

Synthesis and characterization of tin containing polyhedral oligometallasilsesquioxanes (POMSS)

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Tin silicate species have shown good catalytic activity in various oxidation reactions. In an attempt to mimic surface tin species, several tin containing silsesquioxanes have been synthesized. Incompletely condensed silsesquioxanes ($(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ and $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$) were reacted with common tin-precursors, which afforded several silsesquioxane ligated tin compounds. Divalent stannasilsesquioxanes form dimers of the type $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OX})\text{Sn}]_2$ ($\text{X} = \text{H}, \text{SiMe}_3$) with three-coordinated tin centers. The three-coordinated tin(II) are hydrolytically unstable whereas the octahedrally surrounded tetravalent stannasilsesquioxanes $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OX})]\text{Sn}(\text{acac})_2$ ($\text{X} = \text{H}, \text{OSiMe}_3$) are hydrolytically robust. An unprecedented anionic trimeric cluster, $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu_2\text{-OH})_3(\mu_3\text{-OH})\}^-\{\text{HNEt}_3\}^+$, stabilized by bridging hydroxyl groups was formed when the product formed upon reacting $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ with SnCl_4 was slowly hydrolyzed. The stannasilsesquioxanes showed no catalytic activity in oxidation reactions.

Introduction

Tin silicate species have shown good catalytic activity in various oxidation reactions.¹ Tin incorporated silicates were found to be active for the hydroxylation of phenol,² whereas Sn–ZSM-12 and Sn–Al- β catalyze the oxidation of various substituted aryls with moderate selectivity.³ Tin containing zeolite- β and tin exchanged hydrotalcite showed high activity and selectivity for the catalytic Baeyer–Villiger oxidation of cyclic ketones into lactones, as well as the Oppenauer oxidation of primary alcohols.^{1,4}

Titanium silicates, which are believed to be iso-structural to the corresponding tin species, showed remarkable catalytic activity in selective oxidations with H_2O_2 .^{5–7} A general consensus is that the most active and selective sites in the tin and titanium silicates consist of isolated, mononuclear, tetrahedral tin and titanium centers embedded in the surface of the silica framework.⁸

The active sites of titanium silicate catalysts have recently been successfully mimicked by soluble titanium siloxides based on incompletely condensed silsesquioxanes. The catalytic activity of a number of these titanasilsesquioxane complexes with mono-, bi- and terdentate ligated silsesquioxanes $\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_3$, $\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_2(\text{OSiR}^2_3)$, $\text{R}_7\text{Si}_7\text{O}_9(\text{OH})(\text{OSiR}^2_3)_2$, ($\text{R}^1 = c\text{-C}_5\text{H}_9$, $c\text{-C}_6\text{H}_{11}$, $c\text{-C}_7\text{H}_{13}$; $\text{SiR}^2_3 = \text{SiMe}_3$, SiMePh_2) has been reported by the groups of Abbenhuis,⁹ Maschmeijer¹⁰ and Crocker¹¹ (Fig. 1). Terdentately bonded titanasilsesquioxane complexes are hydrolysis stable and proved suitable catalysts for the epoxidation of alkenes in aqueous media. When a hydrophobic pore was simulated by grafting the catalyst on cross-linked polysiloxanes, hydrogen peroxide could be successfully used as oxidant instead of the usual alkyl peroxide.⁹

We were interested whether, in analogy with the titanasilsesquioxanes, stannasilsesquioxane compounds could mimic the

active tin sites incorporated in a silicate framework. In an attempt to model such tin species, we here describe the synthesis and characterization of several silsesquioxane tin compounds.

Results and discussion

Protonolysis of tin amides proved to be an effective route to prepare tin(II) silsesquioxanes. For example, the reaction of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ with $(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$ and $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ selectively afforded the stannasilsesquioxanes $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Sn}]_2$ (**1**) and $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}]_2$ (**2**, Scheme 1). The ^1H NMR spectrum of **1** shows the SiOH resonances as a sharp singlet at 8.92 ppm, which is at low field compared to other silsesquioxane silanols. Isolated silanols such as $(c\text{-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}\text{OH}$ (2.53 ppm), and weakly hydrogen bonding vicinal and geminal silanols like $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ or $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)_2\text{Si}(\text{OH})_2$ show sharp to slightly broadened high field resonances around 2–4 ppm. Strongly hydrogen bonded silanols as observed for $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ and $(c\text{-C}_7\text{H}_{13})_7\text{Si}_6\text{O}_7(\text{OH})_4$ show broad resonances around 6–7 ppm.¹² The low-field SiOH resonance for **1** is probably caused by interaction of the silanol with the tin lone pair. Hydrogen bonding to divalent tin could also explain the broad ν_{OH} stretch vibration at 3145 cm^{-1} , which is a typical frequency for strongly hydrogen bonded hydroxyl groups. However, strongly hydrogen bonded hydroxyls are normally accompanied with broad ^1H NMR resonances, whereas **1** shows a sharp signal. The ^{13}C NMR spectrum of **1** and **2** are very similar and show five methine resonances in a 1:2:2:1:1 ratio, indicative for a C_5 -symmetric ligand system in a highly fluxional system. Compounds **1** and **2** are hydrolysis unstable and upon exposure to moisture they form the free silsesquioxane silanols, as was also found for many metallasilsesquioxanes.¹³

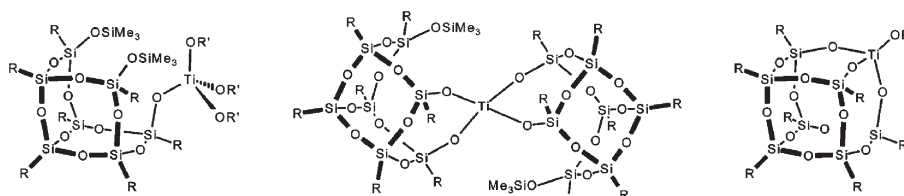
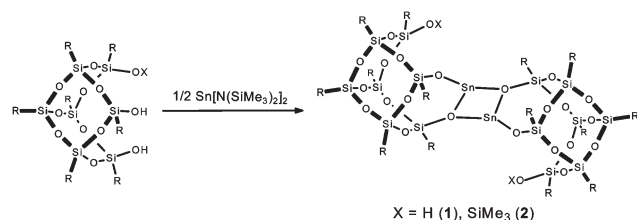


Fig. 1 Examples of monodentate, bidentate and terdentate, titanasilsesquioxane complexes.

