Silsesquioxane Chemistry II. Tin(IV) and Hafnium(IV) Compounds of Silsesquioxanes

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Summary. Four complexes of silsesquioxanes with di- and triorganotin(IV) cations have been prepared; their composition was determined by standard analytical and spectroscopic methods. The results show that complexes containing an organotin(IV) moiety and the ligand in a 1:1 ratio are formed. FTIR spectra are consistent with the presence of Sn–O vibrations in the compounds. The structure of the complexes is discussed on the basis of *Mößbauer* and multinuclear (^{1}H, ^{13}C, ^{119}Sn, and ^{29}Si) NMR spectroscopic measurements. Comparison of the experimental quadrupole splitting (*QS*) with that calculated on the basis of the partial quadrupole splitting (*PQS*) concept revealed that the complexes formed with dialkyltin(IV) cations as well as the trialkyl derivatives have a regular tetrahedral structure. A new organohafnium silsesquioxane derivative ($[Cy_7Si_7O_{12}Hf(C_5Me_5)]$, $Cy =$ cyclohexyl, **5**), was prepared by treatment of $[Cy_7Si_7O_9(OH)_3]$ with $(C_5Me_5)HfMe_3$ under elimination of methane. The molecular structure of **5** was determined by X-ray crystallography.

Keywords. Silsesquioxanes; Organotin(IV) compounds; *Mößbauer* spectroscopy; Organohafnium(IV) compounds; X-Ray crystallography.

Silsesquioxanchemie II. Zinn(IV)- und Hafnium(IV)-Verbindungen von Silsesquioxanen

Zusammenfassung. Vier Komplexe von Silsesquioxanen mit Di- und Triorganozinn(IV)-Kationen wurden hergestellt; ihre Zusammensetzung wurde mit analytischen und spektroskopischen Standardmethoden bestimmt. Die Ergebnisse zeigen, daß in den gebildeten Komplexen Organozinneinheit und Ligand im Verhältnis von 1:1 vorhanden sind. FTIR-Spektren stehen im Einklang mit dem Auftreten von Sn–O-Schwingungen in den Verbindungen. Die Struktur der Komplexe wird auf der Grundlage von *Mößbauer*-Spektren und multinuklearen NMR-Experimenten (^{1}H, ^{13}C, ^{119}Sn, ^{29}Si) diskutiert. Ein Vergleich der experimentell beobachteten Quadrupolaufspaltung (*QS*) mit nach dem Konzept der partiellen Quadrupolaufspaltung (*PQS*) berechneten Werten ergab sowohl für die mit dem Dialkyzinn(IV)-Kation gebildeten Komplexe als auch für die Trialkylderivate eine regelmäßige tetraedrische Struktur. Ein neues Organohafniumsilsesquioxan-

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derivat ([$Cy_7Si_7O_{12}Hf(C_5Me_5)$], Cy = Cyclohexyl, **5**) wurde durch Umsetzung von [$Cy_7Si_7O_9(OH)_3$] mit $(C_5Me_5)HfMe_3$ unter Abspaltung von Methan hergestellt; seine Molekülstruktur wurde mittels Röntgenstrukturanalyse bestimmt.

Introduction

In a recently published review article by *Fehér et al.* [1] it was pointed out that incompletely condensed polyhedral silsesquioxanes (POSS) are an interesting class of ligands for both main group and transition metal elements. They possess a sufficient degree of oligomerization as to be relevant models for highly siliceous materials; furthermore, they retain reactive Si–OH functionalities which allow for their exploitation as ligands in a wide variety of main group and transition metal complexes. The electrochemical behavior of oligometallic sandwich complexes of cyclosiloxanolate ligands has also recently been studied [2].

The most common starting material in this field is the cyclohexyl substituted trisilanol [$Cy_7Si_7O_9(OH)_3$], which is generally prepared by the kinetically controlled hydrolysis of cyclohexyltrichlorosilane.
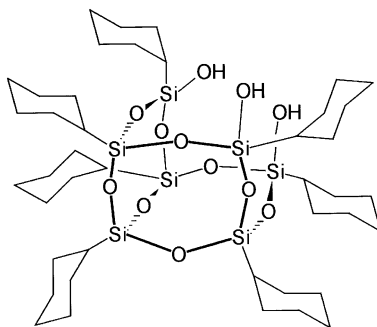
One or two OH groups in [$Cy_7Si_7O_9(OH)_3$] can be selectively blocked by trimethylsilyl substitution to afford the corresponding di- and monosilanols [$Cy_7Si_7O_9(OSiMe_3)(OH)_2$] and [$Cy_7Si_7O_9(OSiMe_3)_2(OH)$], respectively. The amine assisted metathesis reaction of Si–O–H with $L_xM–X$ bonds is quite convenient and has proven to be the most effective method for the synthesis of POSS complexes [1]. Utilizing this method, the mono- and disilanol have been capped with tri- and dialkyltin(IV) cations. The complexes thus formed were characterized by FTIR, multinuclear (^{1}H, ^{13}C, ^{119}Sn, and ^{29}Si) NMR, and *Mößbauer* spectroscopic methods. The latter was applied for the first time to investigate this type of compounds. Further, a new synthetic route has been developed to cap the incompletely condensed silsesquioxane [$Cy_7Si_7O_9(OH)_3$] with a $(C_5Me_5)Hf$ fragment.

