.36 ml, 26.9 mmol) the mixture was allowed to warm up and stirred for an additional 2 h at r.t. Complete conversion was detected both by GC–MS of a derivatized sample ($LiAlH_4$ quench) and by ^{29}Si-NMR. The obtained solution was used without further purification. ^{29}Si-NMR (TMS): δ 37.61, −38.87/−39.11, −40.18, −42.14, −79.63.

4.6. Synthesis of diphenyl(trifluoromethanesulfonyloxy)(undecamethylcyclohexasilanyl)silane (2b)

The synthesis of **2b** was accomplished by the reaction of triphenyl(undecamethylcyclohexasilanyl)silane (12.8 g, 21.6 mmol) with triflic acid (1.89 ml, 21.6 mmol), analogous to **2a**. The toluene solution was used without further purification. ^{29}Si-NMR (TMS): δ 25.16, −38.30, −40.16, −42.49, −79.77.

4.7. Synthesis of methylphenylbis(undecamethylcyclohexasilanyl)silane (3a)

A solution of **2a** (26.9 mmol) in toluene (150 ml) was cooled to 0°C and undecamethylcyclohexasilanyl potassium (26.9 mmol) in DME was added dropwise. After complete conversion, as monitored by GC, the reaction mixture was added to ice-cooled aqueous hydrochloric acid (1 M, 200 ml). The aqueous layer was washed with three portions of toluene and the combined toluene solutions were evaporated to dryness. The brown oily residue was recrystallized twice from isopropanol to give fine colourless crystals (5.9 g, 7.5 mmol, 27.8%). M.p.: 122°C. ^{1}H-NMR (TMS): δ 7.26 (m, 5H), 0.69 to −0.11 (m, 69H). ^{13}C-NMR (TMS): δ 134.97, 127.96, −3.16 to −7.89 (several signals) ^{29}Si-NMR (TMS): δ −29.23, −36.47/−36.56, −40.41/−40.45, −42.93, −74.73. MS (70 eV): m/z (%): 786 (M$^+$, 26%), 728, 13%), 453 (17%), 318 (100%). Anal. Found: C, 44.20; H, 9.46. Calc.: C, 44.35; H, 9.49%.

4.8. Synthesis of diphenylbis(undecamethylcyclohexasilanyl)silane (3b)

The synthesis of **3b** was accomplished by dissolving **2b** (21.6 mmol) in toluene (150 ml) and adding undecamethylcyclohexasilanyl potassium (26.9 mmol) in DME as described for **3a**. After recrystallization from isopropanol, the product was obtained as colourless crystals (6.9 g, 8.1 mmol, 37.6%). M.p.: 110°C. ^{1}H-NMR (TMS): δ 7.31 (m, 10H), 0.45 to −0.12 (m, 66H). ^{13}C-NMR (TMS): δ 137.70, 136.91, 128.53, 127.76, −3.00, −3.99, −4.73, −5.39, −6.14, −6.37. ^{29}Si-NMR (TMS): δ −23.99, −36.27, −40.65, −43.72, −73.22. MS (70 eV): m/z (%): 849 [M$^+$, 14%], 819, 3%), 790 (8%), 761 (4%), 73 (100%). Anal. Found: C, 48.04; H, 9.01. Calc.: C, 48.28; H, 9.08%.

4.9. Synthesis of methylbis(trifluoromethanesulfonyloxy)(undecamethylcyclohexasilanyl)silane (4a)

$Si_6Me_{11}SiMePh_2$ (**1b**) (15.3 g, 28.8 mmol) was dissolved in toluene (150 ml) and cooled to −20°C. Within 30 min neat triflic acid (5.06 ml, 57.6 mmol) was added dropwise. Subsequently, the cooling bath was removed and the reaction mixture was stirred overnight at r.t. The resulting solution was used without further purification for the synthesis of **4b**. ^{29}Si-NMR (TMS): δ 33.72, −39.86, −40.41, −42.21, −77.66.

4.10. Syntheses of dibromomethyl(undecamethylcyclohexasilanyl)silane (4b)

(a) After adding diethyl ether (100 ml) to the solution of silyl triflate **4a** in toluene, lithium bromide (5.0 g, 57.6 mmol) was added at 0°C. The reaction mixture was stirred overnight. Subsequently, the solvents were removed under reduced pressure and the resulting solid residue was dispersed in pentane. Filtration and evaporation of the filtrate resulted in a colourless solid residue of **4b**. Yield: 15.2 g (28.3 mmol, 98.3%).

