$\{[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6](F_3CSO_3)_2\}$: A New Dodecanuclear Organostannoxane

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The new dodecanuclear organostannoxane $\{[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6](F_3CSO_3)_2\}$ (**2**) has been isolated as single crystals from the reaction of trifluoromethanesulfonic acid (F_3CSO_3H) with the decanuclear dibenzyltin(IV)-oxo cluster, $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**), in $[D_3]$acetonitrile, at room temperature. Compound **2** was structurally characterized by X-ray diffraction analysis, multinuclear NMR and IR spectroscopy, mass spectrometry, and thermogravimetry. The structure of **2** can be described as a *football cage* framework containing twelve tin atoms, exhibiting two distinct coordination geometries, penta- and hexacoordinated respectively, and linked together through μ_3-O and μ-OH ligands. Resulting from Sn–C bond cleavage, all tin atoms are only connected to one benzyl ligand. Furthermore, two of the three oxygen atoms of each trifluoromethanesulfonate counteranions are involved in hydrogen bonding interactions with bridging μ-OH groups of two distinct Sn_{12} cations leading to the propagation of a two-dimensional polymeric network.

Key words: Polyhydroxyorganotin(IV) Cluster, Sn-O-Sn Framework, Triflate, Cleavage Reactions, Crystal Structure

Introduction

In the past, numerous examples of organotin(IV) trifluoromethanesulfonate derivatives have been prepared and structurally characterized by single-crystal X-ray analysis. In 2005, J. Beckmann reviewed the state of the art in this domain [1]. In general, organotin triflates are obtained by reaction of organotin oxides with F_3CSO_3H (TfOH) [2], or alternatively from organotin chlorides ($R_{(4-x)}SnCl_x$) with AgO_3SCF_3 [3]. The resulting structures highlight that $F_3CSO_3^-$ can be ionic or non-ionic, with different coordination modes to tin atoms which can be defined as mono-, bi- and tridentate as well as terminal, *pseudo*-terminal, and bridging [4]. In addition to the structural interest, organotin(IV) trifluoromethanesulfonate complexes are active in homogeneous catalysis as Lewis acids for organic reactions, such as the Mukaiyama aldol reaction [5], the Robinson annulation [6], the acetylation of alcohols [7], and the transesterification of dimethyl carbonate with phenol [8].

Recently, we reported the synthesis of the decanuclear dibenzyltin(IV)-oxo cluster $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**) prepared from $(PhCH_2)_2SnO$ and dimethyl carbonate under sealed vial conditions [9]. The study of the reactivity of **1**

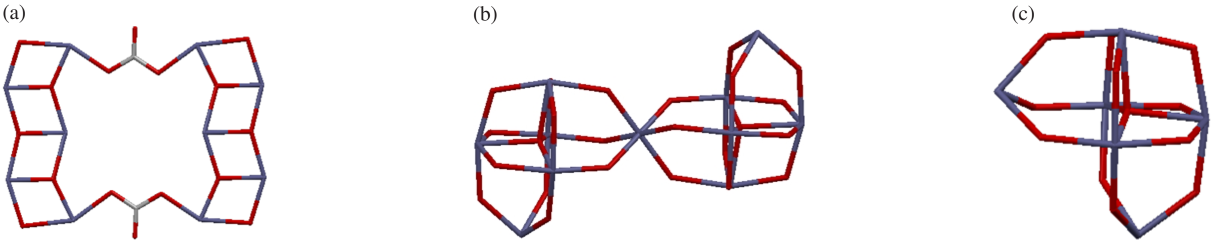

Fig. 1. Examples of shapes previously reported for polyhydroxybenzyltin(IV)-oxo clusters: a) $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**); b) $[(C_7H_7Sn)_6(\mu_4\text{-}O)(\mu\text{-}OH)_{11}(H_2O)_4](OTf)_5$; c) $\{Sn(\mu\text{-}OH)_6[(C_7H_7Sn)_{10}(\mu_4\text{-}O)_2(\mu\text{-}OH)_{16}(H_2O)_2(OTf)_2]\}(OTf)_6$ [9].

