Preparation and structural characterization of trimethyltin(IV) tropolonate. Investigation of a rare methyl-migrational dismutation in the solution, solid and liquid states†

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The synthesis and structural characterisation, by low temperature X-ray diffraction and solid-state NMR, of the highly reactive monomeric $Me_3Sn(trop)$ (**1**) complex has been studied; **1** rearranges into $Me_2Sn(trop)_2$ (**2**) and Me_4Sn by methyl-transfer dismutation. Based on the NMR kinetic data it appears that complex **1** demethylates faster in the solid and liquid than in dilute $CDCl_3$ solution, but with a slower rate than in dilute CD_3OD solution.

Introduction

Toxic triorganotin complexes enter into the ambient environment in the form of insecticides, fungicides and antifouling paints.[1] The degradation products (*via* alkyl group removal from triorganotin complexes) have been detected in the environment and the degradation has been attributed to the action of UV light, chemical cleavage and biological degradation by bacteria.[2] In mammalian organs, the toxic triorganotin complexes are gradually dealkylated to inorganic Sn(IV), and it was shown that a linear peptide derived from the membrane protein stannine is capable of dealkylating trimethyltin complexes.[3] This sequential dealkylation of the tin atom, generally results in a reduction in the toxicity. Recently it was reported that the Bu_3SnCl undergoes redistribution to give Bu_2SnCl_2 and Bu_4Sn under the gas phase conditions that are used in the CVD treatment of glass, but the tetrabutyltin does not survive the conditions of the thermolysis and decomposes into metallic tin, butene and butane.[4] In contrast to thermally induced solid-state methyl migrations in organic molecules which have been the subject of extensive investigations,[5] the solid-state methyl transfer phenomenon in organometallic complexes has been barely exploited. Recently, we have reported that single crystals of the $[Me_3Sn(cupf)]_4$ (cupf = cupferronato anion, $C_6H_5N_2O_2^-$) tetramer demethylate into single crystals of the $[Me_2Sn(cupf)_2]_2$ dimer and volatile Me_4Sn.[6] The demethylation occurred upon heating and it was accompanied by a significant change in the molecular and crystal structure.[6] We have shown that the dismutation proceeded considerably faster in the melt than in the solid state,[6] moreover solvent induced conformational change was held responsible for its demethylation in coordinating solvents, such as DMSO, pyridine and methanol.[7] Therefore, this methyl-migrational dismutation process is a potential source of trimethyltin(IV) complex instability, which prevents the preparation of devised structures *via* crystallization.[7] Although, a series of organotin(IV) tropolonates has been reported[8] the trimethyltin(IV) tropolonato, $Me_3Sn(trop)$, complex remained uncharacterised. This discrepancy between the much studied nature of organotin(IV) tropolonates and the absence of trimethyltin(IV) derivative suggests that this might be due to its high dismutational reactivity which prevents its isolation. Moreover, we have tentatively assumed that this triorganotin(IV) complex also participates into methyl-transfer dismutation not only in coordinating solvents but in the solid- and liquid-states. Herein, we report the successful synthesis of $Me_3Sn(trop)$ (**1**), as well as its X-ray structural determination and NMR analysis both in the solution- and solid-states. In addition, the degradation of **1** into $Me_2Sn(trop)_2$ (**2**) and Me_4Sn has also been investigated in the solution-, solid- and liquid-states.

Results and discussion

Synthesis and structural characterisation of $Me_3Sn(trop)$ (1)

Complex **1** was prepared by metathetical reaction between trimethyltin(IV) chloride and ammonium tropolonate. As suspected, compound **1** shows dismutational activity in methanol, but appears to be stable in *n*-hexane and chloroform solution. Single crystals of **1** were successfully obtained from *n*-hexane, but they diffracted poorly at room temperature. The low-temperature X-ray diffraction measurement reveals that in complex **1** the tin(IV) center is five-coordinated (Fig. 1) in a geometry intermediate between

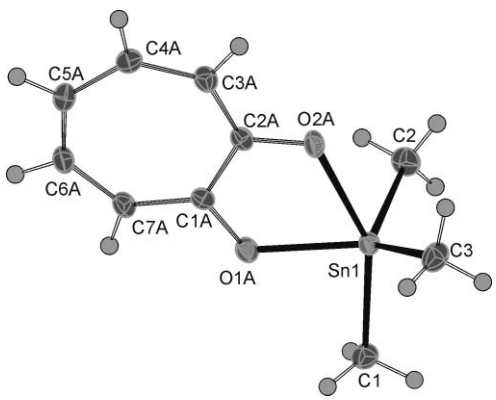

Fig. 1 A view of the molecular structure of complex **1** showing the atom numbering scheme. Non-hydrogen atoms are shown as 50% probability ellipsoids and hydrogen atoms are shown as circles.

