Novel cyclopentadienyl silanes and disilanes: synthesis, structure and gas-phase pyrolysis

Andreas Klipp, Stefan H.A. Petri, Beate Neumann, Hans-Georg Stammler,
Peter Jutzi *

Fakultät für Chemie der Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

Abstract

The new chloro(cyclopentadienyl)silanes $Cp'SiH_yCl_{3-y}$ ($Cp' = Me_4EtC_5$, $y = 1$: **1**; $Cp' = Me_4C_5H$, $y = 1$: **2**; $y = 0$: **3**; $Cp' = Me_3C_5H_2$, $y = 1$: **4** and pentachloro(cyclopentadienyl)disilanes $Cp'Si_2Cl_5$ ($Cp' = Me_5C_5$ **5**, Me_4EtC_5 **6**, Me_4C_5H **7**, $Me_3C_5H_2$ **8**, $Me_3SiC_5H_4$ **9**) are synthesized in good yields via metathesis reactions. Treatment of **1–9** with $LiAlH_4$ leads under Cl–H exchange to the hydridosilyl compounds $Cp'SiH_3$ ($Cp' = Me_4EtC_5$ **10**, Me_4C_5H **11**, $Me_3C_5H_2$ **12**) and to the hydridodisilanyl compounds $Cp'Si_2H_5$ ($Cp' = Me_5C_5$ **13**, Me_4EtC_5 **14**, Me_4C_5H **15**, $Me_3C_5H_2$ **16**, $Me_3SiC_5H_4$ **17**). Complexes **1–17** are characterized by ^1H, ^{13}C, and ^{29}Si-NMR spectroscopy, IR spectroscopy, mass spectrometry and CH-analysis. The structures of **6**, **7** and **9** are determined by single-crystal X-ray diffraction analysis. Pyrolysis studies of the cyclopentadienylsilanes **10–12** and disilanes **13–17** show their suitability as precursors in the MOCVD process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silanes; Disilanes; Cyclopentadienyl ligands; X-ray analysis of cp-disilanes; MOCVD

1. Introduction

Thin silicon films are of great interest because of the many applications they have found in fields such as microelectronics, material science, and optics [1]. For industrial use the most common, well established, and nearly ideal silicon precursors used for the chemical vapor deposition (CVD) of silicon films are the gaseous silane (SiH_4) or disilane (Si_2H_6) [2]. The handling of these highly pyrophoric silanes in laboratory applications needs special precautions and is often problematic. Thus there is a strong demand for alternative precursor molecules that should fulfil the following requirements: (i) sufficient stability to allow for long shelf life; (ii) easy handling without special precautions; (iii) sufficient volatility; and (iv) easy fragmentation to stable gaseous species.

Substituting one hydrogen atom of silane or disilane by an appropriate organic group should lead to compounds which meet these desired requirements. Pentamethylcyclopentadienylsilane ($Me_5C_5SiH_3$; (**18**)) has been proven to be a very good silicon precursor, e.g. in the low temperature remote plasma-enhanced CVD-process, because a homolytic cleavage of the cyclopentadienyl silicon bond takes place easily [3]. The resulting pentamethylcyclopentadienyl radical is very stable and thus prevents carbon deposition and incorporation into the silicon film [4]; in the condensed phase, it reacts preferentially via hydrogen transfer to pentamethylcyclopentadiene and tetramethylfulvene. Modifications at the substituent pattern of the cyclopentadienyl ring or the exchange of the H_3Si group for a H_5Si_2 group should lead to new Si precursors with even better deposition parameters. In this paper we report results on the synthesis and characterization of novel cyclopentadienyl silanes $Cp'SiH_yCl_{3-y}$ ($Cp' = Me_4EtC_5$, $y = 1$: **1**; $y = 3$: **10**; $Cp' = Me_4C_5H$, $y = 1$: **2**; $y = 0$: **3**; $y = 3$: **11**; $Cp' = Me_3C_5H_2$, $y = 1$: **4**; $y = 3$: **12**) and cyclopentadienyl disilanes $Cp'Si_2H_yCl_{5-y}$ ($Cp' = Me_5C_5$, $y = 0$: **5**; $y = 5$: **13**; $Cp' = Me_4EtC_5$, $y = 0$: **6**, $y = 5$: **14**; $Cp' = Me_4C_5H$, $y = 0$: **7**; $y = 5$: **15**; $Cp' = Me_3C_5H_2$, $y = 0$: **8**; $y = 5$: **16**; $Cp' = Me_3SiC_5H_4$, $y = 0$:

* Corresponding author. Tel.: + 49-521-1066181; fax: + 49-521-1066026.

E-mail address: peter.jutzi@uni-bielefeld.de (P. Jutzi).
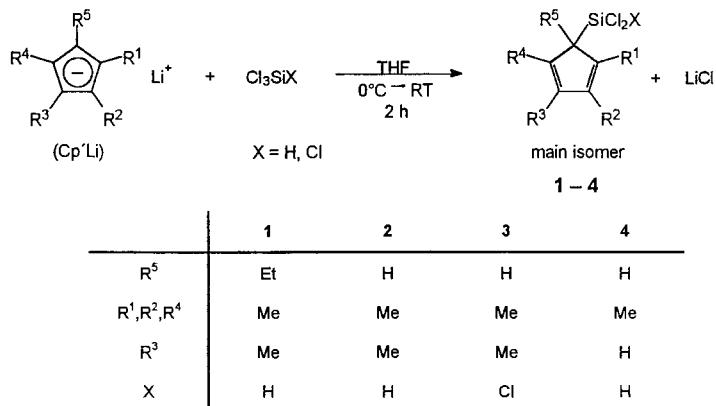
Scheme 1. Synthesis of the chloro(cyclopentadienyl)silanes **1**–**4**.

	1	**2**	**3**	**4**
R^5	Et	H	H	H
R^1, R^2, R^4	Me	Me	Me	Me
R^3	Me	Me	Me	H
X	H	H	Cl	H
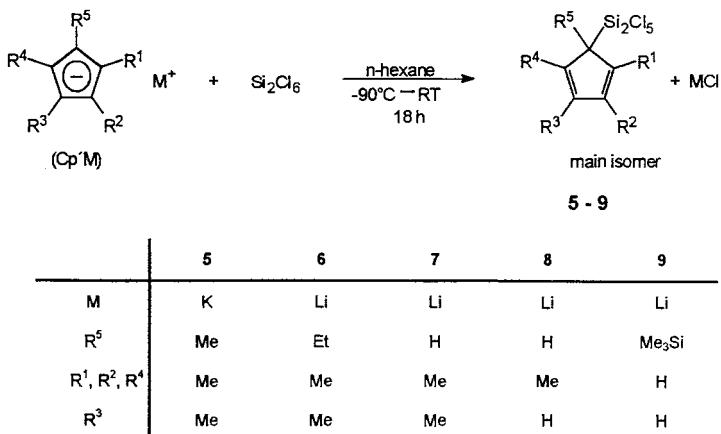
Scheme 2. Synthesis of the pentachloro(cyclopentadienyl)disilanes **5**–**9**.

	5	**6**	**7**	**8**	**9**
M	K	Li	Li	Li	Li
R^5	Me	Et	H	H	Me_3Si
R^1, R^2, R^4	Me	Me	Me	Me	H
R^3	Me	Me	Me	H	H

9; $y = 5$: **17**). Most of the compounds show dynamic behavior (sigmatropic rearrangements) comparable to that of analogous $Cp'SiR_3$ compounds. The volatile hydridosilanes and disilanes **10**–**18** are investigated by gas-phase pyrolysis with regard to their suitability as MOCVD precursors.

2. Results and discussion

2.1. Synthesis

The chloro(cyclopentadienyl)silanes $Cp'SiH_yCl_{3-y}$ ($y = 0, 1$) **1**–**4** are synthesized via metathesis reactions from the corresponding cyclopentadienyl lithium salts and trichlorosilane or tetrachlorosilane in THF at 0°C (Scheme 1). Dropwise addition of the Cp'M suspension to the halogenosilane is necessary to avoid the formation of bis(cyclopentadienyl) derivatives. The products can be recrystallized from pentane (**1**–**3**) or distilled (**4**) for further purification.

The pentachloro(cyclopentadienyl)disilanes $Cp'Si_2Cl_5$ **5**–**9** are synthesized analogously starting from the ap-

propriate cyclopentadienyl lithium or potassium salts and hexachlorodisilane in hexane at low temperature (-80°C) (Scheme 2). At higher temperature a cleavage of the Si–Si bond by the cyclopentadienyl lithium or potassium salt occurs resulting in a polymeric resin and a small amount of Cp'trichlorosilane [5]. The disilanes

	1 / 10	**2 / 3 / 11**	**4 / 12**
R^5	Et	H	H
R^1, R^2, R^4	Me	Me	Me
R^3	Me	Me	H
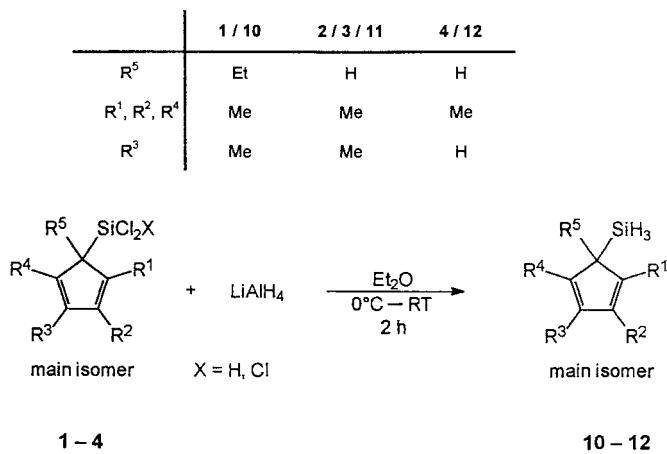
Scheme 3. Synthesis of the cyclopentadienylsilanes **10**–**12**.
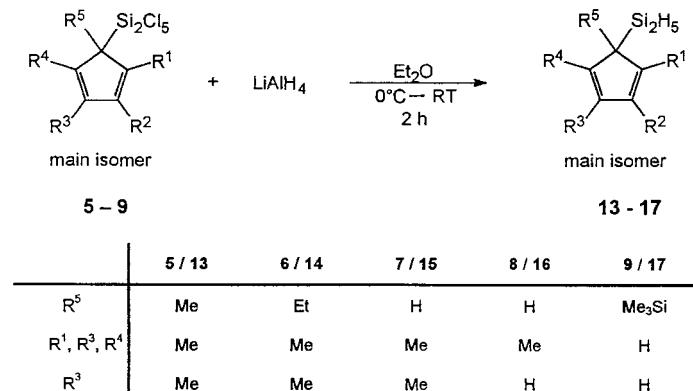
Scheme 4. Synthesis of the cyclopentadienyldisilanes 13–17.

