

# First example of a Sn–C bond cleaved product in the reaction of $\text{Ph}_3\text{SnOSnPh}_3$ with carboxylic acids. 3D-Supramolecular network formation in the X-ray crystal structure of $[\text{Ph}_2\text{Sn}(\text{OH})\text{OC}(\text{O})(\text{R}_f)]_2$ , $\text{R}_f = 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$

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A 1 : 2 reaction of  $\text{Ph}_3\text{SnOSnPh}_3$  **1** with  $\text{R}_f\text{COOH}$  **2** leads to the formation of  $[\text{Ph}_2\text{Sn}(\text{OH})\text{OC}(\text{O})(\text{R}_f)]_2$  **3**, by means of a facile Sn–C bond cleavage process.

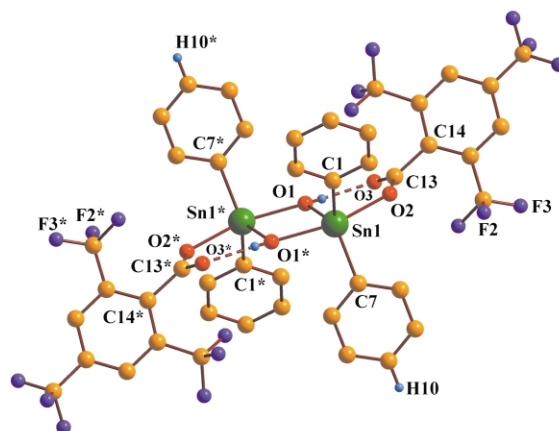
There is considerable interest in the assembly and structural analysis of organotin cages, clusters and coordination polymers. In most instances these compounds are prepared by the reaction of an appropriate organotin precursor such as  $\text{R}_3\text{SnOSnR}_3$ ,  $\text{R}_3\text{SnOH}$ ,  $(\text{R}_2\text{SnO})_n$  or  $\text{RSn}(\text{O})(\text{OH})$  with a carboxylic, phosphinic, phosphonic or sulfonic acid.<sup>1</sup> There have also been some attempts to utilise the lability of the Sn–C bond for the formation of a few structural types involving the organotin motif.<sup>2</sup> The most favourable organotin substrates for this reaction appear to be the allyl tin compounds and such reagents have been used for allyl transfer reactions in organic synthesis. Thus, for example, the tetra-allyl tin,  $\text{Sn}(\text{CH}_2\text{=CH}_2)_4$ , has been used recently for the synthesis of a homoallylic alcohol with a high enantiomeric excess.<sup>3</sup> We also have shown the usefulness of benzyl tin compounds for the construction of complex tetranuclear organotin cages.<sup>4</sup> Although there have been sporadic reports on Sn–Ph bond cleavage involving substrates such as  $\text{PhSn}(\text{O})(\text{OH})$ ,  $\text{Ph}_2\text{SnO}$ ,  $\text{Ph}_3\text{SnOH}$  or  $\text{SnPh}_4$ , these are considerably limited.<sup>2</sup> For example in the reactions of  $\text{Ph}_3\text{SnOSnPh}_3$  with over forty different aliphatic or aromatic carboxylic acids the triorganotin carboxylate,  $\text{Ph}_3\text{SnO}_2\text{CR}$ , is the exclusive product. A similar situation is also found for analogous reactions with (*n*-Bu)<sub>3</sub>SnOSn(*n*-Bu)<sub>3</sub>.<sup>1</sup> We report in the following an unusual Sn–Ph scission in the reaction between  $\text{Ph}_3\text{SnOSnPh}_3$  and  $\text{R}_f\text{COOH}$  leading to the formation of a distannoxane,  $[\text{Ph}_2\text{Sn}(\text{OH})\text{OC}(\text{O})(\text{R}_f)]_2$  **3**, containing two hydroxyl bridges instead of the expected product  $\text{Ph}_3\text{SnO}_2\text{CR}$  **4**.