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† The HTML version of this article has been enhanced with colour images.

Table 1 Selected interatomic bond distances (Å) and bond angles (°) for complex **1**

Sn(1)–C(1)	2.159(3)	Sn(1)–C(2)	2.137(3)
Sn(1)–C(3)	2.140(3)	Sn(1)–O(1A)	2.133(2)
Sn(1)–O(2A)	2.324(2)		
C(1)–Sn(1)–C(2)	109.8(2)	C(2)–Sn(1)–C(3)	118.5(2)
C(3)–Sn(1)–C(1)	105.3(1)	O(1A)–Sn(1)–O(2A)	69.8(1)
C(1)–Sn(1)–O(2A)	152.1(1)	O(1A)–Sn(1)–C(3)	124.8(1)
O(1A)–Sn(1)–C(2)	107.7(1)	C(2)–Sn(1)–O(2A)	88.5(2)
O(1A)–Sn(1)–C(1)	84.3(1)	C(3)–Sn(1)–O(2A)	82.4(1)

square pyramidal (SP) and trigonal-bipyramidal (TBP); $\tau = 0.46$, where values of 0 and 1 are indicative of perfect SP and TBP geometries,[9] respectively. Therefore, the coordination geometry is heavily distorted from that of a regular TBP: the axial C(1)–Sn(1)–O(2A) bond angle is closed from 180° to 152.1(1)°, and the corresponding equatorial bond angles range from 107.7(1) to 124.8(1)° (Table 1). The tropolonato anion is chelated to the metal center forming a five-membered SnO_2C_2 ring and forcing a *cis*-TBP geometry at tin. In this five-membered ring the O–Sn–O bite angle is 69.8(1)°, and the Sn–O bond distances differ by 0.191(2) Å. The structure of **1** is very similar to the triphenyltin(IV) tropolonate, $Ph_3Sn(trop)$,[8g] in which the tropolonato anion is also chelated to the tin(IV), and the metal center is five-coordinate showing an intermediate SP/TBP geometry ($\tau = 0.56$). The structural similarity between **1** and $Ph_3Sn(trop)$ is also reflected by the O–Sn–O bite angles (69.8(1)° and 71.4(1)°) and differential Sn–O distances (0.191(2) Å and 0.141(3) Å).

Fig. 2 shows the ^{119}Sn magic angle spinning (MAS) and the solution ($CDCl_3$) ^{119}Sn NMR spectra of **1**, which remained stable over the course of these experiments. Table 2 lists the principal values of the ^{119}Sn chemical shielding tensor. The solution state ^{119}Sn chemical shift is 70.0 ppm ($CDCl_3$) and the isotropic chemical shift of the MAS ^{119}Sn experiment (δ_{iso}) is 60.6 ppm. These values are in general agreement with the literature data found for trialkyltin(IV) compounds with bidentate ligands,[7,10] and tin coordination number of 4 or 5. The Me–Sn–Me angle calculated from the $^1J(^{119}Sn–^{13}C)$ coupling constant is 112°,[11] which is also

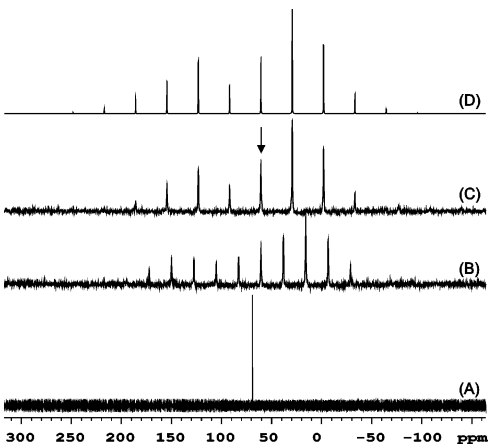

Fig. 2 Above the solution ^{119}Sn NMR of **1** recorded in $CDCl_3$ at 25 °C (A) are the ^{119}Sn MAS spectra (223.6 MHz) of **1** at different spinning rates: (B) $\nu_{rot} = 5$ kHz and (C) $\nu_{rot} = 7$ kHz. The 7 kHz ^{119}Sn MAS spectral simulation is shown on top (D). The isotropic chemical shift (δ_{iso}) is marked with an arrow.

