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Chemistry of decamethylsilicocene: oxidative addition of compounds with X–H bonds (X = F, Cl, Br, O, S)

Peter Jutzi, Ernst-August Bunte, Udo Holtmann, Beate Neumann and Hans-Georg Stammler

Faculty of Chemistry, University of Bielefeld, W-4800 Bielefeld (Germany)

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Abstract

In the reaction of decamethylsilicocene (**1**) with protic substrates HX, the corresponding oxidative addition products **2–9**, **11**, **12**, and **15** of the type $(\sigma\text{-Me}_5C_5)_2Si(H)X$ are formed in good yields. Reactions of the hydrogen halides HF, HCl, and HBr with **1** lead to the silanes **2**, **3** and **4**, respectively. The oxo acids trifluoroacetic acid and propionic acid react with **1** to give the compounds **5** and **6**, respectively. Phenol and *p*-methylphenol add to **1** to give the compounds **7** and **8**, respectively. In the reaction of 4-methyl-catechol with **1**, the oxidative addition product **9** is an intermediate; **9** decomposes with catalytic amounts of water or pyridine to give the *o*-phenylenedioxysilane **10a**. Compound **10b** is obtained from **1** and catechol. Treatment of **1** with cyclohexanone-oxime and ethanal-oxime leads to the addition products **11** and **12**, respectively. The six-membered heterocycles **13** and **14** are formed in the reaction of **1** with the corresponding 1,3-diketones. Oxidative addition products are postulated as intermediates; they rearrange by Cp* migration and Si–O bond formation. The silane **15** is obtained from the reaction of **1** with *p*-methyl-phenylthiol. The new compounds have been characterized by NMR, IR, and mass spectrometry, and in the case of **9**, **10b**, and **13** by an X-ray crystal structure determination as well. The mechanism of the oxidative addition processes is discussed.

1. Introduction

Decamethylsilicocene (**1**), the first silicon(II) compound to be described that is stable under ordinary conditions, can be regarded as an electronically oversaturated and hypercoordinated silylene [1]. The PES data and theoretical calculations indicate that the highest occupied molecular orbitals (HOMOs) in **1** are non-bonding with respect to cyclopentadienyl–silicon interactions, and are located at the π-bonded cyclopentadienyl systems. Lower in energy, but nevertheless still in the HOMO region, is the orbital representing the lone-pair at silicon. Hence, attack of electrophiles should take place either at the cyclopentadienyl π-system or at the silicon lone-pair. Both possibilities have been realized experimentally [2].

In this paper, we describe reactions of **1** with some representative compounds having more or less acidic X–H bonds. In all these reactions, the lone-pair on silicon is involved. As the final result, oxidative addition products with tetravalent silicon are formed, in which the pentamethylcyclopentadienyl ligands are now σ-bonded. The products possess several potential leaving groups (H, X, Me_5C_5) and are therefore of great interest for the preparative chemist. The structures of the new compounds have been elucidated by NMR and IR data and mass spectrometry (MS) and in some cases also by X-ray crystal structure determination. The reaction pathways followed by the X–H substrates in decamethylsilicocene chemistry are compared with those for the corresponding germanium, tin, and lead species.

2. Oxidative addition reactions

We first examined the reactions of decamethylsilicocene (**1**) with hydrogen halides under anhydrous conditions. As a source of hydrogen fluoride we used the pyridine complex $H_5C_5N \cdot HF$. In diethyl ether solution, **1** reacts cleanly with this substrate even at −78°C

Correspondence to: Professor P. Jutzi.

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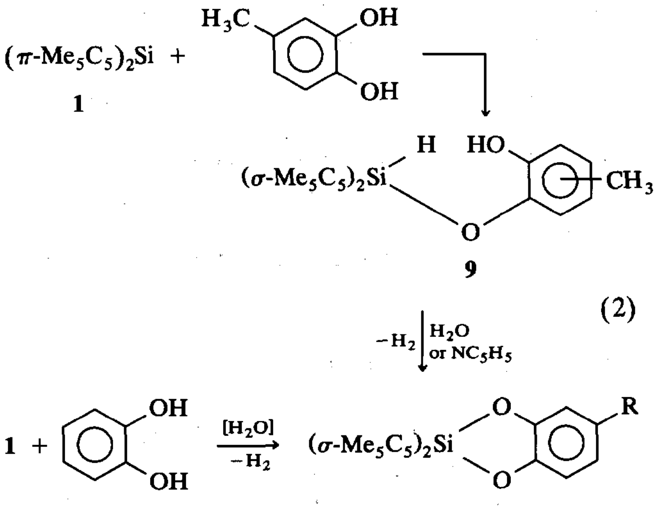
to give the oxidative addition product bis(pentamethylcyclopentadienyl)fluorosilane (**2**). Likewise, bis(pentamethylcyclopentadienyl)chlorosilane (**3**) and -bromosilane (**4**) are formed in good yields in the reaction of **1** with hydrogen chloride and hydrogen bromide, respectively (eqn. (1)). The compounds **2**, **3**, and **4** were isolated by sublimation or crystallization and characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and by MS data.

Similarly, oxo acids can be oxidatively added to **1**. As representative examples we chose the substrates trifluoroacetic acid and propionic acid. At room temperature in diethyl ether solution the compounds bis(pentamethylcyclopentadienyl)trifluoroacetatosilane (**5**) and bis(pentamethylcyclopentadienyl)propionatosilane (**6**), respectively, were formed in high yields (eqn. (1)). They were isolated by crystallization from pentane and characterized by NMR and MS data.