	5 / 13	6 / 14	7 / 15	8 / 16	9 / 17
R^5	Me	Et	H	H	Me$_3$Si
R^1, R^3, R^4	Me	Me	Me	Me	H
R^3	Me	Me	Me	H	H

5–9 are much more sensitive to air and moisture than the monosilanes 1–4. Compounds 5, 6, 7 and 9 can be recrystallized from hexane for further purification.

Treatment of 1–9 with LiAlH$_4$ in diethyl ether leads under Cl–H exchange to the corresponding hydridosilyl 10–12 and hydridodisilanyl compounds 13–17 in good yields (Schemes 3 and 4). In the absence of ether, AlCl$_3$ catalyzed silane redistribution reactions occur, which can result in formation of SiH$_4$, an extremely pyrophoric gas when in contact with air [6].

The pale yellow liquids 10–17 are distilled for further purification. Because the cyclopentadienyl fragment is a very good leaving group and easily gets substituted by other nucleophiles [7], it is absolutely necessary to avoid the presence of impurities of LiAlH$_4$, LiCl and AlCl$_3$ during distillation. The resulting liquids are colorless after distillation but get pale yellow after a short period of time though stored under argon.

2.2. Crystal structures

Crystallization of the crude products 6, 7 and 9 from hexane yields colorless plates suitable for X-ray structure analysis. Crystal structure data and structure refinement parameters are given in Table 1; ORTEP plots of the molecules are shown in Fig. 1 (Tables 2–7).

Compounds 6, 7 and 9 crystallize in the space groups $P2_1/n$, P-1, $P2_1/c$, respectively. As expected, the cyclopentadienyl rings are σ-bound (η^1) with the allylic atom fixed to the pentachlorodisilanyl group. The cyclopentadienyl rings exhibit a diene structure with C–C single bond (1.48 Å) and C=C double bond (1.36 Å) lengths typical for σ-bonded species [8]. The ethyl group and the trimethylsilyl group of compounds 6 and 9 are both bound in allylic position which fits well with the main isomer observed in solution.

The Si–Si and Si–C(1) bond lengths in 6, 7 and 9 are not influenced by the number of alkyl groups bound to

the cyclopentadienyl ring or by the diene system itself as shown in Table 8.

The C$_5$ ring is essentially planar, and the Si–C bond length is typical despite the steric demand of the Cp group, which is evident from the fact that the Cl–Si–Cl bond angles within the SiCl$_2$–SiCl$_3$ moiety are 4–6° less than the tetrahedral angle and the C(1)–Si–Si bond angles are 6–7° more than the tetrahedral angle.

The chlorine atoms of the pentachlorodisilanyl groups in compounds 6, 7 and 9 show a staggered conformation in the solid state.

2.3. Pyrolysis studies

Thin films of silicon are routinely fabricated from gaseous precursor molecules (e.g. SiH$_4$ or Si$_2$H$_6$) by variety of empirically developed chemical vapor deposition techniques. Due to the easy Si–Si bond fission, disilane is thermally less stable than silane and offers comparably lower deposition temperatures and higher deposition rates. The two main decomposition modes are the homolytic cleavage of the Si–Si bond into silyl radicals (SiH$_3$) and the 1,2-hydrogen transfer resulting in silane (SiH$_4$) and silylene (SiH$_2$) [13].

To make a preliminary evaluation of the potential of the silanes 10–12 and 18 and of the disilanes 13–17 as alternative MOCVD precursors for silicon films and to examine their deposition temperature and chemistry, we carried out experiments at a horizontal hot-wall MOCVD reactor. Deposition conditions are shown in Table 9.

Silicon films were deposited at temperatures above 460°C from the cyclopentadienyl disilanes and above 550°C from the cyclopentadienyl silanes; for comparison, polycrystalline silicon is deposited from the decomposition of SiH$_4$ between 630 and 730°C [15].

In order to get information about the fragmentation reactions occurring during CVD, we examined the resulting volatile product mixture. It was collected in a liquid nitrogen cold trap, separated and analyzed by ^{1}H- and ^{29}Si-NMR spectroscopy.

In the case of pentamethylcyclopentadienyldisilane (**13**), the reaction products were identified as pentamethylcyclopentadiene, tetramethylfulvene and pentamethylcyclopentadienylsilane (**18**). This suggests that deposition takes place by a thermally induced ho-

Table 1

Crystal structure data and structure refinement parameters for the cyclopentadienyl-pentachlorodisilanes **6**, **7**, **9** [a]

	Me$_4$EtC$_5$Si$_2$Cl$_5$ (**6**)	Me$_4$C$_5$HSi$_2$Cl$_5$ (**7**)	Me$_3$SiC$_5$H$_4$Si$_2$Cl$_5$ (**9**)
Empirical formula	C$_{11}$H$_{17}$Cl$_5$Si$_2$	C$_9$H$_{13}$Cl$_5$Si$_2$	C$_8$H$_{13}$Cl$_5$Si$_3$
Formula weight	382.68	354.62	370.70
Crystal colour, habit	Colorless, plates	Colorless, plates	Colorless, irregular
Crystal size (mm)	$0.60 \times 0.40 \times 0.05$	$1.00 \times 0.70 \times 0.30$	$0.90 \times 0.50 \times 0.40$
D_{calc} (g cm^{-3})	1.463	1.526	1.489
Wavelength	0.71073	0.71073	0.71073
Space group	$P2_1/n$	P-1	$P2_1/c$
Unit cell dimensions			
a (Å)	9.900(4)	9.137(6)	11.865(3)
b (Å)	13.243(6)	13.476(7)	8.644(3)
c (Å)	13.252(6)	14.048(7)	16.284(5)
α (°)	90	65.65(4)	90
β (°)	91.09(3)	89.96(5)	98.16(2)
γ (°)	90	79.40(5)	90
V (Å^3)	1737.1(13)	1544(2)	1653.2(9)
Z	4	4	4
$F(000)$	784	720	752
Absorption correction	* [d]	*	*
Absorption coefficient (mm^{-1})	0.955	1.068	1.069
θ range for data collection (°)	2.17–27.02	1.60–30.00	1.73–30.00
Reflections collected	3951	9518	5030
Independent reflections	3791 ($R_{int} = 0.0891$)	8994 (Rint $= 0.0270$)	4820 ($R_{int} = 0.0375$)
Parameters	164	297	203
$R_F[I > 2\sigma(I)]$ [b]	0.0739	0.0475	0.0535 for 3728 reflections
$wR_F[I > 2\sigma(I)]$ [c]	0.1509	0.1155	0.1408

[a] $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

[b] $wR_F = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

[c] Definition of the weighting scheme: **6** calc $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$; **7** calc $w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.4656P]$ where $P = (F_o^2 + 2F_c^2)/3$; **9** calc $w = 1/[\sigma^2(F_o^2) + (0.0839P)^2 + 0.9784P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[d] Semi-empirical from Ψ scans.

Me$_4$EtC$_5$Si$_2$Cl$_5$ **6**   Me$_4$C$_5$HSi$_2$Cl$_5$ **7**   Me$_3$SiC$_5$H$_4$Si$_2$Cl$_5$ **9**
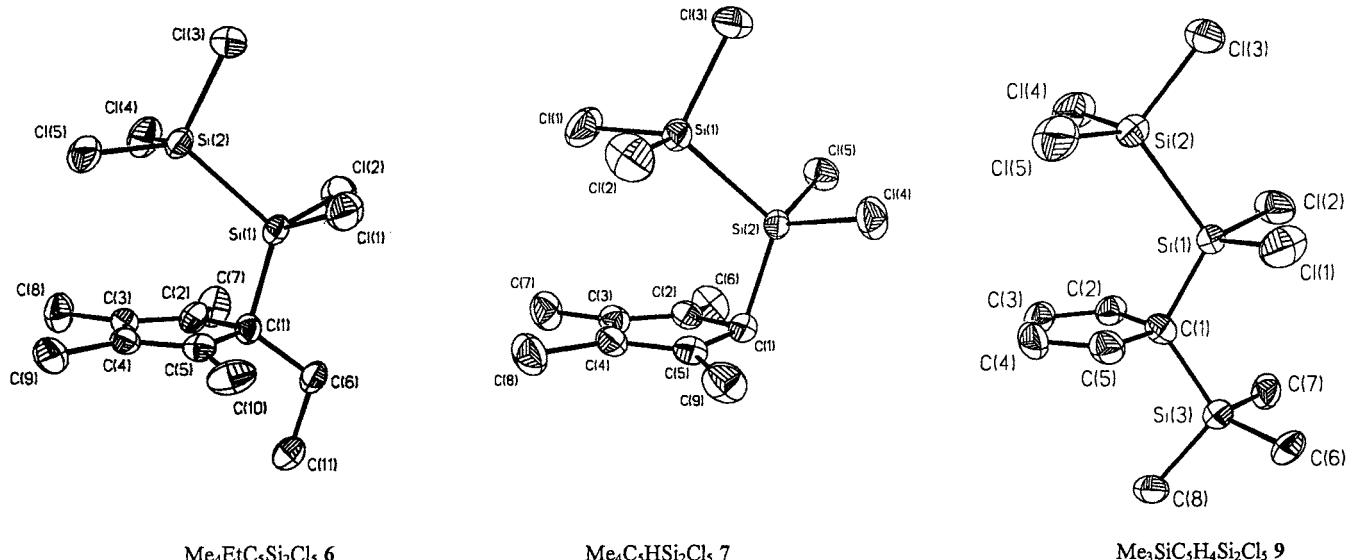
Fig. 1. Molecular structures of **6**, **7** and **9**.