Table 2 ^{119}Sn chemical shielding data for **1** obtained from 7 kHz MAS[a]

Complex **1**	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	η
Solid MAS NMR	60.6	159.1	94.6	−71.9	0.48
Solution NMR ($CDCl_3$)	70.0				
Solution NMR (DMSO)	26.4				

[a] ^{119}Sn chemical shielding tensor principal values are in ppm and are given according to the convention $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$ with estimated errors of less than 1 ppm; the asymmetry parameter is defined as $\eta = (\delta_{22} - \delta_{iso})/(\delta_{33} - \delta_{iso})$.

in line with the solid-state molecular geometry. The asymmetry parameter $\eta = 0.48$ of the chemical shielding tensor rules out axial symmetry in the solid state. The oxygen-attached carbons of the tropolonato ligand were found to be non-equivalent from the analysis of the isotropic chemical shifts in the ^{13}C-MAS NMR spectra as compared to the solution ^{13}C-NMR (see Fig. 3). The quaternary carbon which appears at 175.3 ppm ($CDCl_3$) splits into two distinguishable carbon sites $\delta_{iso} = 171.6$ and 176.6 ppm in the solid-state spectra. This can be explained on the basis of the crystal structure where the tropolonato ligand forms two different Sn–O bond lengths. As a consequence, the two oxygen atoms attached to quaternary carbon atoms experience different chemical shielding in the solid-state.

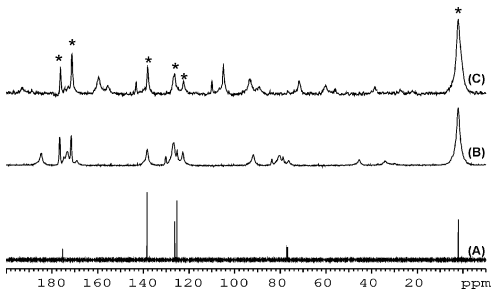

Fig. 3 Above the solution ^{13}C NMR of **1** recorded in $CDCl_3$ at 25 °C (A) are the ^{13}C MAS spectra (150.8 MHz) of **1** at different spinning rates: (B) $\nu_{rot} = 5$ kHz and (C) $\nu_{rot} = 7$ kHz. The identified isotropic chemical shifts (δ_{iso}) are marked with stars.

Methyl-migrational reactivity of complex 1 in the solution-, solid- and liquid-states

To gain insight into the methyl migrational dismutation the rearrangement of $Me_3Sn(trop)$ (**1**) into the $Me_2Sn(trop)_2$ (**2**) and Me_4Sn has been investigated in solution, as well as in the solid- and liquid-states. In the non-polarizing solvent $CDCl_3$ the methyl-migrational dismutation of **1** is nearly infinitely slow (Fig. 4), while, when dissolved in coordinating solvents compound **1** underwent the dismutation process. Precise kinetic data have been collected in methanol-d_4 using ^{1}H-NMR. The solvent has 'captured" the byproduct Me_4Sn and the 2A → B + C stoichiometry of the reaction has been confirmed, suggesting second-order kinetics. To verify this we constructed the $1/[A]$ *vs.* t curve in Fig. 4, which as expected for second-order kinetics, provided a linear fit and the k rate constant of 1.43×10^{-5} l mol^{-1} s^{-1} was determined from the slope. This latter was compared with the $Me_3Sn(cupf)$ dismutation k' rate constant[6] using the same initial $[A]_0 = 0.11$ mol l^{-1} concentration. We found that the two rates are of the same order of magnitude in methanol-d_4, however the tropolonato ligand