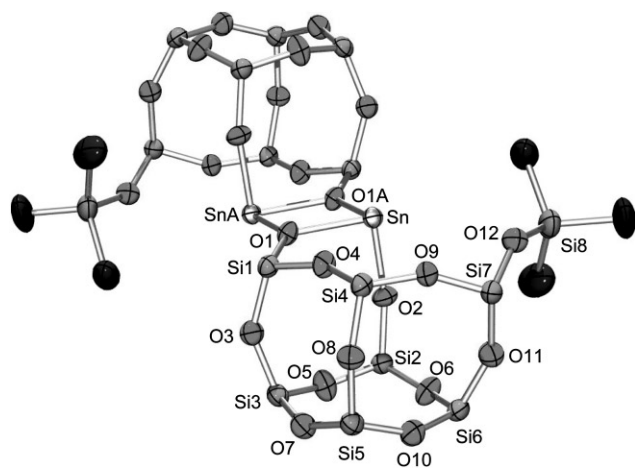
Table 1 Selected interatomic distances and angles for $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}]_2$ (**2**)

Bond distances/Å			Angles/°		
Sn–O1	2.177(3)	Sn–O1–SnA	104.61(13)	O1–Si1–O4	102.97(17)
Sn–O1A	2.172(3)	Sn–O1–Si1	118.63(16)	O2–Si2–O5	111.0(2)
Sn–O2	1.995(3)	SnA–O1–Si1	135.71(18)	O3–Si1–O4	109.99(18)
Si1–O1	1.636(3)	Sn–O2–Si2	156.5(2)	O–Si–O _{av}	109.0(3)
Si1–O3	1.616(3)	O1–Sn–O1A	75.39(13)	Si1–O3–Si3	142.6(2)
Si1–O4	1.627(3)	O1–Sn–O2	92.28(13)	Si1–O4–Si4	152.0(2)
Si2–O2	1.591(3)	O1A–Sn–O2	90.23(14)	Si2–O6–Si6	156.3(3)
Si–O _{av}	1.616(1)	O1–Si1–O3	110.55(18)	Si–O–Si _{av}	150.3(0)

**Scheme 1** Synthesis of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OX})\text{Sn}^{\text{II}}]_2$ ($\text{X} = \text{H}$ (**1**), SiMe_3 (**2**)).

The crystal structure of the dimeric $\text{Sn}(\text{II})$ complex $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}^{\text{II}}]_2$ (**2**) is shown in Fig. 2. Selected bond distances and angles are listed in Table 1. The structure has a center of inversion in the middle of the $(\text{SnO})_2$ ring. The tin centers are three-coordinated and, taking the lone pair into account, the tin atoms are distorted tetrahedrally surrounded. Both silsesquioxane cages are *trans* oriented and nearly perpendicular with respect to the oxygen connected to both the $(\text{SnO})_2$ ring and the cage ($\text{O1–Sn–O2} = 92.28(13)^\circ$, $\text{O1A–Sn–O2} = 90.23(14)^\circ$), consequently stretching the Sn–O2–Si2 ($156.5(2)^\circ$) and Si2–O6–Si6 ($156.3(3)^\circ$) angles somewhat. The four-membered $(\text{SnO})_2$ ring is planar with a strained geometry at each Sn atom with an O1–Sn–O1A angle of $75.39(13)^\circ$ and an Sn–O1–SnA angle of $104.61(13)^\circ$. A similar *trans*-dimer has been described for the bulky tin-alkoxide $[\text{Sn}^{\text{II}}(\text{O}-t\text{-Bu})(\mu\text{-O}-t\text{-Bu})_2]_2$.¹⁴ For this complex, a slightly larger endocyclic O–Sn–O angle of $76(2)^\circ$ and slightly smaller Sn–O bonds for the $(\text{SnO})_2$ ring ($\text{Sn–O} = 2.16(1)$ Å) was found compared to $\text{Sn–O1} = 2.177(3)$ Å and $\text{Sn–O1A} = 2.172(3)$ Å for **2**. Binuclear tin(II) calixarene, prepared from $[t\text{-Bucalix}]_4\text{H}_4$ and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ possess two 3-coordinate tin atoms as well, with an even more strained $(\text{SnO})_2$ ring ($\angle \text{O–Sn–O} = 68.2(1)^\circ$).¹⁴ The Sn–O bonds in the $(\text{SnO})_2$ parallelogram are 2.193(2) and 2.169(2) Å, which are also smaller than observed for **2**. As expected, the distance between the tin atoms and the σ -bonded oxygen atoms is shorter (Sn–O2 , 1.995(3) Å) than the distance between tin and the bridging oxygens.

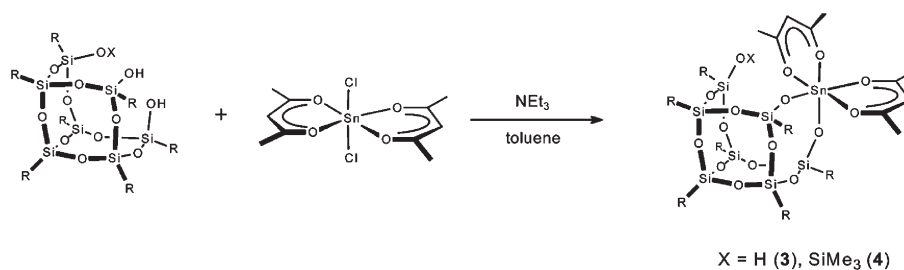
Tetravalent stannasilsesquioxanes are accessible by ammonium salt forming reactions between tetravalent tin halides and silsesquioxanes in the presence of an amine. For example,

**Fig. 2** Molecular structure of $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}]_2$ (**2**); cyclopentyl substituents attached to the silsesquioxane cages are omitted for clarity.