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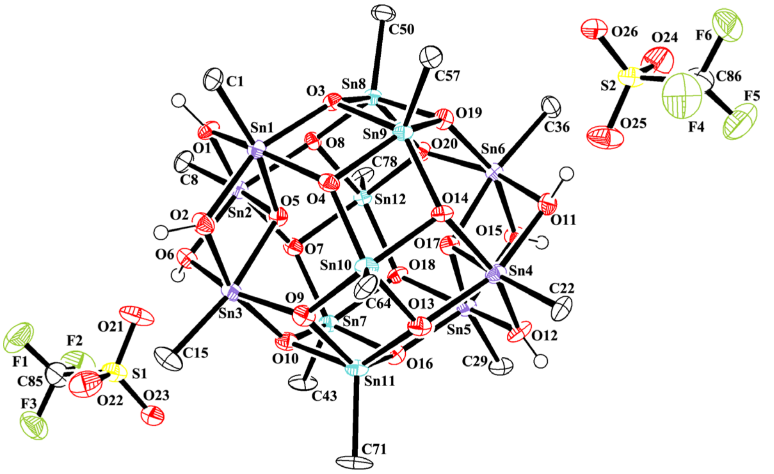

Fig. 2 (color online). ORTEP view of the molecular structure of $\{[(\mathrm{PhCH_2Sn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6](\mathrm{F_3CSO_3})_2\}$ (**2**) with crystallographic numbering scheme (hydrogen atoms, except for OH groups, are omitted for clarity, and only the methylene carbon atoms of the benzyl ligands are shown) (Sn_{sp} light blue, Sn_{oct}, violet, O red, C grey, F green, S yellow). Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Sn1–O1 2.097(5), Sn1–O2 2.106(5), Sn1–O3 2.119(4), Sn1–O4 2.111(5), Sn1–O5 2.087(5), Sn1–C1 2.11(5), Sn8–O3 2.022(4), Sn8–O8 2.032(4), Sn8–O19 2.101(4), Sn8–O20 2.089(4), Sn8–C50 2.147(7); O1–Sn1–O2 95.7(2), O1–Sn1–O3 92.9(2), O1–Sn1–O4 159.1(2), O1–Sn1–O5 74.9(2), O1–Sn1–C1 93.2(11), O2–Sn1–O3 158.7(2), O2–Sn1–O4 89.3(2), O4–Sn1–O3 76.1(2), O5–Sn1–C1 165.8(11), O5–Sn1–O2 75.1(2), O5–Sn1–O3 88.5(2), O5–Sn1–O4 87.0(2), O3–Sn8–O8 97.6(2), O3–Sn8–O19 77.5(2), O3–Sn8–O20 135.8(2), O3–Sn8–C50 116.9(2), O8–Sn8–O19 135.8(2), O8–Sn8–O20 77.3(2), O8–Sn8–C50 109.7(2), O19–Sn8–C50 111.5(2), O20–Sn8–O19 76.9(2), O20–Sn8–C50 105.9(2).

upon successive additions of trifluoromethanesulfonic acid (TfOH) led to the isolation and structural characterization of two novel ionic monobenzyltin(IV) trifluoromethanesulfonate clusters exhibiting unprecedented $\mathrm{Sn_6}$ and $\mathrm{Sn_{11}}$ frameworks (Fig. 1).

Encouraged by previous NMR $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ data which showed the *in situ* formation of additional intermediates, we have continued our investigations of this reaction, in a quest for new benzyltin(IV) triflate species. We describe herein the isolation as well as the solution and solid-state structural characterization of a novel polyhydroxyorganotin(IV) cluster, $\{[(\mathrm{PhCH_2Sn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6](\mathrm{F_3CSO_3})_2\}$ (**2**) which is a new example of the amazing *football cage* $\mathrm{Sn_{12}}$ skeleton.