Next we investigated the oxidative addition reactions of **1** with substrates containing less acidic O–H bonds. In the phenol series phenol itself, *p*-methylphenol, and the *ortho*-diol 4-methylcatechol were chosen as representative examples. In toluene as solvent, the mono alcohols react within one day at room temperature to give bis(pentamethylcyclopentadienyl)phenoxysilane (**7**) and bis(pentamethylcyclopentadienyl)(p-methylphenoxy)silane (**8**), respectively, in good yields (eqn. (1)). Compounds **7** and **8** were isolated by crystallization from petroleum ether and characterized by NMR, IR, and MS data.

$$\underset{\mathbf{1}}{(\pi\text{-}Me_5C_5)_2Si} + HX \longrightarrow \underset{\mathbf{2\text{–}8}}{(\sigma\text{-}Me_5C_5)_2Si(H)X} \qquad (1)$$

(X = F (**2**), Cl (**3**), Br (**4**), F_3CCOO (**5**), H_5C_2COO (**6**), H_5C_6O (**7**), (p-CH_3)H_4C_6O (**8**))



9

(2)

10a,b
(R = CH_3 (**10a**), H (**10b**))

The oxidative addition product bis(pentamethylcyclopentadienyl)(2-hydroxy-4(5)-methyl-phenoxy)silane (**9**) was obtained in good yields from **1** and 4-methylcatechol after a one-day reaction at 0°C in toluene as solvent. Crystallization from pentane gave a nearly 1:1 mixture of the two possible isomers (eqn. (2)). Owing to the presence of OH and SiH functionalities, compound **9** is thermally unstable and decomposes easily [3*]. Nevertheless, it was possible to characterize **9** not only by NMR and IR data but also by an X-ray crystal structure determination (*vide infra*).

Addition of catalytic amounts of water or pyridine leads to a controlled decomposition of **9** with H_2-elimination and to the formation of bis(pentamethylcyclopentadienyl)(3-methyl-*ortho*-phenylenedioxy)silane (**10a**) (eqn. (2)). Compound **10a** was characterized only by NMR spectroscopy, whereas the parent compound **10b** (R = H) was isolated and characterized by an X-ray structure determination (*vide infra*). Compound **10b** is synthesized starting from **1** and catechol (eqn. (2)).

It is noteworthy that aliphatic alcohols such as methanol, ethanol, or propanol do not react with **1** under comparable conditions. Under more drastic conditions, decomposition of **1** takes place with pentamethylcyclopentadiene as the only identified product. This behaviour of **1** contrasts with that of transient silylenes (*vide infra*).

In further experiments we investigated the reactions with O–H bonds in oximes. Slightly more rigorous conditions are necessary to achieve oxidative addition. Thus, treatment of **1** with cyclohexanone-oxime and ethanal-oxime at 60°C for several hours in toluene as solvent gave good yields of the products bis(pentamethylcyclopentadienyl)(cyclohexanone-oximato)silane (**11**) and bis(pentamethylcyclopentadienyl)(ethanal-oximato)-silane (**12**), respectively (eqn. (3)). The compounds were crystallized from hexane (**11**) or petroleum ether (**12**) and characterized by NMR, IR, and MS data.

$$\underset{\mathbf{1}}{(\pi\text{-}Me_5C_5)_2Si} + R_2C{=}NOH \longrightarrow$$

$$\underset{\mathbf{11,\ 12}}{(\sigma\text{-}Me_5C_5)_2Si(H)ON{=}CR_2} \qquad (3)$$

($CR_2 = C_6H_{10}$ (**11**), $CHCH_3$ (**12**))

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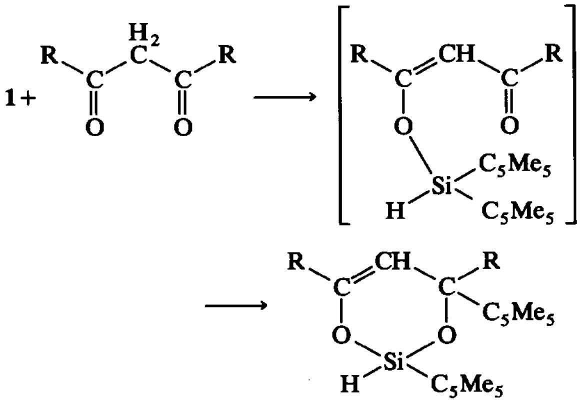
* Reference number with an asterisk indicates a note in the list of references.

1,3-Diketones, capable of keto-enol tautomerism, should also be able to add oxidatively to the silicon atom in **1**. To check this we examined the reaction of **1** with hexafluoroacetylacetone and with acetylacetone. In toluene or benzene as solvent the six-membered ring products 1-pentamethylcyclopentadienyl-3.5-bis-(trifluoromethyl)-5-pentamethylcyclopentadienyl-2.6-dioxa-1-sila-cyclohexene(3) (**13**) and 1-pentamethylcyclopentadienyl-3.5-dimethyl-5-pentamethylcyclopentadienyl-2.6-dioxa-1-silacyclohexene(3) (**14**), respectively, were formed in good yields. They were isolated after crystallization and characterized by NMR, IR, and MS data, and in the case of **13** also by an X-ray crystal structure determination (*vide infra*). To account for the final products **13** and **14**, we assume the formation of intermediate oxidative addition products, in which there is migration of a pentamethylcyclopentadienyl group from silicon to a carbonyl carbon atom with silicon–oxygen bond formation (see eqn. (4)). A comparable rearrangement process with a migrating cyano group (intramolecular cyanosilylation) is known [4].



(4)

13, 14
(R = CF_3 (**13**), CH_3 (**14**))

Finally, we looked at the oxidative addition of S–H compounds. As a representative reagent we chose the aromatic substrate *p*-methylphenylthiol. After reaction of this thiol for one day with **1** at room temperature the compound bis(pentamethylcyclopentadienyl)(*p*-methyl-phenylthio)silane (**15**) was formed in good yield (eqn. (5)). The silane **15** was isolated after crystallization from petroleum ether and characterized by NMR, IR, and MS data.

$$\underset{\mathbf{1}}{(\pi\text{-}Me_5C_5)_2Si} + p\text{-}H_3C\text{-}H_4C_6SH \longrightarrow \underset{\mathbf{15}}{(\sigma\text{-}Me_5C_5)_2Si(H)C_6H_4\text{-}p\text{-}CH_3} \quad (5)$$

It is noteworthy that **1** does not react with aliphatic thiols such as iso-propanethiol under comparable mild conditions. Under more drastic conditions (7 days at 40°C), **1** decomposes to give pentamethylcyclopentadiene as the only identified product.