Results and Discussion

Preparative results

Reactions of [$Cy_7Si_7O_9(OSiMe_3)(OH)_2$] and [$Cy_7Si_7O_9(OSiMe_3)_2(OH)$] with organotin(IV) chlorides were carried out in benzene solution according to Eq.

1: *R* = *n*-Bu   **3**: *R* = Me
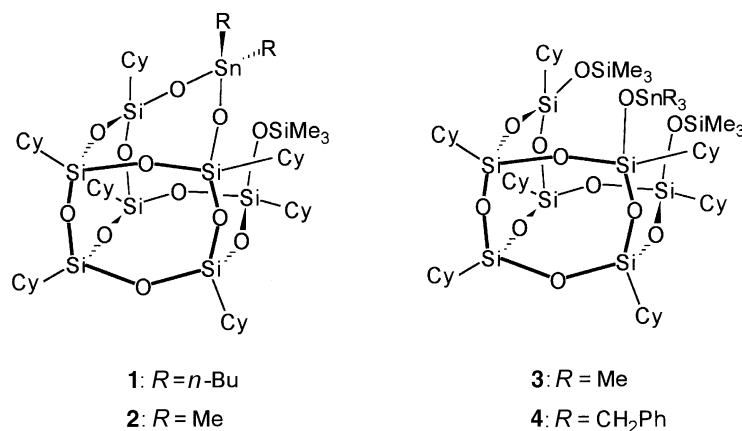
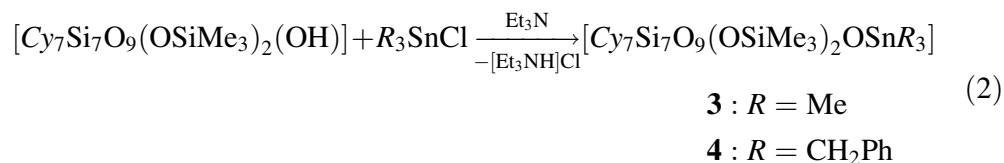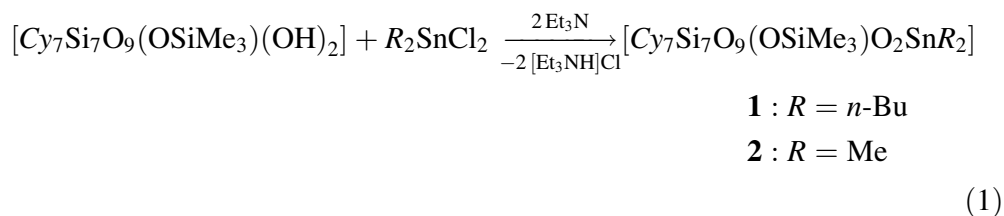**2**: *R* = Me   **4**: *R* = CH₂Ph

Fig. 1. Proposed structures of complexes **1**–**4**

(1) and (2). Appropriate amounts of triethylamine were added in order to trap the eliminated HCl.

$$[Cy_7Si_7O_9(OSiMe_3)(OH)_2] + R_2SnCl_2 \xrightarrow[-2\,[Et_3NH]Cl]{2\,Et_3N} [Cy_7Si_7O_9(OSiMe_3)O_2SnR_2]$$

$$\textbf{1}: R = n\text{-Bu}$$

$$\textbf{2}: R = Me$$

(1)

$$[Cy_7Si_7O_9(OSiMe_3)_2(OH)] + R_3SnCl \xrightarrow[-[Et_3NH]Cl]{Et_3N} [Cy_7Si_7O_9(OSiMe_3)_2OSnR_3]$$

$$\textbf{3}: R = Me$$

$$\textbf{4}: R = CH_2Ph$$

(2)

The analytical data of **1**–**4** clearly demonstrate that complexes with the required stoichiometry were formed *via* substitution of the chloride atoms in the alkyltin(IV) chlorides by hydrogen atoms of the free hydroxyl groups of the ligands, HCl molecules being eliminated (Fig. 1).

