

Synthesis and characterization of new silicon-centred tin-dendrimers $\text{Si}[\text{CH}_2\text{CH}_2\text{SnR}_3]_4$. Single-crystal X-ray structure of the tetrahydrofuran adduct of tetrakis[2-(tribromostannyl)ethyl]silane

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Abstract

A series of novel first-generation silicon-centred tin dendrimers $\text{Si}(\text{CH}_2\text{CH}_2\text{SnR}_3)_4$ [$\text{R} = \text{CH}_3$ (**3**), $t\text{Bu}$ (**4**), $\text{C}\equiv\text{CCH}_3$ (**5**), $\text{C}_6\text{H}_4\text{CH}_3$ -4 (**6**), $\text{C}_6\text{H}_4\text{OCH}_3$ -4 (**7**), $(\text{CH}_2)_4\text{OCH}_2\text{CH}_2\text{OCH}_3$ (**8**), CH_2SiMe_3 (**9**)] was prepared by the reaction of $\text{Si}(\text{CH}_2\text{CH}_2\text{SnBr}_3)_4$ (**2**) with the appropriate Grignard reagent or $\text{LiCH}_2\text{SiMe}_3$ in tetrahydrofuran. The new compounds were characterized by multinuclear NMR studies (^1H , ^{13}C , ^{119}Sn), mass spectrometry (MALDI-TOF, EI) and elemental analyses. The molecular structure of $\text{Si}[\text{CH}_2\text{CH}_2\text{SnBr}_3(\text{THF})_2]_2[\text{CH}_2\text{CH}_2\text{SnBr}_3(\text{THF})_2]_2$ (**2a**) was determined by single-crystal X-ray diffraction.

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1. Introduction

Dendrimers are very promising architectures for the development of materials with novel and improved quality. Their unique chemical properties have generated an increasing attention in the study of these compounds and their chemistry continues to be an attractive research field [1]. The incorporation of metal atoms into the different sites of the dendritic framework opened the way to so-called metallodendrimers [2], new species with very specific properties of great interest for catalysis [3], host-guest chemistry [4], medicinal [5], electro- and photochemical applications [6]. Various kinds of metallodendrimers with mainly transition metal complexes in the periphery have been reported. However, only a few dendrimers with main group metals [7] have been synthesized until now, due to the lack of the required novel preparative techniques.

The hydrometallation reaction of tetraalkenylmetal compounds has been successfully used for the preparation of organosilicon [8] as well as organogermanium dendrimers [9]. A few triorganotin derivatives could be found in the literature, which do classify as dendrimers but which have not been synthesized in this context [10]. Recently, we opened up the field of organotin dendrimers [11], especially for the use as iodine-free X-ray contrast agents [12]. Meanwhile, we developed a method to prepare the first organo-*all*-tin dendrimers by the divergent [13] and the convergent way [14]. Yet, we have not been successful to isolate tin-centred dendrimers $\text{Sn}[(\text{CH}_2)_n\text{SnR}_3]_4$ with $n = 2$ and 3 using the divergent way by hydrostannation of $\text{Sn}(\text{CH}=\text{CH}_2)_4$ and $\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ with Ph_3SnH because of redistribution reactions yielding $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{SnPh}_3$ and $\text{Ph}_3\text{SnCH}_2\text{CH}_2\text{CH}_2\text{SnPh}_3$ instead of the desired products $\text{Sn}(\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$ and $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$, respectively [13]. In contrast, $\text{Si}(\text{CH}=\text{CH}_2)_4$ reacts with Ph_3SnH in high yields forming $\text{Si}(\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$ (**1**), which after bromination yields

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Si(CH₂CH₂SnBr₃)₄ (**2**) as the backbone for silicon-centred dendrimers with tin atoms in the first inner circle [11a]. In this paper, we describe the synthesis and the characterization of some new organotin dendrimers with a silicon nucleus and different peripheral ligands as well as the molecular structure of the THF complex of the starting material Si(CH₂CH₂SnBr₃)₄ (**2**).

2. Results and discussion

2.1. Synthesis and spectroscopy

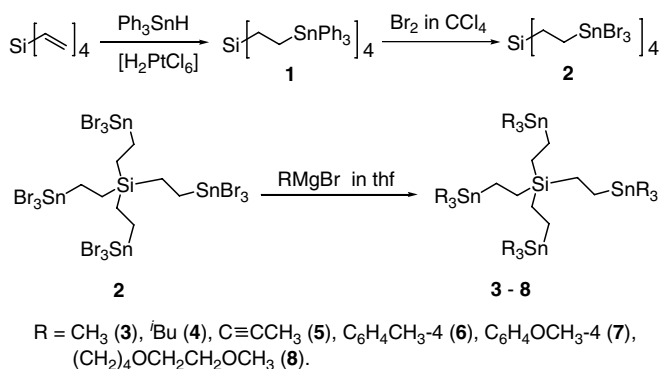
The reactive key compound of the divergent route towards functionalized silicon-centred tin dendrimers, the 12-fold bromine substituted organotin dendrimer tetrakis[2-(tribromostannyl)ethyl]silane (**2**) [11a], was prepared by selective and complete substitution of the phenyl groups of tetrakis[2-(triphenylstannyl)ethyl]silane [11a] (**1**) by bromine as a highly air sensitive white solid, which is hardly soluble in common organic solvents except for tetrahydrofuran. The high reactivity of the Sn–Br bonds in the dendritic backbone allows its further functionalization via coupling reactions with Grignard or organolithium reagents. Thus, treatment of **2** with an excess of the corresponding organomagnesium reagent, followed by workup with water gave tetrakis[2-(trimethylstannyl)ethyl]silane (**3**) and tetrakis[2-(triisobutylstannyl)ethyl]silane (**4**) as white solids in high yield (Scheme 1).

