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Synthesis and characterization of organotin triflate clusters

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Dedicated to Professor Jean-F. Normant on the occasion of his 65th birthday

Abstract

A variety of organotin triflate clusters are obtained by treating dialkyltin oxide with triflic acid (TfOH) in different ratios. When R_2SnO is exposed to 0.5 equivalents of TfOH, 3-hydroxy-1-triflato distannoxanes (**1**) are formed which have a novel sheet-like structure in the solid state. Treatment of R_2SnO with 2/3 or one equivalent of TfOH affords a trinuclear cluster **3** or cationic dimers **2**. The stoichiometry of the novel trinuclear cluster can be confirmed by various chemical reactions as well as elemental analysis. On the basis of ^{119}Sn-NMR study, the equilibrium has been revealed between **2** and **3**. The use of two equivalents of TfOH in the reaction with R_2SnO offers a convenient route for $R_2Sn(OTf)_2$ (**4**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organotin triflate clusters; Dialkyltin oxide; Triflic acid

1. Introduction

Organotin triflates serve as useful Lewis acid catalysts in a wide spectrum of synthetic reactions. The innately weak acidity of organotin compounds can be increased by attaching the strongly electron-withdrawing triflate ligand(s) to tin and, hence, the subtle tuning of the acidity is feasible resulting in unique chemoselectivity. For example, we previously disclosed that dialkyltin bis(triflate)s catalyzed Mukaiyama-aldol reaction in which aldehydes, ketones, and their acetals were completely discriminated [1]. Moreover, Robinson annulation was effected smoothly with the same catalysts thanks to their mildness [2]. Recently, novel cationic organotin triflate dimers were synthesized which exhibited high catalytic activity for acylation of alcohols [3]. In addition to the synthetic utilities, these dimers possess a unique dicationic formulation that originates from the electronic character of the triflate ligand. Thus, we were intrigued to synthesize a variety of organotin triflates in expectation of novel structural features. In this paper, we report the synthesis and characterization of di- and trinuclear organotin triflates together with mononuclear organotin bistriflates.

2. Results and discussion

When dialkyltin oxides were treated with 0.5 equivalents of triflic acid (TfOH) in acetone, 3-hydroxy-1-(triflato)tetraalkyldistannoxanes (**1**) were produced (Eq. (1)). Recrystallization of **1b** from CH_2Cl_2 provided a suitable crystal for X-ray analysis. As illustrated in Fig. 1, this compound involves dimeric ladder structure units typical of distannoxanes [4][1]. Furthermore, the higher order assembly emerges through the intermolecular bridge of the triflates to give rise to a novel sheet-like structures resulting in the 24-membered rings [5]. The selected bond distances and angles are given in Table 1. The ethyl and octyl derivatives, **1a** and **1c**, also could be recrystallized. Unfortunately, however, both compounds failed to give good crystals for X-ray analysis. The same reaction with ^{t}Bu$_2$SnO furnished no identifiable compounds.

As shown in Table 2, ^{119}Sn-NMR spectra of these compounds in CD_3CN exhibited a pair of singlets

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[1] It should be noted that some of C_γ–C_δ bonds in the butyl groups were shorter than the normal distance. We have not yet succeeded in the refinement to obtain reasonable bond lengths despite many attempted measurements even at lower temperatures. However, such disorder of the methyl residue in the butyl group is not of prime importance for the present structural discussion.

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diagnostic of the dimeric formulation A [6]. However, it is not clear at the moment whether the sheet-like structure is retained or not for these compounds in solution.

$$4\,R_2SnO + 2\,TfOH \xrightarrow[\text{acetone}]{} [(TfO)R_2SnOSnR_2OH]_2 \qquad (1)$$

