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$Si(CH_2CH_2SnH_3)_4$ — a unique organotin hydride featuring 12 SnH units in a dendritic molecule. Single-crystal X-ray structures of tetrakis(2-stannylethylene)silane and tetrakis[2-(triphenylstannyl)ethylene]silane

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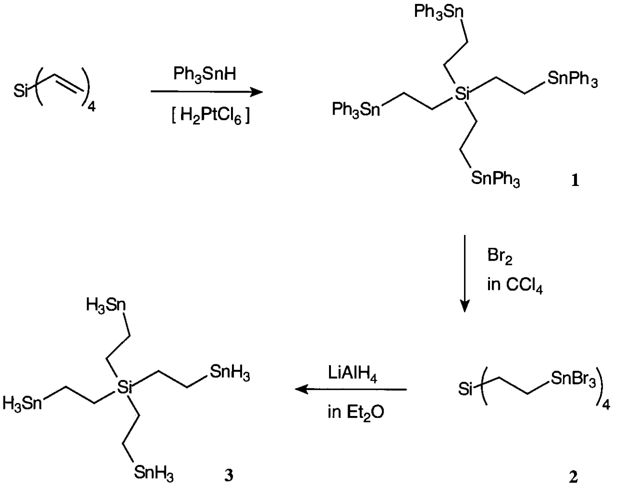
Abstract

Fourfold hydrostannation of tetravinylsilane affords the first generation metallodendrimer $Si(CH_2CH_2SnPh_3)_4$ (**1**). Selective bromination yields $Si(CH_2CH_2SnBr_3)_4$ (**2**), which can be reduced by $LiAlH_4$ to give $Si(CH_2CH_2SnH_3)_4$ (**3**), containing 12 reactive Sn–H bonds. These novel dendritic organotin compounds were characterized by elemental analysis, spectroscopic studies (^1H-, ^{13}C-, ^{119}Sn-NMR; IR) and by single-crystal X-ray structure determination. The molecular structures of **1** and **3** reveal increased conformational constraint in **1**; the average Sn–H bond length in **3** is 1.60(7) Å. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organotin hydride; Dendritic molecule; Metallodendrimer; Organotin dendrimer; Si–Sn dendrimer

1. Introduction

Organotin hydrides occupy a key position in organotin chemistry [1] due to the wide scope of their usability. The remarkable reactivity of the tin–hydrogen bond makes them versatile reagents in organic synthesis [2] as well as valuable synthons in organotin chemistry itself [1a,3]. While the field of organotin chemistry has been developed for 150 years [4], the fast growing area of dendrimer chemistry is a quite young one [5]. Since the first syntheses of dendritic macromolecules 20 years ago, the interest in preparation and applicability of this new class of molecules is prompted by the combination of their beauty and their special properties [6]. Incorporating metal atoms as a core unit, as branching centers, into the branches themselves or into the periphery of the dendrimer leads to so-called metallodendrimers [7]. There is a variety of metal-containing dendrimers known, yet the specific synthesis of tin-based dendrimers has not been reported so far. Merely, a few trimethyltin derivatives that do classify as dendrimers



Scheme 1.

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are scattered around the literature in connection with NMR spectroscopic investigations [8].

We undertook to systematically investigate the syntheses and properties of organotin dendrimers. In the present paper we report on the stepwise synthesis and spectroscopic as well as X-ray structural characterization of tin-containing dendrimers of the first generation with different peripheral substituents. The title compound tetrakis(2-stannylethylene)silane combines the features of a dendritic molecule with the synthetic potential of an organotin hydride, therefore constituting a valuable intermediate for a further approach to surface functionalized or higher order organotin dendrimers with the metal atoms as branching sites.