Related group 4 compounds derived from $[Cy_7Si_7O_9(OH)_3]$ have been reported earlier by *Feher et al.* [1]. The standard synthetic route is similar to that described here for the Sn derivatives and involves treatment of $[Cy_7Si_7O_9(OH)_3]$ with cyclopentadienyl metal trichlorides of Ti, Zr, and Hf in the presence of a base. However, this method has the drawback that it requires the separation of the product from the organoammonium chloride by-product. We report here an alternative route involving treatment of $[Cy_7Si_7O_9(OH)_3]$ with the corresponding trimethyl complexes as exemplified by the reaction with $(C_5Me_5)HfMe_3$ in diethylether solution. The reaction proceeded smoothly at room temperature under elimination of methane and afforded the hitherto unknown (pentamethylcyclopentadienyl)hafnium(IV) complex **5** in 78% yield (Scheme 1).
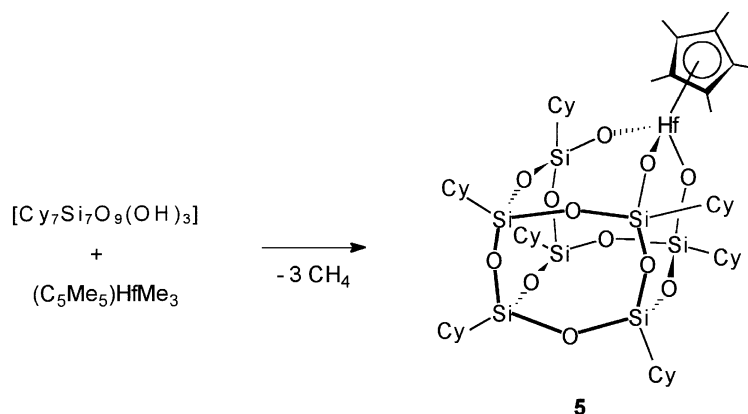
Scheme 1. Synthesis of hafnium complex **5**

Mößbauer measurements

In the case of **1**–**4** *Mößbauer* parameters (*IS* and *QS*) give information about the coordination polyhedra surrounding the tin atom. Certain ranges of *QS* associated with a particular stereochemistry are as following: tetrahedral SnR_2X_2: 1–2.4 mm/s, trigonal bipyramidal *cis*-SnR_2X_3: 3.0–3.5 mm/s, octahedral *cis*-SnR_2X_4: *ca.* 2 mm/s, and octahedral *trans*-SnR_2X_4: *ca.* 4 mm/s. However, it should be emphasized that most compounds have a structure which deviates more or less from these regular polyhedra, and the observed *QS* depends on the angle of $R{-}Sn{-}R$ (Θ) according to Eq. (3)

$$QS = -4[R](1 - (3/4)\sin^2\Theta)^{1/2} \tag{3}$$

A similar treatment may be applied to tetrahedral R_3SnX compounds, many of which show distorted structures. In such a case, *QS* becomes

$$QS = 2[X]_{\text{tetr}} - 3[R]_{\text{tetr}}(1 - 3\cos^2\Theta) \tag{4}$$

so that a reduction in Θ increases the contribution of the *R* groups [4].

