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Ambient Temperature Sn–C Bond Cleavage Reaction Involving the Sn-*n*-butyl Group. Weak F···F Interactions in the Solid State Structure of $[\{n\mathrm{Bu_2SnO_2C{-}C_6H_4\text{-}4\text{-}CF_3}\}_2\mathrm{O}]_2$

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Dedicated to Professor C. N. R. Rao on the Occasion of His 80th Birthday

Keywords: F···F Interactions; Tin; Cleavage reaction; Organostannoxanes

Abstract. The reaction of bis(tri-*n*-butyltin)oxide, $[n\mathrm{Bu_3Sn}]_2\mathrm{O}$, with $\mathrm{HO_2C{-}C_6H_4{-}4\text{-}CF_3}$ ($\mathrm{R_fTol\text{-}CO_2H}$) affords a coordination polymer $[n\mathrm{Bu_3SnO_2C{-}R_fTol}]_n$ (**1**). **1** undergoes hydrolysis in the presence of atmospheric moisture, at room temperature, resulting in the formation of the diorgano stannoxane $[\{n\mathrm{Bu_2SnO_2C{-}R_fTol}\}_2\mathrm{O}]_2$ (**2**). The transformation of **1** to **2** is accompanied by a Sn–C bond cleavage reaction. Formation of **2** also occurs in a direct reaction, involving $[n\mathrm{Bu_3Sn}]_2\mathrm{O}$ and $\mathrm{R_fTol{-}CO_2H}$ in the presence of water. **2** can also be prepared in a 1:1 reaction of di-*n*-butyltin oxide, $[n\mathrm{Bu_2SnO}]_n$ with $\mathrm{R_fTol{-}CO_2H}$. The conversion of **2** from **1** was monitored by ^{119}Sn NMR spectroscopy over a period of eight days. The molecular structure of **2** reveals a tetranuclear assembly consisting of two pairs of structurally distinct six-coordinate tin atoms. Extensive hydrogen-bonding interactions (C-H···O, C-H···F) and weak F···F interactions involving organo-fluorine atoms in the crystal structure result in the formation of a three-dimensional supramolecular architecture for **2**.

Introduction

Organostannoxanes are a family of structurally interesting organometallic compounds.[1] The remarkable structural variability of these compounds has been manifested in several structural forms: ladder, cube, drum, butterfly cluster, O-capped cluster, double O-capped cluster, trigonal prism, football cage.[2] Also, organostannoxanes are known in both molecular forms and coordination polymers.[3] Further, the nuclearity of tin can traverse from one to twelve in these various compounds.[4] The synthesis of organostannoxanes, usually involves the reactions of organotin halides, organotin oxides, -hydroxides, or -oxide-hydroxides with protic acids.[5] In addition to these well-established synthetic procedures, the lability of the Sn–C bond, in certain situations, has also been utilized for preparing new organostannoxanes.[6] Although, Sn–C bond cleavage is most facile in compounds containing Sn-benzyl[6b] or Sn-allyl[6c] motifs, there have been reports, admittedly sparse, on such reactions in compounds containing Sn–Ph[6d] and even Sn–butyl[6e] motifs. Thus, recently, we have utilized such Sn–C bond cleavage reactions for the synthesis of novel organostannoxanes. These include a tetranuclear cage,[7] $[\mathrm{Sn_2(\mu\text{-}OH)_2}]$ cored diorganotin derivative,[6e] and a hydrated organotin cation.[8] One interesting example involves a Sn–Ph scission in the reaction of $[\mathrm{Ph_3Sn}]_2\mathrm{O}$ with perfluoromesityl carboxylic acid, $\mathrm{HO_2C{-}C_6H_2\text{-}2,4,6\text{-}(CF_3)_3}$ ($\mathrm{R_fMes{-}CO_2H}$) leading to the formation of a distannoxane, $[\mathrm{Ph_2Sn(\mu\text{-}OH)O_2C{-}R_fMes}]_2$ instead of the expected product $\mathrm{Ph_3SnO_2C{-}R_fMes}$.[6c] The reason for the facile Sn–C bond cleavage in the above reaction has been suggested as due to the steric and electronic withdrawing character of the perfluoromesityl carboxylate group.