2. Results and discussion

2.1. Synthesis

Utilizing tetravinylsilane as the core molecule, the tin-containing dendrimer tetrakis[2-(triphenylstannyl)ethylene]silane (**1**) could be synthesized in a high-yield hydrostannation reaction (Scheme 1). Triphenyltin hydride, employed in excess, adds cleanly to the olefinic ligands of the educt following the anti-Markownikow rule. Transition-metal catalysis [9] was successfully chosen for this reaction similarly to the synthesis of carbosilane dendrimers via hydrosilylation reaction [10]. The product crystallizes from a cooled tetrahydrofurane, pentane, or cyclopentane solution.

Treating the dendrimer **1** with 12 mol of bromine in a carbon tetrachloride solution resulted in a selective and complete bromodemetallation of the phenyl groups. After a reaction time of 5 days, tetrakis[2-(tribromostannyl)ethylene]silane (**2**) could be isolated as a white, air-sensitive solid. There are only a few examples of cleavage of all three tin-bound aryl groups by bromine reported in the literature [11].

Reduction of dendrimer **2** with lithium aluminum hydride at low temperatures [12] afforded the title compound tetrakis(2-stannylethylene)silane (**3**) in high yield as a viscous liquid, which crystallized upon cooling. This dendritic organotin hydride containing four SnH_3 moieties shows a high sensitivity towards oxygen, temperature and light. Decomposition, indicated by the compound turning brown, occurs at room temperature even in the absence of air, as expected [13], and is accelerated by the exposure to light.

2.2. Spectroscopy

Multinuclear NMR investigations fully characterize the dendritic organotin compounds synthesized. The ^{1}H-NMR spectra of the phenyl- and bromine-substituted derivatives **1** and **2** show typical AA′BB′ and AA′XX′ patterns, respectively, for the hydrogen atoms of the ethylene bridges indicating a hindered rotation of the CH_2CH_2 moieties. Computer simulation of the AA′XX′ spin system in **2** was employed for verification (yielding $J_{AA'} = 24.91$, $J_{XX'} = 21.70$, $J_{AX} = J_{A'X'} = 15.00$, $J_{A'X} = J_{AX'} = 3.92$ Hz) [14]. The larger difference in chemical shifts between the coupling nuclei in **2** reflects the deshielding effect of the tin-bound bromine atoms. In the ^{1}H-NMR spectrum of the hydride-substituted derivative **3**, the ethylenic hydrogen atoms just give rise to one higher order multiplet signal. The tin-bound hydrogen atoms resonate at typical 4.56 ppm with tin satellites surrounding the main signal; the large coupling constant $|^1J(^1H^{117/119}Sn)|$ of 1695.6/1774.5 Hz is characteristic for organotin trihydrides [15].

A comparison of the broad-band decoupled $^{13}C\{^1H\}$-NMR spectra of the organotin derivatives **1**, **2** and **3** reveals a $SiCH_2$ resonance quite unaffected by the varying tin substitution of the dendritic molecules and a CH_2Sn resonance clearly increasing in chemical shift from the hydride- (**3**) over the phenyl- (**1**) to the bromine-substituted derivative (**2**). The nicely observable one-bond and two-bond carbon tin coupling constants $|^1J(^{13}C^{117/119}Sn)|$ and $|^2J(^{13}CSn)|$ are of similar magnitude for **1** and **3** and, as expected [16], clearly larger for the electronegatively substituted **2**. The inverse-gated broad-band decoupled $^{119}Sn\{^1H\}$-NMR spectra supplement the ^{1}H- and ^{13}C-NMR data obtained showing single resonances at chemical shifts of -98.5 for **1**, -301.4 for **2** and -316.3 ppm for **3**.

The IR spectrum of **3** features a strong band at 1852 cm^{-1} indicating a Sn–H stretching frequency similar in size as in $EtSnH_3$ [15b].