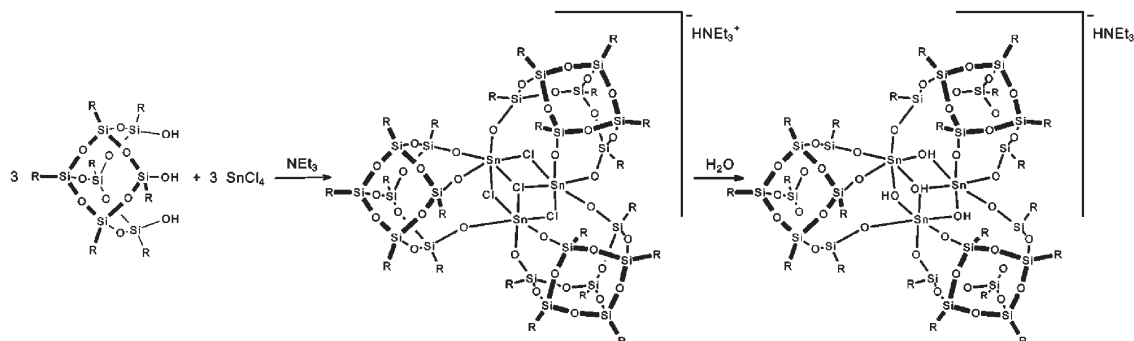
hydrolysis stable stannasilsesquioxane complexes can be obtained by starting from bis(acetylacetonate) tin dichloride, $\text{Cl}_2\text{Sn}(\text{acac})_2$ ($\text{acac} = \text{acetylacetonate}$). When $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ and $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ were treated with $\text{Cl}_2\text{Sn}(\text{acac})_2$ in the presence of NEt_3 , the corresponding products $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Sn}(\text{acac})_2$ (**3**) and $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}(\text{acac})_2$ (**4**) (Scheme 2) could be isolated in good yield. Surprisingly, the third silanol in **3** remains unaffected. Even extensive heating (toluene, reflux) did not lead to protonolysis by the remaining silanol of one of the acetylacetonate ligands to form the putative closed caged $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{Sn}(\text{acac})$. Apparently, coordination of the acetylacetonate ligands to tin affords a highly stable 6-membered metallacycle that can compete with the often observed tendency to form closed caged metallasilsesquioxane complexes. Basset *et al.* reported the synthesis and IR study of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_2\text{Sn}(\text{n-Bu})_2$.¹⁵ Based on a low-frequency shift (3373 cm^{-1}) of the ν_{OH} stretching vibration, an interaction between the tin center and the adjacent silsesquioxane OH group was assumed. In **3**, a similar low-frequency shift of the ν_{OH} stretching vibration (3404 cm^{-1}) was observed as well as a low field shift of the ^1H NMR OH resonance (4.86 ppm), which suggests a similar interaction of the OH with the tin site as was described by Basset. However, **3** contains a coordinatively saturated octahedral tin center that is unlikely to undergo additional interaction with the hydroxyl group. Hydrogen bonding between the hydroxyl and the acetylacetonate ligands is also unlikely since hydrogen bonding generally results in broadening of the ^1H NMR hydroxyl resonance, which is not the case in **3**. Hence, the OH shifts in IR and ^1H NMR spectra are probably not correlated to interactions with the tin center or acetylacetonate ligands and are more likely to be the result of some structural constrain.

Attempts to form tetrahedral stannasilsesquioxane species of the type $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2\text{Sn}]$ or $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{SnX}$ with a terdentately bonded silsesquioxane ligand and a reactive group (X),¹⁶ invariably failed. The reaction between $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ and SnCl_4 is sluggish and produces ill-defined products. This is in sharp contrast with the same reaction with other metal halide precursors such as TiCl_4 , ZrCl_4 and AlCl_3 which selectively afford the corresponding metallasilsesquioxanes $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2\text{M}]$ ($\text{M} = \text{Ti}$, Zr) and $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2\text{Al}]^+\{ \text{HNEt}_3 \}^-\}$, respectively.¹⁷ Treating $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ with an equimolar amount of SnCl_4 in toluene in the presence of NEt_3 afforded an ionic trimer $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu_2\text{-Cl})_3(\mu_3\text{-Cl})\}^-\{ \text{HNEt}_3 \}^+$ (**5**) instead of the expected $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}]\text{SnCl}$. In spite of the poor quality of the dataset of **5**, the preliminary crystal structure revealed that **5** is an anionic trimeric cluster with four bridging chlorides, accompanied by a triethyl ammonium counter ion. The structure of **5** is schematically presented in Scheme 3. In the chloride bridged cluster each tin atom is connected to two different silsesquioxane cages. Three chlorides are μ^2 -bridging while one is μ^3 -bridging between all three tin centers. The seven equi-intense methane resonances in the ^{13}C NMR spectrum of **5** are in agreement with a C_{3v} symmetric structure. The two ^{29}Si NMR resonances of the silsesquioxane framework silicons (3:4 ratio) demonstrate considerable fluxionality on the NMR timescale. The ^{119}Sn NMR resonance of **5** at -614.87 ppm also supports the presence of highly coordinated tin as was observed in the solid state.

The chloride **5** is moisture sensitive and gradually hydrolyses to the corresponding hydroxide species. When for example



Scheme 2 Synthesis of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_7(\text{OX})\text{O}_2\text{Sn}(\text{acac})_2$ ($\text{X} = \text{H}$ (**3**), SiMe_3 (**4**)).



Scheme 3 Synthesis of the trimeric clusters **5** and **6**.

a bromoform solution of **5** was layered with water and left at ambient temperature, large colorless crystals suitable for an X-ray analysis of the hydrolysis product **6** were formed overnight. Complex **6**, $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{OSn}]_3(\mu_2\text{-OH})_3(\mu_3\text{-OH})\}^-\{\text{HNEt}_3\}^+$, is iso-structural to **5** and consists of an anionic cluster where three silsesquioxane cages are held together by three tin atoms with intramolecular bridging hydroxyls.