3. Interpretation of the NMR data

In this discussion we concentrate on the NMR spectra of the comparable compounds **2–9**, **11**, **12**, and **15** of the type $(Me_5C_5)_2Si(H)X$. Since the pentamethylcyclopentadienyl ligands are π-bonded to divalent silicon in **1** and σ-bonded to tetravalent silicon in the oxidative addition products, marked changes are observed in the ^{29}Si, ^{1}H, and ^{13}C NMR spectra. On going from **1** to the oxidative addition products, the ^{29}Si resonance is shifted downfield by about 393 ppm. The δ ^{29}Si shift values as well as the values of the coupling constants $^{2}J(^{29}Si-^{1}H)$ in **2–9**, **11**, **12**, and **15** are as expected from comparison with other $R_2Si(H)X$ compounds [5]; they are listed in Table 1.

Fluxional behaviour is generally observed in Main Group compounds of the type ElC_5Me_5 with σ-bonded pentamethylcyclopentadienyl ligands; it can be attributed to degenerate sigmatropic rearrangements caused by migration of the relevant El unit [6]. For certain Main Group elements the activation energy for such processes can vary drastically with change in the other ligands on the El centre [6,7]. This is not the case for the pentamethylcyclopentadienylsilicon compounds for which the activation energies are only slightly ligand dependent. On the NMR time scale rearrangement processes in pentamethylcyclopentadienylsilicon

TABLE 1. ^{29}Si NMR data for compounds

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**11**	**12**	**15**
δ ^{29}Si (ppm)	4.23	4.73	4.91	5.05	5.26	4.86	4.84	5.12 5.18	4.83	4.77 4.81	5.04
J(SiH) (Hz)	229	224	232	224	224	210	211	210	215	203 211	215

compounds are rather slow; they are easy to detect in the temperature-dependent ^1H or ^{13}C NMR spectra by the presence of three (or five) signals for the different methyl groups and ring-carbon atoms or by more or less broad averaged signals. In the low-temperature ^1H and ^{13}C NMR spectra, sharp signals (coalescence) have never been observed for σ-pentamethylcyclopentadienyl silicon compounds. This is confirmed by the signal patterns in the spectra of the compounds **2–15** (see Experimental section). An example of the element-dependent fluxionality is provided by compounds **13** and **14**; the C-bonded pentamethylcyclopentadienyl groups possess a static structure whereas the Si-bonded groups show dynamic behaviour.

4. Crystal structure data

X-ray crystal structure data for the compounds **9**, **10b**, and **13** are listed in Table 2. Atomic coordinates are given in Tables 3–5. Selected bond lengths and bond angles are listed in Table 6. The molecular structures of **9**, **10b**, and **13** are presented in Figs. 1–3.

The solid-state structure of **9** has a conformation in which the reactive OH and the reactive SiH group are not close together. Furthermore, the two nearly planar pentamethylcyclopentadienyl rings, which show the expected differences in the C–C bond lengths, are not in a parallel orientation; the angle between the two planes in this conformation is 45.3°. All other bis(pentamethylcyclopentadienyl) compounds of Main Group elements so far characterized crystallize with nearly parallel ring systems [8]. The C(1)SiC(11) angle (121.5°) deviates drastically from the expected value for sp^3-hybridized silicon (109.8°); the C(1)–Si distance is rather long (1.903(5) Å). These data are consistent with the well-known steric requirements of a σ-bonded pentamethylcyclopentadienyl ligand. In the structure of **10b** the two nearly planar pentamethylcyclopentadienyl systems show the expected differences in the C–C bond lengths and adopt a parallel sandwich-like, orientation. Some of the bond angles at silicon deviate strongly from the tetrahedral value. The largest change to a smaller value is observed for the O(1)SiO(1a) angle (95.7(3)°) [9*]. Correspondingly, the C(1)SiC(1a)

TABLE 2. X-ray crystal structure data

Compound	**9**	**10b**	**13**
Empirical formula	$C_{27}H_{38}O_2Si$	$C_{26}H_{34}O_2Si$	$C_{25}H_{32}F_6O_2Si$
Crystal size (mm)	0.15 × 0.3 × 1.0	0.6 × 0.8 × 1.0	0.2 × 0.4 × 0.5
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pnn2$	$P2_1/c$
Unit cell dimensions			
a	8.639(6) Å	9.034(6) Å	7.219(4) Å
b	10.661(8) Å	10.381(8) Å	15.494(7) Å
c	14.805(10) Å	12.857(11) Å	22.864(12) Å
α	71.54(5)°	90	90
β	74.80(5)°	90	96.98(4)°
γ	81.43(6)°	90	90
Volume	1244.9(15) $Å^3$	1206(3) $Å^3$	2540(5) $Å^3$
Z	2	2	4
Absorption coefficient	0.109 mm^{-1}	0.110 mm^{-1}	0.150 mm^{-1}
$F(000)$	460	440	1060
Diffractometer	Siemens $P2_1$	Siemens $P2_1$	Siemens $P2_1$
Radiation	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Temperature	128 K	294 K	173 K
2θ range	3–55°	3–55°	3–58°
Scan type	ω	Wyckof	ω
Index ranges	$0 \le h \le 11$, $-13 \le k \le 13$, $-18 \le l \le 19$	$0 \le h \le 11$, $0 \le k \le 13$, $0 \le l \le 16$	$0 \le h \le 9$, $0 \le k \le 21$, $-31 \le l \le 30$
Reflections collected	6034	1618	8438
Independent reflections	5670	1447	6769
Observed reflections	3277 ($F > 4\sigma(F)$)	1111 ($F > 4\sigma(F)$)	2620 ($F > 5\sigma(F)$)
Absorption correction	Face-indexed numerical	Semi-empirical	–
Weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$
Number of parameters	277	132	310
Final R, R_w	0.075, 0.059	0.064, 0.053	0.065, 0.048
Largest difference peak	0.33 e $Å^{-3}$	0.22 e $Å^{-3}$	0.56 e $Å^{-3}$
Largest difference hole	−0.84 e $Å^{-3}$	−0.24 e $Å^{-3}$	−0.40 e $Å^{-3}$