2.3. Crystal structures of 1 and 3

The single-crystal X-ray structure determinations of **1** and **3** for the first time reveal crystallographic data of first generation Si–Sn dendrimers. In both crystal structures, there are four dendrimers in the unit cell. The asymmetric unit of **1** contains a quarter of the dendrimer, whereas half of the dendrimer is found in the asymmetric unit of **3**. The molecular structures of **1** and **3** are shown in Figs. 1 and 2, and selected geometric parameters are presented in Tables 1 and 2. The central Si atom is tetrahedrally coordinated by four dendritic branches. The dendritic backbone is the same for **1** and **3**. However, both dendrimers differ regarding the backbone conformation and the substituents of the Sn atoms that occupy the dendritic surface. The difference in conformation is crystallographically shown by different space group symmetry ($I4_1/a$ and $C2/c$), and it is geometrically shown by the torsion angles Si–C–C–Sn of $-162.5(2)$ (**1**) and $-178.8(4)$ and 175.7(3)° (**3**), where the ideal torsion angle of *trans*-conformation of the Si and Sn atoms about the C–C bond would be

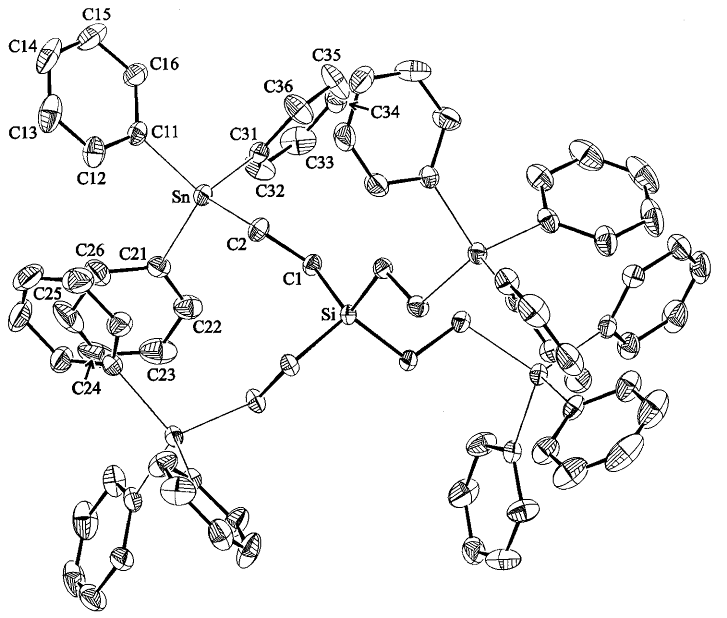

Fig. 1. Solid state structure of $Si(CH_2CH_2SnPh_3)_4$ (**1**) showing the atom labeling scheme. The dendritic backbone $Si(C–C–Sn)_4$ adopts a distorted C_2 symmetry.

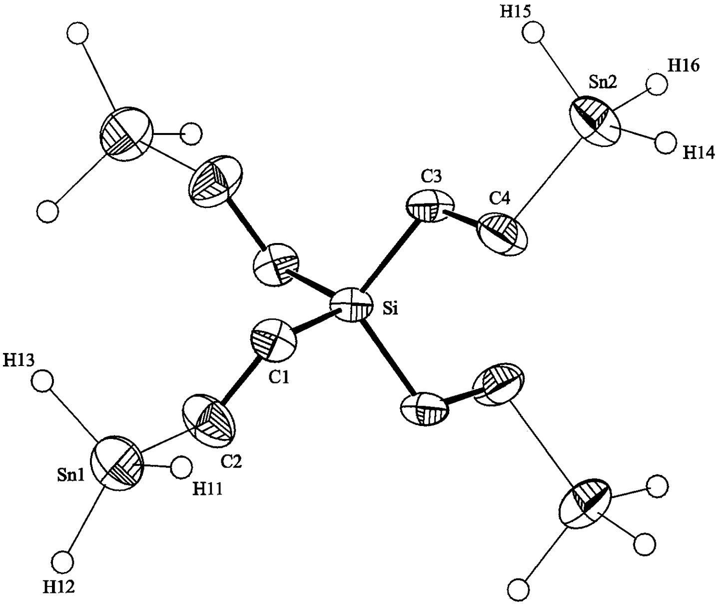

Fig. 2. Solid state structure of $Si(CH_2CH_2SnH_3)_4$ (**3**) showing the atom labeling scheme. The dendritic backbone $Si(C–C–Sn)_4$ adopts a slightly distorted C_2 symmetry.