The crystal structure of **6** is shown in Fig. 3. Selected bond distances and angles of **6** are listed in Table 2. Three of the OH groups in **6** are μ_2 -bridging between two tin atoms and a fourth hydroxyl is μ_3 -bridged between three tin atoms (Fig. 3A, 3B). Each silsesquioxane cage is bonded to two tin atoms, monodentately to one tin atom and bidentately to the other tin atom. Consequently, each tin center is octahedrally surrounded in an almost undistorted manner. The three four-membered rings consisting of $[\text{Sn}(\mu\text{-OH})]_2$ form a portion of an incomplete cube (Fig. 3B). The ammonium counter ion fills the final corner of this cube and most probably forms hydrogen bonding interactions with the three $\text{Sn}(\mu_2\text{-OH})\text{-Sn}$ hydroxyl groups (Fig. 3B). The Sn-O distances range from 2.087(5) Å to 2.137(5) Å for the hydroxyls bridged by two Sn atoms and are somewhat elongated for the hydroxyl bridged by three Sn atoms ($\text{Sn-O}_{\text{av.}} = 2.277(6)$ Å). As expected, the $\text{Sn}(\mu_2\text{-OH})\text{-Sn}$ angles (av.: $112.3(3)^\circ$) are larger than the $\text{Sn}(\mu_3\text{-OH})\text{-Sn}$ angles (av.: $100.9(3)^\circ$). The average length of a Sn-O-Si bond is 1.974(4) Å, which is slightly shorter than the σ -bonded Sn-O2 (1.995(3) Å) in **2**. The Sn-O-Si angle is around 140° for the monodentate link between tin and the silsesquioxane cage and is around 134° for the bidentate link between tin and the silsesquioxane cage (Table 2). Multinuclear tin complexes have been reported in which the tin is coordinated to phosphinates¹⁸ or iron.¹⁹ Reaction of *n*-butylstannic acid with diphenylphosphoric acid results in the hydroxyl bridged $[\{n\text{-BuSn}(\mu_2\text{-OH})\text{O}_2\text{PPh}_2\}_3][\text{Ph}_2\text{PO}_2]^{18}$ and exhibits three four-membered rings just as was observed for **6**. The symmetric structure has Sn-OH distances of 2.12(8) Å, somewhat longer than found for **6**, and $\text{Sn}(\mu_2\text{-OH})\text{-Sn}$ angles of $100.1(2)^\circ$, comparable to those in **6**. The structurally similar trinuclear cluster $[\{\text{BzSn}(\mu_2\text{-OH})(\text{O}_2\text{P}(c\text{-C}_6\text{H}_{11})_2)_3\text{O}\}][\text{O}_2\text{P}(c\text{-C}_6\text{H}_{11})_2]^{18}$ contains an additional oxygen bridged between the three tin atoms similar as the μ_3 -bridged hydroxyl in **6** is capping the three tin atoms. For this complex, $\text{Sn}(\mu_2\text{-OH})$ distances range from 2.05(1) to 2.16(1) Å and $\text{Sn}(\mu_2\text{-OH})\text{-Sn}$ angles from $98.2(6)$ to $99.8(5)^\circ$, this differs slightly from the distances and angles found for $[\{n\text{-BuSn}(\mu_2\text{-OH})\text{O}_2\text{PPh}_2\}_3][\text{Ph}_2\text{PO}_2]$ and **6**. The average Sn-O-Sn angle at the capped oxygen is about 103.3° which is somewhat larger than the $\text{Sn}(\mu_3\text{-OH})\text{-Sn}$ angles observed in **6** (av.: $100.9(3)^\circ$).

The ^1H NMR spectrum of **6** showed two different hydroxyl resonances, one that is sharp (5.61 ppm (3 H)) and shows tin satellites

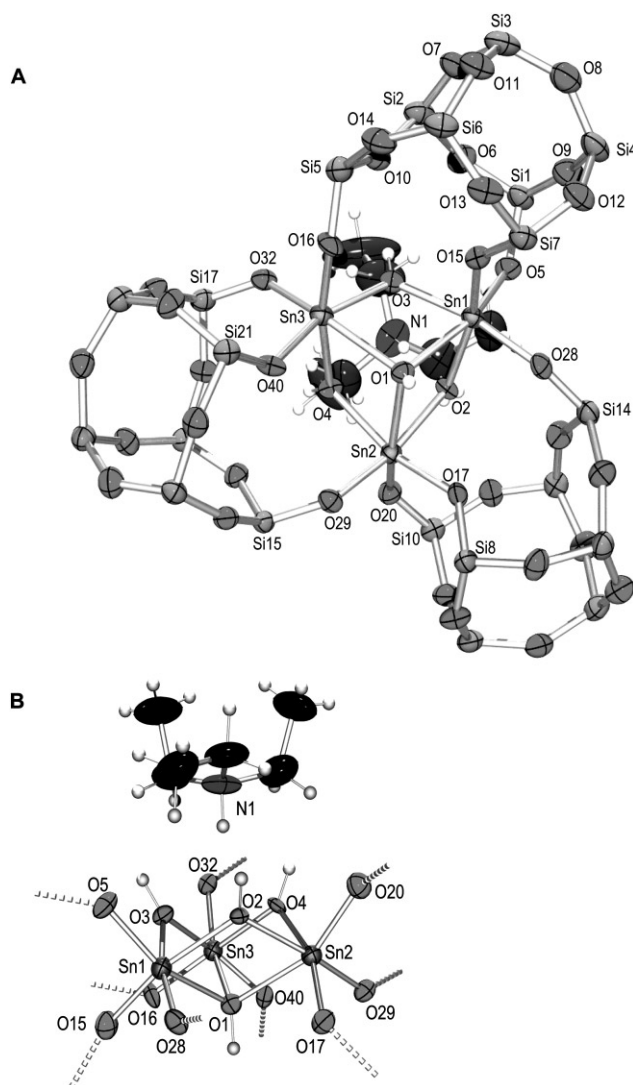
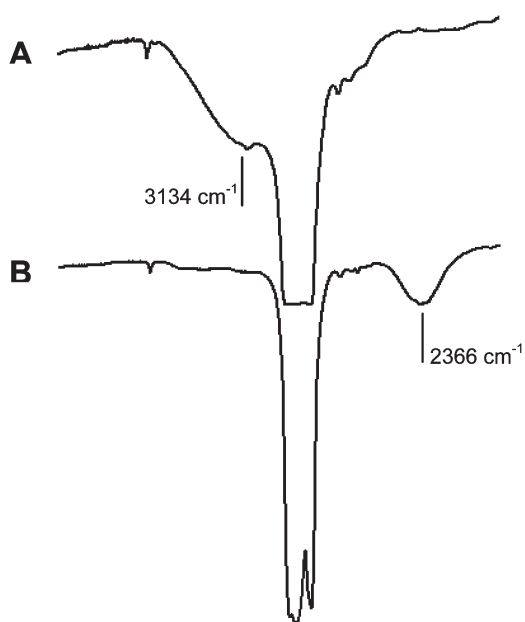


Fig. 3 Crystal structure of $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu_2\text{-OH})_3(\mu_3\text{-OH})\}^-\{\text{HNEt}_3\}^+$ (**6**); A: front view (cyclopentyl substituents attached to the silsesquioxane cages are omitted for clarity), B: selection of the anionic tin-hydroxyl bridged center.