Table 2
Selected bond lengths (Å) and angles (°) for EtMe$_4$C$_5$Si$_2$Cl$_5$ (**6**)

Bond lengths

Si(1)–C(1)	1.893(7)	Si(1)–Cl(2)	2.058(3)
Si(2)–Cl(5)	2.022(3)	Si(2)–Cl(3)	2.034(3)
Si(1)–Cl(1)	2.045(3)	Si(1)–Si(2)	2.327(3)
Si(2)–Cl(4)	2.028(3)	C(1)–C(5)	1.505(8)
C(1)–C(6)	1.524(8)	C(6)–C(11)	1.521(9)
C(2)–C(3)	1.361(8)	C(3)–C(4)	1.445(9)

Bond angles

C(6)–C(1)–Si(1)	112.9(4)	C(1)–Si(1)–Cl(1)	114.0(2)
C(1)–Si(1)–Cl(2)	111.1(2)	C(1)–Si(1)–Si(2)	116.7(2)
Cl(1)–Si(1)–Cl(2)	103.70(12)	C(2)–C(1)–Si(1)	100.9(4)
C(5)–C(1)–Si(1)	100.4(4)		

Table 3
Selected bond lengths (Å) and angles (°) for Me$_4$C$_5$HSi$_2$Cl$_5$ (**7**)

Bond lengths

Si(2)–C(1)	1.866(2)	Si(1)–Cl(1)	2.016(2)
Si(2)–Cl(4)	2.060(2)	C(1)–C(2)	1.500(3)
Si(2)–Cl(5)	2.0482(13)	C(2)–C(3)	1.354(3)
Si(1)–Si(2)	2.336(2)	C(3)–C(4)	1.460(3)
Si(1)–Cl(3)	2.0344(13)	C(4)–C(5)	1.354(3)
Si(1)–Cl(2)	2.036(2)	C(1)–C(5)	1.502(3)

Bond angles

C(1)–Si(2)–Cl(5)	114.23(9)	C(5)–C(1)–Si(2)	102.3(2)
C(1)–Si(2)–Si(1)	115.35(8)	C(2)–C(1)–Si(2)	103.4(2)
Cl(5)–Si(2)–Cl(4)	104.20(6)	C(1)–Si(2)–Cl(4)	112.02(9)

Table 4
Selected bond lengths (Å) and angles (°) for Me$_3$SiC$_5$H$_4$Si$_2$Cl$_5$ (**9**)

Bond lengths

Si(1)–C(1)	1.846(3)		
Si(1)–Cl(1)	2.0354(12)	Si(2)–Cl(4)	2.017(2)
Si(1)–Cl(2)	2.0437(13)	Si(2)–Cl(5)	2.0135(14)
Si(1)–Si(2)	2.3357(13)		
Si(2)–Cl(3)	2.031(2)		

Bond angles

C(2)–C(1)–Si(1)	106.8(2)	C(2)–C(1)–Si(3)	110.0(2)
Si(1)–C(1)–Si(3)	119.0(2)	C(1)–Si(1)–Cl(1)	112.43(12)
C(1)–Si(1)–Cl(2)	112.41(12)	Cl(1)–Si(1)–Cl(2)	106.77(6)
C(1)–Si(1)–Si(2)	115.84(14)	C(5)–C(1)–Si(1)	106.3(2)

molytic fragmentation of the precursor molecules, leading to Me$_5$C$_5$ radicals. These radicals disproportionate via hydrogen transfer to yield Me$_5$C$_5$H and tetramethylfulvene. A second possible fragmentation pathway is the 1,2-hydrogen shift between the two silicon atoms in **13** resulting in pentamethylcyclopentadienylsilane (**18**) and silylene SiH$_2$, a highly reactive decomposition product, which plays an important role in the pyrolysis of Si$_2$H$_6$ and SiH$_4$ [16]. A more detailed investigation of the fragmentation process of **13** is described in Ref. [24]. The partially alkylated cyclopentadienylsilanes **11**–**12** and disilanes **15**–**17** and the compounds **10** and **14** show fragmentation pathways resulting in complex product mixtures.

The Me$_5$C$_5$ substituted silane and disilane, **18** and **13**, seem to us to be the best precursors for the following reasons:

- The sterically demanding Me$_5$C$_5$ ligand renders the attack of reagents like water or oxygen more difficult; as a result, **13** and **18** are stable in air for short time exposure and thus can be easily handled (nonpyrophoric, nonexplosive and noncorrosive; in addition they show good long-term stability).
- Owing to their volatility, **13** and **18** should enable high deposition rates.
- The Me$_5$C$_5$ ligand is known to be a good leaving group, thus facilitating a silicon–carbon bond cleavage at rather low temperatures in the CVD process [17].
- The Me$_5$C$_5$ fragment is a stable entity in the gas phase (as well as the Me$_5$C$_5$H molecule) and does not interact with the growing silicon film (deposition of silicon films without carbon impurities).

3. Conclusions

We have described the synthesis of several new cyclopentadienylsilanes and disilanes. Crystal structures of pentachloro(cyclopentadienyl)disilanes **6**, **7** and **9** reveal the Si$_2$Cl$_5$ fragment to be σ-bound to the cyclopentadienyl ring in allylic position. The volatile hydridosilanes and disilanes **10**–**18** are investigated by gas phase pyrolysis regarding their suitability as MOCVD precursors.

We have shown that under the examined cycopentadienyl silanes and disilanes the best silicon precursor

Table 5
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq} [a] (Å$^2 \times 10^3$) for **6**

	x	y	z	U(eq)
Si(1)	384(2)	7361(1)	4425(1)	27(1)
Si(2)	1560(2)	6666(2)	3089(1)	31(1)
Cl(1)	−1033(2)	6333(2)	4860(1)	46(1)
Cl(2)	−738(2)	8471(2)	3717(2)	50(1)
Cl(3)	132(2)	6055(2)	2149(1)	49(1)
Cl(4)	2494(2)	7758(2)	2288(1)	49(1)
Cl(5)	2910(2)	5557(1)	3400(1)	44(1)
C(1)	1433(6)	7899(5)	5506(5)	28(1)
C(2)	2521(7)	8431(5)	4943(5)	30(2)
C(3)	3639(6)	7832(5)	4942(5)	28(2)
C(4)	3371(6)	6943(5)	5538(5)	29(2)
C(5)	2100(7)	6953(4)	5900(5)	26(1)
C(6)	600(7)	8510(5)	6243(5)	33(2)
C(7)	2393(8)	9466(5)	4491(6)	46(2)
C(8)	4947(7)	8031(6)	4462(6)	49(2)
C(9)	4408(8)	6126(6)	5751(6)	53(2)
C(10)	1477(8)	6250(5)	6626(5)	44(2)
C(11)	1476(7)	8923(6)	7104(5)	43(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq} [a]($\text{Å}^2 \times 10^3$] for **7**

	x	y	z	U(eq)
Si(1)	−662(1)	6524(1)	2546(1)	29(1)
Si(2)	134(1)	8122(1)	1409(1)	23(1)
Cl(1)	972(1)	5219(1)	3404(1)	51(1)
Cl(2)	−2139(1)	6809(1)	3535(1)	50(1)
Cl(3)	−1798(1)	6048(1)	1616(1)	49(1)
Cl(4)	1850(1)	9208(1)	700(1)	39(1)
Cl(5)	1095(1)	7781(1)	231(1)	37(1)
C(1)	1312(2)	8710(2)	2044(2)	27(1)
C(2)	2709(2)	7830(2)	2453(2)	28(1)
C(3)	2642(2)	7243(2)	3495(2)	28(1)
C(4)	1290(3)	7725(2)	3832(2)	29(1)
C(5)	519(3)	8620(2)	3005(2)	28(1)
C(6)	3967(3)	7705(3)	1795(2)	43(1)
C(7)	3792(3)	6282(2)	4218(2)	43(1)
C(8)	900(3)	7272(2)	4950(2)	43(1)
C(9)	−868(3)	9420(2)	2997(2)	42(1)
Si(3)	−4683(1)	7074(1)	7120(1)	28(1)
Si(4)	−3430(1)	6751(1)	8699(1)	25(1)
Cl(6)	−5534(1)	5701(1)	7382(1)	56(1)
Cl(7)	−6450(1)	8378(1)	6662(1)	44(1)
Cl(8)	−3411(1)	7313(1)	5885(1)	39(1)
Cl(9)	−2005(1)	5247(1)	9173(1)	43(1)
Cl(10)	−5071(1)	6500(1)	9720(1)	41(1)
C(10)	−2462(2)	7876(2)	8648(2)	26(1)
C(11)	−1453(3)	8029(2)	7775(2)	29(1)
C(12)	−2088(3)	8968(2)	6938(2)	30(1)
C(13)	−3457(3)	9501(2)	7210(2)	30(1)
C(14)	−3667(2)	8904(2)	8230(2)	28(1)
C(15)	6(3)	7256(2)	7868(3)	46(1)
C(16)	−1508(4)	9437(2)	5871(2)	46(1)
C(17)	−4425(3)	10556(2)	6446(2)	48(1)
C(18)	−4866(3)	9202(2)	8849(2)	43(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

seems to be **13**. This compound shows better CVD relevant properties than the well known **18**, already used in the plasma-enhanced CVD process [18]. Deposition temperatures are lower for **13** than for **18**. Both precursors guarantee the deposition of films without carbon incorporation due to the pronounced leaving group character and stability of the resulting Me$_5$C$_5$ fragment. The Me$_5$C$_5$ substituted silicon precursor have already been successfully applied in the preparation of metal/silicon multilayers [19–21,24] and in the formation of a siloxene like material by deposition of silicon in nanoporous aluminum oxide membranes [22,23] as well as in the deposition of SiO$_2$ [18,19] and of Si$_3$N$_4$ [18].