The reaction of bis(triphenyltin) oxide,  $\text{Ph}_3\text{SnOSnPh}_3$  **1**, and 2,4,6-tris(trifluoromethyl)benzoic acid, 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-COOH **2**, in a 1 : 2 stoichiometry, in benzene under reflux conditions, afforded the distannoxane,  $[\text{Ph}_2\text{Sn}(\text{OH})\text{OC}(\text{O})(\text{R}_f)]_2$  **3**, in about 94% yield (Scheme 1).<sup>†</sup>

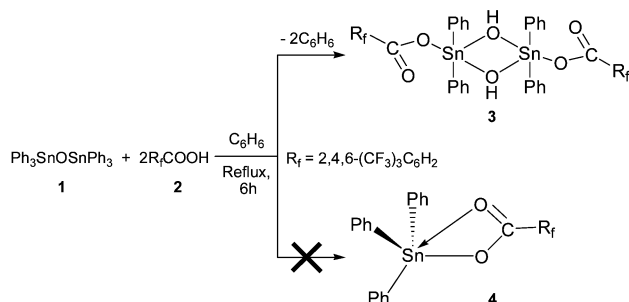
The facile Sn–C bond cleavage occurs as a result of the special electronic and steric requirements of the perfluor-

omesityl carboxylate unit. In contrast, an analogous reaction of  $\text{Ph}_3\text{SnOSnPh}_3$  with mesityl carboxylic acid leads to the formation of the *normal* product,  $\text{Ph}_3\text{SnO}_2\text{C-2,4,6-Me}_3\text{C}_6\text{H}_2$ .<sup>5</sup> Further, the reaction of perfluorobenzoic acid, C<sub>6</sub>F<sub>5</sub>COOH, with  $\text{Ph}_3\text{SnOSnPh}_3$  also leads to the *normal* product.<sup>6</sup> Thus it appears that the unique steric and electronic properties of  $\text{R}_f\text{COOH}$  are responsible for the observed reactivity. A sharp singlet at –316.4 ppm in the <sup>119</sup>Sn NMR (150 MHz, CDCl<sub>3</sub>) spectrum of **3** is indicative of the C<sub>2</sub>O<sub>3</sub> environment around each tin.<sup>1</sup> It is of interest to compare this with the observed chemical shifts of  $\text{Ph}_3\text{SnO}_2\text{CAr}$  (Ar = aromatic group) which occur around –100 ppm.<sup>1</sup> Two singlets at –60.0 and –63.4 ppm are seen in the <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of **3** and are assigned to the fluorine atoms of *ortho* and *para* CF<sub>3</sub> groups. Single crystals of **3** suitable for X-ray diffraction were obtained by vapour diffusing *n*-hexane into its dichloromethane solution at ambient temperature. The compound crystallized in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n* and the molecular structure is shown in Fig. 1.<sup>‡</sup>

The crystal structure of **3** clearly shows the formation of a Sn–C bond cleaved product. Each tin is pentacoordinate and the coordination environment is comprised of two phenyl substituents, one carboxylate moiety and two μ-OH groups. The coordination geometry around each tin is distorted trigonal bipyramidal with the axial positions being occupied by one bridging hydroxy oxygen (O1\*) and the carboxylate oxygen (O2) while the equatorial positions are taken up by the two carbons (C1 and C7) of the phenyl substituents and the other bridging hydroxy oxygen (O1) (Fig. 1). The overall structure is a dimer with the two hydroxy groups acting as μ-bridges



**Fig. 1** Molecular structure of the Sn–C bond cleaved product **3** (where \* = 1 – *x*, 1 – *y*, 1 – *z*). Also shown are the intramolecular hydrogen bonds O1–H100...O3 [O1–H100 0.81(3), H100...O3 1.91(3), O1...O3 2.66(3) Å, O1–H100...O3 153.9(3)°]. The non-interacting hydrogen atoms are omitted for clarity.



**Scheme 1** Synthesis of the Sn–C bond cleaved product **3**.

between the two tin units. This leads to the formation of a central Sn<sub>2</sub>O<sub>2</sub> distannoxane ring.

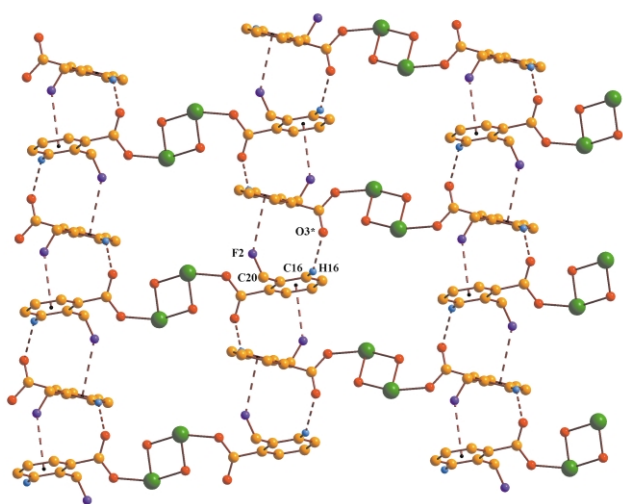
To the best of our knowledge the formation of such a dimeric structure starting from a triorganotin precursor has no precedence in organotin carboxylate chemistry.<sup>1</sup> Other instances of dimeric stannoxane structures include [*t*-Bu<sub>2</sub>Sn(O<sub>2</sub>CCH<sub>3</sub>)(μ-OH)]<sub>2</sub>,<sup>7</sup> [*t*-Bu<sub>2</sub>Sn(OH)Cl]<sub>2</sub>,<sup>8</sup> [Me<sub>2</sub>Sn(OH)NO<sub>3</sub>]<sub>2</sub><sup>9</sup> and [*n*-BuSn(OH)(OSO<sub>2</sub>CF<sub>3</sub>)(H<sub>2</sub>O)]<sub>2</sub>.<sup>10</sup>