The air- and moisture-stable new dendrimers are soluble in all common organic solvents. The ¹H NMR spectrum of **3** shows a sharp singlet signal of the methyl groups attached to the tin atom at 0.05 ppm with typical hydrogen tin coupling constants of $|^2J(^1\text{H}^{117/119}\text{Sn})| = 49.4/51.5$ Hz, whereas the peripheral CH₂ groups of **4** [SnCH₂CH(CH₃)₂] are detected at 0.88 ppm with only one unresolved coupling constant $|^2J(^1\text{H}^{\text{Sn}})| = 48.4$ Hz. According to the relation $|^1J|^3|J|^2|J|^4|J|^4$ mostly being valid for the carbon tin coupling constants, the ¹³C NMR spectra reflect the two carbon atoms attached directly to the tin atom by the largest coupling constants $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 350.6/367.2$ Hz [CH₂CH₂Sn(CH₃)₃] and $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 297.3/310.8$ Hz [CH₂CH₂Sn(CH₃)₃] (**3**), and $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 296.5/310.1$ Hz (CH₂CH₂Sn*i*Bu) and $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 288.8/$

302.5 Hz [SnCH₂CH(CH₃)₂] (**4**), respectively. The carbon atoms next to those appear with the smallest coupling constants $|^2J(^{13}\text{CSn})| = 32.3$ Hz [CH₂CH₂Sn(CH₃)₃] (**3**) or $|^2J(^{13}\text{CSn})| = 31.3$ Hz (CH₂CH₂Sn*i*Bu) and $|^2J(^{13}\text{CSn})| = 17.7$ Hz [SnCH₂CH(CH₃)₂] (**4**), respectively. For each dendrimer, the observation of only one signal in the ¹¹⁹Sn{¹H} NMR spectrum, 6.5 ppm for **3** and –21.2 ppm for **4**, proves the total conversion of the Sn–Br bonds and the high purity of these compounds. The EI MS spectrum of **3** reveals the molecular ion peak centred at *m/z* 796.9 with the well-resolved isotopic multiplets, while **4** gave no satisfactory results: unfortunately, the detectable peaks in the MALDI-MS spectrum correspond to the fragment ions generated from M⁺ by loss of CH₂CH(CH₃)₂ groups.

Tetrakis[2-[tri(2-methylacetylenyl)stannyl]ethyl]silane (**5**) was isolated as a slightly air sensitive yellow powder by the treatment of **2** with an excess of methylacetylenyl-magnesium bromide and subsequent aqueous workup (Scheme 1). It is soluble in both saturated hydrocarbons and aromatic solvents. The ¹³C NMR spectrum of **5** exhibits the resonance of the aliphatic carbon atoms directly attached to the tin atom 4.8 ppm downfield shifted with respect to **3** at 7.54 ppm with an increase in the corresponding tin coupling constant $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 599.7/627.8$ Hz, when compared to the resonance of the parent dendritic backbone in **3**. The largest coupling constant is observed for the peripheral α-carbon atoms (Sn(C≡CCH₃)₃), $|^1J(^{13}\text{C}^{117/119}\text{Sn})| = 755.9/798.1$ Hz, obviously due to the presence of the electron rich triple bond. The ¹¹⁹Sn{¹H} NMR spectrum shows a related effect of the acetylene groups on the tin atoms revealing a very typical resonance for alkyne substituted organotin compounds [15] at –247.9 ppm. This one signal indicates the equivalence of the dendrons. The high purity and monodispersity of **5** is supported by the MALDI-TOF mass spectrum, which confirms that the molecule of mass *m/z* 1105.96 [M + Na]⁺ (Calc. 1106.82) is the only one product of the reaction. In addition, peaks with low intensity arising from the loss of C≡CCH₃ groups via Sn–C bond cleavage also appear. **5** is an interesting starting compound which can be utilized in turn for further functionalization of the dendrimer through hydrometallation [16] or reaction of the triple bonds with transition metal complexes [17] as well as with organoboranes [18].

Tetrakis[2-(tritolylstannyl)ethyl]silane (**6**) and tetrakis[2-(trianisylstannyl)ethyl]silane (**7**) were obtained as air-stable white solids (Scheme 1). The ¹H NMR and ¹³C{¹H} NMR spectra of **6** and **7** resemble those of **1** [11a]. The introduction of the tolyl and anisyl groups shifts the aliphatic α-carbon atoms attached to the tin atoms slightly to 3.12 (**6**) and 3.30 ppm (**7**), respectively, while those in the β-position are not affected distinguishably. The occurrence of singlet signals in the ¹¹⁹Sn{¹H} NMR spectra, –94.5 ppm for **6** and –89.6 ppm for **7** reveals a clean and complete reaction at the periphery without formation of any by-product. The MALDI-TOF mass spectra substantiate the monodispersity of the new dendrimers, revealing the expected molecular



Scheme 1. Synthesis of the dendrimers **3–8**.

ion peaks at m/z 1731.4 $[M + Na]^+$ (Calc. 1731.7) (**6**) and m/z 1923.7 $[M + Na]^+$ (Calc. 1923.7) (**7**), respectively.