4. Experimental

4.1. General data

All manipulations were carried out under purified argon atmosphere using standard vacuum techniques.

The solvents were purified by conventional means and distilled prior to use. Si$_2$Cl$_6$ and LiAlH$_4$ are commercially available and used without further purification. HSiCl$_3$, (CH$_3$)$_3$SiCl and SiCl$_4$ were distilled prior to use. Pentamethylcyclopentadiene [25], ethyltetramethylcyclopentadiene [26], tetramethylcyclopentadiene [27],

Table 7
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U(iso) or U(eq) [a]($\text{Å}^2 \times 10^3$] for **9**

	x	y	z	U(eq)
Si(1)	6929(1)	187(1)	7082(1)	27(1)
Si(2)	7422(1)	−1531(1)	6085(1)	36(1)
Si(3)	7579(1)	1619(1)	8928(1)	35(1)
Cl(1)	5292(1)	−358(1)	7202(1)	60(1)
Cl(2)	6886(1)	2289(1)	6504(1)	55(1)
Cl(3)	6254(1)	−1277(2)	5055(1)	47(1)
Cl(4)	8958(1)	−1072(2)	5747(1)	61(1)
Cl(5)	7364(1)	−3749(1)	6454(1)	63(1)
C(1)	7872(3)	186(4)	8087(2)	29(1)
C(2)	9043(2)	388(4)	7902(2)	32(1)
C(3)	9662(3)	−897(4)	8105(2)	42(1)
C(4)	8930(3)	−2026(4)	8415(2)	47(1)
C(5)	7879(3)	−1417(4)	8401(2)	37(1)
C(6)	6109(5)	1337(12)	9211(4)	45(1)
C(7)	7791(8)	3681(8)	8563(5)	45(1)
C(8)	8679(9)	1287(16)	9854(6)	49(3)
Si(1′)	8038(7)	−165(10)	7917(5)	54(2)
Si(2′)	7579(1)	1619(1)	8928(1)	35(1)
Si(3′)	7422(1)	−1531(1)	6085(1)	36(1)
Cl(1′)	9668(6)	328(8)	7792(4)	73(2)
Cl(2′)	8080(7)	2221(10)	8482(5)	77(2)
Cl(3′)	7566(12)	3708(19)	8512(10)	71(4)
Cl(4′)	6099(15)	1027(23)	9259(12)	88(5)
Cl(5′)	8734(17)	1286(23)	9901(12)	67(5)
C(1′)	7141(15)	−217(21)	6876(14)	45(5)
C(2′)	5971(16)	−390(19)	7125(12)	49(4)
C(3′)	5360(17)	949(26)	6945(17)	75(7)
C(4′)	6126(16)	2017(20)	6640(13)	55(5)
C(5′)	7102(15)	1426(23)	6591(14)	56(5)
C(6′)	8930(21)	−592(21)	5741(15)	22(4)
C(7′)	7860(12)	−3620(19)	6474(10)	22(3)
C(8′)	6345(21)	−1628(25)	5155(15)	21(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8
Si–Si and Si–C bond lengths of **6**, **7** and **9** and in other compounds

	Si–Si (Å)	Si–C(1) (Å)
6	2.327(3)	1.893(7)
7	2.336(2)	1.866(2)
9	2.3357(13)	1.846(3)
Si$_2$Cl$_6$ [9]	2.330	
C$_5$(Si$_2$Me$_5$)$_4$H$_2$ [8]	2.341(3)	1.920(5)
Me$_5$C$_5$SiCl$_3$ [10]		1.867(3)
(Me$_5$C$_5$)$_2$SiCl$_2$ [7]		1.885(5)
Me$_5$C$_5$(CO)$_2$(Me$_3$P)WSi$_2$Cl$_5$ [11]	2.350(3)	
(H$_5$C$_5$)$_2$MoH(SiCl$_2$SiCl$_3$) [12]	2.3394(10)	

Table 9
Deposition conditions of the CVD experiments

	Precursor temperature (°C)	Vapor pressure (mbar)	Minimum temperature for film deposition (°C)
EtMe$_4$C$_5$SiH$_3$ (**10**)	0	0.15	580
Me$_4$C$_5$HSiH$_3$ (**11**)	0	0.1	570
Me$_3$C$_5$H$_2$SiH$_3$ (**12**)	0	1.3	(up to 550 no Si deposition)
Me$_5$C$_5$SiH$_2$SiH$_3$ (**13**)	0	0.05	460
EtMe$_4$C$_5$SiH$_2$SiH$_3$ (**14**)	0–10	0.1	500–520
Me$_4$C$_5$HSiH$_2$SiH$_3$ (**15**)	0	0.3	500–520
Me$_3$C$_5$H$_2$SiH$_2$SiH$_3$ (**16**)	0	0.5–0.6	490–500
Me$_3$SiC$_5$H$_4$SiH$_2$SiH$_3$ (**17**)	0	0.3–0.6	500–520
Me$_5$C$_5$SiH$_3$ (**18**) [7,14]	0	0.3	550

trimethylcyclopentadiene, [28] trimethylsilylcyclopentadiene [29] were prepared as described in the literature. The elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld and the Microanalytical Laboratory BELLER in Göttingen.

The NMR spectra were recorded in C$_6$D$_6$, toluene-d_8 or CDCl$_3$ using a Bruker Avance DRX 500 spectrometer ([1]H 500.1 MHz; [13]C{[1]H} 125.8 MHz, [29]Si 99.36 MHz), Bruker AM 300 ([1]H 300.13 MHz; [13]C 75.47 MHz; [29]Si 59.60 MHz). Chemical shifts are reported in ppm and are referenced to the residual protons in C$_6$D$_6$, C$_7$D$_8$, CDCl$_3$ (^{1}H, ^{13}C) as internal standard and tetramethylsilane ([29]Si) as external standard. IR data were collected using a Bruker Vektor 22 spectrometer. The samples were measured as KBr pellets or in solution between KBr windows. Mass spectrometry was performed using a VG Autospec spectrometer (70 eV EI, 200 μA emission). Only characteristic fragments and isotopes of the highest abundance are listed.

4.1.1. Hot-wall CVD

The experiments were carried out using an externally thermostated quartz reactor [3] (15 mm diameter and 355 mm length) which was evacuated to a base pressure of 10^{-3} mbar. The reactor was heated independently of the precursor evaporator. All manipulations were performed in an atmosphere of dry argon, and no carrier gas was used during the depositions. Deposition was continued until all of the precursor was evaporated.

4.2. General procedure for the synthesis of cyclopentadienylchlorosilanes (1–4)

A suspension of Cp′M in THF is added dropwise to a cooled solution of SiH$_y$Cl$_{4-y}$ in THF (0°C). The solution is allowed to warm up to room temperature (r.t.) and stirred for 2 h. Volatile compounds are removed in vacuo (15 Torr), and the residue is dissolved in hexane. After filtration and evaporation of the solvent, the product can be recrystallized from pentane at −70°C (**1**, **2**, **3**), or distilled (**4**).

4.2.1. Dichloro(ethyltetramethylcyclopentadienyl)silane (1)

EtMe$_4$C$_5$Li (8.50 g, 54.4 mmol); 175 ml THF; 17.6 g (130 mmol) HSiCl$_3$; 50 ml hexane; crystallization from 150 ml pentane at −70°C; mp.: −10°C; yield: 12.2 g (48.9 mmol) 90%. ^{1}H-NMR (CDCl$_3$): $\delta = 0.73$ (t, $^3J_{HH} = 7.4$ Hz, 3H, CH$_2$CH$_3$), 1.81 (s, 6H, ring-CH$_3$), 1.91 (s, 6H, ring-CH$_3$), 2.21 (q, $^3J_{HH} = 7.4$ Hz, 2H, CH$_2$), 3.96 (s, $^1J_{SiH} = 312$ Hz, 1H, SiH). ^{13}C-NMR (CDCl$_3$): $\delta = 11.3, 11.5, 11.7$ (CH$_3$), 18.7 (CH$_2$), 129.1 (br, ring-C). ^{29}Si-NMR (CDCl$_3$): $\delta = -7.5$. MS (EI) m/z (%): 248 (44) [M$^+$], 233 (12) [M$^+$ − CH$_3$], 213 (37) [M$^+$ − Cl], 150 (64) [M$^+$ − SiCl$_2$], 135 (100) [M$^+$ − SiCl$_2$ − CH$_3$]. IR: ν (Si–H) = 2223, 2193 cm^{-1}. Anal. Calc. for C$_{11}$H$_{18}$Cl$_2$Si (249.26) C, 53.01; H, 7.28. Found: C, 52.34; H, 7.26%.

4.2.2. Dichloro(tetramethylcyclopentadienyl)silane (2)

Me$_4$C$_5$HLi (34.6 g, 270 mmol); 800 ml THF; 75.9 g (560 mmol) HSiCl$_3$; 200 ml pentane; crystallization from 150 ml pentane (−70°C); colorless solid; yield: 36.3 g (164 mmol) 61%. ^{1}H-NMR (C$_6$D$_6$): $\delta = 1.65$ (s, 6H, CH$_3$), 1.86 (s, 6H, CH$_3$), 3.12 (br. s, 1H, allyl-H), 4.66 (br, s, $^1J_{SiH} = 298$ Hz, 1H, SiH). ^{13}C-NMR (C$_6$D$_6$): $\delta = 11.4, 14.7$ (vinyl CH$_3$), 48.5 (allyl Cp-C), 140.6 (br, vinyl Cp-C). ^{29}Si-NMR (C$_6$D$_6$): $\delta = -0.6$. MS (EI) m/z (%): 220 (6) [M$^+$], 185 (4) [M$^+$ − Cl], 149 (2) [M$^+$ − 2 × ClH], 122 (100) [M$^+$ − SiCl$_2$], 107 (45) [M$^+$ − SiCl$_2$ − CH$_3$]. IR: ν (Si–H) = 2247 (m) cm^{-1}. Anal. Calc. for C$_9$H$_{14}$Cl$_2$Si (221.20) C, 48.87; H, 6.38. Found: C, 49.41; H, 6.80%.

