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

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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 $(\sigma\text{-Me}_5\text{C}_5)_2\text{Si}(\text{H})\text{X}$ 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*-phenylenedioxy silane 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, Me₅C₅) 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.

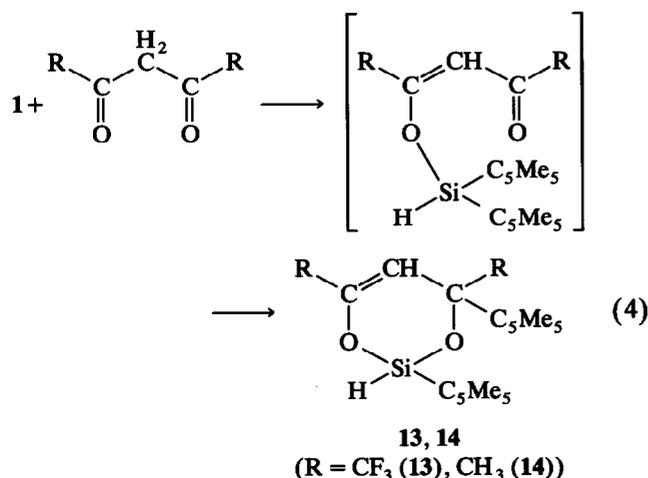
2. Oxidative addition reactions

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 H₅C₅N·HF. In diethyl ether solution, 1 reacts cleanly with this substrate even at –78°C

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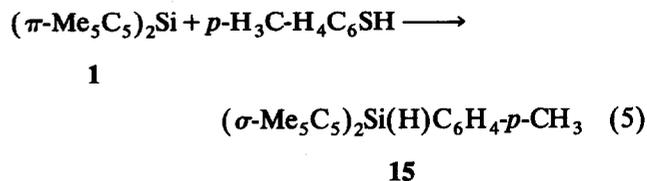
* Dedicated to Professor M.G. Voronkov in recognition of his many contributions to organosilicon chemistry.

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].



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.



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 (Me₅C₅)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 ²⁹Si, ¹H, and ¹³C NMR spectra. On going from **1** to the oxidative addition products, the ²⁹Si resonance is shifted downfield by about 393 ppm. The δ ²⁹Si shift values as well as the values of the coupling constants ²J(²⁹Si-¹H) in **2-9**, **11**, **12**, and **15** are as expected from comparison with other R₂Si(H)X compounds [5]; they are listed in Table 1.

Fluxional behaviour is generally observed in Main Group compounds of the type EIC₅Me₅ with σ-bonded pentamethylcyclopentadienyl ligands; it can be attributed to degenerate sigmatropic rearrangements caused by migration of the relevant EI unit [6]. For certain Main Group elements the activation energy for such processes can vary drastically with change in the other ligands on the EI 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. ²⁹Si 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 ($95.7(3)^\circ$) [9*]. Correspondingly, the C(1)SiC(1a)

TABLE 2. X-ray crystal structure data

Compound	9	10b	13
Empirical formula	$\text{C}_{27}\text{H}_{38}\text{O}_2\text{Si}$	$\text{C}_{26}\text{H}_{34}\text{O}_2\text{Si}$	$\text{C}_{25}\text{H}_{32}\text{F}_6\text{O}_2\text{Si}$
Crystal size (mm)	$0.15 \times 0.3 \times 1.0$	$0.6 \times 0.8 \times 1.0$	$0.2 \times 0.4 \times 0.5$
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pnn2$	$P2_1/c$
Unit cell dimensions			
<i>a</i>	8.639(6) Å	9.034(6) Å	7.219(4) Å
<i>b</i>	10.661(8) Å	10.381(8) Å	15.494(7) Å
<i>c</i>	14.805(10) Å	12.857(11) Å	22.864(12) Å
α	$71.54(5)^\circ$	90	90
β	$74.80(5)^\circ$	90	$96.98(4)^\circ$
γ	$81.43(6)^\circ$	90	90
Volume	$1244.9(15)$ Å ³	$1206(3)$ Å ³	$2540(5)$ Å ³
<i>Z</i>	2	2	4
Absorption coefficient	0.109 mm ⁻¹	0.110 mm ⁻¹	0.150 mm ⁻¹
<i>F</i> (000)	460	440	1060
Diffractometer	Siemens P2 ₁	Siemens P2 ₁	Siemens P2 ₁
Radiation	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)
Temperature	128 K	294 K	173 K
2θ range	$3\text{--}55^\circ$	$3\text{--}55^\circ$	$3\text{--}58^\circ$
Scan type	ω	Wyckof	ω
Index ranges	$0 \leq h \leq 11, -13 \leq k \leq 13, -18 \leq l \leq 19$	$0 \leq h \leq 11, 0 \leq k \leq 13, 0 \leq l \leq 16$	$0 \leq h \leq 9, 0 \leq k \leq 21, -31 \leq l \leq 30$
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 <i>R</i> , <i>R</i> _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 ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) of **9**