For exemplification, a *Mößbauer* spectrum is shown in Fig. 2. All spectra exhibited *IS* and *QS* values which clearly indicated the presence of tin(IV) species within the complexes **1**–**4**. All spectra of the complexes studied comprised only one well developed doublet, suggesting the presence of equivalent environments of tin(IV) centres in these compounds. The *Mößbauer* parameters determined by computer evaluation of the spectra measured at liquid nitrogen temperature are collected in Table 1 together with the suggested configurations. To determine the stereochemical arrangement of the coordination sphere in these organotin(IV) compounds, the experimental *QS* values were calculated on the basis of a simple but general molecular orbital model, according to the *PQS* concept [4, 5] for the symmetries of four-coordinated tin(IV) atoms binding two or three alkyl groups and one or two negatively charged (deprotonated) oxygen atoms from the ligands. The *PQS* values of the different functional groups used in calculations and the calculated *QS* values for tin(IV) in tetrahedral stereochemical arrangements are
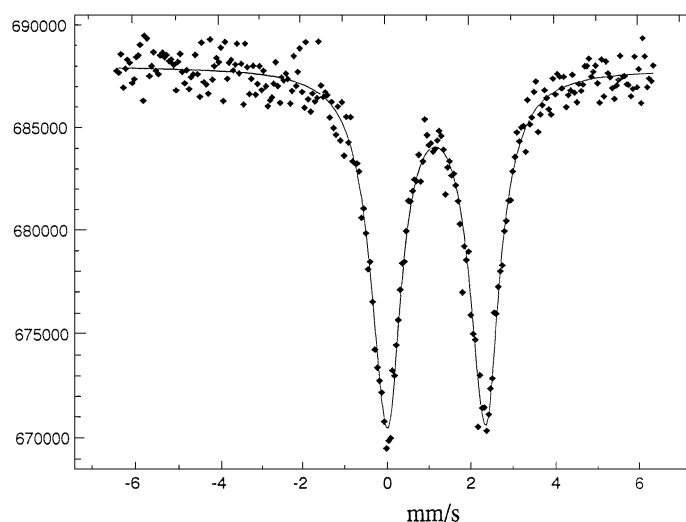
Fig. 2. Mößbauer spectrum of **1** measured at 77 K

Table 1. Experimental and calculated *Mößbauer* parameters for compounds **1**–**4**

	1	**2**	**3**	**4**
IS (mm/s)	1.18(4)	1.07(2)	1.20(4)	1.35(4)
QS_{exp} (mm/s)	2.35(8)	2.29(4)	2.13(9)	1.91(8)
QS_{calc} (mm/s)	2.30	2.30	2.00	1.78
Line width (mm/s)	0.86	0.86	0.83	0.88
Asymmetry (left/right)	1.008	1.021	1.155	1.116
Θ (C–Sn–C)	111.4°	109.2°	108.5°	108.4°

given as *PQS* (mms^{-1}) {Alk}^{tetr} = −1.37, {Ph, Bz} = −1.26, {−O^{-}}^{tetr} = −0.37, and {−OH}^{tetr} = −0.25.

$$QS(\mathrm{T_d}) = 1.15(2\{R\}^{tetr} - 2\{O^{-}\}^{tetr}) \tag{5}$$

Some *PQS* values were taken from the literature [5, 6]. The value of {O^{-}}^{tetr} was calculated *via* equation (6) in Ref. [7].

The evaluation of the *Mößbauer* measurements on the basis of the *PQS* concept and chemical evidence showed that the tin(IV) in the studied alkytin(IV) complexes **1**–**4** is four-coordinated and that all four complexes have a regular tetrahedral structure with a small distortion (Table 1). These findings are consistent with the result obtained by single crystal X-ray diffraction studies on the *bis*(triphenyltin) derivative [$Cy_8Si_8O_{11}(OSnPh_3)_2$] [3].

NMR investigations

The ^{1}H NMR spectra of **1** and **2** show several broad signals in the range from 2.19 to 0.9 which correspond to the protons of the *c*-C_6H_{11} groups. In the ^{1}H NMR spectrum of **2** there are two separated signals for the methyl groups bonded to the central tin atom (at 0.53 and 0.47 ppm) with a coupling constant of 19.62 Hz. It is

impossible to see an analogous picture in the spectrum of **1**, because the proton signals of the *n*-butyl groups are very close to those of the *c*-C_6H_{11} protons. Due to coupling with the tin, the ^{13}C NMR spectra for both **1** and **2** show also two signals with coupling constants of 42.9 and 42.4 Hz, respectively. This may be associated with some steric influence of the bulky $SiMe_3$ group on the alkyl substituents at the Sn atoms in **1** and **2**. The ^{29}Si NMR spectra of the two complexes are very similar and contain six (two signals at −67.4 and −67.5 ppm are very close) singlets for **1** and five singlets for **2** (two signals are too close to be resolved in this case). The shifts observed in the ^{29}Si NMR spectra of **1** and **2** are slightly different from those of the starting silsesquioxane [3]. A ^{119}Sn NMR spectrum of **1** shows just one singlet at −46.14 ppm. In contrast, the ^{119}Sn NMR spectrum of **2** displays a multiplet (signals are very close to each other) at −8.07 ppm. This difference suggests that in contrast to monomeric **1** (the *n*-butyl groups are probably too bulky) complex **2** adopts a dimeric structure in solution. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3** and **4** show two separated signals for the $SiMe_3$ groups, which are however quite close to each other. The ^{29}Si NMR spectra of **3** and **4** also contain a number of signals in a very narrow range corresponding to the siloxane skeleton. The ^{119}Sn NMR spectra of **3** and **4** show singlets at 113.43 and −20.41 ppm, respectively. As expected, the chemical shift in for **3** (113 ppm) is essentially different from those of **1** and **2**. This can be explained by different electronic effects of monosilanol and disilanol ligands on the tin atom. Complexes **3** and **4** have obviously monomeric structures in solution. The NMR data of **5** are also consistent with a monomeric structure in which the incompletely condensed silsesquioxane cube is completed by a $(C_5Me_5)Hf$ fragment.