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3) of **9**

	x	y	z	U_{eq} [a]
Si(1)	2780(1)	4498(1)	2985(1)	29(1)
O(1)	2718(3)	5279(3)	1827(2)	30(1)
O(2)	4877(3)	6351(3)	169(2)	38(1)
C(1)	4962(5)	4139(4)	3088(3)	34(2)
C(2)	5985(5)	3487(4)	2340(3)	29(2)
C(3)	6922(5)	4373(4)	1645(3)	32(2)
C(4)	6682(5)	5634(5)	1871(3)	39(2)
C(5)	5585(5)	5514(4)	2720(3)	39(2)
C(6)	5049(5)	3407(5)	4156(3)	51(2)
C(7)	5998(5)	2043(4)	2437(3)	42(2)
C(8)	8144(5)	4139(5)	759(3)	47(2)
C(9)	7576(6)	6823(5)	1231(4)	62(3)
C(10)	5021(6)	6555(5)	3244(4)	65(3)
C(11)	1362(5)	3132(4)	3410(3)	34(2)
C(12)	1314(5)	2401(4)	4467(3)	38(2)
C(13)	1862(5)	1138(4)	4540(3)	40(2)
C(14)	2228(5)	924(4)	3573(3)	37(2)
C(15)	1915(5)	2067(4)	2912(3)	35(2)
C(16)	−300(5)	3829(4)	3243(3)	49(2)
C(17)	723(6)	3027(5)	5282(3)	54(2)
C(18)	2117(6)	59(5)	5439(3)	57(2)
C(19)	2849(6)	−401(4)	3409(4)	53(2)
C(20)	2063(6)	2316(5)	1834(3)	49(2)
C(21)	2569(5)	6627(4)	1418(3)	27(2)
C(22)	3696(5)	7165(4)	563(3)	31(2)
C(23)	3593(5)	8503(4)	107(3)	40(2)
C(24)	2356(5)	9316(4)	475(3)	40(2)
C(25)	1191(5)	8782(4)	1319(3)	37(2)
C(26)	1323(5)	7433(4)	1784(3)	33(2)
C(27)	−194(6)	9662(5)	1707(3)	53(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

angle is opened to 122.2(4)°, presumably owing to the steric requirements of the pentamethylcyclopentadienyl ligands. The bonding situation around the silicon atom in **10b** is comparable with that in $(Me_5C_5)_2SiCl_2$ [7].

TABLE 4. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3) of **10b**

	x	y	z	U_{eq} [a]
Si(1)	0	5000	0	38(1)
O(1)	709(4)	6026(3)	−876(4)	48(1)
C(1)	1511(6)	4111(5)	708(6)	48(2)
C(2)	2178(6)	4925(6)	1559(6)	57(2)
C(3)	1853(8)	4370(8)	2468(6)	75(3)
C(4)	1059(7)	3192(8)	2293(7)	72(3)
C(5)	862(7)	3005(6)	1294(7)	61(2)
C(6)	2686(6)	3693(6)	−98(6)	72(2)
C(7)	3029(7)	6117(7)	1346(8)	107(4)
C(8)	2332(10)	4835(10)	3506(6)	144(5)
C(9)	621(8)	2327(7)	3159(8)	138(4)
C(10)	227(9)	1832(6)	758(7)	104(3)
C(11)	396(6)	5570(5)	−1860(6)	46(2)
C(12)	771(7)	6162(5)	−2751(6)	59(2)
C(13)	400(9)	5580(6)	−3681(6)	88(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3) of **13**

	x	y	z	U_{eq} [a]
Si(1)	1341(2)	6038(1)	2074(1)	27(1)
F(1)	−574(4)	8505(2)	2728(1)	42(1)
F(2)	1110(4)	8772(2)	2047(1)	53(1)
F(3)	2225(4)	8969(2)	2950(1)	52(1)
F(4)	6261(4)	6834(2)	2360(1)	49(1)
F(5)	7189(4)	6918(2)	3288(1)	49(1)
F(6)	6978(4)	5679(2)	2860(1)	51(1)
O(1)	706(4)	7038(2)	2249(2)	36(1)
O(2)	3238(4)	5854(2)	2525(1)	28(1)
C(1)	1855(7)	7541(3)	2619(2)	27(2)
C(2)	3364(7)	7302(3)	2975(2)	27(2)
C(3)	4102(6)	6381(3)	3001(2)	25(2)
C(4)	1163(8)	8448(3)	2589(2)	36(2)
C(5)	6146(7)	6441(4)	2881(3)	38(2)
C(6)	3842(6)	5918(3)	3601(2)	25(2)
C(7)	4906(7)	6375(3)	4143(2)	31(2)
C(8)	6121(7)	5814(3)	4420(2)	33(2)
C(9)	5992(7)	4977(3)	4116(2)	31(2)
C(10)	4694(7)	5013(3)	3646(2)	31(2)
C(11)	1745(6)	5871(3)	3661(2)	38(2)
C(12)	4501(9)	7272(3)	4346(2)	53(2)
C(13)	7451(8)	5977(4)	4972(2)	54(2)
C(14)	7185(8)	4209(3)	4330(2)	52(2)
C(15)	4061(7)	4278(3)	3243(2)	43(2)
C(16)	1797(7)	5984(3)	1288(2)	29(2)
C(17)	2062(7)	5023(3)	1217(2)	27(2)
C(18)	486(8)	4692(3)	930(2)	35(2)
C(19)	−844(7)	5380(4)	764(2)	38(2)
C(20)	−98(7)	6137(4)	955(2)	36(2)
C(21)	3368(7)	6576(3)	1131(2)	47(2)
C(22)	3799(7)	4538(3)	1457(2)	46(2)
C(23)	123(9)	3754(3)	780(2)	64(3)
C(24)	−2709(7)	5229(4)	412(2)	67(3)
C(25)	−918(8)	7035(4)	856(3)	65(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

No special features are observed in the solid-state structure of **13**. Knowledge of this structure was essential for correct assignment of the ^1H and ^{13}C NMR signals for this compound.