(b) A flask equipped with a reflux condenser cooled to −80°C and charged with methyldiphenyl(undecamethylcyclohexasilanyl)silane (**1a**) (2.70 g, 5.08

mmol) was cooled to −80°C and approximately 15 ml of hydrogen bromide was condensed into the reaction vessel. After 1 h the cooling bath was removed and the solution was refluxed for 2 h, followed by evaporation of excess hydrogen bromide and benzene. GC analysis of the remaining colourless solid showed pure **4b** (2.73 g, 100%). M.p.: 161–163°C. ^{1}H-NMR (TMS): δ 1.12 (s, 3H), 0.36–0.14 (m, 33H). ^{13}C-NMR (TMS): δ 12.64, −3.13, −4.58, −4.85, −6.27, −9.52. ^{29}Si-NMR (TMS): δ 25.63, −38.18, −39.84, −41.74, −67.61. MS (70 eV): m/z (%): 536 [M$^+$, 2%], 463 ($Si_6Me_9Br_2$, 3%), 399 ($Si_6Me_{10}Br$, 23%), 333 (Si_6Me_{11}, 4%), 259 (Si_6Me_6, 18%), 73 ($SiMe_3$, 100%). Anal. Found: C, 26.85; H, 6.76. Calc.: C, 27.13; H, 6.67%.

4.11. Synthesis of dichloromethyl(undecamethylcyclohexasilanyl)silane (4c)

Diethyl ether (100 ml) and lithium chloride (1.43 g, 33.7 mmol) were added to a solution of silyl triflate **4b** (16.8 mmol) and the reaction mixture was stirred for 10 h. After a work-up similar to the synthesis of the bromo derivative (**4b**), **4c** (7.10 g, 15.6 mmol, 94.4%) was obtained as a colourless solid. M.p.: 155–157°C. ^{1}H-NMR (TMS): δ 0.77 (s, 3H), 0.33–0.14 (m, 33H). ^{29}Si-NMR (TMS): δ 40.96, −39.34, −40.40, −42.10, −71.13. MS (70 eV): m/z (%): 446 [M$^+$, 7%], 431 ($Si_7Me_{11}Cl_2$, 1%), 353 ($Si_6Me_{10}Cl$, 11%), 73 ($SiMe_3$, 100%). Anal. Found: C, 32.27; H, 8.14. Calc.: C, 32.18; H, 8.10%.

4.12. Syntheses of the monohalogenated bis(undecamethylcyclohexasilanyl)methylsilyl compounds 5b and 5c

(Si_6Me_{11})$SiMeBr_2$ (**4b**) (12.7 g, 23.7 mmol) or (Si_6Me_{11})$SiMeCl_2$ (**4c**) (7.45 g, 16.6 mmol), respectively, were dissolved in n-pentane (120 ml) and cooled to 0°C. An equimolar amount of a solution of undecamethylcyclohexasilanyl potassium in DME was slowly added and the resulting mixture was stirred for 2 h at r.t. The solvents were removed under reduced pressure and the residue was dispersed in n-pentane. After filtration and evaporation compounds **5b** or **5c**, respectively, were crystallized from n-pentane yielding colourless solids. **5b**: Yield 5.4 g (6.8 mmol, 28.9%), m.p.: 152–155°C. ^{1}H-NMR (TMS): δ 1.12 (s, 3H), 0.55 (s, 6H), 0.53 (s, 6H), 0.45 (s, 6H), 0.42 (s, 6H), 0.39 (s, 6H), 0.23 (m, 36H). ^{29}Si-NMR (TMS): δ 22.92, −34.97/−36.76, −40.68/−40.75, −42.74, −68.83. MS (70 eV): m/z (%): 788 [M$^+$, 5%], 709 ($Si_{13}Me_{23}$, 25%), 376 (Si_7Me_{12}, 70%), 361 (Si_7Me_{11}, 10%), 333 (Si_6Me_{11}, 100%), 73 ($SiMe_3$, 100%). Anal. Found: C, 35.69; H, 8.87. Calc.: C, 34.93; H, 8.79%.

5c: Yield 5.3 g (7.1 mmol, 42.7%), m.p.: 150°C. ^{1}H-NMR (TMS): δ 0.82 (s, 3H), 0.34–0.16 (m, 66H). ^{29}Si-NMR (TMS): δ 33.02, −35.72/−37.42, −40.43/−40.52, −42.75, −69.11. MS (70 eV): m/z (%): 746 [M$^+$, 24%], 411 ($Si_7Me_{12}Cl$, 9%), 376 (Si_7Me_{12}, 46%), 73 ($SiMe_3$, 100%). Anal. Found: C, 37.27; H, 9.44. Calc.: C, 37.01; H, 9.32%.