FTIR investigations

The IR data are also consistent with the formation of well-defined compounds. The IR spectra of the complexes formed with alkyltin(IV) cations (**1**–**3**) show clearly the presence of alkyl groups in the molecules. The characteristic frequencies of the di-*n*-butyltin(IV) oxide **1** in the region of 2300–700 cm^{-1} are weak, and the absorptions related to these in the complexes are generally masked by the strong absorptions of the ligands. In the IR spectra of the complexes, the most characteristic changes occur in the spectral regions of 600–400 cm^{-1}, 1200–1000 cm^{-1}, and 3600–2700 cm^{-1}. Vibration bands characteristic of $(Sn-C)_{as}$ at 544–562 cm^{-1}, $(Sn-C)_s$ at 453–502 cm^{-1} [8], and $(Sn-O)_{as}$ at 640–643 cm^{-1} as well as $(Sn-O)_s$ at 576–619 [9] appeared (Table 2). The changeover from the -C−O vibration of the -COH groups in the ligands to those of the -COSn groups in the complexes caused alterations in the region 1200–1000 cm^{-1}. The interaction of the

Table 2. FTIR data for compounds **1**–**4** (cm^{-1})

	1	2	3	4
$\nu(Sn-C)_{as}$	548	559	544	549
$\nu(Sn-C)_s$	501	502	501	501
$\nu(Sn-O)_{as}$	642	643	641	640
$\nu(Sn-O)_s$	619	618	576	614

alkyltin(IV) cation with the ligands clearly involved the OH groups of the ligands. Accordingly, the free OH stretching absorptions disappeared in the vibration spectra of the complexes.

X-ray structure determination of 5

The measurement was performed using a Siemens SMART CCD diffractometer with MoK_α X-radiation ($\lambda = 0.71073$ Å). A selected crystal of 5 was coated with mineral oil, mounted on a glass fibre, and transferred to a cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. Crystal data of 5: $C_{52}H_{92}HfO_{12}Si_7$, $M = 1284.38$, orthorhombic, space group $Pca2_1$, $a = 2522.92(1)$, $b = 1184.84(1)$ $c = 4216.6(3)$ pm, $V = 12.5927(2)$ nm^3, $Z = 8$, $D_x = 1.355$ Mg·m^{-3}, $F(000) = 5360$, $\lambda = 71.073$ pm, $T = 153(2)$ K, $\mu(MoK_\alpha) = 1.843$ mm^{-1}. Absorption correction by SADABS; $T_{min}/T_{max} = 0.64/1.00$. The structure was solved by direct methods and refined on F^2 to give R(conventional) $= 0.055$ (wR^2, all data $= 0.103$), and GoF $= 1.034$ for 82486 (observed) and 27852 (independent) reflections; $R_{int} = 0.077$ [10]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included using a riding model, except for rigid methyls (*Elack* parameter $x = -0.003(4)$ [11]).

The X-ray structure determination of 5 confirms the presence of a closed silsesquioxane cage in which the open corner of the precursor $[Cy_7Si_7O_9(OH)_3]$ has been capped by a (pentamethylcyclopentadienyl)hafnium fragment. The average Hf–O distance is 195.8 pm, whereas the average Hf–C bond lengths to the C_5Me_5 ligand have been determined as 250.5 pm (Fig. 3).
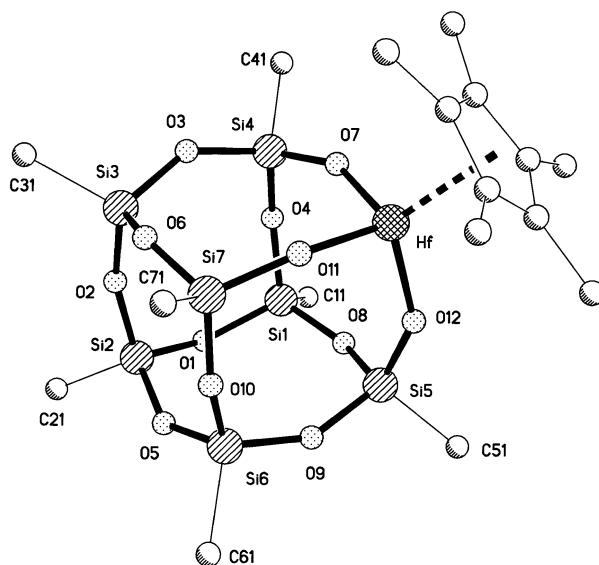