5. Discussion

Oxidative addition reactions of transient silylenes, which are generated by photolysis or thermolysis of appropriate oligosilanes, have been described previously. Most of the recent work in this field was carried out in Weber's group. Dimethylsilylene and methylphenylsilylene are the preferred model substances in the reaction with X–H substrates such as water, methanol, ethanol, i-propanol, t-butanol, neopentyl alcohol, acetone (enol-form), diethylamine, and 2,2-di-

TABLE 6. Selected bond lengths and angles

Compound 9			
C(1)-Si(1)	1.903(5)	C(1)-Si(1)-C(11)	121.5(2)
C(11)-Si(1)	1.888(5)	C(1)-Si(1)-O(1)	109.3(2)
O(1)-Si(1)	1.663(3)	C(11)-Si(1)-O(1)	106.0(2)
O(1)-C(21)	1.373(5)	Si(1)-O(1)-C(21)	126.0(3)
C(22)-O(2)	1.371(5)	O(1)-C(21)-C(22)	116.9(3)
Compound 10b			
Si(1)-C(1)	1.883(6)	C(1)-Si(1)-C(1a)	122.4(4)
Si(1)-O(1)	1.667(5)	O(1)-Si(1)-O(1a)	95.7(3)
O(1)-C(11)	1.381(9)	Si(1)-O(1)-C(11)	108.6(3)
C(11)-C(11a)	1.382(10)	C(1)-Si(1)-O(1a)	106.9(2)
Compound 13			
Si(1)-H(1)	1.439(45)	O(1)-Si(1)-O(2)	104.1(2)
Si(1)-O(1)	1.678(4)	O(1)-Si(1)-C(16)	110.8(2)
Si(1)-O(2)	1.636(3)	Si(1)-O(2)-C(3)	129.0(3)
Si(1)-C(16)	1.869(5)	O(2)-C(3)-C(2)	112.6(4)
C(1)-O(1)	1.357(6)	C(6)-C(3)-C(2)	112.4(4)
C(1)-C(2)	1.330(6)	C(3)-C(2)-C(1)	122.8(4)
C(2)-C(3)	1.522(7)	O(1)-C(1)-C(4)	109.6(4)
C(3)-O(2)	1.440(5)	C(1)-O(1)-Si(1)	120.9(3)
C(3)-C(6)	1.579(7)		

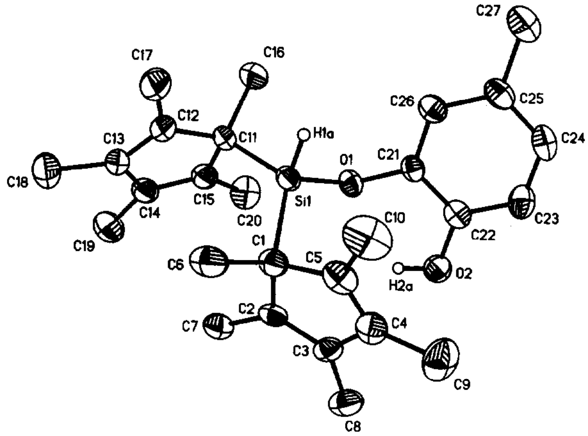


Fig. 1. Molecular structure of **9** [16*].

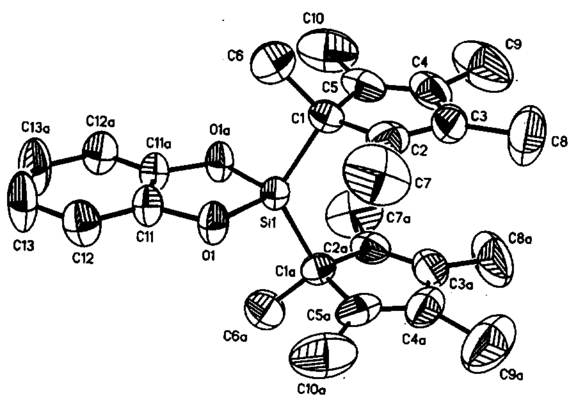


Fig. 2. Molecular structure of **10b** [16*].

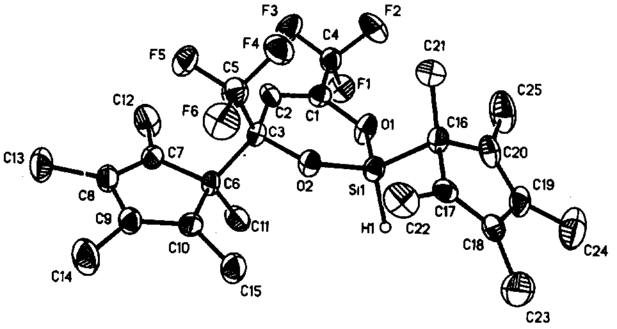


Fig. 3. Molecular structure of **13** [16*].

methylaziridine [10]. Competition studies have been carried out in various solvents, and show that dimethylsilylene is more selective in ether than in hydrocarbon solvents [11]. Furthermore, kinetic isotope effects have been reported for the oxidative addition of alcohols to dimethylsilylene [12]. From these results and from theoretical calculations [13] it has been concluded that a zwitterionic compound, formed by interaction of the lone-pair at oxygen (in the solvent or the substrate) with the vacant p orbital at silicon, is an intermediate in the reactions.

In this context it is noteworthy that decamethylsilicocene (**1**) does not react preferentially with aliphatic alcohols and thio-alcohols; phenols and thiophenols, as well as other more acidic X–H substrates, are the preferred reagents for oxidative addition reactions. From these results we favour (but cannot prove) a mechanism with **1** as the nucleophile and the X–H substrate as the electrophile.

In decamethylsilicocene (**1**) a vacant p-orbital on silicon can only be generated after haptotropic shifts of the pentamethylcyclopentadienyl ligands. Recent experiments in our group indicate, that this process may indeed take place with simultaneous attack of a nucleophile. In this context, we will report on oxidative addition reactions with primary and secondary amines and phosphines in a forthcoming paper.

Several reactions of the heavier homologues of **1**, the decamethylmetallocenes of germanium, tin, and lead, with protic substrates X–H have been described [14]. In all cases studied so far, elimination of pentamethylcyclopentadiene and formation of a divalent germanium, tin, or lead compound is observed. In a recent experiment, we have supported these observations. The reaction of decamethylstannocene with catechol in tetrahydrofuran as solvent leads to pentamethylcyclopentadiene and (*ortho*-phenylenedioxy)stannylene [15*] in high yields (eqn. (6)).

$$(\pi\text{-Me}_5\text{C}_5)_2\text{Sn} + \text{C}_6\text{H}_4(\text{OH})_2 \longrightarrow \text{C}_6\text{H}_4\text{O}_2\text{Sn} + 2\,\text{Me}_5\text{C}_5\text{H} \quad (6)$$

The above findings demonstrate principal differences in the chemistry of decamethylsilicocene (**1**) and its heavier homologues. Whereas oxidative addition reactions dominate the chemistry of **1**, elimination reactions, sometimes as a result of oxidative addition and subsequent reductive elimination processes, dominate the chemistry of the decamethylmetallocenes of germanium, tin, and lead.