4.2.3. Trichloro(tetramethylcyclopentadienyl)silane (3)

Me$_4$C$_5$HLi (34.6 g, 270 mmol); THF; 91.5 g (560 mmol) SiCl$_4$; 200 ml hexane; recrystallization from pentane (−70°C); colorless solid; yield: 45.8 g (179 mmol) 66%; mp.: 18°C. ^{1}H-NMR (CDCl$_3$): $\delta =$ vinyl-isomer: 1.20 (d, $^3J_{HH} = 7.6$ Hz, 3H, allyl-CH$_3$,), 1.79 (s, 3H, CH$_3$), 1.89 (s, 3H, CH$_3$), 2.18 (d, $^4J_{HH} = 2.1$ Hz, 3H, CH$_3$), 3.08 (m, 1H, allyl-H); allyl-isomer: 1.83 (s, 6H, CH$_3$), 2.03 (s, 6H, CH$_3$), 3.28 (br, s, 1H, allyl-H). ^{13}C-NMR (CDCl$_3$): $\delta = 10.6, 11.4, 12.3, 14.1, 14.9, 15.4$

(CH_3), 53.7, 57.7 (allyl Cp–C), 128.5, 131.6, 135.5, 141.5, 151.8, 162.1 (vinyl Cp–C). ^{29}Si-NMR (CDCl$_3$): $\delta = -6.6$, 4.2. Anal. Calc. for $C_9H_{13}Cl_3Si$ (255.65) C, 42.28; H, 5.13; Found: C, 42.56; H, 5.07%.

4.2.4. Dichloro(trimethylcyclopentadienyl)silane (4)

Me$_3$C$_5$H$_2$Li (5.20 g, 45.6 mmol); 150 ml THF; 14.9 g (110 mmol) HSiCl$_3$; 30 ml hexane; purification by distillation; b.p.: 83°C at 9 Torr; yield: 6.80 g (32.8 mmol) 72%. ^{1}H-NMR (C$_6$D$_6$): $\delta = 1.76$ (s, 6H, ring-CH_3), 1.92 (s, 3H, ring-CH_3), 3.18 (br, s, 1H, CpH), 4.71 (s, $^1J_{SiH} = 303$ Hz, 1H, SiH), 5.70 (br, s, 1H, CpH). ^{13}C-NMR (C$_6$D$_6$): $\delta = 13.2$, 15.8 (CH_3), 58.3 (br, allyl-C), 130.9 (vinyl-CH), 135.1, 140.2 (br, vinyl-CMe). ^{29}Si-NMR (CDCl$_3$): $\delta = 0.5$. MS (EI) m/z (%): 206 (9) [M$^+$], 171 (3) [M$^+ -$ Cl], 135 (1) [M$^+ -$ 2 × Cl–H], 108 (100) [M$^+ -$ SiCl$_2$], 93 (85) [C$_7$H$_9^+$], 91 (94) [C$_7$H$_7^+$]. IR: v (Si–H) = 2243 cm^{-1}.

4.3. General procedure for the synthesis of pentachloro(cyclopentadienyl)disilanes (5–9)

A suspension of Cp′M in hexane is added dropwise to a cooled ($-90°C$) solution of hexachlorodisilane in hexane. The solution is allowed to warm up to r.t. and is stirred for 18 h. After filtration and evaporation of the solvent, the residue can be recrystallized from hexane 5, 6, 7, 9 or distilled 8 to yield a colorless solid or a pale yellow liquid, which is sensitive against air and moisture.

4.3.1. Pentachloro(pentamethylcyclopentadienyl)disilane (5)

Si$_2$Cl$_6$ (14.0 g, 52.0 mmol) $-90°C$; 300 ml hexane; suspension of 8.70 g (50.0 mmol) Me$_5$C$_5$K in 230 ml hexane; recrystallization from hexane; colorless, air sensitive solid; sublimation 80°C at 0.06 mbar; yield: 10.04 g (27.0 mmol) 54%. ^{1}H-NMR (C$_6$D$_6$): $\delta = 1.61$ (s, 15H, C$_5$(CH_3)$_5$). ^{1}H-NMR (toluene-d_8, $-70°C$): $\delta = 1.10$ (s, 3H, allylic CH_3), 1.61, 1.81 (s, 12H, vinylic CH_3). ^{13}C-NMR (C$_6$D$_6$): $\delta = 11.8$ (C$_5$(CH$_3$)$_5$). ^{29}Si-NMR (CDCl$_3$): $\delta = -0.9$ (Me$_5$C$_5$SiCl$_2$–), -8.3 (–SiCl$_3$). IR (Nujol): $v = 573$, 450 cm^{-1} (–SiCl$_3$), 542, 530 cm^{-1} (–SiCl$_2$–). MS (EI) m/z (%): 366 (7) [M$^+$], 233 (41) [M$^+ -$ SiCl$_3$], 135 (100) [M$^+ -$ Si$_2$Cl$_5$], 105 (20) [C$_8$H$_9^+$]. Anal. Calc. for C$_{10}$H$_{15}$Cl$_5$Si$_2$ (368.58): C, 32.58; H, 4.10. Found: C, 32.61; H, 4.08%.

4.3.2. Pentachloro(ethyltetramethylcyclopentadienyl)-disilane (6)

Si$_2$Cl$_6$ (12 ml, 69.6 mmol); 150 ml hexane; $-90°C$; suspension of 8.1 g (52.0 mmol) EtMe$_4$C$_5$Li in 150 ml hexane; r.t. 16 h; recrystallization from hexane at $-30°C$; colorless, air sensitive solid, yield: 4.02 g (11 mmol) 20%. ^{1}H-NMR (C$_6$D$_6$): $\delta = 0.43$ (br, s, 3H, CH_3), 1.64 (s, 6H, 2 × CH$_3$), 1.76 (s, 6H, 2 × CH$_3$),

2.01–2.05 (q, 2H, $^3J_{HH} = 7.3$ Hz, CH_2). ^{13}C-NMR (CDCl$_3$, $-50°C$): $\delta = 8.7$ (CH_3), 12.1, 12.3 (CH_3), 18.6 (CH_2), 63.5 (allylic C), 132.5, 144.2 (ring C). ^{29}Si-NMR (C$_6$D$_6$): $\delta = -0.5$ (–SiCl$_2$–SiCl$_3$), -8.7 (SiCl$_2$–SiCl$_3$). IR (KBr): $v = 578$, 570, 463, 415 cm^{-1} (–SiCl). MS (EI) m/z (%): 380 (12) [M$^+$], 365 (5) [M$^+ -$ CH$_3$], 345 (4) [M$^+ -$ Cl], 247 (39) [M$^+ -$ SiCl$_3$], 149 (100) [M$^+ -$ Si$_2$Cl$_5$]. Anal. Calc. for C$_{11}$H$_{17}$Cl$_5$Si$_2$ (382.69): C, 34.52; H, 4.48. Found: C, 34.66; H, 4.56%.

4.3.3. Pentachloro(tetramethylcyclopentadienyl)disilane (7)

Si$_2$Cl$_6$ (28.2 g, 105.0 mmol); $-90°C$; 150 ml hexane; suspension of 10.4 g 80.0 mmol Me$_4$HC$_5$Li in 200 ml hexane; r.t. 20 h; recrystallization from hexane at $-30°C$; colorless air sensitive solid; yield: 19.81 g (55.9 mmol) (70%). ^{1}H-NMR (toluene-d_8, 80°C): $\delta = 1.66$ (s, 6H, 2 × CH_3), 1.85 (s, 6H, 2 × CH_3), 3.57 (s, 1H, allyl CpH). ^{1}H-NMR (toluene-d_8, 20°C): $\delta = 1.62$ (s, 6H, 2 × CH_3), 1.85 (s, 6H, 2 × CH_3), 2.5–3.6 (s, 1H, allyl CpH). ^{1}H-NMR (toluene-d_8, $-80°C$): $\delta = 1.48$ (s, 6H, 2 × CH_3), 1.81 (s, 6H, 2 × CH_3), 2.19 (s, 1H, allyl CpH). ^{13}C-NMR (toluene-d_8 80°C): $\delta = 11.7$ (2 × CH_3), 14.1 (2 × CH_3), 143.0 (br, s, vinyl Cp–C). ^{13}C-NMR (toluene-d_8 20°C): $\delta = 11.7$ (2 × CH_3), 14.1 (2 × CH_3), 57.9 (allyl Cp–C), 143.5 (br, s, vinyl Cp–C). ^{13}C-NMR (toluene-d_8 $-80°C$): $\delta = 11.8$ (2 × CH_3), 14.0 (2 × CH_3), 56.7 (allyl Cp–C), 143.7 (br, vinyl Cp–C). ^{29}Si-NMR (C$_6$D$_6$): $\delta = -0.9$ (–SiCl$_2$–SiCl$_3$), -6.9 (SiCl$_2$–SiCl$_3$). IR (KBr): $v = 2919$, 2861, 2748 cm^{-1} (CH$_3$), 570, 457 cm^{-1} (–SiCl). MS (EI) m/z (%): 352 (10) [M$^+$], 317 (3) [M$^+ -$ Cl], 219 (61) [M$^+ -$ SiCl$_3$], 121 (100) [M$^+ -$ Si$_2$Cl$_5$], 105 (41) [C$_8$H$_9^+$]. Anal. Calc. for C$_9$H$_{13}$Cl$_5$Si$_2$ (354.64): C, 30.48; H, 3.69. Found: C, 30.57; H, 3.95%.