1a: R = Et
1b: R = ^{n}Bu
1c: R = C_8H_{17}

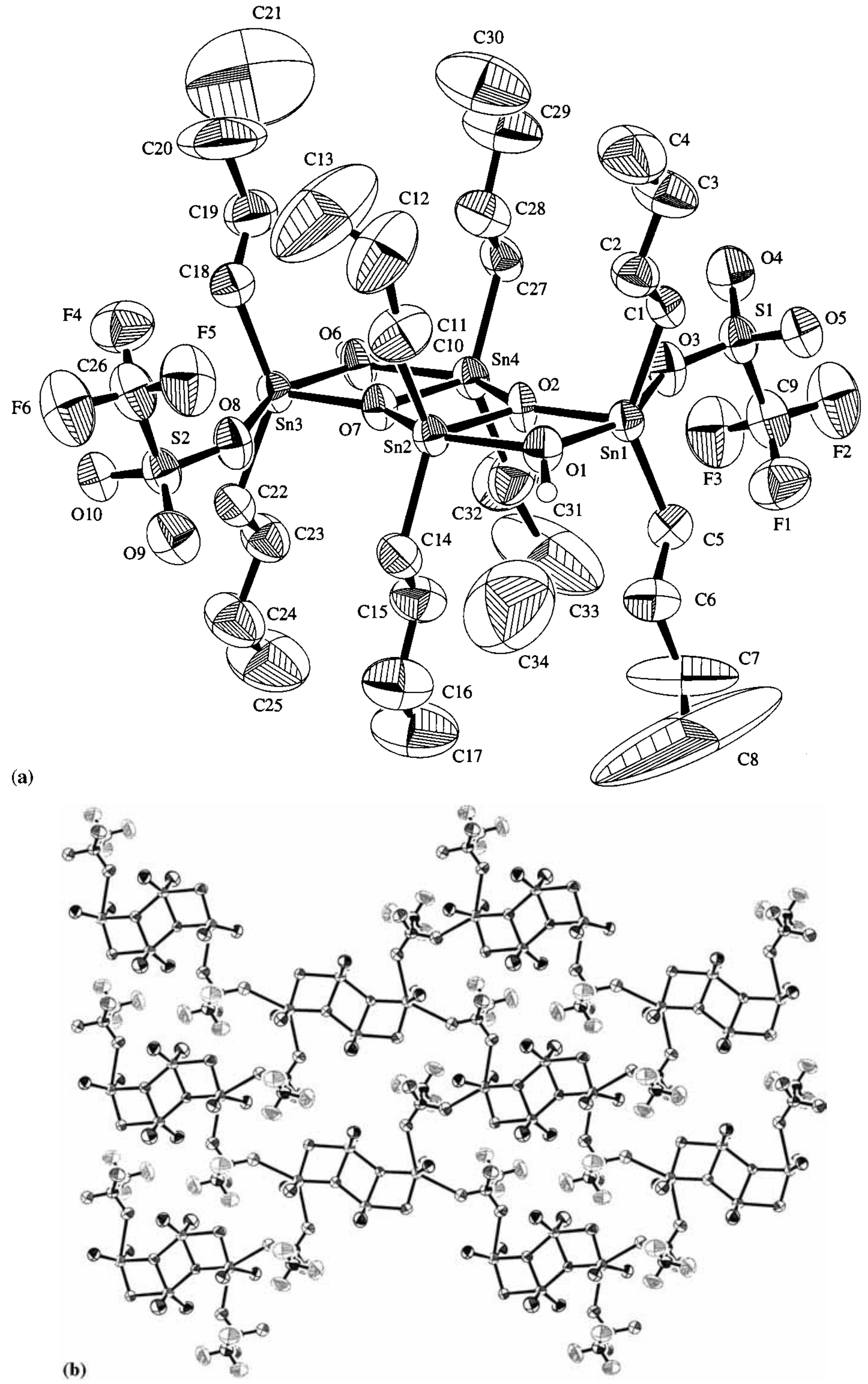


Fig. 1. (a) The ORTEP view of **1b** in dimeric form (thermal ellipsoids for 50% probability). Hydrogen atoms are omitted for clarity. (b) The ORTEP view of **1b** in triflate-bridged form (thermal ellipsoids for 50% probability). The butyl groups are depicted as single atoms for simplicity. (c) Schematic representation of **1b** including Sn–O bond lengths.

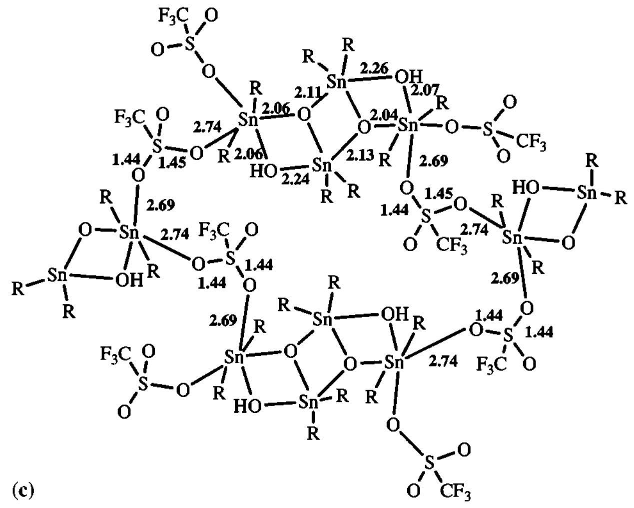
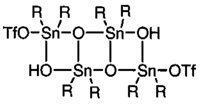


Fig. 1. (*Continued*)