6. Experimental section

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods [benzene, toluene and THF with K; Et_2O, pentane, n-hexane and petroleum ether (40–60) with $LiAlH_4$] and distilled under argon prior to use.

Elemental analyses were performed by the Beller Microanalytical Laboratory, Göttingen. IR spectra were recorded on a Perkin-Elmer or a Mattson–Polaris FTIR spectrophotometer. ^1H, $^{13}C\{^1H\}$, ^{19}F and ^{29}Si NMR spectra were recorded in dry, deoxygenated benzene-d_6, toluene-d_8 or chloroform-d_1 on a Bruker AM 300 instrument. Chemical shifts were referenced to residual solvent signals (C_6D_6 $\delta_H = 7.15$ ppm, $CDCl_3$ $\delta_H = 7.24$ ppm, toluene-d_8 $\delta = 2.09$ ppm). Mass spectra were obtained with a Varian 311 A (EI, 70 eV) and melting points with a Büchi 510 melting point apparatus in closed capillary tubes.

General reaction procedure for compounds 2–6

The appropriate acid was added dropwise to a solution of **1** in Et_2O at −78°C (**2–4**) or at 20°C (**5**, **6**). In the case of compounds **2–4**, the reaction mixture was allowed to warm to room temperature. After removal of the solvents under vacuum, the products were isolated by sublimation or crystallization.

2: 0.76 (2.55 mmol) **1** in 30 ml; 0.82 ml (72.9 mg, 2.55 mmol) HF/pyridine (70% solution); sublimation (10^{-3} mbar, 20°C). Yield: 0.25 g (31%), m.p.: 52°C. ^1H NMR (C_6D_6, δ ppm): 1.66 (s, 30H), 4.23 (d, 1H, ^2J(H–F) = 50.1 Hz). ^{13}C NMR (C_6D_6, δ ppm): 12.3, 63.8, 135.5. ^{29}Si NMR (C_6D_6, δ ppm): 14.1 (dd, ^1J(Si–F) = 327 Hz, ^1J(Si–H) = 229 Hz). MS (m/z): 318 (14, M^+), 183 (100, $M^+ - Cp^*$). Found: C, 74.49; H, 9.90. $C_{20}H_{31}FSi$ (318.55) calc.: C, 75.41; H, 9.81%.

3: 0.86 g (2.85 mmol) **1** in 30 ml; 1.86 ml (2.96 mmol) HCl/Et_2O (1.59 M solution); sublimation (10^{-3} mbar, 20°C). Yield: 0.71 g (72%); m.p.: 74–76°C. ^1H NMR (C_6D_6, δ ppm): 1.62 (s, 30H), 4.73 (s, 1H). ^{13}C NMR (C_6D_6, δ ppm): 12.6, 51.5, 134.2, 137.7. ^{29}Si NMR (C_6D_6, δ ppm): 16.0 (d, ^1J(Si–H) = 224 Hz). MS (m/z): 334 (9, M^+), 199 (100, $M^+ - Cp^*$) 163 (14, Cp^*Si^+). Found: C, 72.46; H, 9.28; Cl, 10.80. $C_{20}H_{31}ClSi$ (335.04) calc.: C, 71.71; H, 9.33; Cl, 10.58%.

4: 0.77 g (2.58 mmol) **1** in 30 ml; 3.30 ml (2.58 mmol) HBr/benzene (0.76 *M* solution); crystallization in pentane. Yield: 0.69 g (70%); m.p.: 95–97°C. ^1H NMR (C_6D_6, δ ppm): 1.72 (s, 30H), 4.91 (s, 1H). ^{13}C NMR (C_6D_6, δ ppm): 12.9, 137.7. ^{29}Si NMR (C_6D_6, δ ppm): 15.0 (d, ^1J(Si–H) = 232 Hz). MS (m/z): 378 (7, M^+), 243 (79, $M^+ - Cp^*$) 163 (4, Cp^*Si^+), 135 (100, Cp^{*+}). Found: C, 64.23; H, 8.29. $C_{20}H_{31}BrSi$ (379.47) calc.: C, 63.31; H, 8.23%.

5: 0.68 g (2.28 mmol) **1** in 30 ml; 0.26 g (2.28 mmol) F_3CCOOH; crystallization in pentane. Yield: 0.88 g (94%); m.p.: 54°C. ^1H NMR (C_6D_6, δ ppm): 1.55 (s, 30H), 5.05 (s, 1H). ^{13}C NMR (C_6D_6, δ ppm): 12.3, 116.6 (q, ^1J(C–F) = 287 Hz), 155.7, 156.3, 178.9. ^{29}Si NMR (C_6D_6, δ ppm): 7.6 (d, ^1J(Si–H) = 224 Hz). MS (m/z): 412 (13, M^+), 277 (16, $M^+ - Cp^*$) 183 (100, Cp^*SiHF^+). Found: C, 64.12; H, 7.60. $C_{22}H_{31}F_3O_2Si$ (412.57) calc.: C, 64.05; H, 7.57%.

6: 0.98 g (3.28 mmol) **1** in 30 ml; 0.24 g (3.28 mmol) EtCOOH; crystallization in pentane. Yield: 1.05 g (86%); m.p.: 78–81°C. ^1H NMR (C_6D_6, δ ppm): 1.03 (t, 3H, ^3J = 7.5 Hz), 1.66 (s, 30H), 2.15 (q, 2H, ^3J = 7.5 Hz), 5.26 (s, 1H). ^{13}C NMR (C_6D_6, δ ppm): 9.5, 12.5, 29.4, 136.9, 172.7. ^{29}Si NMR (C_6D_6, δ ppm): 0.8 (d, ^1J(Si–H) = 224 Hz). MS (m/z): 372 (3, M^+), 237 (100, $M^+ - Cp^*$), 181 (42, $Cp^*CO_2H_2^+$), 163 (15, Cp^*Si^+). Found: C, 73.79; H, 9.50. $C_{23}H_{36}O_2Si$ (372.62) calc.: C, 74.14; H, 9.74%.