Results and Discussion

When an acetonitrile suspension of $[(\mathrm{PhCH_2})_2\text{-}\mathrm{SnO}]_6\{[(\mathrm{PhCH_2})_2\mathrm{SnOH}]_2(\mathrm{CO_3})\}_2$ (**1**) is subjected to a large excess of trifluoromethanesulfonic acid (16 molar equivalents), the tin atoms undergo debenzylation reactions leading, after structural rearrangements, to the formation of $\mathrm{Sn_6}$ and $\mathrm{Sn_{11}}$ polyhydroxymonobenzyltin(IV)-oxo clusters. However, the monitoring of successive additions of $\mathrm{F_3CSO_3H}$ by *in situ* $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR spectroscopy revealed the presence of several supplementary resonances, not clearly identifying, but suggesting the formation of intermediates with penta- and hexacoordinated tin atoms [9]. Indeed, upon reexamining carefully the reaction of **1** with four molar equivalents of $\mathrm{F_3CSO_3H}$, in $[\mathrm{D_3}]$acetonitrile ($\mathrm{CD_3CN}$), we collected, after few days, colorless crystals which were characterized by elemental analysis, HRMS, TGA, IR and NMR spectroscopy, and single-crystal X-ray crystallography, and identified as $\{[(\mathrm{PhCH_2Sn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6](\mathrm{F_3CSO_3})_2\}$ (**2**).

The solid-state structure of **2** consists of a $[(\mathrm{PhCH_2Sn})_{12}(\mu_3\text{-O})_{14}(\mu\text{-OH})_6]$ dication surrounded by two uncoordinated $[\mathrm{F_3CSO_3}]$ anions. An ORTEP view of the cation, together with selected bonds lengths and angles, is shown in Fig. 2. All tin atoms of **2** are bound to only one benzyl ligand in an η^1 mode [Sn–C = 2.14(1) Å (mean)] as a result of partial Sn–C bond cleavage of **1**. The skeleton of the cation is built on a $\mathrm{Sn_{12}O_{20}}$ core which can be described as a *football cage* conformation. The twelve tin centers are linked through two types of oxygen atoms, μ_3-O and μ-OH, and thus display two distinct coordination geometries.

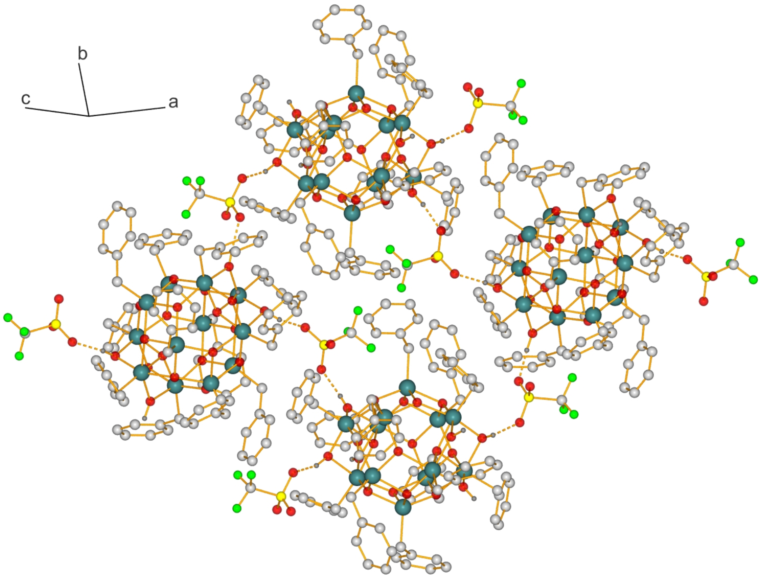

Fig. 3 (color online). Packing diagram for $\{[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6]\text{-}(F_3CSO_3)_2\}$ (**2**), highlighting the 2-D network based on cation-anion hydrogen bonding interactions (dashed lines) (Diamond presentation; Sn blue, O red, C grey, F green, S yellow).