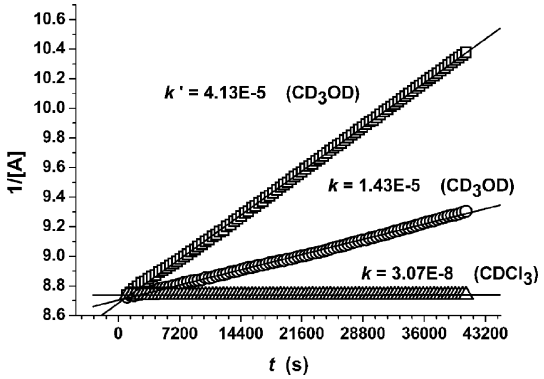

Fig. 4 The $1/[A]$ *versus* t representation of the second-order dismutation kinetics for complex **1** (○ line) and Me_3Sn(cupf)[6] (□ line) in CD_3OD, and for complex **1** (Δ line) in $CDCl_3$ (25 °C, $[A]_0 = 0.11$ mol l^{-1}). The estimated rate constants (k and k') are in l mol^{-1} s^{-1}. Data are from the integral change of the corresponding Me_3Sn(IV) species determined by ^{1}H-NMR.

transforms Me_3Sn(IV) into the Me_2Sn(IV) and Me_4Sn(IV) species three times slower than the cupferronato ligand. When complex **1** was dissolved in a strongly coordinating solvent, DMSO, an upfield shift was observed (26.4 ppm) for the tin, indicating that coordination number five is also possible *via* solvent coordination, as seen for trimethyltin(IV) cupferronate.[6,10] This change in the chemical shift relative to $CDCl_3$ may be indicative of an underlying conformational equilibrium, in which a distorted tetrahedron as well as *cis*- and *trans*-TBP geometries are involved. Such conformational changes are held responsible for inducing the dismutation reaction *via* activation and stabilization of the charge separated species.[7]

After compound **1** was left for a month in open-end vials exposed to direct sunlight ^{119}Sn MAS and solution ^{1}H-NMR ($CDCl_3$) experiments were carried out. The dismutation product **2** was readily identified by both methods (see Fig. 5).

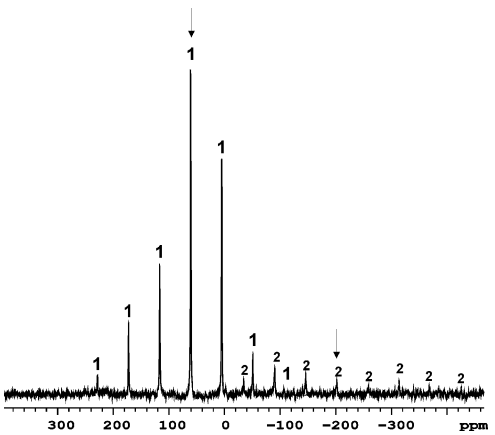

Fig. 5 ^{119}Sn MAS spectra (223.6 MHz) of complex **1** containing the dismutation product **2** at $\nu_{rot} = 12.5$ kHz after **1** was exposed to direct sunlight for a month. The isotropic chemical shifts are marked with arrows.

To get an overview of the kinetics of the solid-state and liquid transformation of **1** into **2** and Me_4Sn, samples of the microcrystalline compound **1** were placed in open-end vials and heated to 40 °C (solid) and 60 °C (liquid), respectively. Although the concept of the rate constant in the crystalline state is ill defined,[12] we set up the plot of the concentration change of complex **1** *versus* time (Fig. 6) as the molar ratios of the methyl-moieties were monitored by solution ^{1}H-NMR spectroscopy. Comparison of the slopes in Fig. 6, suggests that the solid rearranges at a similar rate ($k_{40\,°C} = 5.58 \times 10^{-6}$ l mol^{-1} s^{-1}) as the liquid ($k_{60\,°C} = 6.04 \times 10^{-6}$ l mol^{-1} s^{-1}). Based on these data it appears that complex **1** rearranges faster in the solid and liquid than in $CDCl_3$ solution (see Fig. 4). Nevertheless, the rate constants measured in the solid- and liquid-states are slower than in dilute CD_3OD solution.