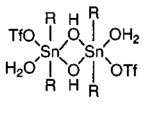
A

Treatment of **1** with further 2 mol of TfOH in acetonitrile afforded hydroxyl-bridged dimers **2** (Eq. (2)). The same compounds were also obtained more conveniently from R_2SnO and 1.0 equivalents of TfOH (Eq. (3)) [3a,c]. These compounds have a four-membered tin–oxygen cycle B or C in the solid state. On the basis of X-ray crystallography, we already revealed that *n*-butyl compound **2b** possessed the non-ionic formulation B whereas the ionic structure C was disclosed for *tert*-butyl derivative **2d**. On the other hand, suitable crystals for X-ray analysis could not be obtained with new compounds, **2a** and **2c**. It is reasonable, nevertheless, to assume the non-ionic structure B for these primary alkyl derivatives, since the cationic structure in the solid state is achievable only when bulky alkyl groups like tertiary butyl and 2-phenylbutyl groups are involved [3c]. In CD_3CN solution, ^{119}Sn-NMR spectra of **2a**, **2b** and **2c** exhibited a singlet with similar chemical shifts (δ -205 to ~ -214 ppm) (Table 2) indicative of cation formation of the ethyl and octyl derivatives, **2a** and **2c**, in solution because the ionic dissociation of **2b** in solution has been fully established [3c]. On the other hand, in acetone-d_6 solution, **2a**–**c** gave rise to two minor signals at around -140 and -170 ppm, respectively, in addition to the main signal at around -210 ppm. By close examination of this minor species we were led to find out an entirely new type of trinuclear cluster.

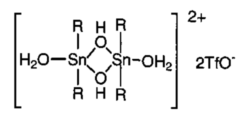
$$1 + 2\,\mathrm{TfOH} \xrightarrow[\mathrm{CH_3CN}]{4\,\mathrm{H_2O}} 2\,[\mathrm{R_2Sn(OH)(OTf)(H_2O)}]_2 \qquad (2)$$

2a: R = Et
2b: R = ^{n}Bu
2c: R = C_8H_{17}
2d: R = ^{t}Bu

$$2\,\mathrm{R_2SnO} + 2\,\mathrm{TfOH} \xrightarrow[\mathrm{CH_3CN}]{2\,\mathrm{H_2O}} \mathbf{2} \qquad (3)$$

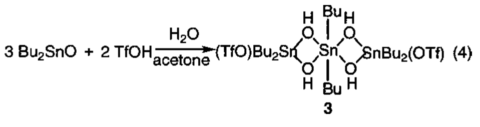


B



C

When Bu_2SnO was treated with 2/3 equivalents of TfOH in acetone, a compound was formed, elemental analysis of which suggested formation of trinuclear species **3** (Eq. (4)). The same compound was also produced by treating **1b** with 2/3 mol of TfOH (Eq. (5)). ^{119}Sn-NMR of this compound in acetone-d_6 exhibited the analogous pattern to that of **2b** but with reversed intensities: signals at -170 and -137 ppm are stronger than that at -204 ppm. Apparently, **2b** and **3** are involved in the equilibrium to each other in acetone (Eq. (6)). The stoichiometry of **3** was further confirmed through monitoring ^{119}Sn-NMR spectra of the following reactions (Eqs. (7) and (8)). In both cases, a set of signals at -170 and -137 ppm, respectively, were observed as main signals together with the minor one at -204 ppm. The ethyl and octyl derivatives exhibited the similar behavior in terms of ^{119}Sn-NMR as described above, yet no discrete trinuclear species could be isolated.



(4)

$$3/2\,[\mathrm{(TfO)Bu_2SnOSnBu_2OH}]_2 + \mathrm{TfOH} \xrightarrow[\mathrm{acetone}]{2\,\mathrm{H_2O}} \mathbf{3}\ (2\ \mathrm{equiv}) \qquad (5)$$

1b

$$3\,[\mathrm{Bu_2Sn(OH)(OTf)(H_2O)}]_2 \overset{-2\,\mathrm{TfOH},\ -4\,\mathrm{H_2O}}{\underset{+2\,\mathrm{TfOH},\ +4\,\mathrm{H_2O}}{\rightleftharpoons}} \mathbf{3}\ (2\ \mathrm{equiv}) \qquad (6)$$

2b

Table 1
Selected bond lengths (Å) and bond angles (°) for **1** [a]