The first six tin atoms (Sn1 to Sn6), located on the two poles of the cage, are coordinated to two bridging OH ligands and to three triply bridging oxygen atoms and exhibit a distorted octahedral coordination geometry (Sn_{oct}). The six other tin atoms (Sn7 to Sn12), positioned on the equator of the cage, are bound to four μ_3-O and reveal a distorted square-pyramidal environment (Sn_{sp}). Remarkably, this Sn-O-Sn arrangement results in the formation of an internal spherical cavity with long Sn···Sn interpole and equatorial distances of 6.85 (Sn1–Sn5) and 6.41 Å (Sn8–Sn11), respectively, which justify the term of *football cage*.

From a supramolecular point of view, the Sn_{12} cages are connected by the trifluoromethanesulfonate anions *via* a two-dimensional hydrogen bonding network. Four of the six bridging OH groups are involved in this interaction [O21···HO6 distance = 2.695(8) Å, O23···HO1 = 2.697(8) Å, O25···HO11 = 2.67(1) Å, O26···HO12 = 2.714(7) Å]. Interestingly, it appears that the third hydroxy group of each pole (O2 and O15, respectively) remains unattainable owing to the steric hindrance of the two benzyl ligands located nearby which prevents any weak interaction of this type. A Diamond view is depicted in Fig. 3.

The IR (ATR) spectrum of **2** revealed a broad absorption centered at 3227 cm^{-1} as well as a weak band at 3609 cm^{-1} which are attributed to OH groups, hydrogen-bonded and free, respectively. Characteristic bands of trifluoromethanesulfonate ligands, in particular $\nu(CF_3)$ and $\nu(SO_3)$, are observed in the stretching region between 1000 and 1300 cm^{-1} [10] while the intense bands located at 1599, 1492, 1453, 756, and 695 cm^{-1} correspond to the benzyl ligands coordinated to tin atoms. Despite the low solubility, the solution $^{119}Sn\{^1H\}$ spectrum of **2** in [D_3]acetonitrile, at 338 K, displays two sharp resonances centered at $\delta = -327.4$ and -514.0 ppm, attributed to the five- and six-coordinate tin atoms, Sn_{sp} and Sn_{oct}, respectively. This observation corroborates the solid-state structure and suggests that the framework of the $[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6]$ dication is preserved in solution. Furthermore, both signals exhibit weak satellite peaks which can be assigned to tin-tin couplings ($^2J\,^{119}Sn\text{-}O\text{-}^{119,117}Sn$) (Fig. 4). The ^{19}F NMR spectrum revealed only one singlet at -79.14 ppm corresponding to CF_3 groups of trifluoromethanesulfonate anions, while the ^1H and $^{13}C\{^1H\}$ NMR spectra distinguished between two sets of signals for the two types of benzyl ligands coordinated to Sn_{sp} and Sn_{oct} atoms. The ESI mass spectrometric analysis of **2** (positive mode) confirms the retention of polynuclear structures displaying several isotope cluster patterns with the most intense one corresponding to $[M]^{2+}$ detected at a mass *m/z* = M/2 (base peak). The thermal stability of **2** was investigated by thermogravimetric (TG) techniques. As shown in Fig. 5, the title compound is stable up to 280 °C and then undergoes three major weight-loss steps initiating at 290 °C (a, 13.43 %), 345 °C (b, 9.60 %), and 700 °C (c, 18.20 %).

