Si–H-containing cyclosilanes and their behaviour in the dehydrogenative polymerization reaction [1]

Edwin Hengge [*], Peter Gspaltl, Erich Pinter

Technical University of Graz, Institute of Inorganic Chemistry, Stremayrg. 16, A-8010 Graz, Austria

Abstract

To study the behaviour of some cyclosilanes containing Si–H bonds in dehydrogenative polymerization, cyclosilanes with Si–H bonds directly on the ring and cyclosilanes with Si–H bonds in silyl- and disilanyl side chains were synthesized and characterized by the usual spectroscopic and analytical methods. The ease of the polymerization is affected by steric hindrance and oligomers can be formed along with other side products. Only 1,4-bis(silyl)decamethylcyclohexasilane gave a polymer. $Cp_2HfCl(Si_6Me_{11})$ was prepared for use as a catalyst.

Keywords: Silicon; Hafnium; Cyclosilanes; Polycyclosilanes; Dehydrogenative polymerization; Hf–Si compounds

1. Introduction

Dehydrogenative polymerization, catalyzed by early transition element cyclopentadienyl derivatives, has been investigated for simple monosilanes [1] and disilanes [2]. No investigations have been carried out with cyclosilanes so far. Cyclosilanes with Si–H bonds have the potential to form polysilanes with cyclosilane units in the polymeric chain or with cyclosilanes as side groups in simple polysilanes. Both structural types promise interesting feature; for example, optical and semiconducting properties. It is known that simple cyclosilanes can form radical anions with completely delocalized electrons, but nothing is known about this behaviour in the case of cyclosilane-containing polysilanes.

Only a few examples of polycyclic silanes are known, and the number of cyclosilane units in these molecules is rather small. We synthesized some linearly-connected five- and six-membered silanes starting from cyclosilanylpotassium compounds. A summary of that work was published recently [3]. Only one annelated cyclosilane is known, it has two permethylated six-membered cyclosilanes connected as in decalin. West and Indrik-

sons [4] made this compound first, and later investigations established the structure and revealed formation of a radical anion [5].

Dehydrogenative polymerization offers a new route to such compounds. Si–H bonds are necessary and two structural types are of interest in this connection, one with the Si–H bond attached directly to the ring and the other with the bond in a side chain. The first type should lead to polymers with cyclosilanes in the main chain, the second to a simple polysilane with cyclosilanes as pendant substituents. In both cases relevant materials were previously unknown, so we made examples of both type. This first investigation involved six-membered rings because of the ready availability of dodecamethylcyclohexasilane.

2. Hydrogen-substituted cyclohexasilanes

Some cyclosilanes are known with hydrogen attached to the ring. Monohydroundecamethylcyclohexasilane was previously known, and made by published methods. By treatment of dodecamethylcyclohexasilane with antimony pentachloride, one methyl group was cleaved from the ring and monochloroundecamethylcyclohexasilane was formed [6]. Hydrogenation with $LiAlH_4$ gave the required compound.

---

[*] Corresponding author.
[1] Dedicated to Professor Robert Corriu.

1,4-Dihydrodecamethylcyclohexasilane was synthesized by action of $LiAlH_4$ on 1,4-dichlorodecamethylcyclohexasilane. The dichloro compound was prepared by reaction of dodecamethylcyclohexasilane with antimony pentachloride [7]; 1,3- and 1,4-dichlorodecamethylcylcohexasilane were formed simultaneously, and we recently developed an improved method for their separation [8].

3. Monofunctional cyclosilanes

Cyclohexasilanes with Si–H-containing side chains were previously unknown. We were interested in mono- and disilanyl side chains with one or more Si–H bonds. We started from undecamethylcyclohexasilanyl-potassium, an improved preparation of which was published recently [9]. Reaction with various chloromethylphenylsilanes led to the corresponding methylphenylsilylcyclohexasilanes. Replacement of the phenyl groups with the triflate group and subsequent reaction with $LiAlH_4$ gave the required derivatives (Scheme 1). The disilanyl derivative was synthesized by a stepwise procedure

because $ClSiPh_2SiPh_2Me$ was not formed in the reaction of Cl_2SiPh_2 with $LiSiPh_2Me$, the only product being $Ph_2MeSiSiPh_2SiPh_2Me$. A better way was to cleave one phenyl group from triphenylsilylundecamethylcyclohexasilane with triflic acid and to treat the product with the $LiSiPh_2Me$ group. The method used to cleave phenyl groups with triflic acid [10] removes only up to two phenyl groups from one Si atom. Therefore, hydrogenation was first necessary, followed by triflic acid cleavage again, as can be seen from Scheme 1.

4. Difunctional cyclosilanes

For the polymerization experiments described later we need cyclosilanes with hydrogen-containing silyl substituents in 1- and 4-positions. The 1,4-disposition seems to be particularly interesting for the formation of polysilanes.