Bond lengths			
Sn(1)–Sn(2)	3.3653(5)	Sn(4)–O(7)	2.049(3)
Sn(1)–O(1)	2.067(3)	Sn(4)–C(27)	2.116(6)
Sn(1)–O(2)	2.040(3)	Sn(4)–C(31)	2.138(7)
Sn(1)–C(1)	2.122(5)	S(1)–O(3)	1.445(4)
Sn(1)–C(5)	2.129(6)	S(1)–O(4)	1.421(4)
Sn(2)–Sn(4)	3.3234(6)	S(1)–O(5)	1.448(4)
Sn(2)–O(1)	2.263(4)	S(1)–C(9)	1.843(8)
Sn(2)–O(2)	2.050(3)	S(2)–O(8)	1.440(4)
Sn(2)–O(7)	2.114(3)	S(2)–O(9)	1.452(4)
Sn(2)–C(10)	2.134(7)	S(2)–O(10)	1.442(4)
Sn(2)–C(14)	2.131(6)	S(2)–C(26)	1.831(7)
Sn(3)–Sn(4)	3.3649(5)	F(1)–C(9)	1.296(8)
Sn(3)–O(6)	2.063(3)	F(2)–C(9)	1.315(7)
Sn(3)–O(7)	2.059(3)	F(3)–C(9)	1.325(7)
Sn(3)–C(18)	2.129(6)	F(4)–C(26)	1.300(8)
Sn(3)–C(22)	2.125(5)	F(5)–C(26)	1.337(8)
Sn(4)–O(2)	2.133(3)	F(6)–C(26)	1.309(7)
Sn(4)–O(6)	2.239(3)		
Bond angles			
Sn(2)–Sn(1)–O(1)	41.1(1)	Sn(4)–Sn(2)–O(7)	36.37(9)
Sn(1)–O(2)–Sn(2)	110.7(1)	Sn(4)–Sn(2)–C(10)	107.1(2)
Sn(1)–O(2)–Sn(4)	144.0(2)	Sn(4)–Sn(2)–C(14)	111.8(2)
Sn(2)–O(2)–Sn(4)	105.2(1)	O(1)–Sn(2)–O(2)	71.4(1)
O(2)–Sn(2)–C(10)	111.1(2)	O(1)–Sn(2)–O(7)	146.1(1)
O(2)–Sn(2)–C(14)	116.3(2)	O(1)–Sn(2)–C(10)	96.2(2)
O(7)–Sn(2)–C(10)	96.8(2)	O(1)–Sn(2)–C(14)	95.4(2)
O(7)–Sn(2)–C(14)	98.7(2)	O(2)–Sn(2)–O(7)	74.6(1)
C(10)–Sn(2)–C(14)	132.5(3)	O(2)–Sn(4)–O(6)	146.0(1)
Sn(4)–Sn(3)–O(6)	40.44(9)	O(2)–Sn(4)–O(7)	74.2(1)
Sn(4)–Sn(3)–O(7)	34.92(9)	O(2)–Sn(4)–C(27)	99.1(2)
Sn(4)–Sn(3)–C(18)	108.1(2)	O(2)–Sn(4)–C(31)	97.3(2)
Sn(4)–Sn(3)–C(22)	111.5(2)	O(6)–Sn(4)–O(7)	71.8(1)
O(6)–Sn(3)–O(7)	75.3(1)	O(6)–Sn(4)–C(27)	95.2(2)
(6)–Sn(3)–C(18)	107.5(2)	O(6)–Sn(4)–C(31)	95.9(2)
O(6)–Sn(3)–C(22)	104.9(2)	O(7)–Sn(4)–C(27)	116.6(2)
O(7)–Sn(3)–C(18)	103.2(2)	O(7)–Sn(4)–C(31)	111.6(2)
O(7)–Sn(3)–C(22)	106.8(2)	C(27)–Sn(4)–C(31)	131.6(3)
Sn(2)–Sn(1)–O(2)	34.72(9)	Sn(1)–O(1)–Sn(2)	101.9(1)
Sn(2)–Sn(1)–C(1)	111.2(1)	C(18)–Sn(3)–C(22)	140.2(2)
Sn(2)–Sn(1)–C(5)	108.4(2)	Sn(2)–Sn(4)–Sn(3)	72.77(1)
O(1)–Sn(1)–O(2)	75.8(1)	Sn(2)–Sn(4)–O(2)	36.53(8)
O(1)–Sn(1)–C(1)	104.9(2)	Sn(2)–Sn(4)–O(6)	109.48(8)
O(1)–Sn(1)–C(5)	107.7(2)	Sn(2)–Sn(4)–O(7)	37.70(9)
O(2)–Sn(1)–C(1)	106.9(2)	Sn(2)–Sn(4)–C(27)	112.0(2)
O(2)–Sn(1)–C(5)	102.8(2)	Sn(2)–Sn(4)–C(31)	108.1(2)
C(1)–Sn(1)–C(5)	140.1(2)	Sn(3)–Sn(4)–O(2)	109.28(8)
Sn(1)–Sn(2)–Sn(4)	72.78(1)	Sn(3)–Sn(4)–O(6)	36.72(8)
Sn(1)–Sn(2)–O(1)	36.93(9)	Sn(3)–Sn(4)–O(7)	35.10(9)
Sn(1)–Sn(2)–O(2)	34.53(8)	Sn(3)–Sn(4)–C(27)	108.6(2)
Sn(1)–Sn(2)–O(7)	109.14(9)	Sn(3)–Sn(4)–C(31)	108.2(2)
Sn(1)–Sn(2)–C(10)	107.8(2)	Sn(3)–O(6)–Sn(4)	102.8(1)
Sn(1)–Sn(2)–C(14)	108.9(2)	Sn(2)–O(7)–Sn(3)	143.9(2)
Sn(4)–Sn(2)–O(1)	109.71(9)	Sn(2)–O(7)–Sn(4)	105.9(1)
Sn(4)–Sn(2)–O(2)	38.27(8)	Sn(3)–O(7)–Sn(4)	110.0(1)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