	<i>x</i>	<i>y</i>	<i>z</i>	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

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) of **10b**

	<i>x</i>	<i>y</i>	<i>z</i>	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 ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) of **13**

	<i>x</i>	<i>y</i>	<i>z</i>	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.

atom in **10b** is comparable with that in $(\text{Me}_5\text{C}_5)_2\text{SiCl}_2$ [7].

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)		

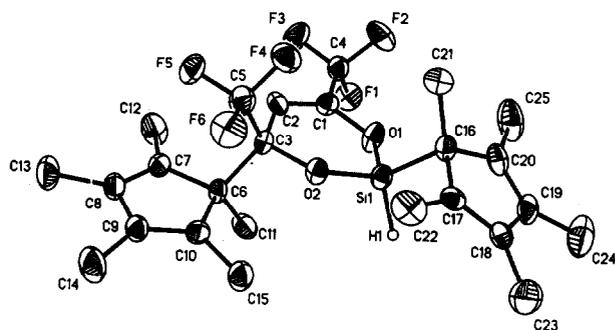


Fig. 3. Molecular structure of 13 [16*].

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)).

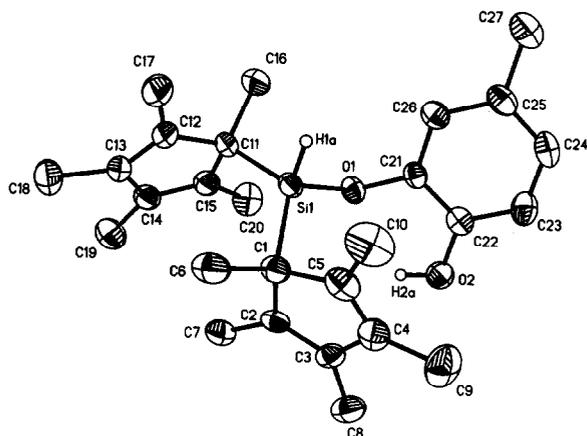
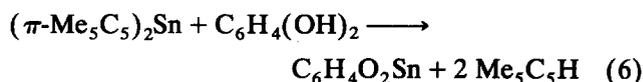


Fig. 1. Molecular structure of 9 [16*].

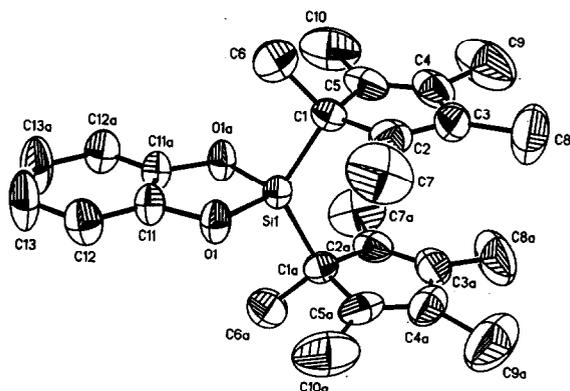


Fig. 2. Molecular structure of 10b [16*].