The starting material was 1,4-dichlorodecamethylcyclohexasilane again, now prepared in the new way [8]. With Ph_3SiLi and $Ph_2MeSiLi$ this gave the corre-
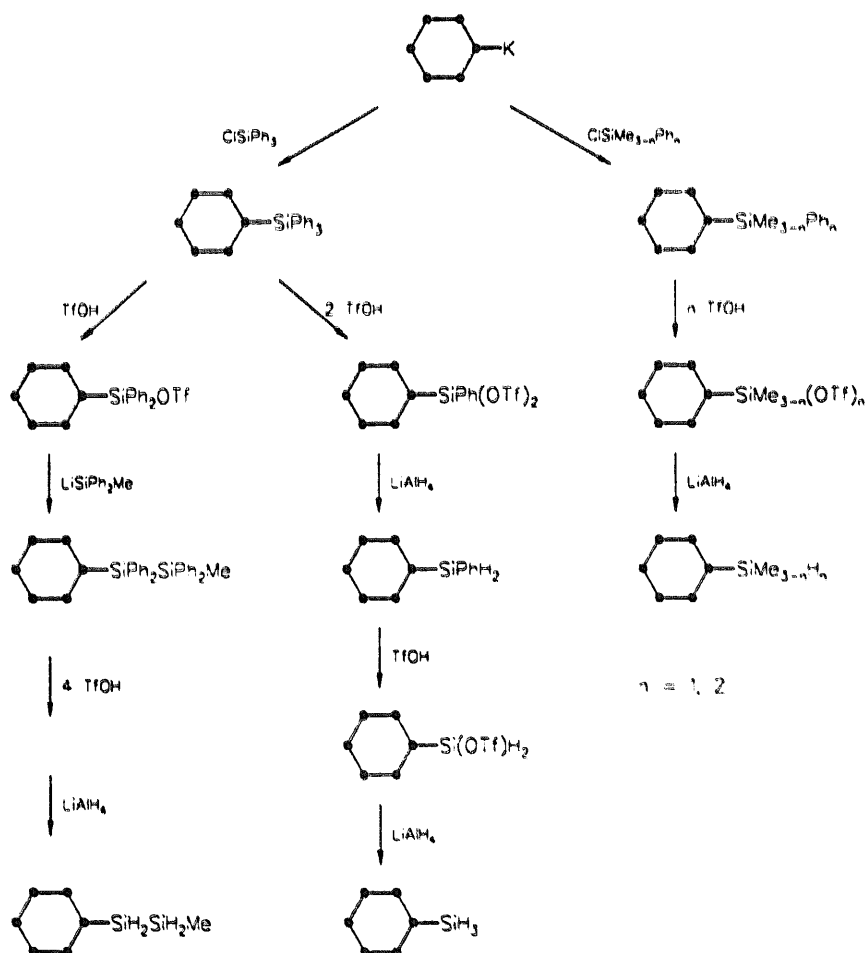
Scheme 1. ● = $SiMe_n$, $n = 1, 2$.
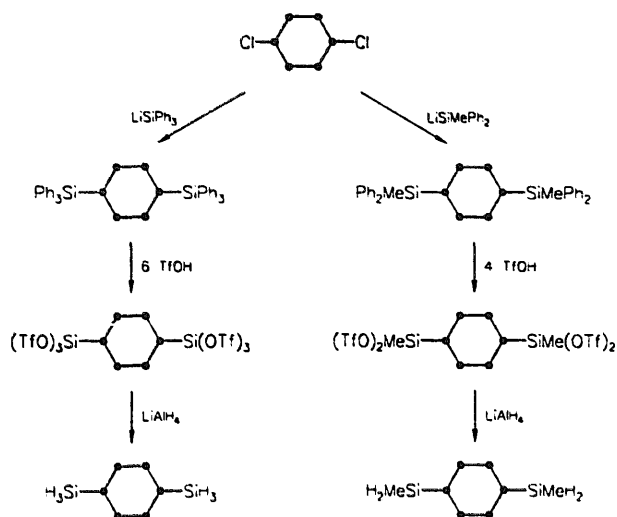
Scheme 2. ● = SiMe$_n$, $n = 1, 2$.

sponding disilylated derivatives (Scheme 2). It was possible to remove all phenyl groups from the cyclosilane with triflic acid in one step; this was expected in the case of the SiPh$_2$Me group but was surprising in the case of the triphenylsilyl group, since for the monosubstituted product only two phenyl groups were split off, and the third could not be removed. After longer reaction time methyl groups were cleaved from the cyclosilane. With the disubstituted derivatives no displacement of the methyl groups occurred, and it was possible to use a longer reaction time and so bring about complete removal of all the phenyl groups. The electronic influence of the groups in the 1- and 4-positions seems to stabilize the Si–methyl bonds.

5. NMR

The ^{29}Si NMR chemical shifts for some silyl-substituted derivatives of (Me$_2$Si)$_6$ are shown in Table 1, and the ^{13}C NMR chemical shifts in Table 2. Substitution of one of the methyls in (Me$_2$Si)$_6$ with a silyl group SiR$_3$ produces four non-equivalent silicons designated α, β, γ, δ, where SiR$_3$ is attached to the α-silicon. Since the resulting methyls can be cis or trans to the substituent, there are seven non-equivalent ring methyls in the ratio 1/2/2/2/2/1/1. This should lead to seven methyl resonances in ^{13}C NMR. The 1,4-disubstituted derivatives of (Me$_2$Si)$_6$ have three different ring methyls (4/4/2) in each isomer (cis or trans), so the ^{13}C NMR spectra of a mixture of these isomers are expected to show six methyl resonances. This is consistent with the observations of West and coworker [11] on mono- and disubstituted derivatives of (Me$_2$Si)$_6$. While the methyl resonances are resolved in many cases, some are too similar to be assigned to particular positions.

6. Cyclosilane-substituted metallocenes

The dehydrogenative polymerization reaction is catalyzed by titanocenes or zirconocenes. Most of the proposed reaction mechanisms involve a silyl derivative of the metallocene as an intermediate. Silyl derivatives can also be used as catalysts [12]. We were interested in looking at the catalytic activities of cyclosilane-substituted metallocenes, and prepared some of these for the first time [13]. In addition, we have now also prepared the corresponding hafnium derivative using the same methods. (Scheme 3).

7. Polymerization reactions

The hydrogen-containing cyclosilanes were subjected to polymerization. The catalysts used were dicyclopentadienyl–dimethylzirconium and the corresponding Ti compound.

Cyclosilanes with hydrogen bonded to the ring directly, such as monohydroundecamethylcyclohexasilane and 1,4-dihydrodecamethylcyclohexasilane, did not react. Probably steric factors prevent formation of the usual intermediates between the catalyst and the cyclosilane.

The hydrides (Si$_6$Me$_{11}$)SiMe$_2$H and (Si$_6$Me$_{11}$)-SiMeH$_2$ react with the catalysts only to a small extent. This is understandable in the case of the monohydro compound because it is known that tertiary hydrosilanes exhibit only very low reactivity [1], but the dihydrogen compounds also react only slowly to give the dimeric species (a 20% yield being observed after several days at elevated temperature). Undecamethylcyclohexasilane and (Si$_6$Me$_{11}$)SiMe$_2$H were formed as side products. Removal of the side chain seems to take place, but migration of the methyl group is also possible. We observed such a methyl migration earlier in similar polymerization reactions. The reaction mechanism of these side reaction is unclear.

Dimerization took place in high yield with (Si$_6$Me$_{11}$)SiH$_3$ to give (Si$_6$Me$_{11}$SiH$_2$)$_2$ as the main product, only 5% of Si$_6$Me$_{11}$H being found. Further oligomerization or polymerization was not possible because of steric hindrance. Dimerization took place mainly with the zirconium catalyst, the Ti catalyst being less reactive.

Disilanyl-substituted cyclosilanes gave a yellow oil containing oligomers ($x = 2–4$, GPC). Oligomerization is accompanied by much Si–Si cleavage (MeSiH$_3$, Si$_6$Me$_{11}$SiH$_3$ were detected by GC/MS). This is understandable in view of the previously postulated reaction mechanism [14].