General procedure for the compounds 7–15

A solution of **1** and the substrate HX in the chosen solvent was stirred at the given temperature for several hours. After removal of the solvents under vacuum the compounds were isolated by sublimation or crystallization.

7: 0.73 g (2.45 mmol) **1**; 0.23 g (2.45 mmol) PhOH, 20 ml toluene; 20°C; 1 d; crystallization from petroleum ether (40–60). Yield: 0.76 g (79%); m.p.: 59°C. ^1H NMR ($CDCl_3$, δ ppm): 1.60 (s, 30H), 4.86 (s, 1H), 6.87–6.91 (m, 3H), 7.19–7.24 (m, 2H). ^{13}C NMR ($CDCl_3$, δ ppm): 11.5, 118.5, 120.9, 129.3, 136.4, 157.3. ^{29}Si NMR ($CDCl_3$, δ ppm): 0.9 (d, ^1J(Si–H) = 210 Hz). IR (KBr, ν cm^{-1}): 2120 (Si–H), MS (m/z): 392 (4, M^+), 257 (100, $M^+ - Cp^*$), 163 (24, Cp^*Si^+). Found: C, 79.44; H, 9.18. $C_{26}H_{36}OSi$ (392.7) calc.: C, 79.53; H, 9.24%.

8: 0.91 g (3.05 mmol) **1**; 0.33 g (3.05 mmol) MePhOH, 20 ml benzene; 20°C; 2 d; crystallization from petroleum ether (40–60). Yield: 0.65 g (52%); m.p.: 67°C. ^1H NMR ($CDCl_3$, δ ppm): 1.54 (s, 30 H), 2.28 (s, 3H), 4.84 (s, 1H), 6.83 (d, 2H, ^3J = 8.3 Hz), 7.04 (d, 2H, ^3J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, δ ppm): 12.4, 20.5, 118.2, 129.8, 130.0, 136. ^{29}Si NMR ($CDCl_3$, δ ppm): 1.0 (d,

^1J(Si–H) = 211 Hz). MS (m/z): 406 (3, M^+), 271 (100, $M^+ - Cp^*$), 163 (24, Cp^*Si^+), 135 (62, Cp^{*+}).

9: 0.82 g (2.75 mmol) **1**; 0.34 g (2.75 mmol) $HOC_6H_3(OH)Me$, 20 ml toluene; 0°C; 1 d; isolation of **9** at 0°C not at room temperature; crystallization from pentane. Yield: 0.72 g (62%, two isomers in a 1:1 ratio); m.p.: 73°C. ^{1}H NMR (C_6D_6, δ ppm): 1.50 (s, 30H), 2.08 and 2.10 (2 s, 3H, two isomers), 5.12 and 5.18 (2 s, 1H, two isomers), 5.47 and 5.58 (2 s, 1H, two isomers). ^{13}C NMR ($CDCl_3$, δ ppm): 12.1, 20.8, 115.3, 115.8, 120.0, 131.3, 136.6, 141.9, 149.2. ^{29}Si NMR ($CDCl_3$, δ ppm): 4.7 (d, ^1J(Si–H) = 210 Hz). IR (KBr, ν cm^{-1}): 3520 (O–H), 2115 (Si–H). MS (m/z): 422 (1, M^+), 286 (13, $M^+ - Cp^*$), 136 (100, Cp^*H^+). Found: C, 75.76; H, 8.82. $C_{27}H_{38}O_2Si$ (422.68) calc.: C, 76.72; H, 9.06%.

10a: 0.05 g (0.19 mmol) **9**; 0.5 ml (0.12 mmol) pyridine/toluene (0.25 M solution), 10 ml toluene; −50°C; 0.5 h; no isolation, but spectroscopic characterisation. ^{1}H NMR (C_6D_6, δ ppm): 1.75 (s, 30H), 2.13 (s, 3H), 6.55 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H), 6.95 (d, ^4J = 1.7 Hz, 1H), 7.04 (d, ^3J = 7.9 Hz, 1H). ^{13}C NMR (C_6D_6, δ ppm): 12.4, 21.2, 112.7, 114.3, 121.4, 130.6, 137.0, 148.5, 150.6. ^{29}Si NMR (C_6D_6, δ ppm): 11.2.

10b: 0.72 g (2.42 mmol) **1**; 0.20 g (2.41 mmol) $C_5H_4(OH)_2$, 0.05 ml H_2O, 10 ml toluene; 60°C; 12 h; crystallization from toluene/pentane 10:1. Yield: 0.56 g (57%); m.p.: 186°C. ^{1}H NMR (C_6D_6, δ ppm): 1.65 (s, 30H), 6.73–6.77 (m, 2H), 7.11–7.14 (m, 2H). ^{13}C NMR (C_6D_6, δ ppm): 12.5, 113.3, 121.3, 138.5, 150.7. ^{29}Si NMR (C_6D_6, δ ppm): 11.0. MS (m/z): 406 (17, M^+), 271 (100, $M^+ - Cp^*$). Found: C, 76.94; H, 8.30. $C_{26}H_{34}O_2Si$ (406.64) calc.: C, 76.80; H, 8.43%.

11: 0.75 g (2.51 mmol) **1**; 0.28 g (2.51 mmol) $H_{10}C_5NOH$, 15 ml toluene; 60°C; 16 h; crystallization from hexane). Yield: 0.72 g (70%); m.p.: 83°C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.45–1.85 (m, 36H), 2.28 (t, 2H, ^3J = 5.6 Hz), 2.57 (t, 2H, ^3J = 5.6 Hz), 4.83 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 12.6, 25.5, 25.9, 26.0, 27.1, 32.2, 163.6. ^{29}Si NMR ($CDCl_3$, δ ppm): 10.1 (d, ^1J(Si–H) = 215 Hz). IR (KBr, ν cm^{-1}): 2104 (Si–H). MS (m/z): 411 (1, M^+), 276 (17, $M^+ - Cp^*$), 142 (100, $M^+ - 2Cp^*$). Found: C, 75.58; H, 9.98. $C_{26}H_{41}NOSi$ (411.69) calc.: C, 75.85; H, 10.04%.