A careful analysis of the X-ray crystal structure of **3** reveals the presence of several intra- and intermolecular secondary interactions. Thus, an intramolecular O–H···O hydrogen bond is found between the uncoordinated carbonyl oxygens O3 or O3\* and the bridging hydroxy groups (Fig. 1). Such an interaction is probably also responsible for the non-participation of these carbonyl oxygens in coordination to the tin centers. Three types of intermolecular interactions are found. First a C–H···O bond (C16–H16···O3\*) between the lone hydrogen of the perfluoromesityl group of one molecule with the free carbonyl oxygen of a neighbouring molecule leads to the generation of a sheet-like architecture (Fig. 2). Further, elaboration of this sheet-structure occurs as a result of a C–F···π interaction (C20–F2···π) between one of the fluorines of the perfluoromesityl group and the centroid of another such group belonging to the neighbouring molecule.

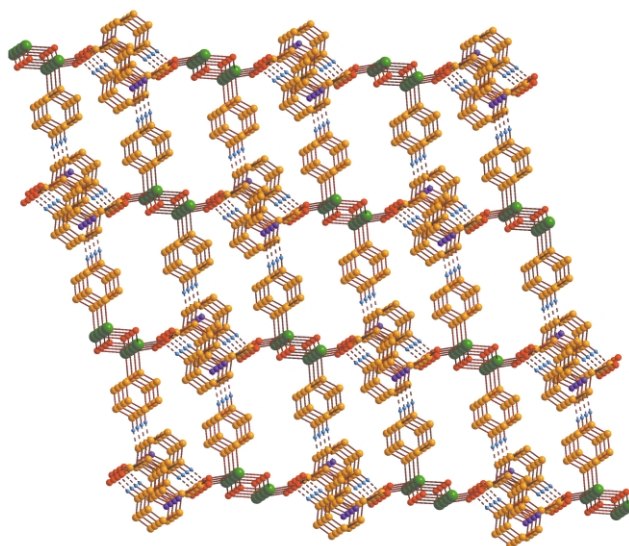
The existence of such C–H···O<sup>11</sup> as well as C–F···π<sup>12</sup> interactions is well documented in recent years. Also recently we have shown that C–H···O interactions in organotin drums [*n*-BuSn(O)OC(O)R]<sub>6</sub>, R = CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub> and 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, leads to the formation of novel two-dimensional supramolecular grids.<sup>13</sup>

The two-dimensional sheet thus formed is taken into the third dimension by intermolecular C–H···F bonds (C10–H10···F3\*) between the hydrogen of the phenyl (C<sub>6</sub>H<sub>5</sub>) group and the fluorine of the perfluoromesityl group (Fig. 3). The metric parameters observed for these C–H···F interactions are quite reasonable.<sup>14</sup>

In summary we observe for the first time the formation of a *diorganodistannoxane* starting from a *triorganotin* precursor. The X-ray crystal structure of the former shows the formation of a three-dimensional supramolecular network as a result of three different intermolecular secondary interactions. In view of this interesting result, the reactions of R<sub>3</sub>COOH with other organotin precursors are under investigation in our laboratory.



**Fig. 2** Intermolecular C–H···O and C–F···π interaction in the 2D-sheet of **3**. The metric parameters: for C16–H16···O3\* contact are C16–H16 0.95(2), H16···O3\* 2.52(1), C16···O3\* 3.34(3) Å, C16–H16···O3\* 144.0(1)° (where \* = 1.5 – x, 0.5 + y, 0.5 – z); for C20–F2···π contact are C20–F2 1.34(1), F2···π 3.08(2), C20···π 4.22(1) Å, C20–F2···π 142.7(1)°. All the phenyl groups on each tin, non-interacting fluorine atoms along with the carbon atoms to which they are attached and all the non-interacting hydrogen atoms are omitted for the sake of clarity.