In the light of these results we examined the 1,4-disubstituted derivatives 1,4-(SiH$_2$Me)$_2$Si$_6$Me$_{10}$ and 1,4-

Table 1

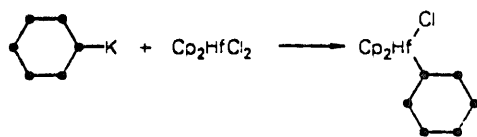^{29}Si chemical shifts for some silyl-substituted derivatives of dodecamethylcyclohexasilane

Compound (solvent a)	δ (ppm) (no. of silicons)					
(Si$_6$Me$_{11}$)SiMePh$_2$(1)	−15.41(1)	−38.12(2)	−40.44(2)	−42.40(1)	−81.35(1)	
(Si$_6$Me$_{11}$)SiMe$_2$Ph(2)	−13.82(1)	−38.50(2)	−40.63(2)	−42.29(1)	−81.90(1)	
(Si$_6$Me$_{11}$)SiPh$_2$SiPh$_2$Me(2)	−21.31(1)	−33.68(1)	−36.83(2)	−40.63(2)	−43.36(1)	−76.54(1)
1,4-(SiPh$_2$Me)$_2$-(Si$_6$Me$_{10}$)(1)	−15.55(2)	−40.40(4)	−80.50(2)			
(Si$_6$Me$_{11}$)SiPh$_2$OTf(1)	25.16(1)	−38.30(2)	−40.16(2)	−42.49(1)	−79.77(1)	
(Si$_6$Me$_{11}$)SiPh(OTf)$_2$(1)	9.87(1)	−38.20(2)	−39.88(2)	−42.42(1)	−76.58(1)	
(Si$_6$Me$_{11}$)SiMe$_2$OTf(1)	52.60(1)	−39.73(2)	−40.41(2)	−42.14(1)	−80.53(1)	
(Si$_6$Me$_{11}$)SiMe(OTf)$_2$(1)	33.72(1)	−39.86(2)	−40.41(2)	−42.21(1)	−77.66(1)	
(Si$_6$Me$_{11}$)SiH$_2$OTf(1)	5.06(1)	−38.64(2)	−40.45(2)	−41.80(1)	−80.53(1)	
1,4-(Si(OTf)$_2$Me)$_2$-(Si$_6$Me$_{10}$)(1)	32.78/32.09(2)	−37.87/−38.05(4)	−77.45/−77.54(2)			
1,4-(Si(OTf)$_3$)$_2$-(Si$_6$Me$_{10}$)(1)	−46.77(4)	−40.25(2)	−82.25(2)			
(Si$_6$Me$_{11}$)SiMe$_2$H(1)	−34.14(1) $^1J_{\text{Si-H}} = 174.19$ Hz	−38.57(2)	−40.72(2)	−41.91(1)	−82.08(1)	
(Si$_6$Me$_{11}$)SiMeH$_2$(1)	−38.28(2)	−40.45(2)	−41.28(1)	−64.81(1) $^1J_{\text{Si-H}} = 181.26$ Hz	−82.45(1)	
(Si$_6$Me$_{11}$)SiPhH$_2$(1)	−38.57(2)	−40.64(2)	−41.81(1)	−57.34(1) $^1J_{\text{Si-H}} = 182.46$ Hz	−82.42(1)	
(Si$_6$Me$_{11}$)SiH$_3$(3)	−38.77(2)	−40.72(2)	−41.68(1)	−83.91(1) $^1J_{\text{Si-H}} = 185.72$ Hz	−99.91(1)	
(Si$_6$Me$_{11}$)SiH$_2$SiH$_2$Me(1)	−38.21(2)	−40.51(2)	−41.80(1)	−65.56(1) $^1J_{\text{Si-H}} = 187.53$ Hz	−79.42(1)	−108.94(1) $^1J_{\text{Si-H}} = 171.73$ Hz
1,4-(SiMeH$_2$)$_2$-(Si$_6$Me$_{10}$)(1)	−37.97(4) $^1J_{\text{Si-H}} = 168.63$ Hz	−65.42(2)	−82.27(2)			
1,4-(SiH$_3$)$_2$-(Si$_6$Me$_{10}$)(1)	−37.84/−38.11(4)	−83.36/−84.27(2)	−98.89($^1J_{\text{Si-H}} = 186.63$ Hz)/−100.82($^1J_{\text{Si-H}} = 175.76$ Hz)(2)			

a 1 = toluene/D$_2$O as an external standard, 2 = CDCl$_3$, 3 = C$_6$D$_6$.

Table 2
^{13}C chemical shifts for some silyl-substituted derivatives of dodecamethylcyclohexasilane

Compound (solvent) [a]	δ (ppm) (no. of carbons)								Phenyl
(Si$_6$Me$_{11}$)SiMePh$_2$(1)	−1.53(1)	−3.14(5)	−4.70(2)	−5.16(3)	−6.55(3)	−9.53(1)			138.81(i), 135.09(o), 128.61(p), 127.96(m)
(Si$_6$Me$_{11}$)SiMe$_2$Ph(1)	−0.69(3)	−3.37(2)	−4.83(2)	−5.25(2)	−6.69(3)	−10.69(1)			141.11(i), 133.83(o), 128.48(p), 127.88(m)
(Si$_6$Me$_{11}$)SiPh$_2$SiPh$_2$Me(1)	−1.78(2)	−2.77(1)	−4.79(4)	−5.40(1)	−6.21(2)	−6.37(1)	−7.60(:)		137.39(i), 137.03(o), 136.32(i), 135.68(o), 128.91(p), 128.65(p), 127.75(m)
1,4-(SiPh$_2$Me)$_2$-(Si$_6$Me$_{10}$)(1)	−1.49(4)	−2.66(4)	−5.11(2)	−9.54(2)					138.75(i), 135.07(o), 128.89(p), 127.97(m)
(Si$_6$Me$_{11}$)SiMe$_2$H(2)	−3.09(2)	−3.25(2)	−4.34(2)	−4.71(2)	−4.94(1)	−5.93(2)	−6.01(1)	−11.19(1)	
(Si$_6$Me$_{11}$)SiMeH$_2$(2)	−3.56(2)	−4.55(2)	−4.97(2)	−5.15(1)	−5.78(2)	−5.88(1)	−9.55(1)	−10.96(1)	
(Si$_6$Me$_{11}$)SiPhH$_2$(2)	−4.10(2)	−5.36(4)	−5.56(1)	−6.37(2)	−6.50(1)	−10.90(1)			
(Si$_6$Me$_{11}$)SiH$_3$(2)	−3.09(2)	−4.03(2)	−4.89(1)	−5.65(2)	−6.45(2)	−9.17(1)	−10.81(1)		
(Si$_6$Me$_{11}$)SiH$_2$SiH$_2$Me(2)	−3.52(2)	−4.68(2)	−4.88(2)	−5.10(1)	−5.69(2)	−5.95(1)	−8.79(1)	−9.43(1)	
1,4-(SiMeH$_2$)$_2$-(Si$_6$Me$_{10}$)(2)	−3.26(4)	−4.62(4)	−9.72(2)	−10.76(2)					
1,4-(SiH$_3$)$_2$-(Si$_6$Me$_{10}$)(2)	−3.59/	−4.52/	−9.83/						
	−3.98(4)	−4.84(4)	−10.25(2)						

[a] 1 = CDCl$_3$, 2 = C$_6$D$_6$.