The reaction of **2** with an excess of 4-(2-methoxyethoxy)butylmagnesium bromide afforded tetrakis{2-[tri{4-(2-methoxyethoxy)butyl}stannyl]ethyl}silane (**8**) in high yield (Scheme 1). In comparison with the signals of the free ligand, the 1H NMR and $^{13}C\{^1H\}$ NMR spectra of **8** show slightly shielded resonances for the 4-(2-methoxyethoxy)butyl groups, as expected. The well-resolved carbon tin coupling constants of the carbon atoms in the butenyl group attached to the tin atoms, $|^1J(^{13}C^{117/119}Sn)| = 290.5/304.1$ Hz, $|^2J(^{13}CSn)| = 18.5$ Hz, $|^3J(^{13}CSn)| = 52.0$ Hz and $|^4J(^{13}CSn)| = 7.6$ Hz, suggest the successful bonding of the ligands to the tin atoms. The monodispersity and purity of the water-soluble dendrimer is documented by only a single resonance detectable in its $^{119}Sn\{^1H\}$ NMR spectrum at -8.1 ppm. The MALDI-TOF mass spectrum also ascertains the completeness of the synthetic route with isotopic multiplets centred at m/z 2212.5 $[M + Na]^+$ (Calc. 2212.0) corresponding to the alkali adduct. Trace signals attributable to defect structures are not detectable.

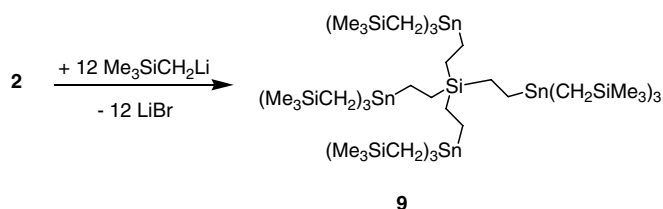
Slowly treatment of **2** with a 25% excess of a diluted solution of Me_3SiCH_2Li in tetrahydrofuran at $0^\circ C$ resulted, after stirring the reaction mixture overnight, in a complete substitution of all 12 bromine atoms and formation of tetrakis[2-{tris(trimethylsilylmethyl)stannyl}ethyl]silane (**9**) as a colorless, viscous oil which did not crystallize (Scheme 2).

The 1H NMR spectrum of **9** shows a sharp singlet signal for the $SiCH_2Sn$ protons at -0.19 ppm with a typical coupling constant of $|^2J(^1H^{117/119}Sn)| = 65.3/68.3$ Hz, whereas the signals for the ethylene protons depict an unresolved multiplet between 0.70 and 0.82 ppm. The ^{13}C NMR spectrum reflects the two carbon atoms attached directly to the tin atom by the largest coupling constants $|^1J(^{13}C^{117/119}Sn)| = 327.8/342.9$ Hz (CH_2CH_2Sn) and $|^1J(^{13}C^{117/119}Sn)| = 204.9/214.7$ Hz ($SnCH_2Si$). The observation of only one signal in the $^{119}Sn\{^1H\}$ NMR spectrum of **9** at 26.2 ppm as well as the MALDI-TOF MS spectrum prove the complete conversion of **2** to the dendrimer **9**.

2.2. X-ray structure of

$Si[CH_2CH_2SnBr_3(THF)_2]_2[CH_2CH_2SnBr_3(THF)_2]_2$ (**2a**)

While single crystals of $Si(CH_2CH_2SnPh_3)_4$ (**1**) and of the very sensitive hydride derivative $Si(CH_2CH_2SnH_3)_4$



Scheme 2. Synthesis of the dendrimer **9**.

could be obtained for X-ray structure determination [11a], crystallization of **2** failed until now due to its low solubility in unpolar as well as in polar solvents. Yet, after cooling the clear filtrate of a sludge of **2** in THF to $-20^\circ C$ needle shaped crystals of a tetrahydrofuran adduct **2a** could be obtained. In vacuum or in a strong stream of nitrogen the crystals lose the coordinated tetrahydrofuran as indicated by elemental analysis of the white powder formed. The X-ray structure of **2a** shows two different types of dendritic branches with one and two coordinating tetrahydrofuran solvent molecules, respectively, resulting in a molecular formula $Si[CH_2CH_2SnBr_3(THF)_2]_2[CH_2CH_2SnBr_3(THF)]_2$ (Fig. 1).

The coordination sphere around the tin atoms of two branches each is distorted trigonal bipyramidal (Sn2) and distorted octahedral (Sn1), respectively. The central silicon atom is tetrahedrally coordinated by four dendritic branches. The conformation of the bromo(tetrahydrofuran)tin dendrimer can be described by the torsion angles $Si-C(1)-C(2)-Sn(1)$ of $-178.5(7)^\circ$ and $Si-C(3)-C(4)-Sn(2)$ of $-168.7(6)^\circ$ (the ideal torsion angle of a *trans*-conformation is 180°). The six $Sn \cdots Sn$ distances in **2a** of $7.881(2)$ Å (mean) are in the same range as in the