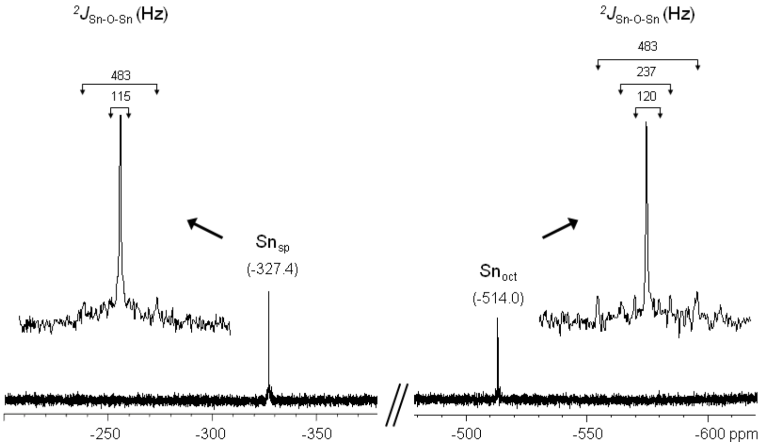

Fig. 4. $^{119}Sn\{^1H\}$ NMR spectrum of **2** in CD_3CN at 338.5 K.

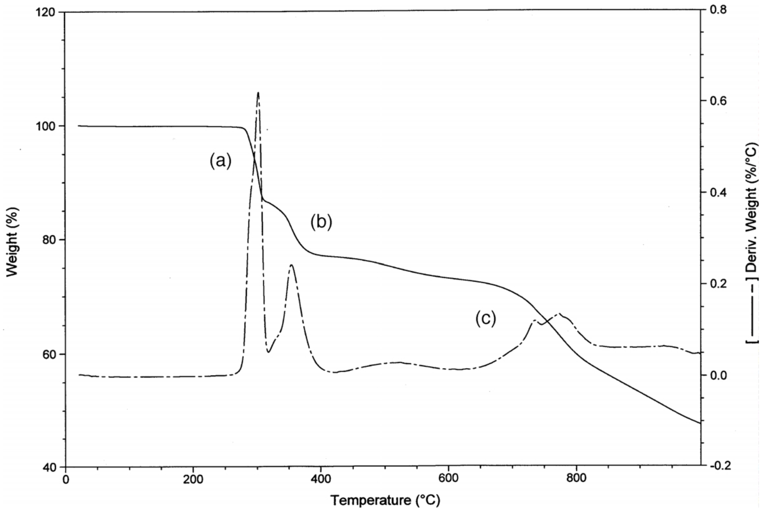

Fig. 5. TG-DTG analyses of **2** at a heating rate of 5 °C min^{-1} under nitrogen.

Fascinatingly, organotin compounds with Sn–O bonds have a large diversity of solid-state structures. Pioneering work in this field dates back to the 1980's and is attributable to Holmes and Chandrasekhar [11]. Since then, a greater variety of shapes has already been identified including prismane, butterfly, ladder, O- and S-capped cluster, drum, cube, double cube, football cage, crown, extended cage, and coordination polymer types [12]. Dodecanuclear organostannoxanes, based on Sn-O-Sn frameworks, have several times been mentioned in the literature and appear to adopt different types of conformations which are described by the authors as triple-ladder [13], cuboctahedron [14], flattened cluster [15], ball [16], extended cage [17], and football cage types [18]. This last architecture pattern is the most frequently depicted one and can be compared with the $[YM_{12}O_{40}]^{n-}$ Keggin structures reported for transition metal polyoxometallates (M = Mo or W; Y is a tetrahedral template) [19]. To this date, eleven crystallographic reports of the type $[(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6][X]$ presenting a football cage framework have been registered in the Cambridge Structural Database: R = *n*-Bu, X = Cl [18a], OH [18b], 4-$CH_3C_6H_4SO_3$ [18c–d], $H_2CHC(O)NHC(CH_3)_3CH_2SO_3$ [18e], $C_6H_4SO_3$, and 2,5-$Me_2C_6H_3SO_3$ [18f]; R = *i*-Pr, X = Cl [18g], $[(i\text{-}PrSn)_4(MoO_4)_{40}(OH)_3]_2$ [18h]; R = Me_3SiCH_2, X = Cl [18i]; R = $PhCH_2$, X = $\{[(PhCH_2)_2Sn]_6(\mu\text{-}3,5\text{-}pyrazoledicarboxylate)_4(\mu\text{-}OH)_2\}$ [18j]. In the past and still recently, these polynuclear entities have aroused a great interest from a structural point of view, and were intensively studied by solution and solid-state NMR spectroscopy [20], and also used as precursors for hybrid materials [18e] and as catalysts [21]. The isolation of $\{[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6](F_3CSO_3)_2\}$ (**2**) has provided a new example of this remarkable class of compounds and is to our knowledge only the second case reported in the benzyl series. Further work is in progress in our laboratory, trying in particular to understand the structural interrelationship connecting **2** to its decanuclear precursor $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**), as well as to its Sn_6 and Sn_{11} descendants.