E. Hengge et al. / Journal of Organometallic Chemistry 521 (1996) 145–155

Scheme 3. ● = SiMe$_n$, n = 1, 2.

(SiH$_3$)$_2$Si$_6$Me$_{10}$. The first compound reacted with Cp$_2$MMe$_2$ (M = Ti, Zr) to form oligomers with x = 2–4 (Scheme 6); the second gave a polymeric product. The molecular weight M_w was found to be (GPC, polystyrol standard) approximately 10500 for reaction with Cp$_2$ZrMe$_2$ and 4200 for reaction with Cp$_2$TiMe$_2$. The polymer is a soluble powder (toluene, THF). Thermogravimetric analysis reveals a transition of the polymer at 160°C, and decomposition starting at approximately 430°C. Analysis and spectroscopic results (NMR, IR) show the compound to be oxygen-free, and no tertiary Si–H group (NMR) could be detected. All these results indicate that the structure is linear.

As mentioned before, in all the proposed reaction mechanisms an intermediate with a silicon-transition element bond is involved. In view of these results on the reactivity of cyclosilanes, we thought it of interest to examine the reactivity of catalysts containing a cyclosilane, and so we used Cp$_2$M(Si$_6$Me$_{11}$)X [(M = Zr, X = Cl, Me) [13]; (M = Hf, X = Cl)]. The behaviour of these catalysts was tested in the reaction with Si$_6$Me$_{11}$SiH$_3$. The activity of the chloro derivatives found was low compared with that of the usual catalysts (Hf < Zr). The activity of Cp$_2$Zr(Si$_6$Me$_{11}$)Me was quite similar to that of Cp$_2$ZrMe$_2$.

In conclusion, the results of polymerization reactions of cyclosilanes with hydrogen-containing side chains

have revealed that steric hindrance is important. Compared with monosilanyl-substituted cyclosilanes, disilanyl-substituted derivatives exhibit much more Si–Si cleavage, though the disilanyl side chain causes lower steric hindrance and the formation of oligomers becomes possible. A second influence is revealed by the fact that the reactivity in metallocene-catalyzed reactions decreases in the order SiH$_3$ > SiH$_2$Me > SiHMe$_2$. So in the case of 1,4-disubstituted cyclosilanes, 1,4-(SiH$_3$)$_2$(Si$_6$Me$_{10}$) reacts to a polymer, whereas 1,4-(SiHMe$_2$)(Si$_6$Me$_{10}$) yields only oligomeric products.

8. Experimental section

8.1. General comments

Unless otherwise noted, all reactions and manipulations were carried out under dry nitrogen or argon. Solvents were dried and distilled prior to use. Melting points were determined with a Büchi melting point apparatus and are uncorrected. C and H analyses were performed with a Heraeus-Mikro-K1 apparatus. NMR spectra (^{1}H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.63 MHz) were recorded on a Bruker MSL 300 spectrometer at 20°C. Samples were dissolved in C$_6$D$_6$ or CDCl$_3$ or toluene with D$_2$O as an external standard. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer. GC-MS data were obtained on a Hewlett-Packard 5890-II model linked to a Hewlett-Packard 5971 mass selective detector. MS data were also obtained on a Kratos Profile spectrometer and a Varian CH-7. Gas chromatography was performed on a cross-linked
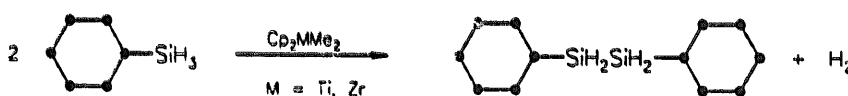
Scheme 4. ● = SiMe$_n$, n = 1, 2.

Scheme 5. ● = SiMe$_n$, n = 1, 2.

R = H, Me
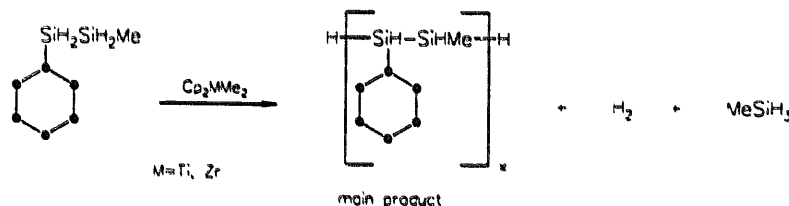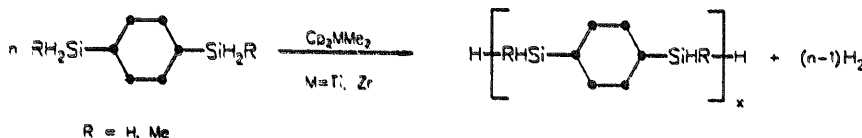
Scheme 6. ● = SiMe$_n$, n = 1, 2.

dimethylpolysiloxane column (25 m × 0.32 mm × 0.1 μm) and helium was used as carrier gas. The molecular weights of polysilanes were measured with a gel permeation chromatograph (Merck-Hitachi L 6200 intelligent pump, Polymer Standards Service columns, Viscotek 200 detector) with polystyrene standards and tetrahydrofuran as solvent.

8.2. Preparation of Si–Ph-substituted cyclohexasilanes

ClSiMe$_2$Ph, ClSiMePh$_2$, ClSiPh$_3$, LiSiMePh$_2$ and LiSiPh$_3$ are well known and readily available compounds. KSi$_6$Me$_{11}$ [9] and 1,4-Cl$_2$(Si$_6$Me$_{10}$) [8] were prepared as reported previously. The compounds were characterized by ^{29}Si NMR and mass spectroscopy.

8.3. General procedure for the preparation of (Si$_6$Me$_{11}$)SiMe$_{3-n}$Ph$_n$, n = 0, 1, 2

In a typical reaction, a solution of the phenylated chlorosilane (50 mmol) in 200 ml of toluene was stirred at 0°C and a solution of 50 mmol of KSi$_6$Me$_{11}$ in dimethoxyethane (200 ml) was added dropwise over 2 h. Once the addition was complete, the mixture was stirred for 2 h, and then added to 300 ml of 1 M HCl/ice. The organic layer was separated and the water layer extracted with toluene (3 × 50 ml). The combined organic layers were dried (Na$_2$SO$_4$) and filtered. The solvent was then evaporated under reduced pressure and the solid residue recrystallized from ^{i}PrOH to give (Si$_6$Me$_{11}$)SiMe$_{3-n}$Ph$_n$ (n = 1, 2, 3).