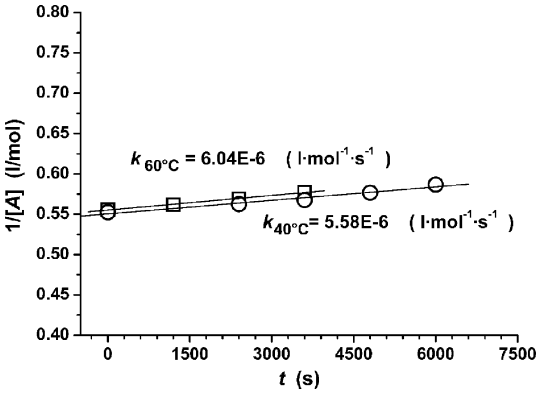

Fig. 6 The $1/[A]$ *versus* t plot used for the estimation of the k rate constant of the second order dismutation process (2A → B + C) for **1** at 40 °C (○ line) and in the liquid at 60 °C (□ line). $[A]$ is the molar concentration of **1**, and t is the time in seconds. An approximate density of 2.0 g cm^{-3} for the liquid was used for the calculation of the initial concentration $[A]_0$.

After 1 hour of heating of **1** at 150 °C the single crystals of **2** crystallized from the melt. The X-ray structure determination confirmed the formation of **2** (Fig. 7), and thus, the demethylation of **1**. The crystal and structural parameters obtained for this melt crystallized dismutation product **2** correspond closely to the results reported previously for $Me_2Sn(trop)_2$ prepared by metathetical reaction between sodium tropolonate and dimethyltin(IV) dichloride.[8e] In the dismutation product **2**, the tin centre is in a distorted *cis*-octahedral geometry, where the methyl substituents at the tin are substantially bent with the bond angle C(1)–Sn(1)–C(2) of 109.3(3)°. The axial C(1)–Sn(1)–O(2A) bond angle is closed from 180° to 160.7(2)°, and the corresponding equatorial bond angles range from 72.6(2) to 107.5(3)°. The tropolonato anions are chelated to the tin centre forming two five-membered SnO_2C_2 rings, with O–Sn–O bite angles of 73.3(1) and 72.6(2)°, respectively. Each tropolonato ligand forms two slightly different Sn–O bond lengths which differ by 0.055(4) and 0.038(4) Å, respectively.

Topochemical rationalisation of the dismutation reactivity in the crystalline state

The reactions occurring in the solid-state are generally induced photochemically[13] and/or thermally,[14] and they proceed either by topochemical or non-topochemical mechanisms.[15] The topochemical mechanism postulate states that the reactions in crystals occur with minimum atomic and molecular motion,[16] whereas recently it was stated that the topochemical reactions without molecular migrations are very rare and not all typical for solid-state reactions.[17] Chemical reactions in the solid state provide an

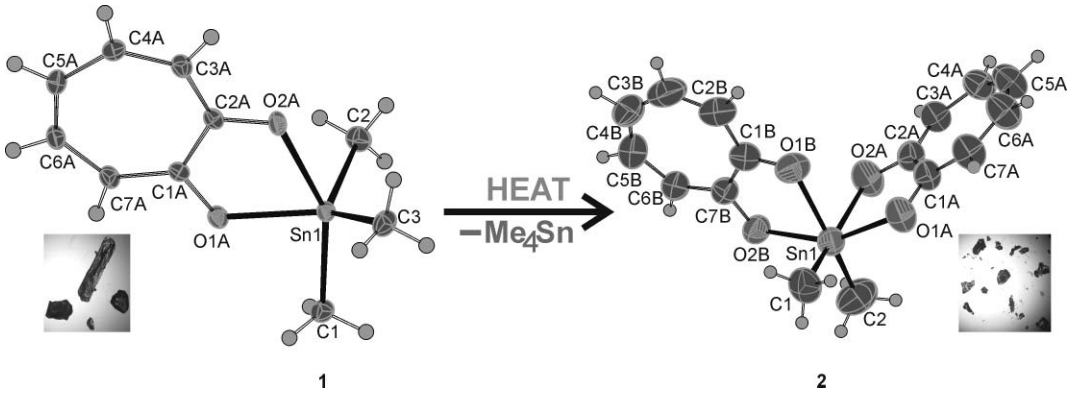

Fig. 7 Thermally induced demethylation of crystals of **1** into crystals of **2** and volatile Me_4Sn.