180°. As expected, the Si–C–C–Sn torsion angles in **3** are closer to the ideal value due to the smaller hydrido substituents on the dendritic surface. The six Sn···Sn distances in **1** of 7.733(2) Å (mean) unexpectedly show about the same magnitude as in **3** with 7.8285(11) Å (mean), and the smallest (5.988(2) Å) and largest (8.6064(12) Å) values are found in **1**. Conclusively, the conformational constraint in **1** is shown in a twisted internal geometry rather than in a stretched dendritic backbone. The reason may be based on the conformational tendency to utilize the internal space of the dendrimer, if there are large phenyl substituents on the surface (**1**). Further evidence for increased conformational constraint in **1** is given by the C–Si–C angles that range from 107.2(3) to 110.63(14)° in **1** and from 108.6(4) to 110.2(3)° in **3**. The Si···Sn distances in **1** (4.7955(8)–4.7958(7) Å) are about the same (0.02 Å shorter) as in **3** (4.809(2)–4.817(2) Å), which indicates that no expansion of a dendrimer (**1**) occurs that has four short ethylene bridges. However, the sum of the bond lengths in a single dendritic branch (Si–C–C–Sn) of **1** with 5.56 Å is slightly larger than in **3** with 5.53 Å (mean). The Sn–C bond length in **1** of 2.136(4) Å is longer than the short Sn–C bond in **3** of 2.126(7) Å (mean). In the dimer of bis[bis(trimethylsilyl)methyl]hydroxystannane [17] a Sn–C bond of 2.149(2) Å (mean) was found despite the different substituents of about the same dimensions as in **1**. Standard Sn–C bond lengths (electron diffraction or microwave spectroscopy) reported in the literature are 2.144(2) Å in $Sn(CH_3)_4$ [18], 2.143(2) Å in CH_3SnH_3, 2.17(5) Å in $(CH_3)_2SnBr_2$ and 2.19(5) Å in CH_3SnCl_3 [19]. Apparently, the more electronegative the substituents of the Sn atom the longer is the Sn–C bond. The average length of the Sn–H bond in **3** of 1.60(7) Å resembles the two values (1.52(5) and 1.63(5) Å) observed in *tert*-butyl-8-(dimethylamino)naphthyl-(−)-menthyltin hydride [20]. In addition, longer Sn–H bonds are reported in the crystal structures of bis[bis(trimethylsilyl)methyl]hydroxystannane (1.73(2) Å) [17] and tris[bis(trimethylsilyl)methyl]stannane (1.90(4) Å) [21]. As expected, the average H–Sn–H angle of 107(3)° in **3** is smaller than the average C–Sn–C angle of 108.4(2)° in **1** (only involving the C atoms of phenyl groups). The thermal motion of the dendritic branches increases with the distance from the central Si atom resulting in thermal parameters of the Sn atoms that are larger than the ones of the Si atom, respectively.

Table 1
Selected bond lengths, distances (Å), angles and torsion angles (°) of **1** [a]