4.3.4. Pentachloro(trimethylcyclopentadienyl)disilane (8)

Si$_2$Cl$_6$ (10 ml, 58.0 mmol); 150 ml hexane; -90 °C; suspension of 4.86 g (42.6 mmol) Me$_3$C$_5$H$_2$Li in 150 ml hexane; 16 h at r.t.; distillation; b.p.: 72°C at 0.15 mbar; yellow liquid; yield: 10.3 g (30.2 mmol) (71%). ^{1}H-NMR (toluene-d_8 + 80°C): $\delta = 1.77$ (s, 6H, 2 × CH_3), 1.88 (s, 3H, CH_3), 4.0–5.56 (br, m, 2H, vinyl CpH) ^{1}H-NMR (toluene-d_8 + 20°C): $\delta = 1.75$ (br, s, 6H, 2 × CH_3), 1.88–1.89 (br, s, 3H, CH_3), 2.5–3.9 (br, s, 1H, allyl CpH), 5.45–6.40 (br, m, 1H, vinyl CpH). ^{1}H-NMR (toluene-d_8 $-40°C$): (5-pentachlorodisilanyl-2,3,5-trimethylcyclopentadiene) (**A**) $\delta = 1.67$, 1.85, 1.98 (3 × s, 9H, 3 × CH_3), 2.65 (1H, allyl CpH), 5.93 (s, 1H, vinyl CpH). (5-pentachlorodisilanyl-1,2,4-trimethylcyclopentadiene) (**B**) $\delta = 1.26$ (s, 3H, CH_3), 1.67 (s, 6H, 2 × CH_3), 5.76 (s, 2H, vinyl CpH). ^{1}H-NMR (toluene-d_8 $-80°C$): (**A**) $\delta = 1.67$, 1.84, 1.97 (3 × s, 9H, 3 × CH_3), 2.30 (1H, allyl CpH), 5.85 (s, 1H, vinyl CpH). (**B**) $\delta = 1.24$ (s, 3H, CH_3), 1.63 (s, 6H, 2 × CH_3), 5.65 (s, 2H, vinyl CpH). ^{13}C-NMR (C$_6$D$_6$): $\delta = 13.7$ (2 ×

CH_3), 15.9 (CH_3), 59.5 (br, s, allyl Cp–*C*), 137.9, 143.0 (vinyl Cp–*C*) ^{13}C-NMR (toluene-d_8, −40°C): (**A**) $\delta = 13.1$, 14.0 ($2 \times CH_3$), 16.2 (CH_3), 58.2 (allyl Cp–*C*), 130.5, 131.6, 138.3, 142.2 (vinyl Cp–*C*). (**B**) $\delta = 12.2$ ($2 \times CH_3$), 14.5 (CH_3), 55.0 (allyl Cp–*C*), 131.3, 148.2 (vinyl Cp–*C*). ^{13}C-NMR (toluene-d_8, −80°C): (**A**) $\delta = 13.1$, 14.0 ($2 \times CH_3$), 16.3 (CH_3), 57.6 (allyl Cp–*C*), 130.5, 131.7, 138.1, 142.2 (vinyl Cp–*C*). (**B**) $\delta = 12.0$ ($2 \times CH_3$), 14.8 (CH_3), 55.0 (allyl Cp–*C*), 131.3, 148.2 (vinyl Cp–*C*). ^{29}Si-NMR (C_6D_6): $\delta = -1.0$ (–*Si*Cl$_2$–SiCl$_3$), −5.0 (SiCl$_2$–*Si*Cl$_3$). ^{29}Si-NMR (toluene-d_8, −80°C): (**A**) $\delta = -0.8$ (–*Si*Cl$_2$–SiCl$_3$), −7.0 (SiCl$_2$–*Si*Cl$_3$).(**B**) $\delta = -0.1$ (–*Si*Cl$_2$–SiCl$_3$), −6.4 (SiCl$_2$–*Si*Cl$_3$). IR (liquid; KBr): $\nu = 2969$, 2920, 2861 cm^{-1} (CH_3), 571, 529, 456, 440 cm^{-1} (–SiCl). MS (EI) m/z (%): 338 (31) [M$^+$], 303 (38) [M$^+$ − Cl], 240 (6) [M$^+$ − SiCl$_2$], 205 (71) [M$^+$ − SiCl$_3$], 107 (100) [M$^+$ − Si$_2$Cl$_5$]. Anal. Calc. for $C_8H_{11}Cl_5Si_2$ (340.61): C, 28.21; H, 3.26. Found: C, 28.14; H, 3.12%.

4.3.5. Pentachloro(trimethylsilylcyclopentadienyl)disilane (**9**)

Si$_2$Cl$_6$ (12 ml, 69.6 mmol); 150 ml hexane; from −70 to −90°C; suspension of 7.51 g (52.1 mmol) CpSiMe$_3$Li; r.t. 20 h; distillation; b.p.: 66°C at 0.2 mbar; pale yellow liquid; at r.t. colorless solid; yield: 13.73 g (37 mmol) (71%). ^{1}H-NMR (C_6D_6): (main isomer): $\delta = -0.06$ (s, 9H, Si(CH_3)$_3$), 6.38–6.39 (d, 2H, $^3J_{HH} = 4.2$ Hz, vinyl Cp*H*), 6.66–6.67 (d, 2H, $^3J_{HH} = 4.2$ Hz, vinyl Cp*H*); (other isomers): $\delta = -0.23$ (s, 9H, Si(CH_3)$_3$), 3.2 (1H, allyl Cp*H*), 6.5 (m, vinyl Cp*H*), 6.60 (m, vinyl Cp*H*) ^{1}H-NMR (toluene-d_8, 80°C): $\delta = -0.12$–0.04 (br, s, 9H, Si(CH_3)$_3$), 6,46 (br, s, 2H, vinyl Cp*H*), 6.70 (br, s, 2H, vinyl Cp*H*). ^{13}C-NMR (C_6D_6): $\delta = -1.3$ (Si(CH_3)$_3$), 59.7 (allyl Cp–*C*), 132.3, 137.5 (vinyl Cp–*C*). ^{29}Si-NMR (C_6D_6): $\delta = 4.0$ (*Si*(CH_3)$_3$), −1.2 (–*Si*Cl$_2$–SiCl$_3$), −6.5 (SiCl$_2$–*Si*Cl$_3$).). IR (KBr): $\nu = 579$, 520, 432 cm^{-1} (–SiCl). MS (EI) m/z (%): 368 (1) [M$^+$], 333 (0.5) [M$^+$ − Cl], 73 [(H$_3$C)$_3$Si$^+$]. Anal. Calc. for $C_8H_{13}Cl_5Si_3$ (370.71): C, 25.92; H, 3.53. Found: C, 25.58; H, 3.59%.

4.4. General procedure for the synthesis of cyclopentadienylsilanes (**10**–**12**)

A solution of the chlorosilanes **1**–**4** in diethylether is added dropwise at 0°C to a suspension of LiAlH$_4$ in diethylether. The reaction mixture is allowed to warm up to r.t. and is stirred for 2 h. The solvent is removed under reduced pressure (50 Torr) and the residue is dissolved in hexane. After filtration the solvent is removed under reduced pressure. The remaining liquid is distilled to give the products in high yields.

4.4.1. (Ethyltetramethylcyclopentadienyl)silane (**10**)

EtMe$_4$C$_5$SiHCl$_2$ (**1**) (11.0 g, 44.1 mmol); 50 ml Et$_2$O; 1.68 g (44.3 mmol) LiAlH$_4$; 95 ml Et$_2$O; distillation; b.p.: 80°C at 15 Torr; yield: 7.00 g (38.8 mmol) 88%. ^{1}H-NMR (toluene d_8, −40°C): $\delta = 0.39$ (t, $^3J_{HH} = 7.2$ Hz, 3H, CH$_2$C*H*$_3$), 1.75 (q, $^3J_{HH} = 7.2$ Hz, 2H, C*H*$_2$), 1.82 (s, 6H, ring-C*H*$_3$), 1.90 (s, 6H, ring-C*H*$_3$), 3.59 (s, $^1J_{SiH} = 198$ Hz, 3H, Si*H*$_3$). ^{1}H-NMR (C_6D_6, 60°C): $\delta = 0.67$ (br, s, 3H, CH$_2$C*H*$_3$), 1.69 (s, 6H, ring-C*H*$_3$), 1.79 (s, 6H, ring-C*H*$_3$), 2.03 (br, s, 2H, C*H*$_2$), 3.52 (s, $^1J_{SiH} = 199$ Hz, 3H, Si*H*$_3$). ^{13}C-NMR (C_6D_6, 60°C): $\delta = 11.1$, 11.6, 14.7 (CH_3), 20.8 (CH_2); (ring-C atoms are not detected) ^{29}Si-NMR (C_6D_6): $\delta = -41.3$. MS (EI) m/z (%): 180 (100) [M$^+$], 165 (37) [M$^+$ − CH$_3$], 151 (37) [M$^+$ − CH$_2$CH$_3$], 150 (34) [M$^+$ − 2 × CH$_3$, EtC$_5$H$^+$], 149 (80) [M$^+$ − SiH$_3$], 133 (71) [M$^+$ − CH$_4$ − SiH$_3$], 119 (65) [M$^+$ − 2 × CH$_3$ − SiH$_3$]. IR: ν (Si–H) = 2170 (m), 2134 (s) cm^{-1}. Anal. Calc. $C_{11}H_{20}Si$ (180.37) C, 73.25; H, 11.17. Found: C, 73.32; H, 11.28%.