extreme case for evaluating the effect of intermolecular forces on a reaction and their influence on a reaction mechanism.[13g] Since most crystals are pure substances, the bimolecular reactions occur between identical partners, and they require precise distances and orientations between reaction partners.[12a] Unfortunately, the topochemical "allowed" distances, *i.e.* suitable intermolecular distances do not guarantee that a reaction will occur.[13a] The knowledge of the crystal structure of a trimethyltin(IV) complex provides a direct rationalisation of the dismutation reaction, but it is difficult to predict the packing motifs for bimolecular reactions in a reliable manner. Moreover, the thermal activation of the dismutation reaction is likely related to the requirement for a reorientation of the molecules relative to each other in order to bring the reacting functions as close as possible in order to react. This is in agreement with the fact that an arrangement of the molecules in the crystal, which would be completely ideal for the dismutation, would be identical with that of the transition state of the reaction, and such a kind of crystal is not isolable.

We have observed that the $[Me_3Sn(cupf)]_4$ tetramer dismutates into the $[Me_2Sn(cupf)_2]_2$ dimer and Me_4Sn proceeds with significant change of the molecular and crystal structure, accordingly the space group $P\bar{4}2_1c$ becomes $P\bar{1}$.[6] In this tetramer the shortest intramolecular C···Sn distance is 4.69 Å, whereas in the crystal lattice, the molecules stack in columns and the shortest intermolecular C···Sn distance between neighbouring molecules is 4.81 Å.[6] These values are somewhat higher than the sum of the van der Waals radii of carbon and tin (3.87 Å) or methyl and tin (4.17 Å). In complex **1**, the shortest intermolecular C···Sn distance is only 4.38 Å, which is shorter than the corresponding distance in the $[Me_3Sn(cupf)]_4$ tetramer. On the basis of the stacking pattern of **1**, it is reasonable to expect that the observed dismutation can occur through a cyclic bimolecular associate (Fig. 8), where the C(3)···Sn(1)^{i} and Sn(1)···O(1A)^{i} contact distances are 4.38 and 4.73 Å, respectively. This cyclic bimolecular system requires only a small degree of reorientation to transfer the methyl- and tropolonato-groups between themselves in a concerted fashion to form **2** and Me_4Sn. The C–H···O hydrogen bond [C(3)···O(1A)^{i} 3.52(1) Å; H(3D)···O(1A)^{i} 2.69 Å, C(3)–H(3D)···O(1A)^{i} 145.0°; symmetry code (i): x, $1/2 - y$, $1/2 + z$] formed between the methyl hydrogen and tropolonato oxygen atoms may facilitate the transfer of the methyl group *via* a jump along the C–H···O contacts (Fig. 8).

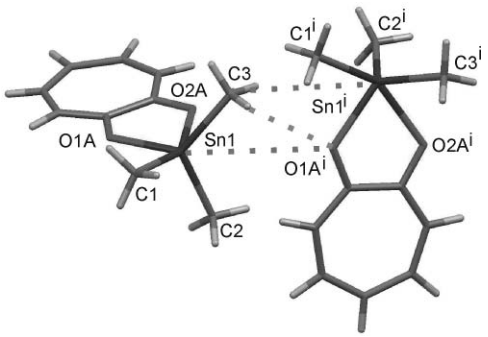

Fig. 8 Section of the crystal structure of **1** showing the potentially reactive pair of neighbouring molecules. Darker lines represent the corresponding C(3)···Sn(1)^{i} and Sn(1)···O(1A)^{i} contacts; the lighter line represents the short C–H···O contact [symmetry code: (i) x, $1/2 - y$, $1/2 + z$].