8.3.1. Triphenylsilylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiPh$_3$

Yield 55%. Spectral data are in accordance with the literature [15]

8.3.2. Diphenylmethylsilylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiMePh$_2$

Yield 52.9%, m.p. 187–190°C.

Anal. Found: C, 54.44; H, 8.82. C$_{24}$H$_{46}$Si$_7$ Calc.: C, 54.26; H, 8.73%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 7.58 (4H), 7.37 (6H), 0.33 (3H), 0.19–0.12 (m, 24H), 0.00 (6H).

Mass spectrum (m/e (relative intensities)): 530 (M$^+$, 25), 383 (7), 333 (Si$_6$Me$_{11}$, 2), 318 (23), 73 (SiMe$_3$, 100).

8.3.3. Phenyldimethylsilylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiMe$_2$Ph

Yield 40%, m.p. 173–175°C.

Anal. Found: C, 48.41; H, 9.35. C$_{19}$H$_{44}$Si$_7$ Calc.: C, 48.64; H, 9.45%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 7.35 (m, 5H), 0.60 (6H), 0.15 (m, 26H), 0.05 (6H).

Mass spectrum (m/e (relative intensities)): 468 (M$^+$, 18), 333 (Si$_6$Me$_{11}$, 2), 318 (8), 303 (3), 73 (SiMe$_3$, 100).

8.4. (2-Methyltetraphenyldisilanyl)undecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiPh$_2$SiPh$_2$Me

A solution of 12.8 g (21.6 mmol) of (Si$_6$Me$_{11}$)SiPh$_3$ in 150 ml of toluene was cooled to −20°C and 1.89 ml (21.6 mmol) of TfOH was added dropwise over 20 min. The mixture was stirred for 12 h at room temperature. Completion of the reaction was checked by means ^{29}Si NMR spectroscopy. The resulting triflate (Si$_6$Me$_{11}$)-SiPh$_2$(OTf) was used without isolation or purification, a solution of 21.6 mmol of LiSiPh$_2$Me in 80 ml of THF being added dropwise over 1 h at 0°C. After stirring for 2 h at room temperature, the mixture was added to 300 ml of 1 M HCl/ice. Work up was as described for (Si$_6$Me$_{11}$)SiMe$_{3-n}$Ph$_n$. The solid residue was recrystallized from ^{i}PrOH.

Yield 11.5 g (74.6%), m.p. 163–164°C.

Anal. Found: C, 60.38; H, 8.02. C$_{36}$H$_{56}$Si$_8$ Calc.: C, 60.60; H, 7.91%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 7.44–7.18 (m, 20H), 0.83 (3H), 0.26 (3H), 0.14–0.09 (m, 18H), −0.06 (6H), −0.22 (6H).

Mass spectrum (m/e (relative intensities)): 712 (M$^+$, 17), 516 (2), 437 (8), 379 (23), 197 (100).

8.5. (Diphenyltrifluoromethanesulfonyloxy)silylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiPh$_2$(OTf)

For ^{29}Si NMR chemical shifts see Table 1.

8.6. 1,4-Bis(diphenylmethylsilyl)decamethylcyclohexasilane 1,4-(SiPh$_2$Me)$_2$(Si$_6$Me$_{10}$) 1,4-bis(triphenylsilyl)decamethylcyclohexasilane 1,4-(SiPh$_3$)$_2$(Si$_6$Me$_{10}$)

A solution of 19.5 g (50 mmol) of 1,4-Cl$_2$(Si$_6$Me$_{10}$) in 200 ml of toluene was cooled to 0°C and a solution of 100 mmol of LiSiPh$_{3-n}$Me$_n$ (n = 0, 1) in THF (200 ml) was added dropwise during 90 min. After 2 h stirring at room temperature, the solution was added to 300 ml of 1 M HCl/ice. Work up was as described for (Si$_6$Me$_{11}$)SiMe$_{3-n}$Ph$_n$. The solid residue was recrystallized from ethyl acetate.

8.6.1. 1,4-Bis(triphenylsilyl)decamethylcyclohexasilane 1,4-(SiPh$_3$)$_2$(Si$_6$Me$_{10}$)

Yield 70%. Spectral data were in accordance with the literature [15].

8.6.2. 1,4-Bis(diphenylmethylsilyl)decamethylcyclohexasilane 1,4-(SiPh₂Me)₂(Si₆Me₁₀)

Yield 31%, m.p. 175–180°C.

Anal. Found: C, 60.32; H, 7.97. $C_{36}H_{56}Si_8$ Calc.: C, 60.60; H, 7.91%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 7.59 (8H), 7.39 (12H), 0.81 (6H), 0.35 (6H), 0.17 (12H), −0.02 (12H).

Mass spectrum (m/z (relative intensities)): 712 (M$^+$, 32), 516 (2), 441 (5), 367 (21), 197 (100).

8.7. General procedure for trifluoromethanesulfonyl-undecamethylcyclohexasilane and 1,4-bis(trifluoro-methanesulfonyl)decamethylcyclohexasilane derivatives

A two-necked flask was charged with 10 mmol of (Si₆Me₁₁)SiPhRR′ [(R = R′ = Me); (R = Ph, R′ = Me); (R = R′ = Ph); (R = Ph, R′ = SiPh₂Me)] or 1,4-(SiPh₂R)₂(Si₆Me₁₀) (R = Me, Ph) and 100 ml of toluene. The stirred solution was cooled to −20°C and 10 mmol of TfOH for (Si₆Me₁₁)SiMe₂Ph, 20 mmol of TfOH for (Si₆Me₁₁)SiMe₂Ph₂, (Si₆Me₁₁)SiPh₃ and (Si₆Me₁₁)SiPh₂SiPh₂Me, 40 mmol of TfOH for 1,4-(SiPh₂Me)₂(Si₆Me₁₀) and 60 mmol of TfOH for 1,4-(SiPh₃)₂(Si₆Me₁₀) were added during 20 min. The mixture was stirred for several hours at room temperature, and completion of the reaction then checked by ^{29}Si NMR spectroscopy. The resulting triflate derivatives (Si₆Me₁₁)SiMe₂(OTf), (Si₆Me₁₁)SiMe(OTf)₂, (Si₆Me₁₁)SiPh(OTf)₂ (Si₆Me₁₁)Si₂Ph₃(OTf)₂Me, 1,4-(Si(OTf)₂Me)₂(Si₆Me₁₀) and 1,4-(Si(OTf)₃)₂(Si₆Me₁₀) were used without isolation or purification. (Si₆Me₁₁)-Si₂Ph₂(OTf)₂Me was always formed mixed with (Si₆Me₁₁)Si₂Ph₃(OTf)Me and (Si₆Me₁₁)Si₂Ph(OTf)₃Me, so characterization by ^{29}Si NMR spectroscopy was not possible. After hydrogenation of (Si₆Me₁₁)-SiPh(OTf)₂ and (Si₆Me₁₁)Si₂Ph₃(OTf)₂Me (vide infra), the remaining phenyl groups were split off by TfOH as described earlier. Because (Si₆Me₁₁)-Si₂H₂(OTf)₂Me was mixed with monophenylated products, a further dephenylation/hydrogenation sequence was carried out in order to give a clean product (vide infra).