Experimental Section

All manipulations were carried out by using standard Schlenk techniques [22], sealed vials [23] and 5 mm NMR tubes. The organic solvents were refluxed over appropriate desiccants, distilled and saturated with argon prior to use. Chemicals were purchased from Aldrich and Acros Organics. The starting compound $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**) was synthesized from $(PhCH_2)_2SnO$ according to a published method [9]. The standard NMR spectra were recorded at 295 and 338 K in CD_3CN on Bruker Avance 300 and II 600 spectrometers. ^1H and ^{13}C chemical shifts (δ, ppm) were determined from the residual solvent signal ($C\mathit{H}Cl_3$ δ = 7.24, $\mathit{C}DCl_3$ δ = 77.00). $^{119}Sn\{^1H\}$ and ^{19}F chemical shifts (δ, ppm) are reported downfield from $(CH_3)_4Sn$ and trifluoromethylbenzene, respectively, used as internal standards. IR spectra were recorded on a Bruker Vector 22 instrument equipped with a Specac Golden Gate™ ATR device. The ESI mass spectrum was obtained on a Bruker microOTOF-Q instrument using an acetonitrile mobile phase. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA Q500 thermoanalyzer using aluminum pans. Samples were heated from r. t. to 1000 °C at a rate of 5 °C min^{-1} under flowing nitrogen gas. The gas flow rate at the sample was 60 mL min^{-1}, while the balance flow rate was 40 mL min^{-1}. Weight loss percentages and onset temperatures were determined using the TA Universal Analysis 2000 software dedicated to the instrument. Elemental analyses were performed at the Institut de Chimie Moléculaire, Université de Bourgogne, Dijon.

Synthesis of $\{[(PhCH_2Sn)_{12}(\mu_3\text{-}O)_{14}(\mu\text{-}OH)_6](F_3CSO_3)_2\}$ *(2)*