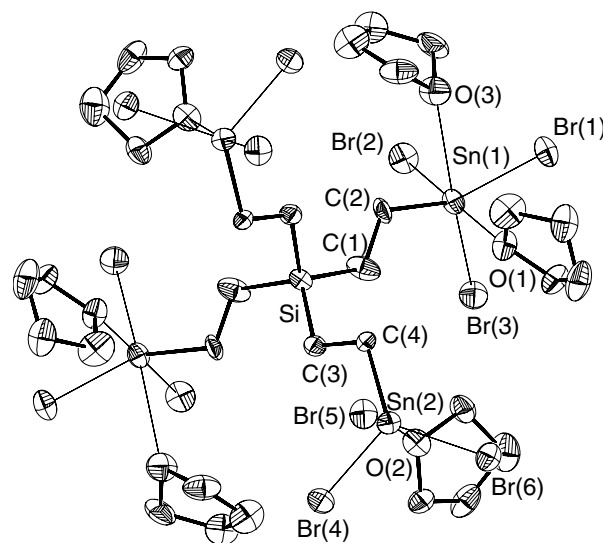


Fig. 1. ORTEP plot [19] of the molecular structure and numbering scheme of **2a** with 40% probability thermal ellipsoids. For clarity, the hydrogen atoms are not depicted. Selected bond lengths and distances (Å), bond and torsion angles ($^\circ$) with estimated standard deviations in parentheses: $Sn(1) \cdots Sn(1')$ 8.210(2), $Sn(1) \cdots Sn(2)$ 7.7020(12), $Sn(1) \cdots Sn(2')$ 7.9658(13), $Sn(2) \cdots Sn(2')$ 7.7384(2), $Si \cdots Sn(1)$ 4.837(2), $Si \cdots Sn(2)$ 4.822(3), $Sn(1)-Br(1)$ 2.476(2), $Sn(1)-Br(2)$ 2.541(2), $Sn(1)-Br(3)$ 2.511(2), $Sn(2)-Br(4)$ 2.472(2), $Sn(2)-Br(5)$ 2.534(2), $Sn(2)-Br(6)$ 2.488(2), $Sn(1)-O(1)$ 2.510(9), $Sn(1)-O(3)$ 2.980(11), $Sn(2)-O(2)$ 2.481(9), $Sn(1)-C(2)$ 2.145(12), $Sn(2)-C(4)$ 2.152(12), $Si-C(1)$ 1.87(2), $Si-C(3)$ 1.889(12), $C(1)-C(2)$ 1.45(2), $C(3)-C(4)$ 1.52(2), $C(2)-Sn(1)-Br(1)$ 140.4(4), $C(2)-Sn(1)-Br(2)$ 100.7(4), $C(2)-Sn(1)-Br(3)$ 109.3(4), $C(4)-Sn(2)-Br(4)$ 116.3(3), $C(4)-Sn(2)-Br(5)$ 103.3(4), $C(4)-Sn(2)-Br(6)$ 125.3(4), $C(1)-Si-C(1')$ 110.2(10), $C(1)-Si-C(3)$ 107.7(7), $C(1)-Si-C(3')$ 109.0(6), $C(3)-Si-C(3')$ 113.2(7), $C(2)-C(1)-Si$ 117.8(11), $C(4)-C(3)-Si$ 114.2(8), $C(1)-C(2)-Sn(1)$ 115.1(10), $C(3)-C(4)-Sn(2)$ 111.3(8), $Si-C(1)-C(2)-Sn(1)$ $-178.5(7)$, $Si-C(3)-C(4)-Sn(2)$ $-168.7(6)$. Applied symmetry operation: ($'$) $-x, y, -z+0.5$.

analogous derivatives $\text{Si}(\text{CH}_2\text{CH}_2\text{SnH}_3)_4$ (7.8285(11) Å) and $\text{Si}(\text{CH}_2\text{CH}_2\text{SnPh}_3)_4$ (**1**) (7.733(2) Å) [11a]. The C–Si–C angles in **2a** show an increased range from 107.7(7)° to 113.2(7)°. Due to the bromo substituents in **2a** the two Sn–C bonds of 2.152(12) Å and 2.145(12) Å are slightly longer than in $\text{Si}(\text{CH}_2\text{CH}_2\text{SnH}_3)_4$ (2.130(7) and 2.122(7) Å) and in **1** (2.136(4) Å) [11a]. The lengths of the Sn–Br bonds are between 2.472(2) Å and 2.541(2) Å. For the lengths of the Sn–O bonds there are two short ones Sn(1)–O(1) of 2.510(9) Å and Sn(2)–O(2) of 2.481(9) Å and a long one Sn(1)–O(3) of 2.980(11) Å found, the latter belonging to the tin atom with two coordinating tetrahydrofuran molecules. Comparisons with other analogous molecules are not possible because there is only one X-ray structure of an organotin trihalide of the type $\text{RSnX}_3(\text{THF})_n$ namely 1- $\text{IC}_6\text{H}_4\text{SnCl}_3(\text{THF})$, described in the literature [20].

The unit cell of **2a** (along the *c*-axis) shows an almost planar arrangement of the THF molecules perpendicular to the *b*-axis (Fig. 2). Each molecule **2** coordinates six THF molecules which are bonded to the tin atoms and which form a ring around the central silicon atom. Thus, there exists a sandwich type structure with the silicon atom and the THF molecules in the central plane, and above and below the Br_3Sn moieties.

3. Conclusion

Novel first generation silicon-centred tin dendrimers carrying peripheral alkyl, acetylenyl, and aryl groups have been prepared by metathetical reactions of $\text{Si}(\text{CH}_2\text{CH}_2\text{SnBr}_3)_4$ with Grignard reagents or $\text{Me}_3\text{Si-CH}_2\text{Li}$. ^1H , ^{13}C , ^{119}Sn NMR spectroscopic as well as MALDI-TOF mass spectrometric investigations evidenced that all synthetic steps proceeded efficiently without steric hindrance and competitive reactions.