The following derivatives were prepared and characterized by ^{29}Si NMR spectroscopy. For ^{29}Si NMR chemical shifts see Table 1.

(Dimethyltrifluoromethanesulfonyloxy)silylundeca-methylcyclohexasilane: (Si₆Me₁₁)SiMe₂(OTf).

(Methylbis(trifluorosmethaneulfonyloxy))silylun-decamethylcyclohexasilane: (Si₆Me₁₁)SiMe(OTf)₂.

(Phenylbis(trifluoromethanesulfonyloxy))silylun-decamethylcyclohexasilane: (Si₆Me₁₁)SiPh(OTf)₂.

(Dihydro(trifluoromethanesulfonyloxy)silyl)unde-camethylcyclohexasilane: (Si₆Me₁₁)Si(OTf)H₂.

1,4-Bis(methylbis(trifluoromethanesulfonyloxy)silyl)

decamethylcyclohexasilane: (1,4-(Si(OTf)₂Me)₂(Si₆-Me₁₀).

1,4-Bis(tris(trifluoromethanesulfonyloxy)silyl)de-camethylcyclohexasilane: 1,4-(Si(OTf)₃)₂(Si₆Me₁₀).

8.8. Silylundecamethylcyclohexasilane and 1,4-bis(silyl)decamethylcyclohexasilane derivatives

To a solution of 10 mmol of (Si₆Me₁₁)Si(OTf)RR′ [(R = R′ = Me); (R = OTf, R′ = Me); (R = OTf, R′ = Ph); (R = H, R′ = OTf); (R = H, R′ = SiH(OTf)Me)] or 1,4-(Si(OTf)₂R)₂(Si₆Me₁₀) (R = Me, OTf) in 100 ml of toluene was added 100 ml of Et₂O. The stirred solution was cooled to 0°C and 0.5 equiv. LiAlH₄ per (OTf) group in Et₂O was added dropwise. The mixture was allowed to warm to room temperature during 1 h and was then added to 100 ml of 1 M HCl/ice. The organic layer was separated and the water layer extracted with pentane (3 × 20 ml). The combined organic layer was dried (Na₂SO₄) and filtered. The solvent was then evaporated under reduced pressure and the solid residue recrystallized from Et₂O.

8.8.1. Dimethylsilylundecamethylcyclohexasilane (Si₆Me₁₁)SiMe₂H

Yield 84.8%, m.p. 122–125°C.

Anal. Found: C, 39.73; H, 10.20. $C_{13}H_{40}Si_7$ Calc.: C, 39.72; H, 10.26%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 4.32 (Si–H), 0.33 (m, 39H).

Mass spectrum (m/z (relative intensities)): 392 (M$^+$, 16), 333 (Si₆Me₁₁, 2), 318 (12), 303 (7), 73 (SiMe₃, 100).

IR (Nujol, CsBr, cm^{-1}): 2091 (Si–H).

8.8.2. Methylsilylundecamethylcyclohexasilane (Si₆Me₁₁)SiMeH₂

Yield 79.7%, m.p. 111–113°C.

Anal. Found: C, 37.89; H, 10.03. $C_{12}H_{38}Si_7$ Calc.: C, 38.03; H, 10.10%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 3.93 (Si–H), 0.24 (m, 36H).

Mass spectrum (m/z (relative intensities)): 378 (M$^+$, 11), 333 (Si₆Me₁₁H, 1), 318 (3), 304 (3), 73 (SiMe₃, 100). IR (Nujol, CsBr, cm^{-1}): 2106 (Si–H).

8.8.3. Phenylsilylundecamethylcyclohexasilane (Si₆Me₁₁)SiPhH₂

Yield 91.9%, m.p. 118–120°C.

Anal. Found: C, 46.09; H, 9.23. $C_{17}H_{40}Si_7$ Calc.: C, 46.29; H, 9.14%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 7.37 (m, 5H), 4.58 (Si–H), 0.21 (m, 33H).

Mass spectrum (m/z (relative intensities)): 440 (M$^+$, 13), 333 (Si$_6$Me$_{11}$, 22), 306 (12), 292 (12), 259 (27), 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 2106 (Si–H).

8.8.4. Silylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiH$_3$

Yield 95.3%, m.p. 105–107°C.

Anal. Found: C, 36.00; H, 10.03. C$_{11}$H$_{36}$Si$_7$ Calc.: C, 36.20; H, 9.94%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 3.50 (Si–H), 0.23 (33H).

Mass spectrum (m/z (relative intensities)): 364 (M$^+$, 16), 333 (Si$_6$Me$_{11}$, 3), 304 (Si$_6$Me$_9$, 4), 290 (3), 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 2122 (Si–H).

8.8.5. 2-Methyldisilanylundecamethylcyclohexasilane (Si$_6$Me$_{11}$)SiH$_2$SiH$_2$Me

Yield 90%, m.p. oil.

Anal. Found: C, 35.74; H, 9.92. C$_{12}$H$_{40}$Si$_8$ Calc.: C, 35.23; H, 9.85%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 3.90 (m, Si–H), 3.26 (t, Si–H), 0.24 (m, 33H).

Mass spectrum (m/z (relative intensities)): 408 (M$^+$, 12), 362 (Si$_6$Me$_{11}$SiH$_2$, 1), 333 (Si$_6$Me$_{11}$, 4), 288 (10), 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 2122 (Si–H), 2100 (Si–H).

8.8.6. 1,4-Bis(methylsilyl)decamethylcyclohexasilane 1,4-(SiMeH$_2$)$_2$(Si$_6$Me$_{10}$)

Yield 85.3%, m.p. 102–103°C.

Anal. Found: C, 35.32; H, 9.91. C$_{12}$H$_{40}$Si$_8$ Calc.: C, 35.23, H, 9.85%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 3.92 (Si–H), 0.25 (m, 36H).

Mass spectrum (m/z (relative intensities)): 408 (M$^+$, 17), 363 (Si$_6$Me$_{10}$SiMeH$_2$, 3), 319 (Si$_6$Me$_{10}$, 1), 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 2108 (Si–H).

8.8.7. 1,4-Bis(silyl)decamethycyclohexasilane 1,4-(SiH$_3$)$_2$(Si$_6$Me$_{10}$)

Yield 63.4%, m.p. 98–100°C.