Sn···Sn′	5.988(2)	C(12)–C(13)	1.370(8)
Sn···Sn″	8.6059(13)	C(13)–C(14)	1.368(11)
Sn···Sn‴	8.6064(12)	C(14)–C(15)	1.368(10)
Sn′···Sn″	8.6064(12)	C(15)–C(16)	1.370(8)
Sn′···Sn‴	8.6059(13)	C(21)–C(22)	1.375(8)
Sn″···Sn‴	5.988(2)	C(21)–C(26)	1.394(8)
Si···Sn	4.7955(8)	C(22)–C(23)	1.379(9)
Si···Sn′	4.7958(7)	C(23)–C(24)	1.362(11)
Sn–C(11)	2.139(5)	C(24)–C(25)	1.355(12)
Sn–C(21)	2.149(5)	C(25)–C(26)	1.379(9)
Sn–C(31)	2.134(5)	C(31)–C(36)	1.376(7)
Sn–C(2)	2.136(4)	C(31)–C(32)	1.379(7)
Si–C(1)	1.875(4)	C(32)–C(33)	1.374(8)
C(1)–C(2)	1.547(6)	C(33)–C(34)	1.365(9)
C(11)–C(16)	1.380(7)	C(34)–C(35)	1.352(9)
C(11)–C(12)	1.394(7)	C(35)–C(36)	1.364(8)
C(2)–Sn–C(11)	113.9(2)	C(15)–C(14)–C(13)	119.6(6)
C(2)–Sn–C(21)	110.8(2)	C(14)–C(15)–C(16)	120.9(7)
C(2)–Sn–C(31)	106.9(2)	C(15)–C(16)–C(11)	120.5(6)
C(11)–Sn–C(21)	107.8(2)	C(22)–C(21)–C(26)	117.7(5)
C(11)–Sn–C(31)	110.4(2)	C(22)–C(21)–Sn	122.6(4)
C(21)–Sn–C(31)	106.9(2)	C(26)–C(21)–Sn	119.7(4)
C(1)–Si–C(1)′	107.2(3)	C(21)–C(22)–C(23)	121.5(7)
C(1)–Si–C(1)″	110.61(14)	C(24)–C(23)–C(22)	119.5(7)
C(1)–Si–C(1)‴	110.63(14)	C(25)–C(24)–C(23)	120.5(7)
C(1)′–Si–C(1)″	110.63(14)	C(24)–C(25)–C(26)	120.4(8)
C(1)′–Si–C(1)‴	110.61(14)	C(25)–C(26)–C(21)	120.4(7)
C(1)″–Si–C(1)‴	107.2(3)	C(36)–C(31)–C(32)	117.1(5)
C(2)–C(1)–Si	113.4(3)	C(36)–C(31)–Sn	119.9(4)
C(1)–C(2)–Sn	112.5(3)	C(32)–C(31)–Sn	123.0(4)
C(16)–C(11)–C(12)	118.0(5)	C(33)–C(32)–C(31)	120.8(6)
C(16)–C(11)–Sn	121.3(4)	C(34)–C(33)–C(32)	120.8(6)
C(12)–C(11)–Sn	120.7(4)	C(35)–C(34)–C(33)	118.6(6)
C(13)–C(12)–C(11)	120.9(6)	C(34)–C(35)–C(36)	121.1(6)
C(14)–C(13)–C(12)	120.1(7)	C(35)–C(36)–C(31)	121.4(5)
Si–C(1)–C(2)–Sn	−162.5(2)		

[a] Symmetry transformations used to generate atoms on equivalent positions: (′) $-x+1$, $-y+0.5$, z; (″) $-y+0.75$, $x-0.25$, $-z+0.75$; (‴) $y+0.25$, $-x+0.75$, $-z+0.75$.

Table 2
Selected bond lengths, distances (Å), angles and torsion angles (°) of **3** [a]