Fig. 3. Molecular structure of one of the two independent molecules of 5; all carbon atoms except for the *ipso*-carbons of the cyclohexyl groups and the Cp^* ring carbons as well as all hydrogen atoms are omitted for clarity; selected bond lengths and angles; Hf-O7 194.9(4), Hf-O11 196.7(4), Hf-O12 195.9(4), Hf-C81 250.3(7), Si1-O1 163.3(5), Si1-C11 185.9(7), average Hf-C distance 250.5(7) pm; O7-Hf-O11 102.7(2), O1-Si2-O5 108.5(2), Si4-O7-Hf 153.2(3), Si2-O5-Si6 144.9(3)°.

Experimental

Preparation of the ligands and the complexes

All manipulations were performed using *Schlenk* and dry box techniques. Solvents were appropriately dried and distilled under nitrogen prior to use. The literature method was used for preparation and purification of the ligand [3]. Di- and trimethyltin(IV)-chlorides as well as $(C_5Me_5)HfCl_3$ were obtained from Aldrich and used as received.

[Cy$_7$Si$_7$O$_9$(OSiMe$_3$)O$_2$SnBu$_2$] (**1**, Cy = c-C$_6$H$_{11}$)

0.82 g (0.78 mmol) of $[Cy_7Si_7O_9(OSiMe_3)(OH)_2]$ were added to a solution of Bu_2SnCl_2 (0.24, 0.78 mmol) and 0.5 ml of triethylamine in 25 ml of benzene. The mixture was stirred for 3 h and then evaporated in vacuum. The residue was extracted with 30 ml of toluene, the extract was filtered and the filtrate was evaporated in vacuum to give white crystals (0.83 g, 82%).

$C_{53}H_{104}O_{12}Si_8Sn$; calcd.: C 49.81, H 7.92; found: C 49.15, H 8.03; ^{1}H NMR (300 MHz, C_6D_6, 20°C): $\delta = 2.19$–1.24 (m, 82H, $CH_2(Bu)+CH_2(c\text{-}C_6H_{11})$), 1.10–0.89 (m, 13H, $CH_2(Bu)+CH$ (c-C_6H_{11})), 0.37 (s, 9H, $SiMe_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20°C): $\delta = 28.26, 28.16, 27.93$, 27.84, 27.69, 27.60, 27.53, 27.42, 27.24, 27.13, 27.07 (CH_2, c-C_6H_{11}), 26.04, 25.75, 25.25, 24.28, 23.86 (CH, c-C_6H_{11}), 21.57, 21.01 (CH_2, Bu), 13.78 (CH_2, Bu), 2.09 ($SiMe_3$), 1.37 (CH_3, Bu) ppm; $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6, 22°C): $\delta = 9.04$ (s, $SiMe_3$), $-64.21, -66.66, -67.50, -69.91$ (s, silox) ppm; $^{119}Sn\{^1H\}$ NMR (112 MHz, C_6D_6, 22°C): $\delta = -46.14$(s) ppm.

[Cy$_7$Si$_7$O$_9$(OSiMe$_3$)O$_2$SnMe$_2$] (**2**)

1.33 g (1.27 mmol) of $[Cy_7Si_7O_9(OSiMe_3)(OH)_2]$ were added to a solution of 0.28 g (1.27 mmol) of Me_2SnCl_2 and 0.7 ml of triethylamine in 30 ml of benzene. The mixture was stirred for three hours; then the mixture was evaporated in vacuum. Work-up as described above yielded a white solid (1.13 g, 75%).