4.13. Syntheses of bis(undecamethylcyclohexasilanyl)-fluoromethylsilane (5d)

(a) (Si_6Me_{11})$_2$SiMeBr (**5b**) (0.60 g, 0.76 mmol) was dissolved in diethyl ether (20 ml) and ZnF_2 (0.80 g, 7.7 mmol) was added. The mixture was heated to reflux for 30 days after which GC analysis indicated quantitative conversion. Filtration, evaporation of the solvent, and recrystallization of the residue from n-pentane yielded 0.26 g (0.36 mmol, 47%) of colourless (Si_6Me_{11})$_2$SiMeF (**5d**).

(b) (Si_6Me_{11})$_2$SiMeBr (**5b**) (0.60 g, 0.76 mmol) was dissolved in diethyl ether (20 ml), tetrabutylammonium difluorotriphenylstannate (0.23 g, 0.36 mmol) was added and the reaction mixture was stirred for 2 days at r.t., followed by the removal of the solvent under reduced pressure and addition of n-pentane. The resulting suspension was filtered and the volatiles evaporated. The colourless residue was recrystallized from n-pentane yielding 0.38 g (0.52 mmol, 69%) of **5d**. ^{29}Si-NMR (TMS): δ 58.21 (d, $^1J_{Si–F}$ 335.6 Hz), −35.88/−37.57 (d, $^3J_{Si–F}$ 5.1 Hz), −39.67/−39.90, −73.85 (d, $^2J_{Si–F}$ 19.1 Hz). ^{19}F-NMR: δ −178.03 (q, $^3J_{F–H}$ 7.9 Hz).

4.14. Synthesis of bis(undecamethylcyclohexasilanyl)-methylsilane (6)

A solution of **5b** (2.51 g, 3.17 mmol) in diethyl ether (30 ml) was cooled to 0°C and an etheral solution of $LiAlH_4$ (1.0 ml, 2.4 M, 2.4 mmol) was added dropwise. The reaction mixture was allowed to warm to r.t. and stirred for another 10 min. The solution was poured into ice-cooled hydrochloric acid (1 M, 40 ml) and the aqueous layer was extracted with three portions of petroleum ether (30 ml each). The combined organic layers were dried over Na_2SO_4 and the solvents evaporated. Yield: 2.20 g (3.09 mmol, 97%) of **6**. M.p.: 140°C. ^{1}H-NMR (TMS): δ 4.20 (q, 1H, $J=5.3$ Hz), 0.49 (d, 3H, $J=5.3$ Hz), 0.51–0.24 (m, 66H). ^{29}Si-NMR (TMS): δ −36.88/−37.83, −40.25/−40.57, −42.08, −65.65 ($^1J_{Si–H}$ 160.4 Hz), −75.83. IR: 2073 ($\nu_{Si–H}$) cm^{-1}. MS (70 eV): m/z (%): 710 [M$^+$, 43%], 505 ($Si_{10}Me_{15}$, 9%), 333 (Si_6Me_{11}, 15%), 303 (Si_6Me_9, 41), 73 ($SiMe_3$, 100%). Anal. Found: C, 38.91; H, 9.99. Calc.: C, 38.80; H, 9.91%.

Crystal data for **6**: $C_{23}H_{70}Si_{13}$, $M=711.96$, monoclinic, space group $P2_1/c$, $a=9.8621(1)$, $b=13.7906(1)$, $c=34.9563(3)$ Å, $\beta=96.500(1)°$, $V=4723.65(7)$ Å^3, T (K) $=150$, $Z=4$, $\mu=0.367$ mm^{-1} (Mo–K$_\alpha$). Colourless plates of dimensions $0.22\times0.08\times0.05$ mm^3. 8144 independent reflections ($2.4 \leq 2\theta \leq 50.00°$). $R_1 = 0.0851$ for 5049 data ($I > 2\sigma(I)$ and $wR_2 = 0.1445$ for all data. The crystals were removed from the Schlenk flask under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fibre, and immediately placed in the low-temperature nitrogen stream of the diffractometer [9]. The data set was collected using a Siemens SMART system at −123°C (Oxford Instruments Cryojet low-temperature device), complete with three-circle goniometer and CCD detector operating at −54°C, employing monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS [10]. The crystal structure was solved by direct methods, as included in the SHELX program package [11]. Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93) [12]. The hydrogen at Si-1 was located in a difference Fourier map and included in the refinement by using distance restraints and U_{eq} of 1.2 of the carrier Si atom. All other hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups with U_{iso} constrained at 1.2 for non-methyl groups, and 1.5 for methyl groups times U_{eq} of the carrier C atom. Scattering factors were those provided with the SHELX program system.