Table 2 Selected interatomic distances and angles for $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu\text{-OH})_4\}^-\{\text{HNEt}_3\}^+$ (**6**)

Bond distances/Å			Angles/°		
Sn1–O28	1.951(6)	O1–Sn1–O28	98.8(2)	O15–Sn1–O28	95.2(3)
Sn1–O15	1.972(6)	O1–Sn1–O15	89.5(2)	O5–Si1–O9	112.1(4)
Sn1–O5	1.994(6)	O1–Sn1–O5	158.6(2)	O6–Si1–O9	108.5(4)
Sn1–O1	2.261(6)	O1–Sn1–O2	72.8(2)	O–Si–O _{av}	109.19(6)
Sn1–O2	2.118(5)	O1–Sn1–O3	72.6(2)	Sn1–O1–Sn2	101.9(2)
Sn1–O3	2.125(6)	O2–Sn1–O3	82.0(2)	Sn1–O1–Sn3	100.8(2)
Si1–O5	1.617(6)	O2–Sn1–O5	95.4(2)	Sn2–O1–Sn3	100.1(2)
Si5–O16	1.588(7)	O2–Sn1–O15	162.2(2)	Sn1–O2–Sn2	111.9(2)
Si7–O15	1.588(7)	O2–Sn1–O28	89.6(2)	Sn1–O3–Sn3	112.8(3)
Si–O _{av}	1.62(1)	O3–Sn1–O5	88.4(2)	Sn2–O4–Sn3	112.2(2)
		O3–Sn1–O15	90.9(2)	Si1–O5–Sn1	130.7(4)
		O3–Sn1–O28	169.4(2)	Si7–O15–Sn1	139.4(4)
		O5–Sn1–O15	100.7(3)	Si14–O28–Sn1	140.1(4)
		O5–Sn1–O28	99.0(3)	Si–O–Si _{av}	149.52(6)

($^3J(^1\text{H}\text{--}^{118}\text{Sn}/^{119}\text{Sn}) = 12\text{ Hz}$) and one which is broad (6.33 ppm, 1 H). Hence, the exchange of the μ_2 - and μ_3 -hydroxyls is slow on the NMR time-scale. The FT-IR spectrum of **6** (Nujol mull) reveals a broad vibration band at 3134 cm^{-1} (Fig. 4A), characteristic for hydrogen bonded OH groups. When D_2O is added to THF solutions of **6**, after a few hours stirring at room temperature, the hydroxyl protons are exchanged by deuterium. The broad band at 3134 cm^{-1} has been replaced by a new band located at 2366 cm^{-1} that can be assigned to bridging Sn–OD. The same IR spectrum is obtained when the tin-chloride species **5** is treated with D_2O , all the chlorides are exchanged by OD groups and the infrared spectrum shows the same broad vibration at 2366 cm^{-1} (Fig. 4B).

**Fig. 4** FT-IR spectra recorded as a Nujol mull of **6** (A) and deuterated **6** (B).

The stannasilsesquioxanes **3**, **4** and **6** have been screened for possible catalytic activity in Baeyer–Villiger oxidation of cyclohexanone (H_2O_2), Oppenauer oxidation of isopropanol by cyclohexanone and epoxidation of cyclooctene (TBHP). Not completely unexpected, none of the three complexes showed any catalytic activity. The fact that even the intramolecular hydroxyl group in **3** was unable to replace the tin bonded acetylacetonato ligand makes the possibility of H_2O_2 or TBHP intermolecularly replacing the acetylacetonate very slim. The active species in tin silicalites are thought to be tetrahedrally coordinated and Lewis acidic, whereas all the three octahedral stannasilsesquioxane complexes are coordinatively saturated. Moreover, the Lewis acidity in complex **6** is strongly reduced by both aggregation to give octahedral tin centers, as well as forming an anionic complex. The steric crowding around

the tin centers and the electronically saturated nature of **6** prevents coordination of nucleophilic substrates.

Concluding remarks

Several interesting stannasilsesquioxane complexes could be prepared with 3-coordinated Sn(II) atoms and with octahedrally coordinated Sn(IV) centers. Attempts to prepare tetrahedral Sn(IV) silsesquioxane complexes failed. While the divalent stannasilsesquioxanes readily hydrolyze to give the free silsesquioxane ligands, the octahedral Sn(IV) species (**3**, **4**, **6**) are stable in the presence of water, neither do they react with oxidizing agent (H_2O_2 , TBHP). The lack of reactivity of these stannasilsesquioxanes clearly indicates that structurally they do not resemble the active sites in tin-silicalite oxidation catalysts. Nevertheless, they reveal interesting structural features such as the instability of tetrahedral structures and the high tendency to form octahedral structures. This tendency to form octahedrally coordinated tin species contrasts the titanasilsesquioxane complexes that form stable neutral tetrahedral complexes or labile Lewis base adducts thereof. Probably the difference in ionic radii between titanium and tin (Ti^{4+} 4-coordinated = 0.56 Å , Sn^{4+} 4-coordinated = 0.69 Å)¹⁹ is responsible for this different behaviour as the same was observed for zirconium (Zr^{4+} 4-coordinated = 0.73 Å).²⁰ Whereas the tetrahedral complex $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2]\text{Ti}$ does not interact with Lewis bases, the zirconium analogue readily forms the octahedral bis(THF) adduct $[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2]\text{Zr} \cdot 2\text{THF}$.¹⁷