Sn(1)···Sn(2)	8.4292(8)	Si–C(1)	1.887(6)
Sn(1)···Sn(1)′	7.0078(11)	Si–C(3)	1.877(6)
Sn(1)···Sn(2)′	8.1953(8)	C(1)–C(2)	1.511(10)
Sn(2)···Sn(1)′	8.1953(8)	C(3)–C(4)	1.528(10)
Sn(2)···Sn(2)′	6.7139(11)	Sn(1)–H(11)	1.59(6)
Sn(1)′···Sn(2)′	8.4292(8)	Sn(1)–H(12)	1.60(6)
Si···Sn(1)	4.817(2)	Sn(1)–H(13)	1.60(5)
Si···Sn(2)	4.809(2)	Sn(2)–H(14)	1.60(6)
Sn(1)–C(2)	2.122(7)	Sn(2)–H(15)	1.61(6)
Sn(2)–C(4)	2.130(7)	Sn(2)–H(16)	1.60(7)
C(1)–Si–C(3)	110.2(3)	C(2)–Sn(1)–H(13)	109(2)
C(1)–Si–C(1)′	108.6(4)	C(4)–Sn(2)–H(14)	114(2)
C(3)–Si–C(1)′	109.6(3)	C(4)–Sn(2)–H(15)	107(2)
C(3)–Si–C(3)′	108.7(4)	C(4)–Sn(2)–H(16)	116(2)
C(2)–C(1)–Si	112.4(4)	H(11)–Sn(1)–H(12)	108(3)
C(4)–C(3)–Si	113.9(4)	H(11)–Sn(1)–H(13)	107(3)
C(1)–C(2)–Sn(1)	114.7(5)	H(12)–Sn(1)–H(13)	108(3)
C(3)–C(4)–Sn(2)	112.0(4)	H(14)–Sn(2)–H(15)	107(3)
C(2)–Sn(1)–H(11)	104(2)	H(14)–Sn(2)–H(16)	106(3)
C(2)–Sn(1)–H(12)	120(2)	H(15)–Sn(2)–H(16)	106(3)
Si–C(1)–C(2)–Sn(1)	−178.8(4)	Si–C(3)–C(4)–Sn(2)	175.7(3)

[a] Applied symmetry operations: (′) $-x$, y, $-z+0.5$.

3. Conclusions

We systematically opened up the field of organotin dendrimers. In a divergent approach, first generation metallodendendrimers with ethylene bridges connecting a central silicon atom with the tin branching sites could be synthesized. The all-phenyl-substitution at tin was selectively transformed into bromine- or hydride-substitution, respectively. The high reactivity of the 12 Sn–H bonds of the dendritic organotin hydride formed is being utilized for further functionalization of the dendrimer via 12-fold hydrostannation reaction. This ongoing investigation aims to prepare water-soluble tin-based metallodendrimers as iodine-free X-ray contrast agents [22] and will be reported soon.

4. Experimental

All reactions were carried out in a protective atmosphere of nitrogen using dried, freshly distilled solvents. CH analyses were performed on a Perkin–Elmer CHNS/O Analyzer 2400. NMR spectra were recorded on a Bruker spectrometer ARX 200 (^{1}H at 200 MHz, ^{13}C{^{1}H} at 50.32 MHz) and ARX 400 (^{119}Sn{^{1}H inverse gated} at 149.21 MHz). Chemical shifts are referenced to tetramethylsilane (^{1}H and ^{13}C) and tetramethylstannane (^{119}Sn), respectively. The IR spectrum was recorded on a Nicolet Magna 750 spectrometer.

*4.1. $Si(CH_2CH_2SnPh_3)_4$ (**1**)*

Triphenyltin hydride (26.3 g, 75.0 mmol) was treated with tetravinylsilane (2.04 g, 15.0 mmol) and five drops of a 0.1 M solution of hexachloroplatinic acid in *i*-propanol. After vigorously stirring the reaction mixture for 24 h at room temperature (r.t.), pentane was added to the viscous product to give a solid, which was filtered off and washed 4 × with pentane. Recrystallization from cyclopentane yielded **1** as colorless crystals (20.8 g, 90%). M.p.: 148°C. Anal. Calc. for $C_{80}H_{76}SiSn_4$: C, 62.38; H, 4.97. Found: C, 62.27; H, 4.89%. ^{1}H-NMR ($CDCl_3$, ppm): δ 1.07 (m, $SiCH_2$, 8H), 1.41 (m, CH_2Sn, 8H), 7.30–7.50 (m, Ph-$CH_{3/4/5}$, 36H), 7.50–7.80 (m, Ph-$CH_{2/6}$, 24H). Concentration of the sample causes a lowfield shift of the aliphatic signals by 0.50 and of the aromatic signals by 0.35 ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): δ 3.16 (CSn; $|^{1}J(^{13}C^{117/119}Sn)|$ 371.6/388.4 Hz), 6.45 (SiC; $|^{2}J(^{13}CSn)|$ 34.6 Hz), 128.48 (Ph-$C_{3/5}$; $|^{3}J(^{13}CSn)|$ 46.8 Hz), 128.82 (Ph-C_4; $|^{4}J(^{13}CSn)|$ 10.9 Hz), 137.05 (Ph-$C_{2/6}$; $|^{2}J(^{13}CSn)|$ 34.5 Hz), 138.83 (Ph-C_1; $|^{1}J(^{13}C^{117/119}Sn)|$ 451.5/472.5 Hz). ^{119}Sn{^{1}H}-NMR ($CDCl_3$, ppm): δ −98.5.