$$\tfrac{1}{2}\,\underset{\textbf{1b}}{[(TfO)Bu_2SnOSnBu_2(OH)]_2} + \underset{\textbf{4b}}{Bu_2Sn(OTf)_2} \xrightarrow[\text{acetone}]{+2\,H_2O,\ -TfOH} \textbf{3} \qquad (7)$$

$$\underset{\textbf{2b}}{[Bu_2Sn(OH)(OTf)(H_2O)]_2} + Bu_2SnO \xrightarrow{-H_2O} \textbf{3} \qquad (8)$$

Finally, exposure of **3** to one equivalent of TfOH, or more simply, exposure of R_2SnO to two equivalents of TfOH yielded $R_2Sn(OTf)_2$ (**4**) (Eq. (9)). Although **4b** was prepared previously by treating Bu_2SnCl_2 with AgOTf [7], the present procedure is apparently simpler and cheaper.

$$R_2SnO + 2\,TfOH \xrightarrow[CH_3CN]{-H_2O} R_2Sn(OTf)_2 \qquad (9)$$

$$\begin{array}{l} \textbf{4a}\text{: } R = Et \\ \textbf{4b}\text{: } R = {}^{n}Bu \\ \textbf{4c}\text{: } R = C_8H_{17} \end{array}$$

It should be noted that water was not deliberately added in all experiments described above. Even though we used dry solvents, a trace amount of the water present there was involved in the reaction. Thus, the hydration or dehydration seems to occur totally depending on the thermodynamic stability of the products.

In summary, various organotin triflates with unique structures have been prepared. Scheme 1 summarizes the action of TfOH on organotin oxides or hydroxides leading to the stepwise formation of the organotin triflates. By changing the amount of TfOH, the triflato ligand/tin ratio can be controlled in a wide range. Rather surprisingly, the di- and trinuclear organotin triflates thus obtained are hydrolytically stable in sharp contrast to $R_2Sn(OTf)_2$ which are gradually hydrolyzed in air. Due to the strong electron-withdrawing character of the triflato ligand, the unprecedented association of organotin moieties emerged. This suggests the potential usefulness of organotin triflates in obtaining structurally novel compounds.

3. Experimental

All reactions were carried out under nitrogen, unless otherwise noted. CH_3CN, $CHCl_3$, CH_2Cl_2 and acetone were distilled from calcium hydride. NMR spectra were recorded at 25°C on Bruker-400, JEOL Lambda 300 and JEOL Lambda 500 instruments and calibrated with Me_4Si, trifluoromethylbenzene or Me_4Sn as an internal standard. Elemental analyses were performed with the Perkin Elmer PE 2400. Et_2SnO, *n*-Bu_2SnO, $(C_8H_{17})_2SnO$ and TfOH were purchased and used without purification. The cationic dimer **2b** [3c], **2d** [3c] and **4b** [7] were prepared according to the literature methods.

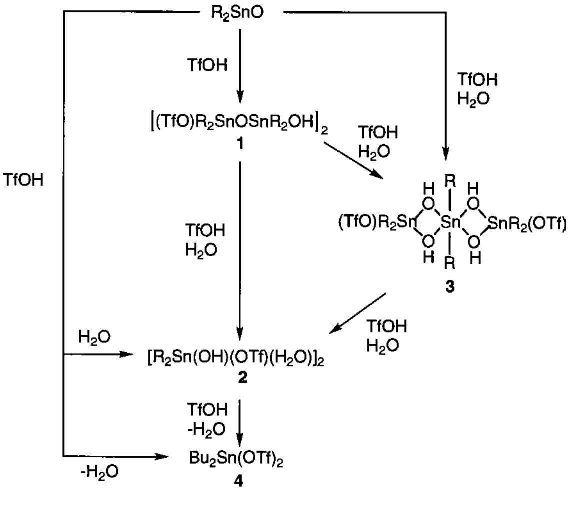
*3.1. Preparation of [(TfO)Bu₂SnOSnBu₂OH]₂ (**1b**) from n-Bu₂SnO and TfOH (representative procedure)*