In order to test the generality of this approach (Sn–C bond cleavage approach), we have utilized perfluoro-*p*-tolyl carboxylic acid, $\mathrm{HO_2C{-}C_6H_4\text{-}4\text{-}CF_3}$ ($\mathrm{R_fTol{-}CO_2H}$) which is sterically less encumbered than $\mathrm{R_fMes{-}CO_2H}$ and contains only one strong electron withdrawing group ($-\mathrm{CF_3}$). Accordingly, herein we report the reaction of bis(tri-*n*-butyltin)oxide, $(n\mathrm{Bu_3Sn})_2\mathrm{O}$ with $\mathrm{HO_2C{-}C_6H_4\text{-}4\text{-}CF_3}$ ($\mathrm{R_fTol{-}CO_2H}$) which affords the expected tri-*n*-butyltin carboxylate coordination polymer $[n\mathrm{Bu_3SnO_2C{-}R_fTol}]_n$ (**1**). The influence of the $-\mathrm{CF_3}$ group, however, is manifested in a facile ambient temperature hydrolysis of **1**, involving the Sn–C bond cleavage of the Sn-*n*-butyl substituent, leading to the formation of $[\{n\mathrm{Bu_2SnO_2C{-}R_fTol}\}_2\mathrm{O}]_2$ (**2**). We could prepare **2**, in a direct Sn–C bond cleavage reaction from $[n\mathrm{Bu_3Sn}]_2\mathrm{O}$ as well as in a normal re-

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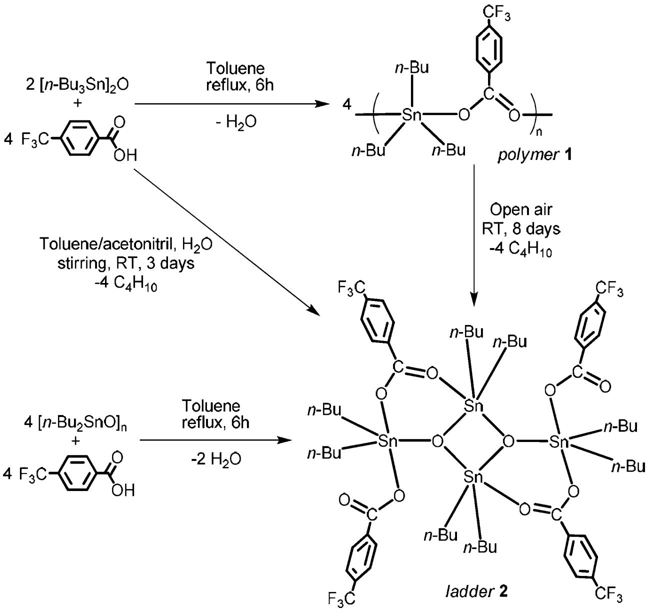
action involving $[n\text{Bu}_2\text{SnO}]_n$. On the other hand, from several interactions involving halogen atoms, those containing fluorine, the F···F and C–H···F interactions, are attracting attention recently due to several reasons including their role in the medicinal chemistry.[6d,9]

The crystal structure of **2** reveals, that due to rich intermolecular C–H···O, C–H···F and weak F···F interactions, a 3D-supramolecular architecture is realized in the solid-state. These results are discussed herein.

Results and Discussion

Synthetic Aspects

The reaction of $[n\text{Bu}_3\text{Sn}]_2\text{O}$ with two equivalents of R_fTol–CO_2H in toluene leads to the formation of mononuclear triorganotin carboxylate **1** (Scheme 1) which is a viscous oil. Based on the molecular structures of this family of compounds[3b] we presume that it should possess a polymeric structure. However, this could not be confirmed since attempts to crystallize it afforded, through a Sn–C bond cleavage reaction, **2** (see below). The ^{119}Sn NMR spectrum of **1** shows a single resonance at $\delta = 63$ ppm. It is known that triorganotin carboxylates that are coordination polymers in the solid-state break down in solution, typically into their monomeric form.