4. Experimental

All manipulations involving air sensitive compounds were carried out in dry, oxygen-free solvents under an inert atmosphere of nitrogen using standard Schlenk techniques. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Elemental analyses were performed on a Perkin–Elmer Series II CHNS/O Analyzer 2400. The NMR spectra were recorded on Bruker ARX 200 (^1H , 200 MHz; ^{13}C , 50 MHz) and ARX 400 (^1H , 400 MHz; ^{13}C , 100.64 MHz; ^{119}Sn , 149.21 MHz) spectrometers at ambient temperature. Chemical shifts are reported in ppm and referenced to the ^1H and ^{13}C residues of the deuterated solvents. Chemical shifts for ^{119}Sn are given relative to $(\text{CH}_3)_4\text{Sn}$. IR spectra were obtained on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311 A/AMD Instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities are given in parentheses.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed in the reflection mode of an Applied Biosystems Voyager-Elite mass spectrometer equipped with a nitrogen laser emitting at 337 nm. Acceleration voltage was set to 20 kV and 25 kV, respectively, with positive or negative ionization. The mass spectrometers were externally calibrated with a mix of three synthesized peptides. Trans-indolacrylic acid (IAA) was used as a MALDI matrix at concentrations of 0.2 M and 10 mM in THF/ CH_3CN (3:1), respectively. Sample solutions were prepared with an approximate concentration of 1 mM in THF or CH_2Cl_2 . Solutions containing 2 mM of CH_3COONa , KCl, or AgI were used as ionization agents. Sonification was applied to speed up mixing. One microlitre of the sample was mixed with 1 μl

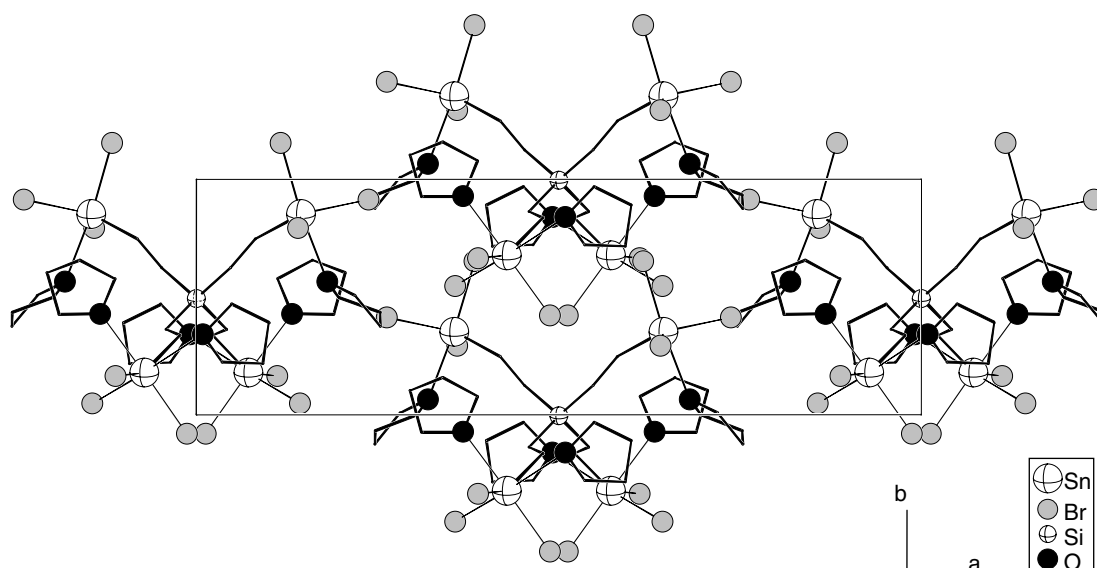


Fig. 2. The content of the unit cell of **2a** viewed along the *c*-axis depicts the almost planar arrangement of the THF rings in the crystal structure [21].

of the matrix solution and 1 μ l of the resulting mixture was deposited on a stainless-steel flat plate and allowed to dry at room temperature.

CH_3I , $t\text{BuBr}$, $\text{CH}_3\text{C}\equiv\text{CBr}$, $\text{CH}_3\text{C}_6\text{H}_4\text{Br-4}$, $\text{CH}_3\text{O-C}_6\text{H}_4\text{Br-4}$, $\text{Br}(\text{CH}_2)_2\text{Br}$, $\text{Br}(\text{CH}_2)_4\text{Br}$, Mg, Ph_3SnCl , LiAlH_4 , *trans*-indolacrylic acid and α -cyano-4-hydroxycinnamic acid were used as purchased. Ph_3SnH [22], $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2)_4\text{Br}$ [23], $\text{Me}_3\text{SiCH}_2\text{Li}$ [24], **1** [11a] and **2** [11a] were prepared according to published procedures.

4.1. *Si(CH₂CH₂SnPh₃)₄ (1)* [11a]

MS MALDI-TOF (IAA, THF): 1563.4 $[\text{M} + \text{Na}]^+$ (Calc. 1563.18), 1602.5 $[\text{M} + \text{Na} + \text{K}]^+$ (Calc. 1602.18) and 1672.6 $[\text{M} + \text{Na} + \text{Ag}]^+$ (Calc. 1671.01).

4.2. *Synthesis of Si(CH₂CH₂SnMe₃)₄ (3)*

A solution of **2** (5.19 g, 3.30 mmol) in THF (50 ml) was placed in a 250 ml three-necked Schlenk flask equipped with a reflux condenser and a dropping funnel. After cooling to 0 °C, 54.20 ml of a solution of CH_3MgBr in THF (0.95 M, 51.48 mmol) was dropped in slowly. The brown reaction mixture was stirred for 1 h at this temperature, heated to 75 °C for 5 h and stirred for 12 h at room temperature. The resulting solution was hydrolyzed carefully with water at 0 °C and filtered with a d4-frit. The residue was extracted three times with diethyl ether (20 ml). The combined organic fractions were washed twice with an aqueous solution of NH_4Cl and twice with an aqueous solution of NaCl . Drying over Na_2SO_4 and evaporation of the solvent in vacuum (10^{-2} mbar) gave **3** as a white solid.