4.4.2. (Tetramethylcyclopentadienyl)silane (**11**)

Me$_4$C$_5$HSiHCl$_2$ (**2**) (30.0 g, 136 mmol); 165 ml Et$_2$O; 5.20 g (137 mmol) LiAlH$_4$; 300 ml Et$_2$O; purification by distillation; b.p.: 66–67°C at 15 Torr; yield: 15.5 g (102 mmol) 75%. Alternatively: 35.0 g (137 mmol) Me$_4$C$_5$HSiCl$_3$ (**3**); 175 ml Et$_2$O; 5.20 g LiAlH$_4$; 350 ml Et$_2$O yield: 16.3 g (107 mmol) 78%. ^{1}H-NMR (C_6D_6): $\delta = 1.75$ (s, 6H, C*H*$_3$), 1.90 (s, 6H, C*H*$_3$), 2.56 (m, 1H, allyl-*H*), 3.56 (d, $^2J_{HH} = 3.1$ Hz, $^1J_{SiH} = 201$ Hz, 3H, Si*H*$_3$). ^{13}C-NMR (C_6D_6): $\delta = 11.3$ (CH_3), 12.9 (CH_3), 47.0 (allyl Cp–*C*), 133.2, 136.0 (vinyl Cp–*C*). ^{29}Si-NMR (C_6D_6): $\delta = -52.1$(*Si*H$_3$). MS (EI) m/z (%): 152 (100) [M$^+$], 149 (24) [M$^+$ − 3 × H], 137 (35) [M$^+$ − CH$_3$], 121 (90) [M$^+$ − SiH$_3$]. IR: ν (Si–H) = 2146 (m) cm^{-1}. Anal. Calc. for $C_9H_{16}Si$ (152.31) C, 70.97; H, 10.59. Found: C, 70.84; H, 10.73%.

4.4.3. (Trimethylcyclopentadienyl)silane (**12**)

Me$_3$C$_5$H$_2$SiHCl$_2$ (**4**) (2.50 g, 12.1 mmol); 15 ml Et$_2$O; 0.46 (12.1 mmol) LiAlH$_4$; 15 ml Et$_2$O; purification by distillation; b.p.: 60°C at 25 Torr; yield: 1.45 g (10.5 mmol) 87%. ^{1}H-NMR (C_6D_6): $\delta = 1.81$(s, 3H, C*H*$_3$), 1.87(s, 3H, C*H*$_3$), 1.97 (s, 3H, C*H*$_3$), 2.59 (s, 1H, allyl-*H*), 3.54 (d, $^1J_{SiH} = 202$ Hz, $^3J_{HH} = 2.3$ Hz, 3H, Si*H*$_3$), 6.03 (s, 1H, vinyl-*H*). ^{13}C-NMR (C_6D_6): $\delta = 12.7$ (CH_3), 15.4 (CH_3), 48.0 (allyl-*C*), 131.3 (vinyl-*C*H), 134.3, 134.8, 141.2 (vinyl-*C*Me). ^{29}Si-NMR (C_6D_6): $\delta = -50.1$. MS (EI) m/z (%): 138 (100) [M$^+$], 123 (74) [M$^+$ − CH$_3$], 107 (95) [M$^+$ − SiH$_3$], 93 (39) [C$_7$H$_9^+$], 91 (74) [C$_7$H$_7^+$]. IR: ν (Si–H) = 2149 cm^{-1}. Anal. Calc. for $C_8H_{14}Si$ (138.29) C, 69.48; H, 10.20. Found: C, 70.39; H, 10.72%.

4.5. General procedure for the synthesis of cyclopentadienyldisilanes (13–17)

A solution of the pentachloro(cyclopentadienyl)disilane in diethylether is added dropwise at 0°C to a suspension of LiAlH$_4$ in diethylether. The reaction mixture is allowed to warm up to r.t. and is stirred for 2 h. The solvent is removed under reduced pressure (30 Torr), and the residue is dissolved in hexane. After filtration the solvent is removed under reduced pressure. The remaining liquid is distilled to give the product in high yields.

4.5.1. (Pentamethylcyclopentadienyl)disilane (13)

LiAlH$_4$ (2.30 g, 61.0 mmol); 100 ml Et$_2$O; 0°C; 8.87 g (24.0 mmol) Me$_5$C$_5$Si$_2$Cl$_5$ (5) in 80 ml Et$_2$O; 3 h at r.t.; distillation b.p.: 70°C at 6 mbar; colorless liquid; yield: 3.48 g (18.0 mmol) (74%). ^{1}H-NMR (CDCl$_3$): $\delta = 1.56–1.84$ (s, 15H, C$_5$(CH$_3$)$_5$), 2.60 (s, 3H, $^1J_{SiH} = $ 195 Hz, –SiH$_3$), 3.88 (s, 2H, $^1J_{SiH} = 195$ Hz, –SiH$_2$–).^{1}H-NMR (CDCl$_3$, 0°C): $\delta = 1.30$ (br, s, 3H, allyl CH$_3$), 1.76–1.82 (s, 12H, vinyl CH$_3$), 2.52–2.54 (m, 3H, –SiH$_3$), 3.83–3.85 (m, 2H, –SiH$_2$–). ^{1}H-NMR (CDCl$_3$, −10°C): $\delta = 1.29$ (br, s, 3H, allyl CH$_3$), 1.76–1.81 (s, 12H, vinyl CH$_3$), 2.52–2.53 (m, 3H, SiH$_3$), 3.83–3.85 (m, 2H, –SiH$_2$–).^{1}H-NMR (CDCl$_3$, −20°C): $\delta = 1.28$ (s, 3H, allyl CH$_3$), 1.80 (s, 6H, 2 × CH$_3$), 1.86 (s, 6H, 2 × CH$_3$), 2.51–2.52 (m, 3H, –SiH$_3$), 3.83–3.84(m, 2H, –SiH$_2$–). ^{1}H-NMR (CDCl$_3$, −40°C): $\delta =$ 1.17 (s, 3H, –C(CH$_3$),.1.80 (s, 6H, –C(CH$_3$), 1.86 (s, 6H, C(CH$_3$), 2.48–2.49 (t, 3H, $^1J_{SiH} = 190$ Hz, –SiH$_3$), 3.83–3.84 (m, 2H, $^1J_{SiH} = 190$ Hz, –SiH$_2$–). ^{13}C-NMR (CDCl$_3$): $\delta = 11.1–15.6$ (C$_5$(CH$_3$)$_5$), 135.5–137.7 (C$_5$(CH$_3$)$_5$. ^{29}Si-NMR (CDCl$_3$): $\delta = −40.1$ (Me$_5$C$_5$SiH$_2$SiH$_3$) ($^1J_{SiH} = 189.1$ Hz), −102.5 (Me$_5$C$_5$SiH$_2$SiH$_3$) ($^1J_{SiH} = 194.4$ Hz) ($^2J_{SiH} = 9.5$ Hz). IR (liquid; KBr): $\nu = 2137$ cm^{-1} (–SiH$_2$), 2110 cm^{-1} (–SiH$_3$), 940, 878, 760 cm^{-1} (SiH). MS (EI) m/z (%): 196 (61) [M$^+$], 165 (100) [M$^+$ − SiH$_3$], 135 (15) [M$^+$ − Si$_2$H$_5$], 105 (20) [C$_8$H$_9^+$]. Anal. Calc. for C$_{10}$H$_{20}$Si$_2$ (196.36): C, 61.14; H, 10.26. Found: C, 61.22; H, 10.51%.

4.5.2. (Ethyltetramethylcyclopentadienyl)disilane (14)

LiAlH$_4$ (0.70 g, 18.4 mmol); 30 ml Et$_2$O; 0°C; 3.50 g (9.00 mmol) EtMe$_4$C$_5$Si$_2$Cl$_5$ (6) in 20 ml Et$_2$O; 2 h at r.t.; distillation b.p.: 72°C at 5 mbar; colorless liquid; yield: 0.49 g (2.30 mmol) (26%). ^{1}H-NMR (CDCl$_3$, −40°C): (main isomer) $\delta = 0.31–0.34$ (t, 3H, $^3J_{HH} = $ 7.3 Hz CH$_3$), 1.79 (s, 6H, 2 × CH$_3$), 1.82 (s, 6H, 2 × CH$_3$), 2.24–2.25 (q, 2H, $^3J_{HH} = 7.3$ Hz, CH$_2$), 2.48–2.49 (t, 3H,$^3J_{HH} = 2.6$ Hz, SiH$_3$), 3.77–3.78 (q, 2H, $^3J_{HH} = 2.6$ Hz, SiH$_2$); (other isomers) $\delta = 0.97–$ 0.99 (m, 3H, CH$_3$), 1.87 (s, 6H, 2 × CH$_3$), 1.89 (s, 6H, 2 × CH$_3$); (CH$_2$ not detected), 2.55–2.56 (m, 3H, SiH$_3$), 3.80 (m, 2H, SiH$_2$); ^{1}H-NMR (CDCl$_3$, 50°C): $\delta = 0.68–$

0.76 (br, s, 3H, CH$_3$), 1.76 (s, 6H, 2 × CH$_3$), 1.82 (s, 6H, 2 × CH$_3$), 2.61–2.62 (t, 3H, $^3J_{HH} = 2.6$ Hz, SiH$_3$), 3.81–3.82 (q, 2H, $^3J_{HH} = 2.6$ Hz, SiH$_2$). ^{13}C-NMR (CDCl$_3$, −40°C): $\delta = 10.6–10.7$ (CH$_3$), 11.1 (CH$_3$), 22.9 (CH$_2$), 56.4 (allyl Cp–C), 134.7, 136.1 (vinyl Cp–C). ^{29}Si-NMR (CDCl$_3$): $\delta = −43.1$ (–SiH$_2$SiH$_3$); ($^1J_{SiH} = 187.3$ Hz). − 103.4 (–SiH$_2$SiH$_3$); ($^1J_{SiH} = 194.0$ Hz) ($^2J_{Si} = 9.4$ Hz).. IR (liquid; KBr): $\nu = 2140$ cm^{-1} (–SiH), 2115, 940, 878, 758 cm^{-1}(SiH). MS (EI) m/z (%): 210 (20) [M$^+$], 180 (10) [M$^+$ − SiH$_2$], 179 (53) [M$^+$ − SiH$_3$], 177 (33) [M$^+$ − Si$_2$H$_5$], 149 (100) [C$_5$Me$_4$Et$^+$]. Anal. Calc. for C$_{10}$H$_{22}$Si$_2$ (210.47): C, 62.78; H, 10.54. Found: C, 62.58; H, 10.72%.