Experimental

General comments

Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF), Na/K alloy (hexanes, benzene- d_6) and Na/benzophenone (Et_2O) or dried over 4 Å molecular sieves (NEt_3 , chloroform- d_1 , THF- d_8) and stored under argon. ^1H - and ^{13}C -NMR spectra were recorded on Varian Mercury 400 spectrometers (25 °C , ^1H NMR: 400 MHz , ^{13}C NMR: 100.6 MHz). ^{29}Si - and ^{119}Sn -NMR spectra were recorded on a Varian Indigo 500 spectrometer (25 °C , ^{29}Si NMR: 99.3 MHz , ^{119}Sn NMR: 186.4 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H , ^{13}C NMR) or external standards (^{29}Si : $\text{SiMe}_4 = 0\text{ ppm}$, ^{119}Sn : $\text{SnMe}_4 = 0\text{ ppm}$). In some cases, the ^{119}Sn -NMR signals were fairly broad due to partially relaxed $^{119}\text{Sn}\text{--Cl}$ coupling, therefore short acquisition times ($< 0.3\text{ s}$) were used in those cases. Fourier Transformed Infrared spectra were recorded at room temperature on a Nicolet Avatar™ 360 spectrophotometer. Spectra were recorded as Nujol-mulls (prepared under inert atmosphere, glovebox). Elemental analyses were carried out at the Mikroanalytic Laboratory H. Kolbe in Mülheim an der Ruhr, Germany; quoted data are the average of at least two independent measurements. Starting materials $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$,¹² $(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$,¹² $(c\text{-C}_5\text{H}_9)_7$

$\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$,¹² $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$ ²¹ and $\text{Cl}_2\text{Sn}(\text{Acac})_2$ ²² were prepared following referred literature procedures.

$[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Sn}]_2$ (1)

$(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$ (1.00 g, 1.03 mmol) was added in one portion to a hexane (50 mL) solution of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (0.45 g, 1.06 mmol) cooled to -78°C . The mixture was allowed to gently warm to room temperature and was stirred overnight affording a clear solution with a white precipitate. Volatiles were removed *in vacuo* and the residue washed with cold (*ca.* 0°C) hexane (2×5 mL), extracted with heptane, filtered and allowed to cool to room temperature overnight. IR (Nujol): $\nu_{\text{OH}} = 3145\text{ cm}^{-1}$. ^1H NMR (400 MHz, benzene- d_6 , 25°C , δ): 8.92 (s, 1H, SiOH), 2.11 (m, 14H, $\text{CH}_2\text{-C}_6\text{H}_{11}$), 1.63 (m, 28H, $\text{CH}_2\text{-C}_6\text{H}_{11}$), 1.30 (m, 14H, $\text{CH}_2\text{-C}_6\text{H}_{11}$). ^{13}C NMR (100.6 MHz, benzene- d_6 , 25°C , δ): 28.67, 28.57, 28.53, 28.34, 27.97, 27.88, 27.41 ($\text{CH}_2\text{-C}_6\text{H}_{11}$), 25.50, 25.01, 24.53, 24.47, 24.42 ($\text{CH-C}_6\text{H}_{11}$, 1:2:2:1:1 ratio). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.8 MHz, benzene- d_6 , 25°C , δ): -58.54, -61.55, -67.73, -67.84, -68.32 ($7 \times (\equiv\text{O})_3\text{SiC}_5\text{H}_9$, ratio 2:1:1:1:2). $^{119}\text{Sn}\{^1\text{H}\}$ (186.4 MHz, benzene- d_6 , 25°C , δ): -336.89. (Found: C, 41.97; H, 6.37. $\text{C}_{70}\text{H}_{128}\text{O}_{24}\text{Si}_{14}\text{Sn}_2$ requires C, 42.37; H, 6.50%).

$[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}]_2$ (2)

$(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ (1.00 g, 1.06 mmol) and $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$ (0.46 g, 1.06 mmol) were weighed in a Schlenk vessel and cooled to -40°C . Subsequently hexane (30 mL) was added and the mixture was allowed to gently warm to room temperature and was stirred for three hours at room temperature. The hexane solution was concentrated and stored at -4°C , which afforded crystals suitable for X-ray determination. ^1H NMR (400 MHz, benzene- d_6 , 25°C , δ): 1.96 (m, 14H, $\text{CH}_2\text{-C}_5\text{H}_9$), 1.77 (m, 28H, $\text{CH}_2\text{-C}_5\text{H}_9$), 1.69 (m, 14H, $\text{CH-C}_5\text{H}_9$), 1.19 (m, 7H, $\text{CH-C}_5\text{H}_9$), 0.43 (s, 9H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (100.6 MHz, benzene- d_6 , 25°C , δ): 29.01, 28.91, 28.85, 28.74, 28.68, 28.51, 28.48, 28.18, 28.11, 28.10, 27.99 ($\text{CH}_2\text{-C}_5\text{H}_9$), 25.40, 25.05, 24.42, 23.45 ($\text{CH-C}_5\text{H}_9$), 2.93 ($\text{Si}(\text{CH}_3)_3$). $^{119}\text{Sn}\{^1\text{H}\}$ (186.4 MHz, benzene- d_6 , 25°C , δ): -372.69. (Found: C, 42.34; H, 6.68. $\text{C}_{76}\text{H}_{144}\text{O}_{24}\text{Si}_{16}\text{Sn}_2$ requires C, 42.88; H, 6.82%).

$(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OH})\text{Sn}(\text{acac})_2$ (3)