Scheme 1. Synthesis of the organostannoxanes **1** and **2**.

Efforts to crystallize **1** resulted in the formation of **2**. The conditions for this were optimized and block shaped crystals of **2** were isolated when neat **1** in the form of a viscous oil was kept undisturbed in open air for 8 days. Since the formation of **2** involves a Sn–C bond cleavage and hydrolysis, we reacted $[n\text{Bu}_3\text{Sn}]_2\text{O}$ and R_fTol–CO_2H in the presence of water in a mixture of solvents (1:2 toluene and acetonitrile) at room temperature for 3 days (Scheme 1). Interestingly, this *direct* reaction, which involves a facile ambient temperature Sn–butyl bond cleavage reaction, afforded **2** in very good yield (see Experimental Section). We also performed a 1:1 reaction of the diorganotin oxide, $(n\text{Bu}_2\text{SnO})_n$ with R_fTol–CO_2H. This reaction also affords **2** in nearly quantitative yields (see Experimental Section). Compound **2** shows two resonances at $\delta = -254$ and -272 ppm in its ^{119}Sn NMR spectrum indicating the presence of two types of tin atoms in its molecular structure. These values are comparable to the literature precedents.[4c] The ^{19}F NMR spectrum of both **1** and **2** show singlets that resonate at $\delta = -69$ and -67 ppm, respectively.

The hydrolysis of **1** was monitored by using ^{119}Sn NMR spectroscopy at various time intervals. Thus, compound **1** shows a single resonance at $\delta = 63$ ppm (Figure 1a). After two days, a new signal appears at $\delta = -271$ ppm indicating the onset of hydrolysis and increase of the coordination number around tin (Figure 1b). After five days, three new signals ($\delta = -201$, -262, and -269 ppm) appeared along with the one at $\delta = -271$ ppm observed previously, (Figure 1c). Finally, after eight days two signals, corresponding to **2** were observed at $\delta = -254$ and $\delta = -272$ ppm indicating the complete conversion of **1** to **2** (Figure 1d). At this point we are unable to offer a detailed mechanism regarding this conversion except to note that the reaction appears to be more facile in an open atmosphere, in light. In dark, the reaction appears to be very sluggish.