A suspension of *n*-Bu_2SnO (498 mg, 2.0 mmol) and TfOH (150 mg, 1.0 mmol) in acetone (50 ml) was

Table 2
^{119}Sn-NMR chemical shift data of organotin triflate clusters

Compound	δ (ppm)	
	In CD_3CN	In acetone-d_6 [a]
1a	−152, −156	−152, −157
1b	−146, −150	−147, −150
1c	−149, −152	−149, −152
2a	−214	−214 (−143, −166)
2b	−210	−204 (−137, −170)
2c	−205	−205 (−139, −169)
2d	−250	−249
3	−137, −170	−137, −170 (−204)
4a	−367	
4b	−342	−342
4c	−343	−343

[a] Minor signals are indicated in parentheses.



Scheme 1.

stirred under reflux. After 15 h, a clear solution resulted, and filtration followed by evaporation afforded crude products which were recrystallized from hot CH_2Cl_2 to furnish **1b** (596 mg, 92%). M.p. 223–226°C; ^{1}H-NMR (500 MHz, acetone-d_6): δ 0.81–0.96 (m, 12H), 1.27–1.85 (m, 24H); ^{13}C-NMR (75 MHz, CD_3CN): δ 12.1, 12.2, 23.8, 25.5, 25.7, 25.8, 25.9, 26.2, 119.27 (q, $^1J_{C-F} = 319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ −78.7; ^{119}Sn-NMR (112 MHz, CD_3CN): δ −146, −150; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ −147, −150; IR (Nujol, cm^{-1}): 3450, 2960, 1460, 1380, 1270, 1230, 1170, 1020; Anal. Calc. for $C_{17}H_{37}F_3O_5SSn_2$: C, 31.51; H, 5.76. Found: C, 31.43; H, 5.58%.

The other distannoxanes were prepared analogously.

1a: m.p. 245–247°C; ^{1}H-NMR (500 MHz, acetone-d_6): δ 1.42–1.47 (m, 12H), 1.90–2.06 (m, 8H); ^{13}C-NMR (125 MHz, acetone-d_6): δ 7.8 ($^1J_{C-Sn} = 342$ Hz), 26.8, 26.9, 119.4 (q, $^1J_{C-F} = 319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ −78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ −152, −156; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ −152, −157; IR (Nujol, cm^{-1}): 3550, 2900, 1460, 1380, 1280, 1240, 1220, 1170, 1030; Anal. Calc. for $C_9H_{21}F_3O_5SSn_2$: C, 20.18; H, 3.95. Found: C, 20.18; H, 3.82%.

1c: m.p. 106–108°C; ^{1}H-NMR (500 MHz, acetone-d_6): δ 0.82–0.95 (m, 12H), 1.22–1.45 (m, 48H), 1.48–1.95 (m, 8H), 5.09 (br, 2H); ^{13}C-NMR (125 MHz, acetone-d_6): δ 12.6, 12.7, 21.6, 21.7, 21.8, 21.9, 23.7, 23.8, 24.0, 24.1, 24.2, 25.9, 31.0, 31.1, 33.3, 33.9, 119.4 (q, $^1J_{C-F} = 319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ −78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ −149, −152; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ −149, −152; IR (Nujol, cm^{-1}): 3540, 2900, 1460, 1380, 1270, 1230, 1170, 1030; Anal. Calc. for $C_{33}H_{69}F_3O_5SSn_2$: C, 45.43; H, 7.97. Found: C, 45.44; H, 7.89%.

3.2. Preparation of *[Et$_2$Sn(OH)(OTf)(H$_2$O)]$_2$* (**2a**) *from* **1a** *and TfOH (representative procedure)*

A solution of **1a** (536 mg, 0.5 mmol) and TfOH (150 mg, 1.0 mmol) in acetonitrile (30 ml) was stirred at room temperature. After 5 h, filtration followed by evaporation afforded crude products which were washed with CH_2Cl_2 to furnish **2a** (576 mg, 80%). M.p. 190–192°C; ^{1}H-NMR (300 MHz, acetone-d_6): δ 1.42 (t, $J = 7.3$ Hz, 6H), 1.60–1.92 (m, 4H); ^{13}C-NMR (75 MHz, acetone-d_6): δ 7.6, 7.8, 20.3, 21.6, 119.4 (q, $^1J_{C-F} = 319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ −78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ −214; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ −214; IR (Nujol, cm^{-1}): 3350, 2900, 1650, 1460, 1380, 1260, 1220, 1170, 1040; Anal. Calc. for $C_{10}H_{24}F_6O_9S_2Sn_2$ as the mono-hydrated species: C, 17.06; H, 3.44. Found: C, 17.00; H, 3.24%.