Anal. Found: C, 31.88, H, 9.53. C$_{10}$H$_{36}$Si$_8$ Calc.: C, 31.51; H, 9.52%.

For ^{29}Si NMR chemical shifts see Table 1, for ^{13}C NMR chemical shifts see Table 2.

^{1}H NMR (ppm): 3.47 (Si–H)/3.46 (Si–H), 0.25 (m, 30H).

Mass spectrum (m/z (relative intensities)): 380 (M$^+$, 12), 349 (Si$_6$Me$_{10}$SiH$_3$, 1), 319 (Si$_6$Me$_{10}$, 1) 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 2122 (Si–H).

8.9. Chloro(undecamethylcyclohexasilanyl)-bis(η^5-cyclopentadienyl)hafnium (η^5-C$_5$H$_5$)$_2$Hf(Si$_6$Me$_{11}$)Cl

A two-necked flask was charged with 2.50 g (6.59 mmol) of Cp$_2$HfCl$_2$ and n-pentane (30 ml). The stirred solution was cooled to −55°C and a solution of 6.59 mmol of KSi$_6$Me$_{11}$ in 25 ml of DME was added dropwise. The stirred mixture was allowed to warm to room temperature during 2 h and the solution then evaporated to dryness and the residue extracted with n-pentane (2 × 20 ml). The combined extracts were concentrated by removing 50% of the solvent and cooling to −70°C. After 2 days orange crystals had been formed. Purification was by fractional crystallization from n-pentane.

Yield 1.80 g (40.3%), m.p. 175–179°C.

Anal. Found: C, 37.41; H, 6.45. C$_{21}$H$_{43}$ClHfSi$_6$ Calc.: C, 37.20; H, 6.39%.

^{29}Si NMR (ppm): −16.66, −30.74, −38.12, 42.84.

^{1}H NMR (ppm): 5.80 (Cp, 10H), 0.50 (m, 33H).

^{13}C NMR (ppm): 110.16, −0.69, −0.92, −2.86, −3.64, −4.44, −4.97, −5.84.

Mass spectrum (m/z (relative intensities)): 678 (M$^+$, 3), 639 (2), 380 (11), 334 (Si$_6$Me$_{11}$, 46), 73 (SiMe$_3$, 100).

IR (Nujol, CsBr, cm^{-1}): 1243 s, 1017 s, 812 vs, 795 s, 780 m, 768 m, 683 m, 648 m, 400 w.

8.10. Polymerisation of (Si$_6$Me$_{11}$)SiMeRH (R = Me, H) and 1,4-(SiMeH$_2$)$_2$(Si$_6$Me$_{10}$) catalyzed by Cp$_2$MMe$_2$ (M = Ti, Zr)

A Schlenk flask was charged with 1 mmol of the hydrosilane and 2 ml of toluene and 2 mol.% of catalyst was added. The catalyst dissolved immediately. The mixture was heated to 80°C, the color turning to orange (Cp$_2$ZrMe$_2$) or dark green (Cp$_2$TiMe$_2$). The mixture was heated for 2 days and the catalyst was then inactivated by exposure to air for a few minutes. Removal of the volatiles left a yellow product.

8.10.1. (Si$_6$Me$_{11}$)SiMe$_2$H and Cp$_2$TiMe$_2$

5% of [(Si$_6$Me$_{11}$)SiMe$_2$]$_2$ and 3% of Si$_6$Me$_{11}$H (spectral data were in accordance with the literature [16]). The rest is unreacted product.

8.10.2. (Si$_6$Me$_{11}$)SiMe$_2$H and Cp$_2$ZrMe$_2$

5% of [(Si$_6$Me$_{11}$)SiMe$_2$]$_2$ and 2% of Si$_6$Me$_{11}$H (spectral data were in accordance with the literature [16]). The rest is unreacted product.

8.10.3. $(Si_6Me_{11})SiMeH_2$ and Cp_2TiMe_2

18% of $Si_6Me_{11}H$, 11% of $(Si_6Me_{11})SiMe_2H$ and 17% of $[(Si_6Me_{11})SiMeH]_2$, which could be isolated by Kugelrohr distillation.

Spectral data of $[(Si_6Me_{11})SiMeH]_2$. ^{29}Si NMR (ppm): $-37.36/-38.03$, $-40.\,\!8/-40.52$, -41.94, -67.63 ($^1J_{Si-H} = 171.73$), -76.65. ^{1}H NMR (ppm): 4.02 (Si–H), 0.42 (m, 72H). Mass spectrum (m/z (relative intensities)): 754 (M$^+$, 53), 696 (2), 563 (3), 334 (Si$_6$Me$_{11}$, 73), 73 (SiMe$_3$, 100).

8.10.4. $(Si_6Me_{11})SiMeH_2$ and Cp_2ZrMe_2

20% of $[(Si_6Me_{11})SiMeH]_2$ and 8% of $Si_6Me_{11}H$.

8.10.5. $1,4\text{-}(SiMeH_2)_2(Si_6Me_{10})$ and Cp_2TiMe_2

50% yield (oligomeric products), GPC: $M_w = 1800$, $M_n = 900$, $DP = 2\text{–}4$, $M_w/M_n = 2.0$. ^{29}Si NMR (ppm): -39.0 (m), 67.8 (m), -75.7, 82.6 (m). ^{1}H NMR (ppm): 3.9 (Si–H), 0.33 (m). IR (Nujol, CsBr, cm^{-1}): 2103 (Si–H). $1,4\text{-}H_2(Si_6Me_{10})$ and $1\text{-}SiMeH_2\text{-}4\text{-}H\text{-}(Si_6Me_{10})$ were detected as by-products.

8.10.6. $1,4\text{-}(SiMeH_2)_2(Si_6Me_{10})$ and Cp_2ZrMe_2

50% yield (oligomer products), GPC: $M_w = 1600$, $M_n = 800$, $DP = 2\text{–}4$, $M_w/M_n = 2.0$. ^{29}Si NMR (ppm): -38.5 (m), -67.3 (m), -76.1 (m), -82.6 (m). ^{1}H NMR (ppm): 4.0 (Si–H), 0.32 (m). IR (Nujol, CsBr, cm^{-1}): 2103 (Si–H). $1,4\text{-}H_2(Si_6Me_{10})$ and $1\text{-}SiMeH_2\text{-}4\text{-}H\text{-}(Si_6Me_{10})$ were detected as by-products.

8.11. Polymerization of $(Si_6Me_{11})SiH_2R$ $(R = H, SiH_2Me)$ and $1,4\text{-}(SiH_3)_2(Si_6Me_{10})$ catalyzed by Cp_2MMe_2 $(M = Ti, Zr)$

A Schlenk flask was charged with 1 mmol of the hydrosilane and 2 ml of toluene, and 2 mol.% of catalyst was added. The catalyst dissolved immediately. After an induction period of between 1 and 3 h the mixture turned dark green (Cp_2TiMe_2) or orange (Cp_2ZrMe_2), with strong gas evolution. It was stirred for 24 h and the catalyst then deactivated by exposure to the air for a few minutes. The volatiles were then removed under reduced pressure.