**Fig. 3** 3D-Supramolecular network of **3** arising out of the C–H···F interaction between the 2D-sheets shown in Fig. 2. The metric parameters for this C10–H10···F3\* contact are C10–H10 0.95(3), H10···F3\* 2.49(2), C10···F3\* 3.44(4) Å, C10–H10···F3\* 173.9(2)° (where \* = 2 – x, 1 – y, 1 – z). The non-interacting phenyl group on each tin, non-interacting fluorine atoms along with the carbon atoms to which they are attached and all the non-interacting hydrogen atoms are omitted for the sake of clarity.

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## Notes and references

† *Synthesis and characterization data for 3*: The stoichiometries of the reactants are: Ph<sub>3</sub>SnOSnPh<sub>3</sub> (0.55 g, 0.8 mmol) and 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>COOH (0.50 g, 1.5 mmol). Mp: 240 °C (decomp.). Anal. Calcd. for C<sub>44</sub>H<sub>26</sub>F<sub>18</sub>O<sub>6</sub>Sn<sub>2</sub>: C, 42.96; H, 2.13. Found: C, 43.02; H, 2.29%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.06(s, 4H, aromatic); 7.68–7.70 (d, 8H, aromatic, J = 7.31 Hz); 7.34–7.41 (m, 12H, aromatic).

‡ *Crystal data and structure refinement for 3*: C<sub>44</sub>H<sub>26</sub>F<sub>18</sub>O<sub>6</sub>Sn<sub>2</sub>, M = 1230.03, monoclinic, a = 14.2793(6), b = 8.4503(4), c = 19.1407(8) Å, β = 102.7370(10)°, U = 2252.77(17) Å<sup>3</sup>, T = 150(2) K, space group P2<sub>1</sub>/n (no. 14), Z = 2, μ(Mo–Kα) = 1.231 mm<sup>–1</sup>, 11361 reflections measured, 3963 unique (R<sub>int</sub> = 0.0305). Final R indices [I > 2σ(I)]: R1 = 0.0214, wR2 = 0.0572. R indices (all data): R1 = 0.0225, wR2 = 0.0578. CCDC 200423. See <http://www.rsc.org/suppdata/cc/b2/b212409b/> for crystallographic data in CIF or other electronic format.

- V. Chandrasekhar, S. Nagendran and V. Baskar, *Coord. Chem. Rev.*, 2002, **235**, 1; R. R. Holmes, *Acc. Chem. Res.*, 1989, **22**, 190; E. R. T. Tiekink, *Trends Organomet. Chem.*, 1994, **1**, 71.
- K. C. K. Swamy, M. A. Said, S. Nagabrahamanandachari, D. M. Poojary and A. Clearfield, *J. Chem. Soc., Dalton Trans.*, 1998, 1645.
- K. M. Waltz, J. Gavenonis and P. J. Walsh, *Angew. Chem., Int. Ed.*, 2002, **41**, 3697.
- V. Chandrasekhar, V. Baskar, A. Steiner and S. Zacchini, *Organometallics*, 2002, **21**, 4528.
- V. Chandrasekhar, S. Nagendran, K. Gopal and A. Steiner, unpublished results.
- R. Willem, A. Bouhdid, M. Biesemans, J. C. Martins, D. de Vos, E. R. T. Tiekink and M. Gielen, *J. Organomet. Chem.*, 1996, **514**, 203.
- V. B. Mokul, V. K. Jain and E. R. T. Tiekink, *J. Organomet. Chem.*, 1992, **431**, 283.
- H. Puff, H. Hevendehl, K. Höfer, H. Reuter and W. Shuh, *J. Organomet. Chem.*, 1985, **287**, 163; D. Dakternieks, K. Jurkschat, S. van Dreumel and E. R. T. Tiekink, *Inorg. Chem.*, 1997, **36**, 2023.
- A. M. Domingos and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1974, 475.
- K. Sakamoto, H. Ikeda, H. Akashi, T. Fukuyama, A. Orita and J. Otera, *Organometallics*, 2000, **19**, 3242.
- G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
- M. D. Prasanna and T. N. Guru Row, *Crystal Eng.*, 2000, **3**, 135.
- V. Chandrasekhar, S. Nagendran, S. Bansal, A. W. Cordes and A. Vij, *Organometallics*, 2002, **21**, 3297.
- G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond In Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.