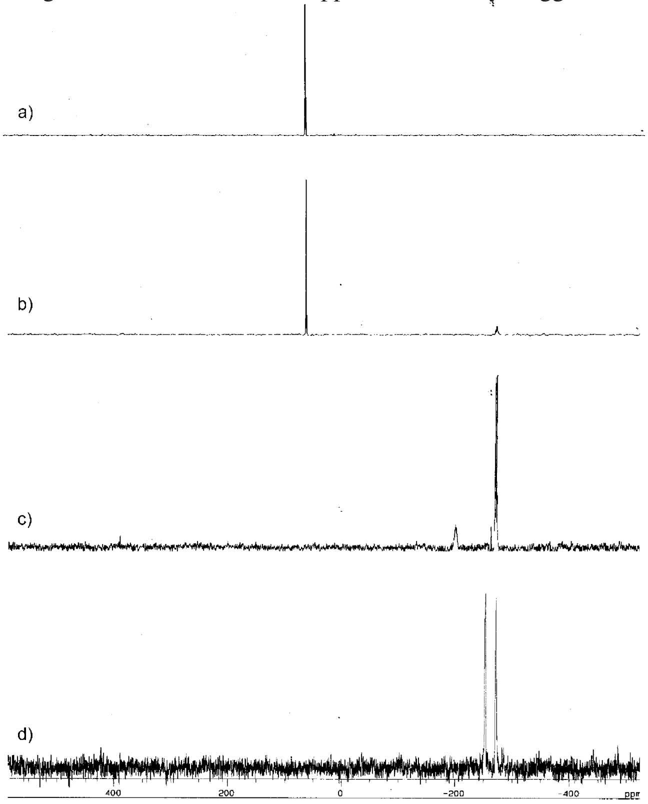


Figure 1. Monitoring the conversion of **1** to **2** by ^{119}Sn NMR spectroscopy. (a) Compound **1**. (b) After 2 days. (c) After 5 days. (d) After 8 days. Note that the chemical shifts at this stage *exactly* match that of **2**.

Molecular and Supramolecular Structures

The molecular structure of compound **2** is shown in Figure 2 and its selected bond parameters are summarized in the caption

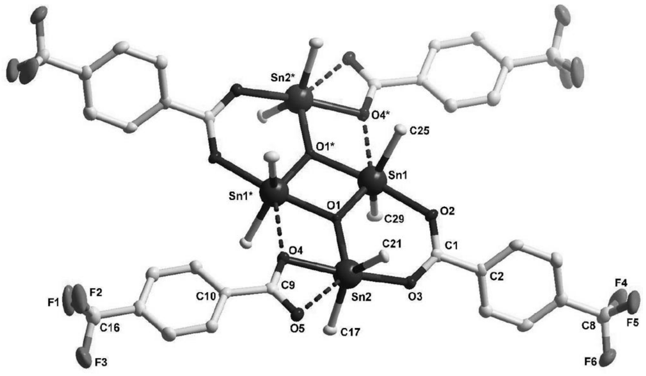


Figure 2. Molecular structure of **2**. The unlabeled atoms are symmetry related to the labeled atoms. Selected bond parameters are as follows: Sn1–O1 2.051(2), Sn1–O1* 2.142(2), Sn1–O2 2.290(2), Sn1–O4* 2.815(3), Sn1–C25 2.122(4), Sn1–C29 2.126(4), Sn2–O1 2.048(2), Sn2–O3 2.312(3), Sn2–O4 2.196(2), Sn2–O5 2.818(7), Sn2–C21 2.123(4), Sn2–C17 2.130(4) Å; C25–Sn1–C29 143.55(15), O2–Sn1–O1* 162.91(9), O1–Sn1–O4* 140.38(8), C21–Sn2–C17 139.31(14), O3–Sn2–O4 166.15(9), O1–Sn2–O5 129.35(3)°.

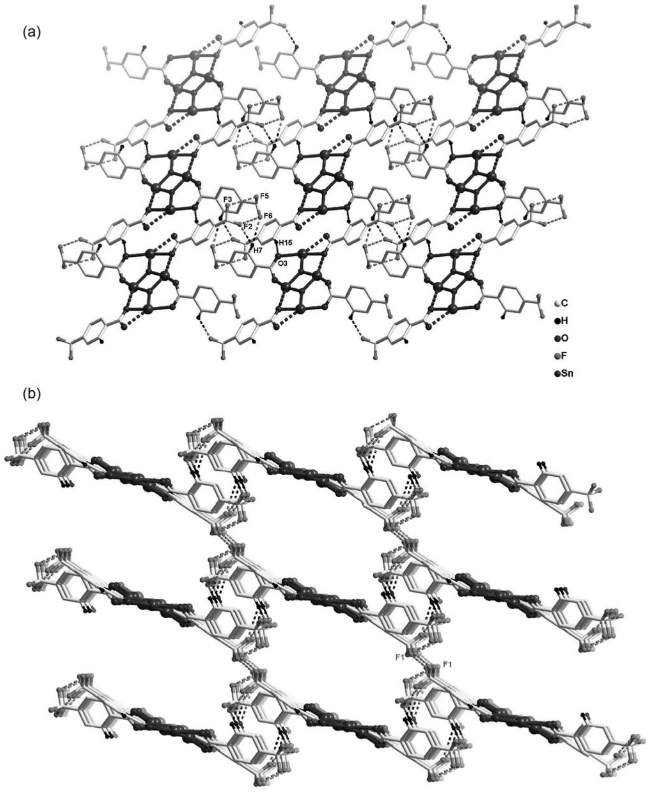


Figure 3. (a) View showing the two-dimensional staircase like network. One fluorine atom of the CF_3 group is omitted for clarity. (b) Three-dimensional supramolecular network formed by C–H···O, C–H···F, and weak F···F interactions in **2**.