12: 0.62 g (2.08 mmol) **1**; 0.12 g (2.08 mmol) H_3CHNOH, 20 ml toluene; 60°C; 6 h; crystallization from petroleum ether (40–60). Yield: 0.53 g (71%, two isomers in 1:1 ratio); m.p.: 64°C. ^{1}H NMR ($CDCl_3$, δ ppm): 1.50–1.70 (m, 33H), 4.77 and 4.81 (2 s, 1H, two isomers), 7.00 (q, ^3J = 5.3 Hz). ^{13}C NMR ($CDCl_3$, δ ppm): 1.3 and 11.7 (two isomers), 12.8, 132.8, 136.0, 150.4. ^{29}Si NMR ($CDCl_3$, δ ppm): 2.1 (d, ^1J(Si–H) = 203 Hz), 11.5 (d, ^1J(Si–H) = 219 Hz). IR (KBr, ν cm^{-1}): 2114 (Si–H). MS (m/z): 357 (9, M^+), 222 (68, $M^+ - Cp^*$), 135 (68, Cp^{*+}), 88 (100, $M^+ - 2Cp^{*+}$ H). Found: C, 73.75; H, 9.91. $C_{22}H_{35}NOSi$ (357.6) calc.: C, 73.89; H, 9.86%.

13: 1.02 g (3.42 mmol) **1**; 2.00 g (9.59 mmol) $F_3COCH_2CCOCF_3$, 15 ml toluene; 20°C; 14 h; sublimation (10^{-2} mbar, 60°C) then crystallization from acetonitrile/toluene 10:1. Yield: 1.30 g (75 %); m.p.: 77°C. ^{1}H NMR (C_6D_6, δ ppm): 1.02 (s, 3H, Cp^*–C), 1.57 (s, 3H, Cp^*–C), 1.63 (s, 3H, Cp^*–C), 1.67 (s, 3H, Cp^*–C), 1.80 (s, 15H, Cp^*–Si), 1.93 (s, 3H, Cp^*–C), 2.92 (s, 1H), 5.63 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 10.6, 12.7, 17.9, 61.1, 83.2 (q, ^2J(C–F) = 29.5 Hz), 104.2, 119.4 (q, ^1J(C–F) = 272 Hz), 124.3 (q, ^1J(C–F) = 287 Hz), 134.4 (Cp^*–C), 134.8 (Cp^*–C), 137.4 (Cp^*–C), 139.7 (Cp^*–C), 142.5 (q, ^2J(C–F) = 37 Hz). ^{13}C NMR (toluene-d_8, 100°C, δ ppm): 10.8, 10.9, 11.1, 12.7, 18.00, 62.0, 84.1 (q, ^2J(C–F) = 29.8 Hz), 105.0, 121.1 (Cp^*–Si), 135.6 (Cp^*–C), 136.3 (Cp^*–C), 138.1 (Cp^*–C), 140.1 (Cp^*–C), 143.5 (q, ^2J(C–F) = 36.1 Hz). ^{19}F NMR ($CDCl_3$, δ ppm): −74.5 (s, 3F), −76.1 (s, 3F). ^{29}Si NMR ($CDCl_3$, δ ppm): −38.1 (d, ^1J(Si–H) = 301 Hz). IR (KBr, ν cm^{-1}): 2250 (Si–H). MS (m/z): 506 (5, M^+), 371 (29, $M^+ - Cp^*$), 135 (100, Cp^{*+}). Found: C, 59.61; H, 6.62. $C_{25}H_{32}O_2F_6Si$ (506.60) calc.: C, 59.27; H, 6.37%.

14: 0.83 g (2.79 mmol) **1**; 1.00 g (10.00 mmol) $H_3COCH_2CCOCH_3$, 10 ml benzene; 50°C; 2 d; crystallization from petroleum ether (40–60). Yield: 0.71 g (64%); m.p.: 104°C. ^{1}H NMR (C_6D_6, δ ppm): 1.22 (s, 3H), 1.23 (s, 3H), 1.69 (s, 3H), 1.74 (s, 3H), 1.78 (s, 3H), 1.89 (s, 15H, Cp^*–Si), 2.01 (s, 3H), 3.39 (s, 1H), 4.51 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 11.1 12.9, 16.2, 22.0, 25.6, 64.7, 79.7, 108.5, 135.0 (Cp^*–C), 136.1 (Cp^*–C), 138.4 (Cp^*–C), 141.4 (Cp^*–C), 147.1. ^{29}Si NMR ($CDCl_3$, δ ppm): −32.8 (d, ^1J(Si–H) = 283 Hz). IR (KBr, ν cm^{-1}): 2210 (Si–H). MS (m/z): 398 (1, M^+), 263 (100, $M^+ - Cp^*$), 135 (24, Cp^{*+}). Found: C, 75.17; H, 9.51. $C_{25}H_{38}O_2Si$ (398.66) calc.: C, 75.32; H, 9.61%.

15: 0.95 g (3.20 mmol) **1**; 0.39 g (3.20 mmol) MePhSH, 20 ml toluene; 20°C; 1 d; crystallization from petroleum ether (40–60). Yield: 0.82 g (61%); m.p.: 85°C. ^{1}H NMR (C_6D_6, δ ppm): 1.78 (s, 30H), 2.02 (s, 3H), 5.04 (s, 1H), 6.86–6.88 (m, 2H), 7.52–7.54 (m, 2H). ^{13}C NMR (C_6D_6, δ ppm): 11.6, 20.9, 55.5, 129.8, 131.8, 134.5, 136.7. ^{29}Si NMR (C_6D_6, δ ppm): 18.8 (d, ^1J(Si–H) = 215 Hz). IR (KBr, ν cm^{-1}): 2114 (Si–H). MS (m/z): 422 (6, M^+), 287 (100, $M^+ - Cp^*$), 163 (76, Cp^*Si^+). Found: C, 76.02; H, 9.21. $C_{27}H_{38}SSi$ (422. 75) calc.: C, 76.71; H, 9.06%.

Acknowledgments

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