2c: m.p. 53–54°C; ^{1}H-NMR (500 MHz, acetone-d_6): δ 0.83–1.00 (m, 12H), 1.23–1.51 (m, 40H), 1.65–2.05 (m, 16H), 6.16 (s, 2H); ^{13}C-NMR (125 MHz, acetone-d_6): δ 12.5, 12.6, 21.5, 21.6, 23.2, 23.5, 23.8, 28.1, 28.2, 30.9, 31.0, 32.4, 32.8, 33.2, 33.3, 33.9, 119.2 (q, $^1J_{C-F} = 319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ −78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ −205; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ −205; IR (Nujol, cm^{-1}): 3400, 2900, 1660, 1460, 1380, 1260, 1180, 1020; Anal. Calc. for $C_{34}H_{70}F_6O_8S_2Sn_2$ as the non-hydrated species: C, 39.94; H, 6.90. Found: C, 39.88; H, 6.91%.

3.3. Preparation of *[n-Bu$_2$Sn(OH)(OTf)(H$_2$O)]$_2$* (**2b**) *from n-Bu$_2$SnO and TfOH*

A suspension of *n*-Bu_2SnO (498 mg, 2.0 mmol) and TfOH (300 mg, 2.0 mmol) in acetonitrile (30 ml) was stirred at room temperature. After 5 h, a clear solution resulted, and filtration followed by evaporation afforded crude products which were recrystallized from hot CH_2Cl_2 to furnish **2b** (726 mg, 87%).

The other compounds **2a** and **2c** were obtained analogously.

3.4. Preparation of $[(TfO)n\text{-}Bu_2Sn(\mu\text{-}OH)_2Sn(n\text{-}Bu)_2(\mu\text{-}OH)_2Sn(n\text{-}Bu)_2(OTf)]$ (**3**) from $n\text{-}Bu_2SnO$ and TfOH

A suspension of n-Bu_2SnO (498 mg, 2.0 mmol) and TfOH (201 mg, 1.34 mmol) in acetone (50 ml) was stirred at room temperature. After 24 h, a clear solution resulted, and filtration followed by evaporation afforded crude products which were reprecipitated from $CHCl_3$ to furnish **3** (617 mg, 90%). M.p. 75–76°C; ^{1}H-NMR (300 MHz, acetone-d_6): δ 0.93 (t, $J=$ 7.1 Hz, 18H), 1.30–1.45 (m, 12H), 1.55–1.85 (m, 24H); ^{13}C-NMR (75 MHz, acetone-d_6): δ 13.8, 13.9, 27.3, 27.4, 27.5, 27.6, 28.4, 119.3 (q, $^1J_{C-F}=319$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ -78.1; ^{119}Sn-NMR (112 MHz, CD_3CN): δ -137, -170; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ -137, -170; IR (Nujol, cm^{-1}): 3400, 2900, 1650, 1460, 1380, 1240, 1180, 1030; Anal. Calc. for $C_{26}H_{58}F_6O_{10}S_2Sn_3$: C, 29.29; H, 5.48. Found: C, 29.33; H, 5.49%.

3.5. Preparation of $n\text{-}Bu_2Sn(OTf)_2$ (**4b**) [7] from $n\text{-}Bu_2SnO$ and TfOH (representative procedure)

A suspension of n-Bu_2SnO (498 mg, 2.0 mmol) and TfOH (300 mg, 2.0 mmol) in acetonitrile (30 ml) was stirred at room temperature. After 5 h, a clear solution resulted, and filtration followed by evaporation afforded crude products. After water was removed as an azeotrope with toluene under reduced pressure, the crude products were washed with CH_2Cl_2 to furnish n-$Bu_2Sn(OTf)_2$ (**4b**) (515 mg, 97%).

The other bis(triflates) were prepared analogously. **4a**: m.p. 254–256°C; ^{1}H-NMR (500 MHz, acetone-d_6): δ 1.43–1.47 (m, 6H), 2.02–2.07 (m, 4H); ^{13}C-NMR (125 MHz, acetone-d_6): δ 7.8 ($J_{C-Sn}=282.5$ Hz), 26.8 ($J_{C-Sn}=342.5$ Hz), 119.4 ($J_{C-F}=318.8$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ -78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ -367; IR (Nujol, cm^{-1}): 3350, 2900, 1640, 1460, 1380, 1280, 1250, 1160, 1040; Anal. Calc. for $C_6H_{10}F_6O_6S_2Sn$ as the non-hydrated species: C, 15.17; H, 2.12. Found: C, 15.19; H, 2.21%.