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; Et₂O, pentane, n-hexane and petroleum ether (40–60) with LiAlH₄] 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, ¹³C{¹H}, ¹⁹F and ²⁹Si 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 (C₆D₆ δ_H = 7.15 ppm, CDCl₃ δ_H = 7.24 ppm, toluene-*d*₈ δ = 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 Et₂O 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 (C₆D₆, δ ppm): 1.66 (s, 30H), 4.23 (d, 1H, ²J(H–F) = 50.1 Hz). ¹³C NMR (C₆D₆, δ ppm): 12.3, 63.8, 135.5. ²⁹Si NMR (C₆D₆, 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. C₂₀H₃₁FSi (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/Et₂O (1.59 M solution); sublimation (10^{–3} mbar, 20°C). Yield: 0.71 g (72%), m.p.: 74–76°C. ¹H NMR (C₆D₆, δ ppm): 1.62 (s, 30H), 4.73 (s, 1H). ¹³C NMR (C₆D₆, δ ppm): 12.6, 51.5, 134.2, 137.7. ²⁹Si NMR (C₆D₆, 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. C₂₀H₃₁ClSi (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 (C₆D₆, δ ppm): 1.72 (s, 30H), 4.91 (s, 1H). ¹³C NMR (C₆D₆, δ ppm): 12.9, 137.7. ²⁹Si NMR (C₆D₆, 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^{*}Si⁺). Found: C, 64.23; H, 8.29. C₂₀H₃₁BrSi (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) F₃CCOOH; crystallization in pentane. Yield: 0.88 g (94%); m.p.: 54°C. ¹H NMR (C₆D₆, δ ppm): 1.55 (s, 30H), 5.05 (s, 1H). ¹³C NMR (C₆D₆, δ ppm): 12.3, 116.6 (q, ¹J(C–F) = 287 Hz), 155.7, 156.3, 178.9. ²⁹Si NMR (C₆D₆, 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. C₂₂H₃₁F₃O₂Si (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 (C₆D₆, 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). ¹³C NMR (C₆D₆, δ ppm): 9.5, 12.5, 29.4, 136.9, 172.7. ²⁹Si NMR (C₆D₆, δ ppm): 0.8 (d, ¹J(Si–H) = 224 Hz). MS (*m/z*): 372 (3, M⁺), 237 (100, M⁺–Cp^{*}), 181 (42, Cp^{*}CO₂H₂⁺), 163 (15, Cp^{*}Si⁺). Found: C, 73.79; H, 9.50. C₂₃H₃₆O₂Si (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 (CDCl₃, δ ppm): 1.60 (s, 30H), 4.86 (s, 1H), 6.87–6.91 (m, 3H), 7.19–7.24 (m, 2H). ¹³C NMR (CDCl₃, δ ppm): 11.5, 118.5, 120.9, 129.3, 136.4, 157.3. ²⁹Si NMR (CDCl₃, 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. C₂₆H₃₆O₂Si (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 (CDCl₃, 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). ¹³C NMR (CDCl₃, δ ppm): 12.4, 20.5, 118.2, 129.8, 130.0, 136. ²⁹Si NMR (CDCl₃, δ ppm): 1.0 (d,

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

9: 0.82 g (2.75 mmol) **1**; 0.34 g (2.75 mmol) $\text{HOC}_6\text{H}_3(\text{OH})\text{Me}$, 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 . ^1H 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, $^1J(\text{Si-H}) = 210$ Hz). IR (KBr, ν cm^{-1}): 3520 (O-H), 2115 (Si-H). MS (m/z): 422 (1, M^+), 286 (13, $M^+ - \text{Cp}^*$), 136 (100, Cp^*H^+). Found: C, 75.76; H, 8.82. $\text{C}_{27}\text{H}_{38}\text{O}_2\text{Si}$ (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. ^1H 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) $\text{C}_5\text{H}_4(\text{OH})_2$, 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 . ^1H 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, $M^+ - \text{Cp}^*$). Found: C, 76.94; H, 8.30. $\text{C}_{26}\text{H}_{34}\text{O}_2\text{Si}$ (406.64) calc.: C, 76.80; H, 8.43%.