*4.15. Syntheses of bis(undecamethylcyclohexasilanyl)-methylsilane (**6**) and benzylbis-(undecamethylcyclohexasilanyl)methylsilane (**7**)*

Sodium (0.20 g, 8.7 mmol) was added to a solution of $(Si_6Me_{11})_2SiMeBr$ (**5b**) (2.00 g, 2.53 mmol) in toluene (20 ml). The stirred mixture was refluxed for 48 h and subsequently filtered. The volatiles were evaporated, the residue purified chromatographically using silica gel 60 and *n*-heptane, resulting in 0.53 g (0.74 mmol, 58%) of **6** and 0.51 g (0.63 mmol, 50%) of **7**.

7: ^{1}H-NMR (TMS): δ 7.18 (m, 5H), 2.73 (s, 2H), 0.54–0.19 (m, 69H). ^{13}C-NMR (TMS): δ 141.43, 129.77, 129.15, 125.41, 26.80, 0.61, −1.67 to −6.68 (several signals). ^{29}Si-NMR (TMS): δ −18.82, −35.73/−36.75, −40.17/−40.28, −42.86, −73.05. MS (70 eV): *m*/*z* (%): 800 [M$^+$, 15%], 467 ($Si_7Me_{12}Bn$, 9%), 319 (Si_6Me_{10}, 44%), 73 ($SiMe_3$, 100%). Anal. Found: C, 45.14; H, 9.60. Calc.: C, 44.93; H, 9.55%.

*4.16. Synthesis of tris(trimethylsilyl)(undecamethylcyclohexasilanyl)silane (**8**)*

Tris(trimethylsilyl)silyl potassium (0.485 g, 1.69 mmol) in toluene (2 ml) was added dropwise to an ice-cooled solution of bromoundecamethylcyclohexasilane (0.934 g, 1.69 mmol) in toluene (10 ml) within 30 min. After stirring for further 2 h GC–MS analysis showed complete conversion, hence, the suspension was poured into 2 M aqueous H_2SO_4. The aqueous layer was extracted with toluene, the combined organic layers were dried with Na_2SO_4, followed by evaporation of the solvents. Subsequent recrystallization of the colourless residue from *n*-pentane yielded 0.952 g (1.63 mmol, 97%) of **8**. M.p.: 117–121°C. ^{1}H-NMR (TMS): δ 2.18 (s, 3H), 0.31–0.16 (m, 57H). ^{13}C-NMR (TMS): δ 3.96, −2.10 to −6.23 (several signals). ^{29}Si-NMR (TMS): δ −9.61, −35.87, −39.22, −43.29, −70.20, −126.47. MS (70 eV): *m*/*z* (%): 580 [M$^+$, 0.3%], 333 (Si_6Me_{11}, 15%), 232 (Si_4Me_8, 51%) 73 ($SiMe_3$, 100%).

*4.17. Synthesis of bis(trimethylsilyl)(undecamethylcyclohexasilanyl)silyl potassium (**9**)*

Compound **8** (0.82 g, 1.41 mmol) and potassium *tert*-butoxide (0.16 g, 1.41 mmol) were dissolved in 10 ml THF. The reaction mixture was stirred at r.t. and after 4 h GC–MS analysis showed complete conversion. The solvent was removed under reduced pressure and 2 ml of toluene were condensed onto the residue. The solution was used for the synthesis of **10** without further purification. ^{29}Si-NMR (TMS): δ −5.39, −38.37, −40.37, −42.21, −64.84, −184.54. MS (70 eV) (ethyl bromide quench): *m*/*z* (%): 536 [M$^+$, 6%], 333 (Si_6Me_{11}, 30%), 73 ($SiMe_3$, 100%).

*4.18. Synthesis of bis(trimethylsilyl)bis(undecamethylcyclohexasilanyl)silan (**10**)*

Compound **9** (1.41 mmol) in toluene was added dropwise to an ice-cooled solution of bromoundecamethylcyclohexasilane (0.587 g, 1.41 mmol) in 5 ml of toluene. The mixture was allowed to warm to r.t. and stirred for 1 h. Work-up proceeded with pouring the reaction mixture into 2 M H_2SO_4, followed by extraction with toluene, drying, and evaporation. The remaining residue was sublimated (0.1 mbar, 125°C) yielding 0.81 g (0.96 mmol, 68%) of pure crystalline **10**. ^{29}Si-NMR (TMS): δ −9.39, −32.74, −37.45, −41.59, −67.09, −109.74. MS (70 eV): *m*/*z* (%): 842 [M$^+$, 1%], 492 (Si_9Me_{16}, 17%), 333 (Si_6Me_{11}, 14%), 131 (Si_2Me_5, 11%) 73 ($SiMe_3$, 100%).

5. Supplementary material

Full details have been deposited with the Cambridge Cystallographic Data Centre (CCDC 101461) and are also available in CIF format from the authors.

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