*4.2. $Si(CH_2CH_2SnBr_3)_4$ (**2**)*

A stirred solution of **1** (20.0 g, 13.0 mmol) in CCl_4 (100 ml) was treated dropwise with bromine (24.9 g, 156 mmol) at −15°C under exclusion of light. Stirring of the reaction mixture was continued for 5 days at r.t., during which the product formed as a white precipitate. Filtration, washing the residue 5 × with a mixture of pentane, diethyl ether and chloroform and removal of the solvents in vacuo yielded **2** as a white solid (14.5 g, 71%). M.p.: decomposition starting at 150°C. Anal. Calc. for $C_8H_{16}Br_{12}SiSn_4$: C, 6.11; H, 1.02. Found: C, 6.36; H, 1.16%. ^{1}H-NMR (C_4D_8O, ppm): δ 1.37 (m, $SiCH_2$, 8H), 2.57 (m, CH_2Sn, 8H). ^{13}C{^{1}H}-NMR (C_4D_8O, ppm): δ 9.22 (SiC; $|^{2}J(^{13}C^{117/119}Sn)|$ 94.3/98.5 Hz), 35.55 (CSn; $|^{1}J(^{13}C^{117/119}Sn)|$ 680.3/712.1 Hz). ^{119}Sn{^{1}H}-NMR (C_4D_8O, ppm): δ −301.4.

*4.3. $Si(CH_2CH_2SnH_3)_4$ (**3**)*

A suspension of **2** (10.0 g, 6.35 mmol) in diethyl ether (50 ml) was slowly added to a stirred suspension of lithium aluminum hydride (2.17 g, 57.2 mmol) in diethyl ether (60 ml) at −35°C. After stirring the reaction mixture for 2 h at r.t., water (3.4 ml, 190 mmol) in dioxane (10 ml) was added dropwise at −5°C, and the mixture was stirred for another 15 min at r.t. Filtration, followed by washing of the residue with diethyl ether and drying of the combined filtrate over anhydrous sodium sulfate yielded a yellow solution. After removal of the solvent, a viscous liquid remained, which upon cooling at −28°C afforded **3** as colorless crystals (3.6 g, 90%). M.p.: −25°C. Anal. Calc. for $C_8H_{28}SiSn_4$: C, 15.32; H, 4.50. Found: C, 15.23; H, 3.86%. ^{1}H-NMR (C_6D_6, ppm): δ 0.40–1.20 (m, $SiCH_2CH_2Sn$, 16H), 4.56 (m, SnH_3, 12H; $|^{1}J(^{1}H^{117/119}Sn)|$ 1695.6/1774.5 Hz). ^{13}C{^{1}H}-NMR (C_6D_6, ppm): δ −1.65 (CSn; $|^{1}J(^{13}C^{117/119}Sn)|$ 390.5/408.4 Hz), 10.07 (SiC; $|^{2}J(^{13}CSn)|$ 37.1 Hz). ^{119}Sn{^{1}H}-NMR (C_6D_6, ppm): δ −316.3. IR (cm^{-1}): ν(Sn–H) 1853 (s; KBr/film).