4c: m.p. 94–96°C; ^{1}H-NMR (300 MHz, acetone-d_6): δ 0.88 (t, $J=7.0$ Hz, 3H), 1.20–1.45 (m, 10H), 1.80–1.90 (m, 2H), 1.90–2.20 (m, 2H); ^{13}C-NMR (75 MHz, acetone-d_6): δ 12.5, 21.5, 23.1, 27.9, 28.1, 30.8, 31.8, 33.1, 119.2 (q, $^1J_{C-F}=315.0$ Hz); ^{19}F-NMR (376 MHz, CD_3CN): δ -78.3; ^{119}Sn-NMR (112 MHz, CD_3CN): δ -343; ^{119}Sn-NMR (112 MHz, acetone-d_6): δ -343; IR (Nujol, cm^{-1}): 3330, 2900, 1630, 1460, 1380, 1290, 1240, 1190, 1020; Anal. Calc. for $C_{18}H_{36}F_6O_7S_2Sn$ as the non-hydrated species: C, 32.69; H, 5.49. Found: C, 32.93; H, 5.51%.

3.6. Crystallography

3.6.1. Data collection and refinement

Data were collected on a Rigaku-RAXIS-IV automatic diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda=0.71070$ Å) for unit-cell determination. The structure could be successfully solved by direct method (SAR-92) [8] and subsequently refined by difference Fourier techniques (DIRDIF-94) [9]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. All calculations were performed using the TEXSAN crystallographic software package [10]. Crystal data for **1b**: crystal dimensions $0.30\times0.30\times0.10$ mm^3; $C_{34}H_{74}O_{10}F_6S_2Sn_4$, $M_r=1295.82$; monoclinic, space group $P2_1/n$ (no. 14), $a=9.714(1)$, $b=21.016(2)$, $c=26.172(2)$ Å, $\beta=98.263(9)°$, $V=5287.66$ Å^3, $Z=4$, $\rho_{calc}=1.63$ g cm^{-3}, $2\theta_{max}=55.0°$, $T=263$ K, 11265 reflections measured, refinement based on 8823 reflections. $F_{000}=2576$, GOF on $F=1.50$; no. of parameters $=506$; $R=0.048$ $[I>4\sigma(I)]$, $wR=0.096$, largest positive and negative difference peaks $+1.00$ and -0.90 e Å^{-3}. Selected bond distances and angles are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 143838 (form I). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] (a) T. Sato, J. Otera, H. Nozaki, J. Am. Chem. Soc. 112 (1990) 901. (b) T. Sato, Y. Wakahara, J. Otera, H. Nozaki, Tetrahedron 47 (1991) 9773.

[2] T. Sato, Y. Wakahara, J. Otera, H. Nozaki, Tetrahedron Lett. 31 (1990) 1581.

[3] (a) K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, J. Otera, Organometallics 18 (1999) 3555. (b) S. Durand, K. Sakamoto, T. Fukuhara, A. Orita, J. Otera, A. Duthie, D. Dakternieks, M. Schulte, K. Jurkschat, Organometallics 19 (2000) 3220. (c) K. Sakamoto, H. Ikeda, H. Akashi, T. Fukuyama, A. Orita, J. Otera, Organometallics 19 (2000) 3242.

[4] A. Orita, K. Sakamoto, H. Ikeda, J. Xiang, J. Otera, Chem. Lett. (2000) in press.

[5] Methyltin oxide with a graphite-like structure: (a) B. Räke, P. Müller, H.W. Roesky, I. Usón, Angew. Chem. Int. Ed. Engl. 38 (1999) 2050. Distannoxanes with three-dimensional structures: (b) D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, Organometallics 13 (1994) 4121. (c) M. Mehring, M. Schürmann, H. Reuter, D. Dakternieks, K. Jurkschat, Angew. Chem. Int. Ed. Engl. 36 (1997) 1112.

[6] (a) J. Otera, T. Yano, K. Nakashima, R. Okawara, Chem. Lett. (1984) 2109. (b) T. Yano, K. Nakashima, J. Otera, R. Okawara, Organometallics 4 (1985) 1501.

[7] C.A. Obafemi, J.A. Obaleye, M.S. Akanni, Synth. React. Inorg. Met. Org. Chem. 16 (1986) 777.

[8] H.-F. Fan, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, 1991.

[9] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

[10] Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.