$(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ (1.29 g, 1.47 mmol) and $\text{Cl}_2\text{Sn}(\text{acac})_2$ (0.57 g, 1.47 mmol) were dissolved in toluene, an excess of NEt_3 was added (2 mL) and the whole was stirred at 80°C overnight. The formed $\text{Et}_3\text{N}(\text{H})\text{Cl}$ was removed by filtration and the toluene was removed under reduced pressure. Hexane (50 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a white powder remained (1.59 g, 91%, 1.34 mmol). IR (Nujol): $\nu_{\text{OH}} = 3404\text{ cm}^{-1}$. ^1H NMR (400 MHz, chloroform- d_1 , 25°C , δ): 5.58 (s, CH-acac , 1H), 5.56 (s, CH-acac , 1H), 4.86 (s, SiOH, 1H), 2.19, 2.10, 2.04, 2.01 ($4 \times \text{s}$, $\text{CH}_3\text{-acac}$, 12H), 1.71 (br s, $\text{CH}_2\text{-C}_5\text{H}_9$, 14H), 1.55 (br s, $\text{CH}_2\text{-C}_5\text{H}_9$, 42H), 0.94 (m, $\text{CH-C}_5\text{H}_9$, 7H). ^{13}C NMR (100.6 MHz, chloroform- d_1 , 25°C , δ): 196.93, 196.05, 195.00, 194.49 ($4 \times \text{C}(\text{=O})\text{-acac}$), 102.29, 101.97 ($2 \times \text{CH-acac}$), 28.04, 27.88, 27.81, 27.78, 27.64, 27.56, 27.50, 27.46, 27.29, 27.15, 27.07, 27.01 ($\text{CH}_2\text{-C}_5\text{H}_9$), 24.26, 23.99, 22.95, 22.78, 22.73, 22.45, 22.41 ($\text{CH-C}_5\text{H}_9$, 1:1:1:1:1:1 ratio). ^{29}Si NMR (99.8 MHz, benzene- d_6 , 25°C , δ): -55.87 (SiOH), -62.04, -63.49, -64.42, -65.47, -66.04, -68.05 ($6 \times (\equiv\text{O})_3\text{SiC}_5\text{H}_9$, ratio 1:1:1:1:1:1). ^{119}Sn NMR (186.4 MHz, benzene- d_6 , 25°C , δ): -731.82. (Found: C, 45.45; H, 6.60. $\text{C}_{45}\text{H}_{78}\text{O}_{16}\text{Si}_7\text{Sn}$ requires C, 45.40; H, 6.60%).

$(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{Sn}(\text{acac})_2$ (4)

To a mixture of the solids $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)(\text{OH})_2$ (1.50 g, 1.58 mmol) and $\text{Cl}_2\text{Sn}(\text{acac})_2$ (0.61 g, 1.57 mmol) was added 50 mL of toluene. Subsequently excess NEt_3 was added (about 2 mL) and the mixture was stirred at 80°C overnight. The next day $\text{Et}_3\text{N}(\text{H})\text{Cl}$ was removed by filtration and the toluene was removed under reduced pressure. Hexane (50 mL) was added and thorough evaporation removed the last traces of toluene together with the

hexanes and a white powder remained (1.09 g, 55%, 0.86 mmol). ^1H NMR (400 MHz, chloroform- d_1 , 25°C , δ): 5.54 (s, CH-acac , 1H), 5.52 (s, CH-acac , 1H), 2.18, 2.10, 2.02, 2.00 ($4 \times \text{s}$, $\text{CH}_3\text{-acac}$, 12H), 1.72 (br s, $\text{CH}_2\text{-C}_5\text{H}_9$, 14H), 1.51 (br s, $\text{CH}_2\text{-C}_5\text{H}_9$, 42H), 0.92 (m, $\text{CH-C}_5\text{H}_9$, 7H), 0.15 (s, $\text{Si}(\text{CH}_3)_3$, 9H). ^{13}C NMR (100.6 MHz, chloroform- d_1 , 25°C , δ): 196.24, 195.21, 194.63, 194.59 ($4 \times \text{C}(\text{=O})\text{-acac}$), 102.03, 101.79 ($2 \times \text{CH-acac}$), 28.06, 27.92, 27.82, 27.76, 27.64, 27.60, 27.53, 27.39, 27.32, 27.27, 27.23, 27.15, 27.09, 27.07, 27.03, 27.00, 26.96 ($\text{CH}_2\text{-C}_5\text{H}_9$), 24.64, 24.59, 24.42, 24.15, 23.40, 22.64, 22.56 ($\text{CH-C}_5\text{H}_9$, 1:1:1:1:1:1 ratio), 1.96 ($\text{Si}(\text{CH}_3)_3$). ^{29}Si NMR (99.8 MHz, benzene- d_6 , 25°C , δ): 9.12 (OSiMe_3), -63.40, -64.19, -64.80, -65.26, -65.78, -67.28, -68.58 ($7 \times (\equiv\text{O})_3\text{SiC}_5\text{H}_9$, 1:1:1:1:1:1 ratio). ^{119}Sn NMR (186.4 MHz, benzene- d_6 , 25°C , δ): -739.68. (Found: C, 48.15; H, 7.10. $\text{C}_{48}\text{H}_{86}\text{O}_{16}\text{Si}_8\text{Sn}\cdot\text{C}_6\text{H}_{14}$ requires C, 48.09; H, 7.47%).

$\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu\text{-Cl})_4\}^-\{\text{HNEt}_3\}^+$ (5)

An excess of NEt_3 (3.5 mL) was added to a suspension of $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$ (5.00 g, 5.71 mmol) in toluene (100 mL). The mixture was cooled to 0°C and a toluene solution (20 mL) of SnCl_4 (1.49 g, 5.71 mmol) was slowly added. The mixture was allowed to warm to room temperature and was stirred overnight. The formed ammonium salt was filtered-off and the toluene was removed under reduced pressure. Hexane (20 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a pale pink solid remained. Yield 94% (5.73 g, 1.80 mmol). ^1H NMR (400 MHz, benzene- d_6 , 25°C , δ): 3.08 (q, $\text{N}(\text{CH}_2\text{CH}_3)_3$, 6H), 2.27 (m, 21H, $\text{CH}_2\text{-C}_5\text{H}_9$), 1.82 (m, 147H, $\text{CH}_2\text{-C}_5\text{H}_9$), 1.21 (m, 21H, $\text{CH-C}_5\text{H}_9$), 0.90 (t, 9H, $\text{N}(\text{CH}_2\text{CH}_3)_3$). ^{13}C NMR (100.6 MHz, benzene- d_6 , 25°C , δ): 47.59 ($\text{HN}(\text{CH}_2\text{CH}_3)_3$), 29.07, 28.94, 28.88, 28.72, 28.31, 28.25, 28.19, 28.13, 28.07, 27.98, 27.91, 27.87, 27.71, 27.59, 27.53 ($\text{CH}_2\text{-C}_5\text{H}_9$), 26.35, 25.14, 24.36, 24.03, 23.44, 23.26, 22.87 ($\text{CH-C}_5\text{H}_9$, 1:1:1:1:1:1 ratio), 9.19 ($\text{HN}(\text{CH}_2\text{CH}_3)_3$). ^{29}Si NMR (99.8 MHz, THF- d_8 , 25°C , δ): -66.50; -65.10 ($7 \times (\equiv\text{O})_3\text{SiC}_5\text{H}_9$, 4:3 ratio). ^{119}Sn NMR (186.4 MHz, benzene- d_6 , 25°C , δ): -614.87. (Found: C, 41.17; H, 6.38. $\text{C}_{111}\text{H}_{205}\text{Cl}_4\text{NO}_3\text{Si}_{21}\text{Sn}_3$ requires C, 41.44; H, 6.42%).