of this figure. The molecular structure of **2** shows that four carboxylate ligands present in this compound are supported by a planar $[Sn_4O_2]$ core and adopt the familiar *ladder* framework with two central (Sn1 and Sn1*) and two terminal tin atoms (Sn2 and Sn2*). The Sn–O distances in the central $[Sn_2O_2]$ core [Sn1–O1 2.051(2) and Sn1–O1* 2.142(2) Å] are comparable with literature precedents.[2b,3d] All the tin atoms are present in a distorted trigonal bipyramidal arrangement (2C, 3O). Also, an additional carboxylate oxygen (O5 with terminal tin atom Sn2 and O4* with central tin atom Sn1) is involved in a sixth weaker bonding interaction [Sn2–O5 2.818(7) Å and Sn1–O4* 2.815(3) Å] with a tin atom along its trigonal bipyramidal face (Figure 2). Considering that the sum of the van der Waals radii of tin and oxygen is 3.7 Å[10] the coordination arrangement around the tin atoms (Sn1 and Sn2) can be assumed to be distorted octahedral. The carboxylate ligands are involved in both anisobidentate chelating (Sn2–O4 and Sn2–O5) as well as isobidentate bridging (Sn1–O2 and Sn2–O3) coordination modes. The carboxylate groups in **2** are nearly in the same plane as that of the aromatic ring (with a deviation of 9.7° for terminal chelating R_fTol–CO_2 and 29.2° for central bridging R_fTol–CO_2) and are comparable with our previous observations.[3d]

There is a great interest in the assembly of ordered supramolecular structures through crystal engineering because of the potential for realizing new types of functional solids.[11] Many types of secondary interactions are known to mediate supramolecular assembly formation in organic and inorganic compounds. These include O–H···O, N–H···O, and N–H···N (strong interactions); C–H···O, C–H···π, π···π, C–H···*X* and *X*···*X* (*X* = halogen) interactions (weak interactions) etc.[11] Since **2** contain many fluorine atoms in the periphery we examined its solid-state crystal structure in greater detail. The supramolecular organization in this compound may be considered in a step-wise manner. At the first-level, each molecule interacts with two other neighbors by means of two-proton acceptor and two-proton donor type of C–H···O bonding interactions along with two types of F···F interactions to form a linear one-dimensional tape (Figure 3a). In this interaction, a proton (H15) on the R_fTol–CO_2 moiety is intermolecularly hydrogen-bonded with the carboxylate oxygen (O3) of the central R_fTol–CO_2 ligand [H15···O3 2.683(7) Å, 167.73(22)°, symmetry code: 2–*x*, 1–*y*, 1–*z*]. Similarly, two of the fluorine atoms (F2 and F3) present in the terminal R_fTol–CO_2 ligands interact very weakly with two other fluorine atoms (F6 and F5) present in the central R_fTol–CO_2 ligands in the form of CF_2 dimer [F2···F6 3.016(11) Å, symmetry code: 2–*x*, 1–*y*, 1–*z*; F3···F5 3.277(11) Å, symmetry code. 2–*x*, 1–*y*, 1–*z*]. At the second-level, two such one-dimensional networks are interconnected by means of H···F interactions to form a *staircase* like two-dimensional supramolecular network (Figure 3a). Here, one of the protons (H7) on the central R_fTol–CO_2 ligand is hydrogen bonded with two fluorine atoms (F2 and F6) of two different *ladder* molecules in a bifurcated manner [H7···F2 2.822(8) Å, 134.14(29)°, symmetry code: *x*, *y*, –1+*z*; H7···F6 2.797(6) Å, 132.19(27)°, symmetry code: 2–*x*, 1–*y*, *z*]. Finally, these *staircase* like two-dimensional networks are interconnected by other F···F interactions to afford a three-dimensional supramolecular assembly (Figure 3b). The bonding parameter for this interaction is: F1···F1 3.065(9) and its symmetry code is 3–*x*, –*y*, 2–*z*.