Yield: 2.52 g (96 %), m.p. 57 °C. ^1H NMR (400.13 MHz, CDCl_3): δ 0.62–0.76 (m, 16H, $\text{CH}_2\text{CH}_2\text{SnMe}_3$), 0.052 [s, 36H, $\text{CH}_2\text{CH}_2\text{Sn}(\text{CH}_3)_3$, $^2J(^1\text{H}^{117/119}\text{Sn}) = 49.4/51.5$ Hz], $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3): δ -10.71 [SnCH_3 , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 297.3/310.8$ Hz], 2.76 [SnCH_2 , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 350.6/367.2$ Hz], 6.18 [SiCH_2 , $^2J(^{13}\text{CSn}) = 32.3$ Hz], $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ 6.5. EI MS [103 °C; *m/z* (%): 796.9 (5.7) $[\text{M}]^+$, 616.9 (2) $[\text{M}-\text{Sn}(\text{CH}_3)_3-\text{CH}_3]^+$, 426.1 (46) $[\text{M}-\text{C}_2\text{H}_4\text{Sn}(\text{CH}_3)_3-\text{C}_2\text{H}_4\text{Sn}(\text{CH}_3)_2]^+$, 398.01 (41.7) $[\text{M}-2\text{C}_2\text{H}_4\text{Sn}(\text{CH}_3)_3-\text{CH}_3]^+$, 165.1 (100) $[\text{Sn}(\text{CH}_3)_3]^+$, 120.0 (2) $[\text{Sn}]^+$. Anal. Calc. for $\text{C}_{20}\text{H}_{52}\text{SiSn}_4$ (795.48 g/mol): C, 30.20; H, 6.59. Found: C, 30.07; H, 6.52%.

4.3. *Synthesis of Si(CH₂CH₂Sn^{*i*}Bu₃)₄ (4)*

In analogy to the synthesis of **3**, a solution of **2** (5.00 g, 3.18 mmol) in THF (50 ml) was reacted at 0 °C with 70.87 ml (49.61 mmol) of a solution of $t\text{BuMgBr}$ (0.70 M) in THF. After the reaction and analogous workup, **4** was isolated as a white solid.

Yield: 3.64 g (88 %), m.p. 33 °C. ^1H NMR (200.13 MHz, CDCl_3): δ 0.70–0.76 (m, 16H, $\text{CH}_2\text{CH}_2\text{Sn}$), 0.88 (d, 24H,

$\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^2J(^1\text{HSn}) = 48.4$ Hz), 0.96 (d, 72H, $\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^3J(^1\text{HSn}) = 124.0$ Hz), 1.74–2.10 (m, 12H, $\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ 2.95 ($\text{CH}_2\text{CH}_2\text{Sn}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 296.5/310.5$ Hz), 6.55 (SiCH_2 , $^2J(^{13}\text{CSn}) = 31.3$ Hz), 21.85 ($\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 288.8/302.5$ Hz), 26.93 ($\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^3J(^{13}\text{C}^{117/119}\text{Sn}) = 36.2/37.9$ Hz), 27.16 ($\text{Sn}[\text{CH}_2\text{CH}(\text{CH}_3)_2]_3$, $^2J(^{13}\text{CSn}) = 17.7$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ -21.2. MS MALDI-TOF (IAA, THF): 1200.5 $[\text{M}-\text{CH}_2\text{CH}(\text{CH}_3)_2-\text{CH}(\text{CH}_3)_2]^+$. Anal. Calc. for $\text{C}_{56}\text{H}_{124}\text{SiSn}_4$ (1300.45 g/mol): C, 51.72; H, 9.61. Found: C, 51.55; H, 9.56%.

4.4. *Synthesis of Si[CH₂CH₂Sn(C≡CCH₃)₃]₄ (5)*

In analogy to the synthesis of **3**, a solution of **2** (4.57 g, 2.90 mmol) in THF (50 ml) was reacted at 0 °C with 60.32 ml (45.24 mmol) of a solution of $\text{CH}_3\text{C}\equiv\text{CMgBr}$ (0.75 M). After the reaction and analogous workup, **5** was obtained as a yellow solid.

Yield: 2.80 g (89 %), m.p. 128 °C. ^1H NMR (200.13 MHz, CDCl_3): δ 0.80–0.98 (m, 8H, SiCH_2), 0.96 (s, 36H, CH_3 , $^4J(^1\text{HSn}) = 14.4$ Hz), 1.00–1.20 (m, 8H, SnCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ 4.92 (CH_3 , $^3J(^{13}\text{CSn}) = 15.0$ Hz), 5.44 (SiCH_2 , $^2J(^{13}\text{CSn}) = 47.5$ Hz), 7.54 (SnCH_2 , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 599.7/627.8$ Hz), 76.26 ($\text{SnC}\equiv\text{C}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 755.9/798.1$ Hz), 107.75 ($\text{SnC}\equiv\text{C}$, $^2J(^{13}\text{C}^{117/119}\text{Sn}) = 155.3/162.4$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ -247.9. MS MALDI-TOF (IAA, THF): 1105.96 $[\text{M} + \text{Na}]^+$ (Calc. 1106.82), 1029.81 $[\text{M}-\text{C}\equiv\text{CCH}_3-\text{CH}_3]^+$. Anal. Calc. for $\text{C}_{44}\text{H}_{52}\text{SiSn}_4$ (1083.74 g/mol): C, 48.76; H, 4.84. Found: C, 48.63; H, 4.74%.