$\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu\text{-OH})_4\}^-\{\text{HNEt}_3\}^+$ (6)

A CHBr_3 solution (20 mL) of **5** (2.74 g, 0.85 mmol) was layered with water (10 mL). The next day, large colorless crystals of **6**, suitable for an X-ray crystal structure analysis, had formed (39% (1.03 g, 0.33 mmol). IR (Nujol, cm^{-1}): 3134 (br s, ν_{OH}). ^1H NMR (300 MHz, chloroform- d_1 , 50°C , δ): 7.96 (s-broad, 1H, HNEt_3), 6.33 (s-broad, 1H, $\mu\text{-OH}$), 5.61 (t, 3H, $\mu\text{-OH}$, $^3J_{\text{HH-118Sn/119Sn}} = 12\text{ Hz}$), 3.42 (m, 6H, $\text{HN}(\text{CH}_2\text{CH}_3)_3$), 1.78 (m, 42H $\text{CH}_2\text{-C}_5\text{H}_9$), 1.56 (m, 135H, $\text{CH}_2\text{-C}_5\text{H}_9 + \text{HN}(\text{CH}_2\text{CH}_3)_3$), 0.99 (m, 18 H, $\text{CH-C}_5\text{H}_9$), 0.77 (m, 3 H, $\text{CH-C}_5\text{H}_9$). ^{13}C NMR (75 MHz, chloroform- d_1 , 50°C , δ): 47.57 ($\text{HN}(\text{CH}_2\text{CH}_3)_3$), 28.31, 28.08, 27.81, 27.50, 27.32, 27.10 ($\text{CH}_2\text{-C}_5\text{H}_9$), 25.66, 24.73, 23.93, 23.40, 23.03, 22.92, 22.84, 22.65, 22.49 ($\text{CH-C}_5\text{H}_9$), 9.18 ($\text{HN}(\text{CH}_2\text{CH}_3)_3$). ^{29}Si NMR (99.8 MHz, THF- d_8 , 25°C , δ): -57.81, -65.69, -67.22 ($7 \times (\equiv\text{O})_3\text{SiC}_5\text{H}_9$, 3:1:3 ratio). ^{119}Sn NMR (186.4 MHz, THF- d_8 , 25°C , δ): -659.44. (Found: C, 42.27; H, 6.57. $\text{C}_{111}\text{H}_{209}\text{NO}_4\text{Si}_{21}\text{Sn}_3$ requires C, 42.41; H, 6.70%). The deuterated analogue of **6**, $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Sn}]_3(\mu\text{-OD})_4\}^-\{\text{DNEt}_3\}^+$, was prepared in the same way starting from **5** (2.1 g, 0.65 mmol) using D_2O . Yield 45% (0.92 g, 0.30 mmol). IR (Nujol, cm^{-1}): 2366 (br s, ν_{OH}).

Crystal structure determination of **2** and **6**

Suitable crystals of **2** and **6** were selected, mounted on a thin, glass fiber using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω -scans at 0° , 90° , and 180° in ϕ . Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.²³ The raw data were routinely processed with XPREP, which flags units cells with possible higher symmetry settings or

super lattices.²⁴ Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2 . Bromoform was cocrystallized in the asymmetric unit of **6**. The data set was treated with the Squeeze routine of PLATON.²⁴ Most non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.²⁵ **2**: Mo K α radiation ($\lambda = 0.71073$ Å), $T = 203(2)$ K, $0.2 \times 0.2 \times 0.1$, $C_{76}H_{144}O_{24}Si_{16}Sn_2$, $M_r = 2128.73$, triclinic, $P-1$, $a = 11.0773(9)$ Å, $b = 14.6916(12)$ Å, $c = 16.5481(14)$ Å, $a = 100.6690(10)^\circ$, $\beta = 95.106(2)^\circ$, $\gamma = 101.9760(10)^\circ$, $V = 2578.0(4)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 1.371$ g cm⁻³, θ range (min., max.) = 1.26, 28.68, $h: -14 \rightarrow 14$; $k: -19 \rightarrow 19$; $l: 0 \rightarrow 22$, $F(000) = 1116$ e⁻, $\mu(\text{Mo K}\alpha) = 7.34$ cm⁻¹, total data = 22979, unique data = 11772, $wR(F^2) = 0.1455$, $R(F) = 0.0539$, GOF = 1.012, max. residual electron density 0.859 and -0.694 e Å⁻³. **6**: Mo K α radiation ($\lambda = 0.71073$ Å), $T = 203(2)$ K, $0.3 \times 0.3 \times 0.1$, $C_{111}H_{209}NO_{40}Si_{21}Sn_3CHBr_3$, $M_r = 3396.50$, triclinic, $P-1$, $a = 14.584(3)$ Å, $b = 20.826(4)$ Å, $c = 27.208(5)$ Å, $a = 93.022(3)^\circ$, $\beta = 90.817(3)^\circ$, $\gamma = 94.583(3)^\circ$, $V = 8224(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.372$ g cm⁻³, θ range (min., max.) = 1.20, 24.71, $h: -17 \rightarrow 17$; $k: -24 \rightarrow 24$; $l: -31 \rightarrow 32$, $F(000) = 3516$ e⁻, $\mu(\text{Mo K}\alpha) = 14.00$ cm⁻¹, total data = 55220, unique data = 27527, $wR(F^2) = 0.1940$, $R(F) = 0.0793$, GOF = 1.114, max. residual electron density 1.242, and -0.787 e Å⁻³.

CCDC reference numbers 238581 (**6**) and 238582 (**2**).

See <http://www.rsc.org/suppdata/dt/b4/b407471h/> for crystallographic data in CIF or other electronic format.

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