Summary

We have observed an interesting and rare ambient temperature Sn–C bond cleavage involving the crystallization of the triorganotin carboxylate, $[n\mathrm{Bu_3SnO_2C–R_fTol}]_n$ (**1**) affording $[\{n\mathrm{Bu_2SnO_2C–R_fTol}\}_2\mathrm{O}]_2$ (**2**). **2** could also be prepared in two *direct* reactions: one, involving the reaction of $(n\mathrm{Bu_3Sn})_2\mathrm{O}$ with $\mathrm{R_fTol–CO_2H}$ in presence of water and another involving the reaction of $(n\mathrm{Bu_2SnO})_n$ with $\mathrm{R_fTol–CO_2H}$. The conversion of **1** into **2** could be monitored by ^{119}Sn NMR; the conversion is slow, takes 8 days, but is quantitative. The crystal structure of **2** reveals the presence of an interesting 3D supramolecular structure formed as a result of intermolecular C–H···O, C–H···F, and weak F···F interactions.

Experimental Section

Reagents and General Procedures: Solvents and other general reagents used in this work were purified according to standard procedures. The following chemicals were purchased and used as such without further purification: $(n\mathrm{Bu_3Sn})_2\mathrm{O}$, $[n\mathrm{Bu_2SnO}]_n$, $\mathrm{R_fTol–CO_2H}$ (all from Aldrich, USA).

Instrumentation: Melting points were recorded using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out with a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^{1}H, ^{19}F and ^{119}Sn NMR spectra were recorded in $\mathrm{CDCl_3}$ solutions with a JEOL JNM Lambda spectrometer operating at 400.0, 376.0, and 150.0 MHz respectively. The chemical shifts are referenced with respect to tetramethylsilane (for ^{1}H), $\mathrm{CFCl_3}$ (for ^{19}F) and tetramethyltin (for ^{119}Sn). All the ^{119}Sn NMR spectra were recorded under broadband decoupled conditions.

$[n\mathrm{Bu_3SnO_2C–R_fTol}]_n$ (1): A mixture of $[n\mathrm{Bu_3Sn}]_2\mathrm{O}$ (0.36 g, 0.60 mmol) and $\mathrm{R_fTol–CO_2H}$ (0.23 g, 1.20 mmol) in toluene (60 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The reaction mixture was filtered and evaporated to afford the corresponding product as viscous oil. Yield: 0.56 g (96.6 %). $\mathrm{C_{20}H_{31}O_2F_3Sn}$: calcd. C 50.13, H 6.52 %; found: C 49.79, H 6.18 %. **^{1}H NMR** (ppm): δ = 0.75 (t, J = 7.21 Hz, 9 H, *n*-butyl $\mathrm{C}H_3$), 1.21–1.69 (m, 18 H, *n*-butyl $\mathrm{C}H_2$), 7.65 (br., 2 H, aromatic C*H*), 8.09 (br., 2 H, aromatic C*H*). **^{19}F NMR** (ppm): δ = –69 (s). **^{119}Sn NMR** (ppm): δ = +63 (s).

$[\{n\mathrm{Bu_2SnO_2C–R_fTol}\}_2\mathrm{O}]_2$ (2): Three synthetic procedures were utilized for the preparation of **2**.

Method A: Colorless block shaped crystals were obtained from **1** (0.56 g, 1.17 mmol) (viscous oil) when kept undisturbed in open air for a period of 8 d and are identified as **2** by single-crystal X-ray analysis. Yield: 0.21 g (40.7 %, isolated crystals).