Triflic acid (10.9 μL, 0.124 mmol) was added to $[(PhCH_2)_2SnO]_6\{[(PhCH_2)_2SnOH]_2(CO_3)\}_2$ (**1**) (0.102 g, 0.031 mmol) suspended in CD_3CN (0.5 mL) and led rapidly to a complete dissolution of the starting tin complex. After exposure to air for few days at r. t., suitable colorless single crystals were grown from the clear solution, characterized finally as **2** (yield = 0.030 g, 31 %). – IR: ν = 3609 (OH, free), 3227 (OH, H-bonded), 3059 (C-H), 3026 (C-H), 1648, 1599 (C=C), 1492, 1453, 1407, 1279 (SO_3), 1237 (CF_3), 1224, 1170 (CF_3), 1027 (SO_3), 909, 819, 756, 695 (C=C-H), 679, 610 (C-S), 579, 533 cm^{-1}. – ^1H NMR (600.132 MHz, CD_3CN, 338 K): δ = 2.39 (s, $SnC\mathit{H_2}Ph$, 12H), 2.52 (s, $SnC\mathit{H_2}Ph$, 12H), 6.80 – 7.40 (m, $SnCH_2\mathit{Ph}$, 60H). – ^{19}F NMR (282.404 MHz, 13 MHz, CD_3CN, 298 K): $\delta = -79.14$ (s, $\mathit{F_3}CSO_3^-$). – $^{13}C\{^1H\}$ NMR (150.902 MHz, CD_3CN, 338 K): δ = 139.2 (C_{ipso} $SnCH_2\mathit{Ph}$), 136.1 (C_{ipso} $SnCH_2\mathit{Ph}$), 130.4 ($C_{o/m}$ $SnCH_2\mathit{Ph}$), 130.1 ($C_{o/m}$ $SnCH_2\mathit{Ph}$), 130.0 ($C_{o/m}$ $SnCH_2\mathit{Ph}$), 129.9 ($C_{o/m}$ $SnCH_2\mathit{Ph}$), 127.6 (C_p $SnCH_2\mathit{Ph}$), 126.55 (C_p $SnCH_2\mathit{Ph}$), 35.7 ($Sn\mathit{C}H_2Ph$), 29.4 ($Sn\mathit{C}H_2Ph$). – $^{119}Sn\{^1H\}$ NMR (111.920 MHz, CD_3CN, 296.5 K): $\delta = -325.9$ (s, $6Sn_{sp}$), -512.8 (s, $6Sn_{oct}$). – $^{119}Sn\{^1H\}$ NMR (223.792 MHz, CD_3CN, 338.5 K): $\delta = -327.4$ (s, $6Sn_{sp}$, $^2J^{119}Sn\text{-}O\text{-}^{119,117}Sn$ = 483, 115 Hz), -514.0 (s, $6Sn_{oct}$, $^2J^{119}Sn\text{-}O\text{-}^{119,117}Sn$ = 483, 237, 120 Hz). – HRMS ((+)-ESI): *m/z* = 1428.7211 (calcd. 1428.7139 for $C_{42}H_{45}O_{10}Sn_6$, $[M]^{2+}$ at a mass *m/z* = M/2), 2857.4431 (calcd. 2857.4284 for $C_{84}H_{90}O_{20}Sn_{12}$, $[M]^+$), 2896.4514 (calcd. 2896.3921 for $C_{84}H_{90}O_{20}Sn_{12}K$, $[M+K]^+$), 3006.3896 (calcd. 3006.3804 for $C_{85}H_{90}F_3O_{23}SSn_{12}$, $[M+OTf]^+$). – $C_{86}H_{90}F_6O_{26}S_2Sn_{12}\cdot CH_3CN$ (3183.08): calcd. C 33.20, H 2.94, N 0.44, S 2.01; found C 33.44, H 3.01, N 0.27, S 2.97.

Crystal structure determination

Formula $C_{84}H_{90}O_{20}Sn_{12}\cdot 2(CF_3SO_3)$, M = 3141.98, colorless crystal: $0.2 \times 0.08 \times 0.08$ mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 20.8304(3), b = 16.4676(2), c = 32.5296(4) Å, β = 118.561(1)°, V = 9800.4(2) $Å^3$, Z = 4, D_{calcd} = 2.13 g cm^{-3}, μ = 3.1 mm^{-1}, Nonius Kappa CCD diffractometer, λ = 0.71073 Å, T = 115 K, mixture of ϕ rotations and ω scans, 41567 reflections collected (index ranges: h: −27 / 26; k: −21 / 21; l: −42 / 42), $((\sin\theta)/\lambda_{max}$ = 0.65 $Å^{-1}$, 22360 independent (R_{int} = 0.0435) and 16789 observed reflections [$I \geq 2\,\sigma(I)$], 1250 refined parameters, 174 restraints, R indices for observed reflections: R_1 = 0.0510, wR_2 = 0.0852, R indices for all data: R_1 = 0.0784, wR_2 = 0.0955, goodness-of-fit = 1.174, maximum residual electron density 0.87 / −0.91 e $Å^{-3}$. The structure was solved using Direct Methods (SIR 92) [24] and refined with full-matrix least-squares methods based on F^2 (SHELX-97) [25] with the aid of the WINGX program [26]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined as riding atoms. Two benzyl groups (C1–C7 and C64–C70 were found disordered over two positions with occupation factors converged to 0.60 : 0.40). Programs used for the representation of the molecular and crystal structures: ORTEP [27], DIAMOND [28].

CCDC 800927 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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