4.5.3. (Tetramethylcyclopentadienyl)disilane (15)

LiAlH$_4$ (3.76 g, 99.1 mmol); 100 ml Et$_2$O; 0°C; 14.1 g (39.8 mmol) Me$_4$C$_5$HSi$_2$Cl$_5$ 7 in 50 ml diethylether; 3 h at r.t.; distillation; b.p.: 71°C at 8 mbar; colorless liquid; yield: 2.33 g (12.8 mmol) (32%). ^{1}H-NMR (toluene-d_8, −80°C): $\delta = 1.77$ (s, 6H, 2 × CH$_3$), 1.88 (s, 6H, 2 × CH$_3$), 2.51 (s, 1H, allyl CpH), 2.83–2.85 (m, 3H, SiH$_3$), 4.02 (m, 2H, SiH$_2$). ^{1}H-NMR (C$_6$D$_6$): $\delta = 1.73$ (s, 6H, 2 ×), 1.84 (s, 6H, 2 × CH$_3$), 2.81–2.82 (t, 3H,$^3J_{HH} = 2.6$ Hz, SiH$_3$), 2.75–2.80 (s, 1H, allyl CpH), 3.98–3.99 (q, 2H, $^3J_{HH} = 2.6$ Hz, SiH$_2$). ^{1}H-NMR (CDCl$_3$): $\delta = 1.8$ (s, 6H, 2 ×), 1.93 (s, 6H, 2 ×), 2.63–2.64 (t, 3H,$^3J_{HH} = 2.4$ Hz, SiH$_3$), 3.09 (s, 1H, allyl CpH), 3.90–3.91 (m, 2H, SiH$_2$). ^{1}H-NMR (toluene-d_8, 80°C): $\delta = 1.71$ (s, 6H, 2 × CH$_3$), 1.84 (s, 6H, 2 × CH$_3$), 2.75–2.76 (m, 3H, SiH$_3$), 2.89–2.95 (br, s, 1H, allyl CpH), 3.91–3.92 (m, 2H, SiH$_2$). ^{13}C-NMR (toluene-d_8, −80°C): $\delta = 11.1$, 12.8 (CH$_3$) 46.6 (allyl Cp–C), 133.2, 135.9 (vinyl Cp–C). ^{13}C-NMR (C$_6$D$_6$): $\delta = 10.9$ (CH$_3$), 12.9 (CH$_3$), 47.3 (allyl Cp–C), 133.4, 136.4 (vinyl Cp–C). ^{13}C-NMR (toluene-d_8, 80°C): $\delta = 10.9$, 12.9 (CH$_3$) 48.8 (allyl Cp–C), 133.1, 136.5 (vinyl Cp–C). ^{29}Si-NMR (C$_6$D$_6$): $\delta = −54.6$ (–SiH$_2$SiH$_3$); ($^1J_{SiH} = $ 190.8 Hz). − 105.2 (–SiH$_2$SiH$_3$); ($^1J_{SiH} = 192.4$ Hz). IR (liquid; KBr): $\nu = 2967$, 2913, 2856 cm^{-1} (–CH$_3$), 2138, 940, 878, 777 cm^{-1} (–SiH). MS (EI) m/z (%): 182 (32) [M$^+$], 151 (70) [M$^+$ − SiH$_3$], 123 (100), 122 (44) [M$^+$ − Si$_2$H$_4$], 121 (36) [M$^+$ − Si$_2$H$_5$], 105 (20) [C$_8$H$_9^+$]. Anal. Calc. for C$_9$H$_{18}$Si$_2$ (182.41): C, 59.26; H, 9.95. Found: C, 59.24; H, 10.01%.

4.5.4. (Trimethylcyclopentadienyl)disilane (16)

LiAlH$_4$ (2.0 g, 52.7 mmol); 100 ml Et$_2$O; 0°C; 8.59 g (25.2 mmol) Me$_3$C$_5$H$_2$Si$_2$Cl$_5$ (8) in 50 ml Et$_2$O; r.t. 2 h; distillation; colorless, air sensitive liquid; b.p.: 53°C at 6 mbar; yield: 2.23 g (13.3 mmol) (53%). ^{1}H-NMR (toluene d_8, −80°C): $\delta = 1.78$, 1.80, 1.89 (s, 9H, 3 × CH$_3$), 2.46 (br, s, 1H, allyl CpH), 3.21–3.22 (t, 3H,$^3J_{HH} = 2.5$ Hz, SiH$_3$), 3.90 (m, 2H, SiH$_2$), 5.94 (s, 1H, vinyl CpH). ^{1}H-NMR (C$_6$D$_6$): $\delta = 1.79$, 1.80 (s, 6H, 2 × CH$_3$), 1.91 (s, 3H, CH$_3$), 2.84 (br, s, 1H, allyl CpH), 2.89–2.90 (t, 3H, $^3J_{HH} = 2.7$ Hz, SiH$_3$), 3.90 (m, 2H, SiH$_2$), 5.98 (s,

1H, vinyl CpH). ^{1}H-NMR (CDCl$_3$): δ = 1.86, 1.93 (s, 6H, 2 × CH_3), 2.04 (s, 3H, CH_3), 2.75–2.76 (t, 3H, SiH_3), 3.20 (br, s, 1H, allyl CpH), 3.89 (m, 2H, SiH_2), 6.06 (s, 1H, vinyl CpH). ^{1}H-NMR (toluene d_8, 80°C): δ = 1.78 (s, 6H, 2 × CH_3), 1.91 (s, 6H, CH_3), 2.85–2.86 (t, 3H, $^3J_{HH}$ = 2.7 Hz, SiH_3), 3.86 (m, 2H, SiH_2), 5.00–6.3 (s, 1H, vinyl CpH). ^{13}C-NMR (CDCl$_3$): δ = 12.2, 12.7 (CH_3), 15.3 (CH_3), 48.0 (allyl Cp–C), 131.1, 134.6, 135.1, 140.9 (vinyl Cp–C). ^{13}C-NMR (C$_6$D$_6$): δ = 12.3, 12.8 (CH_3), 15.3 (CH_3), 48.1 (allyl Cp–C), 131.6, 134.5, 135.2, 140.8 (vinyl Cp–C). ^{29}Si-NMR (C$_6$D$_6$): δ = −56.4 (–SiH$_2$SiH$_3$); ($^1J_{SiH}$ = 193.7 Hz), −105.5 (–SiH$_2$$SiH_3$); ($^1J_{SiH}$ = 195.0 Hz). IR (liquid; KBr): v = 3043, 2964, 2912 cm^{-1} (–CH$_3$), 2139, 2123, 940, 878, 771 cm^{-1} (–SiH). MS (EI) m/z (%): 168 (100) [M$^+$], 138 (8) [M$^+$ − SiH$_2$], 137 (54) [M$^+$ − SiH$_3$], 107 (16) [M$^+$ − Si$_2$H$_5$]. Anal. Calc. for C$_8$H$_{16}$Si$_2$ (168.39): C, 57.06; H, 9.58. Found: C, 56.83; H, 9.55%.

4.5.5. (Trimethylsilylcyclopentadienyl)disilane (17)

LiAlH$_4$ (1.66 g, 43.7 mmol); 80 ml Et$_2$O; 0°C; 7.83 g (21.1 mmol) Me$_3$SiC$_5$H$_4$Si$_2$Cl$_5$ (9); 40 ml Et$_2$O; r.t. and stirred for 2 h; distillation; colorless, air sensitive liquid; b.p.: 72°C at 12 Torr; yield: 2.60 g (13.0 mmol) (62%). ^{1}H-NMR (C$_6$D$_6$): δ = −0.04 (s, 9H, Si(CH_3)$_3$), 2.94–2.95 (t, 3H, $^3J_{HH}$ = 2.7 Hz, SiH_3), 4.02–4.04 (q, 2H, $^3J_{HH}$ = 2.7 Hz, SiH_2), 6.35 (s, 2H, vinyl CpH), 6.66 (s, 2H, vinyl CpH). ^{1}H-NMR (CDCl$_3$): δ = 0.02 (s, 9H, Si(CH_3)$_3$), 2.76–2.77 (m, 3H, SiH_3), 3.96 (m, 2H, SiH_2), 6.49 (s, 2H, vinyl CpH), 6.74 (s, 2H, vinyl CpH). ^{13}C-NMR (CDCl$_3$): δ = −2.1 (Si(CH_3)$_3$), 48.5 (allyl Cp–C), 131.1, 136.4 (vinyl Cp–C). ^{29}Si-NMR (C$_6$D$_6$): δ = 1.0 (Si(CH$_3$)$_3$), −67.5 (–SiH$_2$SiH$_3$); ($^1J_{SiH}$ = 195.3 Hz), −105.3 (–SiH$_2$$SiH_3$); ($^1J_{SiH}$ = 195.7 Hz) ($^2J_{SiH}$ = 9.8 Hz). ^{29}Si-NMR (CDCl$_3$): δ = 1.0 (Si(CH$_3$)$_3$), −67.4 (–SiH$_2$SiH$_3$), −105.3 (–SiH$_2$$SiH_3$). IR (liquid; KBr): v = 2140, 2125, 935, 863, 771, 733 cm^{-1} (–SiH). MS (EI) m/z (%): 198 (7) [M$^+$], 167 (21) [M$^+$ − SiH$_3$], 137 (17) [M$^+$ − Si$_2$H$_5$], 73 (100) [(H$_3$C)$_3$Si$^+$]. Anal. Calc. for C$_8$H$_{18}$Si$_2$ (198.49): C, 48.41; H, 9.14. Found: C, 48.68; H, 9.22%.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153990 for compond **6**, CCDC no. 153991 for compound **7**, CCDC no. 153992 for compound **9**. 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).

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