Method B: A mixture of $[n\mathrm{Bu_3Sn}]_2\mathrm{O}$ (0.72 g, 1.2 mmol) and $\mathrm{R_fTol–CO_2H}$ (0.46 g, 2.4 mmol) was taken in a mixture of solvents toluene (20 mL) and acetonitrile (40 mL). To the mixture was added $\mathrm{H_2O}$ (0.5 mL) and stirred at room temperature for 3 d. The reaction mixture was filtered, the filtrate stripped of the solvent and the residue obtained was identified and characterized as **2**. Yield: 0.86 g (83.3 %).

Method C: A mixture of $[n\mathrm{Bu_2SnO}]_n$ (0.50 g, 2.00 mmol) and $\mathrm{R_fTol–CO_2H}$ (0.38 g, 2.0 mmol) in toluene (60 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The reaction mixture was filtered, the filtrate stripped of the solvent and the residue obtained was identified and characterized as **2**. Yield: 0.80 g (93.1 %).

M.p.: 155 °C. $\mathrm{C_{64}H_{88}O_{10}F_{12}Sn_4}$: calcd. C 44.69; H 5.16 %; found: C, 44.41; H, 5.30 %. **^{1}H NMR** (ppm): δ = 0.81 (t, J = 7.31 Hz, 24 H, *n*-butyl $\mathrm{C}H_3$), 1.35–1.66 (m, 48 H, *n*-butyl $\mathrm{C}H_2$'s), 7.81 (m, 16 H, aromatic C*H*). **^{19}F NMR** (ppm): δ = –67 (s). **^{119}Sn NMR** (ppm): δ = –254 (s), –272 (s). Colorless crystals were obtained from slow diffusion of diethyl ether into the dichloromethane solution of **2**.

X-ray Crystallography: Suitable crystals for single-crystal X-ray diffractions were loaded with a Bruker AXS Smart Apex CCD diffractometer. SMART software package (version 5.628) was used for collecting data frames, SAINT software package (version 6.45) for integration of the intensity and scaling and SADABS was used for absorption correction. The structure was solved and refined by full-matrix least-squares on F^2 using SHELXTL software package.[12] Non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms with occupancy $>$ 0.5 were included in idealized positions and their positions were refined isotropically by a riding model. Figure 2 and Figure 3 and its bonding parameters were obtained from DIAMOND 3.1 software package.[13]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-974962 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Crystallographic Data for 2 : Empirical formula $\mathrm{C_{64}H_{88}O_{10}F_{12}Sn_4}$; Size $0.2\times0.2\times0.1$ mm^3; M_w = 1720.10 g; triclinic; $P\bar{1}$; a = 11.083(5) Å; b = 11.871(5) Å; c = 14.229(5) Å; α = 84.706(5)°; β = 80.842(5)°; γ = 69.376(5)°; V = 1728.4(12) Å^3; Z = 2; T = 153(2) K; θ range: 4.13 to 25.02°; 9119 reflections collected, 5997 independent reflections (R_{int} = 0.0193); R_1 = 0.0332, wR_2 = 0.0751 [for $I > 2\sigma(I)$]; R_1 = 0.0395, wR_2 = 0.0779 (for all data); GOF = 1.030; maximum and minimum electron densities = 1.191 and –0.662 e·Å^{-3} respectively.

Supporting Information (see footnote on the first page of this article): Crystallographic Information File (CIF) and bond lengths, bond angles table for compound **2**. This materials are available free of charge via the Internet at http://pubs.acs.org.

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Ambient Temperature Sn–C Bond Cleavage Reaction Involving the Sn-*n*-butyl Group. Weak F···F Interactions in the Solid State Structure of $[\{n\mathrm{Bu_2SnO_2C{-}C_6H_4\text{-}4\text{-}CF_3}\}_2\mathrm{O}]_2$