$C_{47}H_{92}O_{12}Si_8Sn$; calcd.: C 47.35, H 7.72; found: C 47.27, H 7.64; ^{1}H NMR (300 MHz, C_6D_6, 20°C): $\delta = 2.14$–1.26 (m, 70H, $CH_2(c\text{-}C_6H_{11})$), 1.09–0.96 (m, 7H, $CH(c\text{-}C_6H_{11})$), 0.53 and 0.47 (s, 6H, CH_3), 0.34 (s, 9H, $SiMe_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20°C): $\delta = 28.51, 28.43$, 28.36, 28.21, 28.13, 27.97, 27.93, 27.79, 27.71, 27.67, 27.56 (CH_2, c-C_6H_{11}), 26.11, 25.99, 25.48, 24.56, 24.15 (CH, c-C_6H_{11}), 2.94 ($SiMe_3$), 0.79, 0.22 (CH_3) ppm; $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6, 22°C): $\delta = 9.31$ (s, $SiMe_3$), $-63.75, -66.80, -67.61, -69.91$ (s, silox) ppm; $^{119}Sn\{^1H\}$ NMR (112 MHz, C_6D_6, 22°C): $\delta = -8.07$(s) ppm.

[Cy$_7$Si$_7$O$_9$(OSiMe$_3$)$_2$OSnMe$_3$] (**3**)

0.84 g (0.75 mmol) of $[Cy_7Si_7O_9(OSiMe_3)_2(OH)]$ were added to a mixture of 0.15 g (0.75 mmol) of Me_3SnCl and 0.25 ml of triethylamine in 30 ml of benzene. The mixture was stirred for 3 h, evaporated to dryness, and the residue was extracted with 40 ml of hexane. The extract was filtered, and the filtrate was evaporated in vacuum to give a white solid (0.74 g, 77%).

$C_{51}H_{104}O_{12}Si_9Sn$; calcd.: C 47.85, H 8.13; found: C 47.32, H 7.96; ^{1}H NMR (300 MHz, C_6D_6, 24°C): $\delta = 2.17$–1.31 (m, 70H, $CH_2(c\text{-}C_6H_{11})$), 1.07–0.93 (m, 7H, $CH(c\text{-}C_6H_{11})$), 0.52–0.23 (m, 27H, CH_3+SiMe_3) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 24°C): $\delta = 27.78, 27.70, 27.61, 27.44$, 27.40, 27.34, 27.30, 27.19, 27.16, 27.07, 27.02 (CH_2, c-C_6H_{11}), 26.89, 26.74, 26.69, 25.21, 23.80 (CH, c-C_6H_{11}), 1.86 and 0.80 ($SiMe_3$), -2.31 and -2.85 (CH_3) ppm; $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6, 22°C): $\delta = 9.88, 8.75$ (s, $SiMe_3$), $-58.97, -65.09, -67.07, -67.92, -68.06, -68.24, -69.06$, $-69.78, -70.09$ (s, silox) ppm; $^{119}Sn\{^1H\}$ NMR (112 MHz, C_6D_6, 25°C): $\delta = 113.43$(s) ppm.

$[Cy_7Si_7O_9(OSiMe_3)_2OSn(CH_2Ph)_3]$ (**4**)

0.96 g (0.86 mmol) of $[Cy_7Si_7O_9(OSiMe_3)_2(OH)]$ were added to 0.37 g (0.86 mmol) of $(PhCh_2)_3SnCl$ and 0.5 ml of triethylamine in 30 ml of benzene and stirred for 3 h. The mixture was evaporated in vacuum and the residue was extracted with 50 ml of hexane. The extract was filtered and the solution was evaporated in vacuum to give a slightly yellow wax-like solid (0.96 g, 74%).

$C_{69}H_{116}O_{12}Si_9Sn$; calcd.: C 54.94, H 7.7; found: C 54.65, H 7.87; ^1H NMR (300 MHz, C_6D_6, 24°C): $\delta = 7.11$–6.69 (m, 15H, C_6H_5), 2.73 (s, 6H, CH_2), 2.14–1.22 (m, 70H, $CH_2(c\text{-}C_6H_{11})$), 1.08–0.93 (m, 7H, $CH(c\text{-}C_6H_{11})$), 0.36 (s, 18H, $SiMe_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 24°C): $\delta = 139.49$, 129.02, 124.64 (C_6H_5), 46.75 (CH_2), 28.37, 28.23, 28.15, 27.93, 27.89, 27.86, 27.74, 27.70, 27.63, 27.59, 27.49 (CH_2, $c\text{-}C_6H_{11}$), 27.32, 27.25, 25.61, 24.77, 24.37 (CH, $c\text{-}C_6H_{11}$), 2.15 ($SiMe_3$) ppm; $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6, 22°C): $\delta = 9.89$, 9.15 (s, $SiMe_3$), −58.93, −65.03, −67.06, −68.04, i 68.22, −68.8, −69.13, −69.70 (s, silox) ppm; $^{119}Sn\{^1H\}$ NMR (112 MHz, C_6D_6, 25°C): $\delta = -20.41$(s) ppm.