11: 0.75 g (2.51 mmol) **1**; 0.28 g (2.51 mmol) $\text{H}_{10}\text{C}_5\text{NOH}$, 15 ml toluene; 60°C ; 16 h; crystallization from hexane. Yield: 0.72 g (70%); m.p.: 83°C . ^1H 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, $^1J(\text{Si-H}) = 215$ Hz). IR (KBr, ν cm^{-1}): 2104 (Si-H). MS (m/z): 411 (1, M^+), 276 (17, $M^+ - \text{Cp}^*$), 142 (100, $M^+ - 2\text{Cp}^*$). Found: C, 75.58; H, 9.98. $\text{C}_{26}\text{H}_{41}\text{NOSi}$ (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 . ^1H 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, $^1J(\text{Si-H}) = 203$ Hz), 11.5 (d, $^1J(\text{Si-H}) = 219$ Hz). IR (KBr, ν cm^{-1}): 2114 (Si-H). MS (m/z): 357 (9, M^+), 222 (68, $M^+ -$

Cp^*), 135 (68, Cp^{*+}), 88 (100, $M^+ - 2\text{Cp}^{*+}$ H). Found: C, 73.75; H, 9.91. $\text{C}_{22}\text{H}_{35}\text{NOSi}$ (357.6) calc.: C, 73.89; H, 9.86%.

13: 1.02 g (3.42 mmol) **1**; 2.00 g (9.59 mmol) $\text{F}_3\text{COCH}_2\text{CCOFCF}_3$, 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 . ^1H 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, $^2J(\text{C-F}) = 29.5$ Hz), 104.2, 119.4 (q, $^1J(\text{C-F}) = 272$ Hz), 124.3 (q, $^1J(\text{C-F}) = 287$ Hz), 134.4 (Cp^*-C), 134.8 (Cp^*-C), 137.4 (Cp^*-C), 139.7 (Cp^*-C), 142.5 (q, $^2J(\text{C-F}) = 37$ 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, $^2J(\text{C-F}) = 29.8$ 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, $^2J(\text{C-F}) = 36.1$ 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, $^1J(\text{Si-H}) = 301$ Hz). IR (KBr, ν cm^{-1}): 2250 (Si-H). MS (m/z): 506 (5, M^+), 371 (29, $M^+ - \text{Cp}^*$), 135 (100, Cp^{*+}). Found: C, 59.61; H, 6.62. $\text{C}_{25}\text{H}_{32}\text{O}_2\text{F}_6\text{Si}$ (506.60) calc.: C, 59.27; H, 6.37%.

14: 0.83 g (2.79 mmol) **1**; 1.00 g (10.00 mmol) $\text{H}_3\text{COCH}_2\text{CCOCH}_3$, 10 ml benzene; 50°C ; 2 d; crystallization from petroleum ether (40–60). Yield: 0.71 g (64%); m.p.: 104°C . ^1H 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, $^1J(\text{Si-H}) = 283$ Hz). IR (KBr, ν cm^{-1}): 2210 (Si-H). MS (m/z): 398 (1, M^+), 263 (100, $M^+ - \text{Cp}^*$), 135 (24, Cp^{*+}). Found: C, 75.17; H, 9.51. $\text{C}_{25}\text{H}_{38}\text{O}_2\text{Si}$ (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 . ^1H 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, $^1J(\text{Si-H}) = 215$ Hz). IR (KBr, ν cm^{-1}): 2114 (Si-H). MS (m/z): 422 (6, M^+), 287 (100, $M^+ - \text{Cp}^*$), 163 (76, Cp^*Si^+). Found: C, 76.02; H, 9.21. $\text{C}_{27}\text{H}_{38}\text{SSi}$ (422.75) calc.: C, 76.71; H, 9.06%.

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