*4.4. Single-crystal X-ray structure determination for **1** and **3***

Single crystals of $Si[CH_2CH_2Sn(C_6H_5)_3]_4$ (**1**) were obtained from a cyclopentane solution at 245 K and single crystals of $Si(CH_2CH_2SnH_3)_4$ (**3**) were grown without solvent at 245 K. Crystallographic measurements were made on an Enraf Nonius CAD-4 (**1**) and on a Siemens SMART CCD diffractometer (**3**) equipped with low temperature devices. Summaries of crystal data, data collection and refinement parameters are given in Table 3. Lattice parameters for **1** were derived from the setting angles of 25 reflections in the range of $13° \leq 2\theta \leq 30°$. Data were collected in the ω–2θ scan mode. Intensity data were corrected for Lorentz and polarization effects [23]. Structure solution was performed by direct methods (SHELXS-86) [24] and subsequent difference Fourier synthesis (SHELXL-93) [25] in the space group $I4_1/a$. Data for **3** were collected over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle for the crystal, and each exposure covered 0.3° scan in ω. Lattice parameters were derived from the setting angles of 8192 reflections [26]. The space group of **3** is $C2/c$. Structure solution was performed by direct methods and subsequent difference Fourier synthesis (SHELXTL) [27]. Full-matrix least-squares refinement was performed on F^2 for **1** and **3**. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included by using a riding model with $d(C–H) = 0.96$ Å, $U_{iso} = 0.08$ Å^2. In the case of **3** the Sn–H bonds and the distances between neighboring H atoms were restrained to be equal (SADI). Scattering

Table 3
Crystal data and details of data collection and structure refinement for **1** and **3**

	1	**3**
Crystal data		
Chemical formula	$C_{80}H_{76}SiSn_4$	$C_8H_{28}SiSn_4$
Formula weight (g mol^{-1})	1540.3	627.2
Crystal size (mm^3); color	0.39 × 0.33 × 0.30; colorless	1.20 × 0.96 × 0.70; colorless
Crystal system	tetragonal	monoclinic
Space group	$I4_1/a$	$C2/c$
Z (molecules)	4	4
a (Å)	18.027(6)	17.7394(2)
b (Å)	18.032(5)	8.6269(2)
c (Å)	21.571(3)	14.7225(2)
β (°)	90	112.764(1)
V (Å^3)	7012(3)	2077.57(6)
D_{calc} (g cm^{-3})	1.459	2.005
F(000)	3080	1160
μ(Mo–K$_\alpha$) (mm^{-1})	1.467	4.786
Data collection		
Diffractometer	Enraf Nonius CAD-4	Siemens SMART CCD
T (K)	193(2)	173(2)
Radiation (Mo–K$_\alpha$) (Å)	0.71069	0.71073
2θ Range (°)	$3 \leq 2\theta \leq 48$	$2 \leq 2\theta \leq 55$
Aperture (mm)	2.20	–
Scan angle (°)	$1.17 + 0.35 \tan \theta$	–
Reflections collected	11 112	7670
Reflections unique	2729	2382
Refinement		
Abs. Correction; max./min.	–	SADABS; 0.0805/0.0261
Refl. Observed, $I > 2\sigma(I)$	2047	1572
Data/restraints/ parameters	2724/0/192	2382/30/78
Goodness of fit [a]	1.072	1.020
R_1 $I > 2\sigma(I)$/all data [b]	0.0320/0.0562	0.0486/0.0854
wR_2 $I > 2\sigma(I)$/all data [c]	0.0719/0.0865	0.1101/0.1249
Larg. diff. Peak/hole (e Å^{-3})	0.476/−0.554	0.612/−1.262

[a] $\text{GOOF} = [\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$.

[b] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$.

[c] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 10.2425P]$ for **1** and $w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$ for **3** where $P = (F_o^2 + 2F_c^2)/3$.

factors were taken from Ref. [28]. After all atoms had been added to the model of the structure of **3** an empirical absorption correction SADABS [29] was applied: effective transmission, max.: 0.0805, min.: 0.0261. Geometrical calculations were performed with PLATON [30]. The ORTEP [31] illustrations depict thermal ellipsoids which are scaled to 35% (**1**) and 40% (**3**) probability level.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 139854 (**1**) and CCDC 139855 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).).

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