$[Cy_7Si_7O_{12}Hf(C_5Me_5)]$ (**5**)

56 mmol MeLi (35 ml 1.6 M ether solution) were added to a suspension of 7.7 g (18.4 mmol) Cp^*HfCl_3 in 200 ml ether at −78°C, stirred for 5 h, and warmed up slowly to 20°C. The mixture was cooled down again to −78°C, and 17.9 g (18.4 mmol) $[Cy_7Si_7O_9(OH)_3]$ were added during 2 h. The solution was stirred overnight; then the solvent was evaporated in vacuum, and the residue was extracted with 150 ml of pentane. The extract was filtered and the solvent was removed partially in vacuum to give colorless crystals (17 g, 78%).

$C_{52}H_{92}HfO_{12}Si_7$; calcd.: C 48.63, H 7.17; found: C 48.05, H 6.94; ^1H NMR (400 MHz, C_6D_6, 24°C): $\delta = 2.09$ (s, 15H, C_5Me_5), 1.73 (m, 35H, $CH_2(c\text{-}C_6H_{11})$), 1.24 (m, 35H, $CH_2(c\text{-}C_6H_{11})$), 0.71 (m, 7H, $CH(c\text{-}C_6H_{11})$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 24°C): $\delta = 120.50$ (C_5Me_5), 28.50, 28.36, 28.30, 27.93, 27.84, 27.75, 27.65 (CH_2, $c\text{-}C_6H_{11}$), 25.04, 24.36, 24.33 (3:3:1, CH, $c\text{-}C_6H_{11}$), 10.64 (C_5Me_5) ppm; IR (KBr): $\nu = 2922$ vs, 2849 vs, 2666 vw, 1448 m, 1354 w, 1347 w, 1275 m, 1268 m, 1196 s, 1107 vs, 1027 vs, 1001 m, 930 s, 894 m, 848 m, 825 w, 759 w, 742 w, 689 w, 670 w, 648 w, 618 w, 556 m, 546 m, 515 s, 491 m, 467 s cm^{-1}.

Measurements

Microanalyses were carried out at the Department of Chemistry, Otto-von-Guericke-University, Magdeburg. The analytical data showed that complexes with a stoichiometry of ligand: organotin(IV) = 1:1 were formed. IR spectra in the region of 4000–200 cm^{-1} were recorded in KBr pellets using a Perkin Elmer 2000 FTIR spectrometer. The ^{119}Sn *Mößbauer* spectra were recorded at 77 K on a RANGER spectrometer in constant accelerating mode with a source activity of 0.4 GBq. Computer evaluation was used to determine isomer shift (*IS*) and quadrupole splitting (*QS*) values. The spectra were analyzed as *Lorentzian* lines by least-squares fitting. The reproducibility of the *Mößbauer* parameters was found to be ±0.02 mm/s (*IS*) and 0.04 mm/s (*QS*), respectively, in each measurement. The *IS* values are referred to that of $CaSnO_3$.

Acknowledgements

References

[1] Fehér FJ, Budzichowski TA (1995) Polyhedron **14**: 3239 and references therein

[2] Borsari M, Gavioli G, Zucci C, Pályi G, Pesaro R, Ugo R, Shchegolikhina OI, Zhdanov AA (1997) Inorg Chim Acta **258**: 139

[3] Fehér FJ, Newman DA, Walzer JF (1989) J Am Chem Soc **111**: 1741

[4] Parish RV (1984) Structure and Bonding in Tin Compounds. In: Long GJ (ed) Mößbauer Spectroscopy Applied to Inorganic Chemistry. Plenum Press, New York London

[5] Bancroft GM, Kumar Das VG, Sham TK, Clark MG (1976) J Chem Soc Dalton Trans 643

[6] Korecz L, Saghier AA, Burger K, Tzschach A, Jurkschat A (1982) Inorg Chim Acta **58**: 243

[7] Bancroft GM, Sham TK (1976) J Chem Soc Dalton Trans 467

[8] Pellerito L, Ruisi G, Barbieri R, Lo Giudice MT (1977) Inorg Chim Acta **21**: L33

[9] Bucher FK, Gerrard W, Money EF, Rees RG, Williams HA (1964) Spectrochim Acta **20**: 51

[10] Sheldrick GM (1995) SHELXTL, Structure Determination Software Programs, Version 5.03 (PC), Siemens Analytical X-Ray Instruments. Madison, WI. Additional material to the structure determination may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany, referring to the deposition number CSD-410524

[11] Flack HD (1983) Acta Cryst **A39**: 876