4.5. *Synthesis of Si[CH₂CH₂Sn(C₆H₄CH₃-4)₃]₄ (6)*

In analogy to the synthesis of **3**, a solution of **2** (3.51 g, 2.23 mmol) in THF (50 ml) was treated at 0 °C with 40.93 ml (34.79 mmol) of a solution of tolylmagnesium bromide (0.85 M) in THF. After the reaction and analogous workup, **6** was isolated as a white solid.

Yield: 3.01 g (79 %), m.p. 120 °C. ^1H NMR (400.13 MHz, CDCl_3): δ 0.85–1.04 (m, 8H, SiCH_2), 1.21–1.41 (m, 8H, SnCH_2), 2.36 (s, 36H, CH_3), 7.15 (d, 24H, Ph-*H^{meta}*), 7.41 (d, 24H, Ph-*H^{ortho}*), $^3J(^1\text{HSn}) = 43.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3): δ 3.12 (SnCH_2 , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 375.3/390.9$ Hz), 6.34 (SiCH_2 , $^2J(^{13}\text{CSn}) = 35.0$ Hz), 21.41 (CH_3), 129.30 (Ph-*C^{meta}*), $^3J(^{13}\text{CSn}) = 48.9$ Hz), 135.25 (Ph-*C^{para}*), $^4J(^{13}\text{CSn}) = 11.3$ Hz), 137.04 (Ph-*C^{ortho}*), $^2J(^{13}\text{CSn}) = 36.0$ Hz), 138.39 (Ph-*C^{ipso}*), $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 458.1/478.5$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ -94.5. MS MALDI-TOF (IAA, THF): 1731.4 $[\text{M} + \text{Na}]^+$ (Calc. 1731.7), 1771.9 $[\text{M} + \text{Na} + \text{K}]^+$, 1826 $[\text{M} + 5\text{Na}]^+$, 1921.9 $[\text{M} + 2\text{Ag}]^+$. Anal. Calc. for $\text{C}_{92}\text{H}_{100}\text{SiSn}_4$ (1708.65 g/mol): C, 64.67; H, 5.90. Found: C, 64.55; H, 5.80%.

4.6. Synthesis of $\text{Si}[\text{CH}_2\text{CH}_2\text{Sn}(\text{C}_6\text{H}_4\text{OCH}_3\text{-}4)_3]_4$ (**7**)

In analogy to the synthesis of **3**, a solution of **2** (3.16 g, 2.01 mmol) in THF (50 ml) was reacted with 34.84 ml (31.36 mmol) of a solution of anisylmagnesium bromide (0.90 M) in THF. After the reaction, the analogous workup gave **7** as a white solid.

Yield: 2.79 g (73 %), m.p. 58 °C. ^1H NMR (200.13 MHz, CDCl_3): δ 0.78–1.06 (m, 8H, SiCH_2), 1.20–1.41 (m, 8H, SnCH_2), 3.78 (s, 36H, CH_3), 6.89 (d, 24H, $\text{Ph-H}^{\text{meta}}$), 7.40 (d, 24H, $\text{Ph-H}^{\text{ortho}}$, $^3J(^1\text{H}\text{Sn}) = 42.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ 3.30 (SnCH_2 , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 378.0/395.2$ Hz), 6.48 (SiCH_2 , $^2J(^{13}\text{CSn}) = 34.4$ Hz), 54.92 (CH_3), 114.35 ($\text{Ph-C}^{\text{meta}}$, $^3J(^{13}\text{CSn}) = 51.1$ Hz), 129.45 ($\text{Ph-C}^{\text{ipso}}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 469.4/492.0$ Hz), 138.08 ($\text{Ph-C}^{\text{ortho}}$, $^2J(^{13}\text{CSn}) = 39.8$ Hz), 160.21 ($\text{Ph-C}^{\text{para}}$, $^4J(^{13}\text{CSn}) = 11.2$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ -89.6. MS MALDI-TOF (IAA, THF): 1923.7 $[\text{M} + \text{Na}]^+$ (Calc. 1923.7), 1962.7 $[\text{M} + \text{K}]^+$, 2001.9 $[\text{M} + 2\text{K}]^+$. Anal. Calc. for $\text{C}_{92}\text{H}_{100}\text{O}_{12}\text{SiSn}_4$ (1900.64 g/mol): C, 58.24; H, 5.30. Found: C, 57.97; H, 5.19%.

4.7. Synthesis of $\text{Si}[\text{CH}_2\text{CH}_2\text{Sn}\{(\text{CH}_2)_4\text{OCH}_2\text{-CH}_2\text{OCH}_3\}_3]_4$ (**8**)

In analogy to the synthesis of **3**, a solution of **2** (3.10 g, 1.97 mmol) in THF (50 ml) was treated with 76.81 ml (30.72 mmol) of a solution of 1-bromomagnesium[4-(2-methoxyethoxy)butane] (0.40 M) in THF. After the reaction and analogous workup, **8** was isolated as a colorless viscous liquid.