It must be pointed out that the mechanism of demethylation of **1** cannot be deduced directly based on its crystal structure, since the formation of ions during the reaction cannot be ruled out.[14n,o] Thus, the solid state transformation of **1** into **2** and volatile Me_4Sn can also be triggered by the formation of Me_3Sn^+, trop$^-$ and $Me_2Sn(trop)^+$, Me^- ions. The destruction of the crystal lattice, which is an inevitable consequence of the dismutation reaction, will create voids through which the diffusion of potentially formed ions may be facilitated. Therefore, the trop$^-$ and $Me_2Sn(trop)^+$, and the Me_3Sn^+ and Me^- ions are then free to condense with one another forming $Me_2Sn(trop)_2$ and Me_4Sn, respectively. Nevertheless, at the present time whether free ions exist in the crystal during the reaction, or whether the removal of tropolonate and methyl groups occurs in a concerted fashion, remains unanswered at the present time. However, we must point out that both **1** and **2** crystallized in space group $P2_1/c$, and as a consequence, the molecular packing of **1** shows some obvious similarities to that of its dismutation product **2**. The molecules **1** are linked into dimers (Fig. 9) by C–H···O contacts [C(3A)···O(2A)^{ii} 3.46(1) Å; H(3A)···O(2A)^{ii} 2.63 Å, C(3A)–H(3A)···O(2A)^{ii} 149.0°; symmetry code (ii): $-x$, $-y$, $-z$]. Accordingly, the molecules **2** are also linked into dimers (Fig. 9), the single difference being that the latter is set up by two sets of C–H···O hydrogen bonds [C(3A)···O(2A)^{ii} 3.27(1) Å; H(3A)···O(2A)^{ii} 2.35 Å, C(3A)–H(3A)···O(2A)^{ii} 173.1° and C(4A)···O(2B)^{ii} 3.49(1) Å; H(4A)···O(2B)^{ii} 2.66 Å,

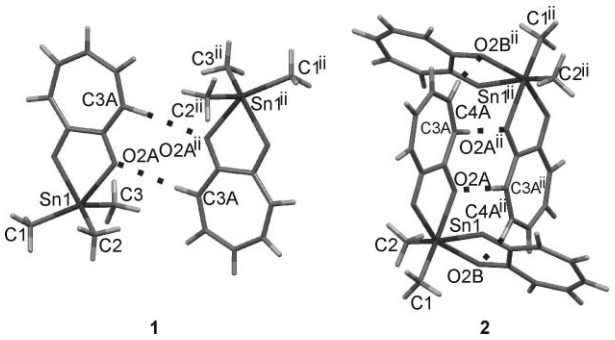

Fig. 9 View illustrating the C–H · · · O bonded dimers of **1** and **2**.

C(4A)–H(4A) · · · O(2B)^{ii} 149.5 Symmetry code (ii): $-x, -y, -z$]. Therefore, it is possible to see why at least in principle the solid-state transformation between **1** and **2** is apparently facile since it also allows the conservation of the hydrogen-bonding direction.

Experimental

Trimethyltin(IV) chloride and tropolone were purchased from Aldrich as pure compounds and used as received. The preparation and purification of the complexes were carried out in the open air or in a dry atmosphere.

Preparation of Me_3Sn(trop) (1)

To a 10 ml aqueous solution of trimethyltin chloride (0.88 g, 4.41 mmol) and tropolone (0.538 g, 4.41 mmol) a few drops of aqueous ammonia were added. A pale yellow precipitate appeared gradually. After stirring for half an hour at room temperature, the precipitate was filtered off and washed with a small amount of water. This waxy precipitate was dissolved in *n*-hexane and the resulting yellow solution was placed in a refrigerator. After a few days, yellow blocky crystals were obtained, mp = 55–56 °C. Yields, 0.92 g (3.23 mmol, 73.0%). Anal. Calc. for $C_{10}H_{14}O_2Sn$: C, 42.15; H, 4.95. Found: C, 42.4; H, 5.1%. ^{1}H-NMR (599.9 MHz, $CDCl_3$): δ 0.41 (s, $^2J(^{117}Sn/^{119}Sn–^1H)$ = 52.9/55.2 Hz, 9 H, CH_3), 6.92–6.99 (m, J = 9.2, 1.0 Hz, 1 H, CH), 7.28–7.34 (m, J = 10.4, 1.0 Hz, 2H, CH), 7.35–7.42 (m, J = 10.4, 9.2, 1.0 Hz, 2H, CH). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ −2.0 (s, $^1J(^{117}Sn/^{119}Sn–^{13}C)$ = 404/421 Hz, CH_3), 125.3 (s, $^3J(^{117}Sn/^{119}Sn–^{13}C)$ = 13.1/13.1 Hz, CH), 126.3 (s, CH), 138.4 (s, CH), 175.3 (s, $^2J(^{117}Sn/^{119}Sn–^{13}C)$ = 9.7/9.7 Hz, C). ^{119}Sn-NMR (223.6 MHz, $CDCl_3$): δ 70.0 ppm.