8.11.1. $(Si_6Me_{11})SiH_3$ and Cp_2TiMe_2

30% $[(Si_6Me_{11})SiH_2]_2$, 10% $Si_6Me_{11}H$ and 60% charged starting material $[(Si_6Me_{11})SiH_2]_2$ were isolated by Kugelrohr distillation.

Spectral data of $[(Si_6Me_{11})SiH_2]_2$. M.p. 134°C. ^{29}Si NMR (ppm): -37.40, -39.93, -41.07, -78.09, -108.60 ($^1J_{Si-H} = 177.39$ Hz). ^{1}H NMR (ppm): 3.50 (Si–H), 0.30 (m, 66H). IR (Nujol, CsBr, cm^{-1}): 2098 (Si–H). Mass spectrum (m/z (relative intensities)): 726 (M$^+$, 8), 485 (3), 425 (4), 334 (16), 66 (100).

8.11.2. $(Si_6Me_{11})SiH_3$ and Cp_2ZrMe_2

95% $[(Si_6Me_{11})SiH_2]_2$ and 5% $Si_6Me_{11}H$.

8.11.3. $(Si_6Me_{11})SiH_2SiH_2Me$ and Cp_2TiMe_2

70% yield (oligomer products), GPC: $M_w = 1800$, $M_n = 1800$, $DP = 2\text{–}4$, $M_w/M_n = 1.4$. ^{29}Si NMR (ppm): -21.7, -39.2 (m), -68.0, -77.9 (m), -82.8, -105.8. ^{1}H NMR (ppm): 3.5 (Si–H), 0.35 (m). IR (Nujol, CsBr, cm^{-1}): 2095 (Si–H). $Si_6Me_{11}H$, $(Si_6Me_{11})SiH_3$ and $MeSiH_3$ were by-products (detected by GC-MS).

8.11.4. $(Si_6Me_{11})SiH_2SiH_2Me$ and Cp_2ZrMe_2

90% yield (oligomer products), GPC: $M_w = 1700$, $M_n = 1300$, $DP = 2\text{–}3$, $M_w/M_n = 1.4$. ^{29}Si NMR (ppm): -19.6, -38.7 (m), -72.1 (m), -77.8, -78.6. ^{1}H NMR (ppm): 3.6 (Si–H), 0.45 (m), IR (Nujol, CsBr, cm^{-1}): 2091 (Si–H). $Si_6Me_{11}H$, $(Si_6Me_{11})SiH_3$ and $MeSiH_3$ were by-products (detected by GC-MS).

8.11.5. $1,4\text{-}(SiH_3)_2(Si_6Me_{10})$ and Cp_2TiMe_2

98% yield (oligomer products), m.p. $> 360°C$. GPC: $M_w = 4200$, $M_n = 2300$, $M_w/M_n = 1.8$. ^{29}Si NMR (ppm): -37.9 (m), -68.5, -76.5, -78.9 (m), -100.9, -106.7, -109.7. ^{1}H NMR (ppm): 3.66 (m, Si–H), 1.3, 0.33 (m). IR (Nujol, CsBr, cm^{-1}): 2089 (Si–H). $1,4\text{-}H_2(Si_6Me_{10})$ could be detected as a by-product by GC-MS.

8.11.6. $1,4\text{-}(SiH_3)_2(Si_6Me_{10})$ and Cp_2ZrMe_2

98% yield (oligomer products), m.p. $> 360°C$. GPC: $M_w = 10500$, $M_n = 4200$, $M_w/M_n = 2.5$. ^{29}Si NMR (ppm): $-38\,3$ (m), -78.2 (m), -83.3, -107.3, -108.7, -112.8. ^{1}H NMR (ppm): 3.59 (m, Si–H), 2.68, 2.27, 0.35 (m). IR (Nujol, CsBr, cm^{-1}): 2089 (Si–H). $1,4\text{-}H_2(Si_6Me_{10})$ could be detected as a by-product by GC-MS.

Acknowledgements

References

[1] C. Aitken, J.F. Harrod and E. Samuel, *J. Organomet. Chem.*, 279 (1985) C11.

[2] E. Hengge and M. Weinberger, *J. Organomet. Chem.*, 433 (1992) 21. E. Hengge and M. Weinberger, *J. Organomet. Chem.*, 441 (1992) 397. H.-G. Woo, J.F. Walzer and T.D. Tilley, *J. Am. Chem. Soc.*, 114 (1992) 7047. Y. Mu, C. Aitken, B. Cote, J.F. Harrod and E. Samuel, *Can. J. Chem.*, 69 (1991) 264. J. Corey, *Adv. Silicon Chem.*, 1 (1991) 327.

[3] E. Hengge and R. Janoschek, *Chem. Rev.*, 95 (1995) 1495.

[4] R. West and A. Indriksons, *J. Organomet. Chem.*, 94 (1972) 611.

[5] P.K. Jenkner, E. Hengge, R. Czaputa and C. Kratky, *J. Organomet. Chem.*, **446** (1993) 83.

[6] W. Wojnowski, B. Dreczewski, A. Herman, K. Peters, E.M. Peters and H.G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, **24** (1985) 992.

[7] F.K. Mitter and E. Hengge, *J. Organomet. Chem.*, **47** (1987) 332.

[8] A. Spielberger, P. Gspaltl, H. Siegl, E. Hengge and K. Gruber, *J. Organomet. Chem.*, **499** (1995) 241.

[9] F. Uhlig, P. Gspaltl, M. Trabi and E. Hengge, *J. Organomet. Chem.*, **493** (1995) 33.

[10] W. Uhlig, *Chem. Ber.*, **125** (1992) 47.

[11] B.J. Helmer and R. West, *J. Organomet. Chem.*, **236** (1982) 21.

[12] T.D. Tilley, *Acc. Chem. Res.*, **26** (1993) 22.

[13] E. Hengge, E. Pinter, M. Eibl and F. Uhlig, *Bull. Soc. Chim. Fr.*, **132** (1995) 509.

[14] E. Hengge and M. Weinberger, *J. Organomet. Chem.*, **443** (1993) 167.

[15] F. Uhlig, B. Stadelmann, A. Zechmann, P. Lassacher, H. Stüger and E. Hengge, *Phosphorus, Sulfur and Silicon*, **90** (1994) 29.

[16] F.K. Mitter, G.I. Pollhammer and E. Hengge, *J. Organomet. Chem.*, **314** (1986) 1.