Yield: 3.37 g (78 %). ^1H NMR (200.13 MHz, CDCl_3): δ 0.48–0.56 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{Sn}$), 0.64–0.79 (m, 24H, $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.31–1.61 (m, 48H, $\text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{O}$), 3.26 (s, 36H, CH_3), 3.30–3.40 (m, 24H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.40–3.50 (m, 48H, $\text{OCH}_2\text{-CH}_2\text{OCH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ 0.42 ($\text{CH}_2\text{CH}_2\text{Sn}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 300.5/314.4$ Hz), 6.24 (SiCH_2 , $^2J(^{13}\text{CSn}) = 31.1$ Hz), 8.12 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 290.5/304.1$ Hz), 23.23 ($\text{SnCH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{O}$, $^2J(^{13}\text{CSn}) = 18.5$ Hz), 33.97 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{-CH}_2\text{O}$, $^3J(^{13}\text{CSn}) = 52.0$ Hz), 58.66 (CH_3), 69.92 ($\text{OCH}_2\text{CH}_2\text{OCH}_3$), 70.71 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$, $^4J(^{13}\text{CSn}) = 7.6$ Hz), 71.66 ($\text{OCH}_2\text{CH}_2\text{OCH}_3$). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ -8.1. MS MALDI-TOF (IAA, THF): 2212.5 $[\text{M} + \text{Na}]^+$ (Calc. 2212.0), 2267.6 $[\text{M} + 2\text{K}]^+$, 2415.8 $[\text{M} + 3\text{Na} + 4\text{K}]^+$. Anal. Calc. for $\text{C}_{92}\text{H}_{196}\text{O}_{24}\text{SiSn}_4$ (2189.40 g/mol): C, 50.47; H, 9.02. Found: C, 50.25; H, 8.91%.

4.8. Synthesis of $\text{Si}[\text{CH}_2\text{CH}_2\text{Sn}(\text{CH}_2\text{SiMe}_3)_3]_4$ (**9**)

In analogy to the synthesis of **3**, a solution of **2** (4.2 g, 2.67 mmol) in THF (50 ml) was treated with $\text{Me}_3\text{SiCH}_2\text{Li}$ (3.92 g, 41.65 mmol) in THF. After the reaction and analogous workup, **9** was isolated as a colorless viscous oil.

Table 1

Crystal data and details of data collection of **2a**

Formula	$\text{C}_{32}\text{H}_{64}\text{Br}_{12}\text{O}_6\text{SiSn}_4$
Formula weight (g mol ⁻¹)	2007
Crystal size (mm ³); color, shape	0.74 × 0.13 × 0.10; colorless needles
Crystal system	monoclinic
Space group	$C2/c$
Z (formula units)	4
a (Å)	28.5550(6)
b (Å)	8.06170(10)
c (Å)	27.6869(5)
α (°)	90
β (°)	119.5630(10)
γ (°)	90
V (Å ³)	5543.8(2)
D_{calc} (g cm ⁻³)	2.404
F(000)	3752
μ (mm ⁻¹)	10.488
2 θ Range (°)	3 ≤ 2 θ ≤ 55
Number of reflection, collected/unique [R_{int}]	20280/6364 [0.1150]
Number of reflection, observation $I > 2\sigma(I)$	3518
Index range	$h = -20 \rightarrow 37$, $k = -10 \rightarrow 10$, $l = -35 \rightarrow 35$
Data/restraints/parameters	6364/0/249
$R_1 I > 2\sigma(I)$ /all data ^a	0.0739/0.1444
$wR_2 I > 2\sigma(I)$ /all data ^b	0.1506/0.1808
Goodness-of-fit ^c	0.999
Weight details a/b^d	0.077/0
Difference in peak/hole (e Å ⁻³)	1.831/-1.340
Absorption correction, maximum/minimum	SADABS, 0.0342/0.0050

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$$

$$^b wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

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

$$^d w = 1 / [\sum^2(F_o^2) + (aP)^2 + bP], P = (F_o^2 + 2F_c^2) / 3$$

Yield: 2.36 g (53 %). ^1H NMR (200.13 MHz, CDCl_3): δ -0.19 (s, 24H, SnCH_2Si , $^2J(^1\text{H}^{117/119}\text{Sn}) = 65.3/68.3$ Hz), 0.04 (s, 108H, SiCH_3), 0.70–0.82 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{Sn}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3): δ -3.33 (SnCH_2Si , $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 204.9/214.7$ Hz), 1.97 (SiCH_3), 6.19 ($\text{SiCH}_2\text{CH}_2\text{Sn}$, $^1J(^{13}\text{C}^{117/119}\text{Sn}) = 327.8/342.9$ Hz), 6.91 ($\text{SiCH}_2\text{CH}_2\text{Sn}$, $^2J(^{13}\text{CSn}) = 32.5$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (149.21 MHz, CDCl_3): δ 26.2. MS MALDI-TOF (IAA, THF): 1671.35 $[\text{M} - \text{CH}_3 + \text{Na}]^+$ (Calc. 1669.62). Anal. Calc. for $\text{C}_{56}\text{H}_{148}\text{Si}_{13}\text{Sn}_4$ (1661.66 g/mol): C, 40.48; H, 8.89. Found: C, 40.07; H, 8.63%.

4.9. X-ray structural analysis of **2a**

Single crystals of **2a** were obtained from a tetrahydrofuran solution of **2** at 253 K. The crystal data and details of data collection are given in Table 1. Data were collected on a Siemens SMART CCD diffractometer [25] (graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) with an area detector by use of ω scans at 173 K. The single-crystal structure was solved by direct methods with

SHELXS-97 [26] and refined on F^2 using all observed reflections with SHELXL-97 [27]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions ($C-H = 0.96 \text{ \AA}$) and assigned to isotropic displacement parameters ($U_{eq} = 0.08 \text{ \AA}^2$). SADABS [28] was used to perform area-detector scaling and absorption correction. The geometrical aspects of the structure were analyzed by using PLATON software [29].

5. Supplementary data

CCDC-606541 contains the supplementary crystallographic data. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/contz/retriving.html or an application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

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