X-Ray crystallography

Crystal data and refinement parameters are summarized in Table 3. Crystals of **1** and **2** were mounted in Paratone-N oil within a conventional cryo-loop, and intensity data were collected on a Rigaku R-AXIS RAPID image plate diffractometer (λ(Mo-K$_\alpha$ radiation) = 0.71070 Å), fitted with an X-stream low temperature attachment. Several scans in the ϕ and ω direction were made to increase the number of redundant reflections, which were averaged over the refinement cycles. The structures were solved by direct methods (SIR92)[18] and refined by full-matrix least-squares (SHELXL-97).[19] All calculations were carried out using the WinGX package of crystallographic programs.[20] All non-hydrogen atoms were refined anisotropically in F^2 mode. Hydrogen atomic positions were generated from assumed geometries. The riding model was applied for the hydrogen atoms. In addition, the riding methyl hydrogen atoms were allowed to rotate freely during refinement.

CCDC reference numbers 621188 and 621189.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613692c

Table 3 Crystal data and structure refinement parameters for complexes **1** and **2**, respectively

Complex	**1**	**2**
Empirical formula	$C_{10}H_{14}O_2Sn$	$C_{16}H_{16}O_4Sn$
Formula mass	284.90	390.98
Crystal size/mm	0.17 × 0.20 × 0.35	0.23 × 0.41 × 0.41
Colour	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
T/°C	−180	22
θ Range for data collection/°	3.08 ≤ θ ≤ 27.45	3.14 ≤ θ ≤ 27.67
a/Å	10.572(6)	10.732(4)
b/Å	8.576(4)	14.192(6)
c/Å	12.235(7)	10.561(4)
β /°	99.83(2)	98.24(4)
V/Å^3	1093.0(1)	1591.9(2)
Z	4	4
d_{calc}/Mg m^{-3}	1.731	1.631
μ/mm^{-1}	2.305	1.617
F(000)	560	776
Index ranges	−13 ≤ h ≤ 13 −10 ≤ k ≤ 11 −15 ≤ l ≤ 15	−12 ≤ h ≤ 11 −16 ≤ k ≤ 16 −12 ≤ l ≤ 12
No. of collected reflns.	9308	10055
No. of indep. reflns./R_{int}	2493/0.036	2750/0.031
No. of obsd. reflns. $I > 2\sigma(I)$	2195	2242
No. of parameters	121	192
GOOF	1.26	1.25
$R1$ (obsd. data)	0.0238	0.0329
$wR2$ (all data)	0.0712	0.1223
Largest diff. peak, hole/e Å^{-3}	0.57, −0.73	0.61, −0.60

NMR spectroscopy

NMR experiments were carried out on Varian Inova (400 MHz for ^{1}H) and Varian NMR SYSTEM (600 MHz for ^{1}H) spectrometers using a switchable broadband X{^{1}H}, and a direct detection double tuneable pfg 5 mm X{^{1}H–^{19}F} probe (X = ^{13}C, ^{119}Sn) respectively. Solid-state MAS spectra were recorded using a 3.2 mm HXY Varian Chemagnetics and a 6.0 mm HXY Varian Chemagnetics tunable MAS probes in HX double resonance (DR) mode. For ^{13}C and ^{119}Sn MAS experiments recycle delays of 30 and 45 s and ^{1}H decoupling field strengths of 57 and 92 kHz were used. Chemical shifts in the solid state were referenced to adamantane (δ_{13C} = 29.5, 38.6 ppm) and tetracyclohexyltin (δ_{119Sn} = −97.4 ppm). Solution ^{1}H chemical shifts are referenced to the residual solvent signals. ^{119}Sn shifts are given relative to the internal reference Me_4Sn. Deuterated (99.98 atom%) solvents were purchased from Merck® GmBH, Germany. ^{119}Sn-NMR spectra were recorded by using a 5 s recycle delay and WALTZ[21] proton decoupling during acquisition. Spectra were processed in VnmrJ® 2.1B. Solid-state simulations were performed by Varian software: STARS®.

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