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# Oligomethylene-Bridged Dinuclear Triorganotin Triflates and Diphenylphosphinates. Ion Pairing in the Solid State and Electrolytic Dissociation in Solution of $[Ph_2Sn(CH_2)_nSnPh_2X](O_3SCF_3)$ ($X = OH, O_2PPh_2$; $n = 1-3$)

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The condensation of $[Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2]$ (**1**−**3**; $n = 1-3$) with $HO_3SCF_3$ and $HO_2PPh_2$ provided $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**4**−**6**; $n = 1-3$) and $[Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (**10**−**12**; $n = 1-3$), respectively. The reaction of $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**4**−**6**; $n = 1-3$) with $HO_2PPh_2$ and $NaO_2PPh_2$ gave rise to the formation of $[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)$ (**7**−**9**; $n = 1-3$) and $[Ph_2(OH)Sn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (**13**−**15**; $n = 1-3$), respectively. In the solid state, compounds **4**−**9** comprise ion pairs of cationic cyclo-$[Ph_2SnCH_2SnPh_2(OH)]_2^{2+}$, cyclo-$[Ph_2Sn(CH_2)_nSnPh_2(OH)]^+$ ($n$ = 2, 3), and cyclo-$[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)]^+$ ($n = 1-3$) and triflate anions. In MeCN, the eight-membered-ring system cyclo-$[Ph_2SnCH_2SnPh_2(OH)]_2^{2+}$ appears to be in equilibrium with the four-membered-ring system cyclo-$[Ph_2SnCH_2SnPh_2(OH)]^+$. In contrast, compounds **10**−**15** show no ionic character. Compounds **1**−**15** were characterized by multinuclear NMR spectroscopy in solution and in the solid state, IR spectroscopy, conductivity measurements, electrospray mass spectrometry, osmometric molecular weight determinations, and X-ray crystallography (**4**, **5**, **7**, and **12**).

## Introduction

Triorganotin cations stabilized by neutral donor solvents and ligands, $[R_3SnL_n]^+$ (L = neutral molecule; $n$ = 1, 2; R = alkyl, aryl), and free triorganotin cations ("stannylium cations") $[R_3Sn]^+$ have attracted considerable attention in the last 80 years.[1,2] In 1923, Kraus and Callis reported that solutions of $Me_3SnCl$ in ethanol show substantial electric conductivities, attributable to the electrolytic dissociation of $Me_3SnCl$ into $[Me_3Sn(EtOH)_2]^+$ cations and chloride anions.[3] In the early 1960s, Tobias provided the first spectroscopic evidence for the existence of hydrated $[R_3Sn(H_2O)_2]^+$ (R = alkyl, aryl) in aqueous media.[4] Shortly thereafter, Wada and Okawara isolated the first hydrated triorganotin cation, $[Me_3Sn(H_2O)_2](BPh_4)$,[5] in the solid state; however, it was not until the 1980s that Davies et al. and Blaschette et al. reported the first fully characterized analogues, $[Bu_3Sn(H_2O)_2][C_5(CO_2Me)_5]$[6] and $[Me_3Sn(H_2O)_2][N(SO_2Me)_2]$.[7] In the late 1960s, Kitching and Kumar Das described a number of trimethyltin cations $[Me_3SnL_2](BPh_4)$ stabilized by solvents and neutral ligands, such as L = DMSO, DMF, DMA, $Ph_3PO$, and $Ph_3AsO$.[8] More recently, similar complexes were prepared with MeCN and $NH_3$, e.g. $[c\text{-}Hex_3Sn(MeCN)_2](SbF_6)$,[9] $[t\text{-}Bu_3Sn(MeCN)_2](BPh_4)$,[10] and $[Me_3Sn(NH_3)_2][N(SO_2Me)_2]$,[11] and fully characterized. Triorganotin cations having intramolecularly coordinating donor ("built-in") ligands, e.g. $\{[Me_2N(CH_2)_3]_2SnPh\}X$ (X = Br, I, $PF_6$) and $[1,5\text{-}(Me_2NCH_2)_2C_6H_3SnBu_2]Br$, were also reported.[12]

Somewhat disguised cases of triorganotin cations stabilized by neutral ligands are the di- and trinuclear species $[Et_3SnOH(SnEt_3)][B(C_6F_5)_4]$[13] and $[Me_3SnOH(SnMe_3)HOSnMe_3]X$ (X = I, Br),[14] which may be re-

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(2) For the preparation and full characterization of the first free triorganotin cation, $[R_3Sn][B(C_6F_5)_4]$ (R = 2,4,6-triisopropylphenyl), see: (a) Lambert, J. B.; Lin, L.; Keinan, S.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 6022. For closely related work, see: (b) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. (c) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253. (d) Lambert, J. B.; Lin, L. *J. Org. Chem.* **2001**, *66*, 8537.

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10.1021/om049773c CCC: $27.50

garded as the complexes $[R_3SnL_n]^+$ with one ($n = 1$) or two ($n = 2$) neutral ligands L = $R_3SnOH$ (R = Me, Et).

We now describe a number of oligomethylene-bridged dinuclear triorganotin triflates, $[Ph_2Sn(CH_2)_nSnPh_2X](O_3SCF_3)$ (X = OH, $O_2PPh_2$; $n = 1-3$), which comprise ion pairs of oligomethylene-bridged dinuclear triorganotin cations and triflate anions in the solid state that undergo electrolytic dissociation in MeCN. Also reported are oligomethylene-bridged dinuclear triorganotin diphenylphosphinates, $[Ph_2XSn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (X = OH, $O_2PPh_2$; $n = 1-3$), which show no evidence of ionic character.

## Results and Discussion

The starting materials $[Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2]$ (**1**−**3**; $n = 1-3$) were prepared by base hydrolysis of the corresponding species $[Ph_2(I)Sn(CH_2)_nSn(I)Ph_2]$ ($n = 1-3$), similar to a procedure reported for compound **1** by Gielen and Jurkschat (eq 1).[15] Compounds **1**−**3** were

$$Ph_2(I)Sn(CH_2)_nSn(I)Ph_2 \xrightarrow[-2NaI]{2NaOH} Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2 \quad (1)$$
$$\mathbf{1-3};\ n = 1-3$$

obtained as amorphous solids that are insoluble in most solvents at room temperature and condense when heated.[15] Compounds **1**−**3** show sharp IR bands (KBr) near 3600 $cm^{-1}$,[15] which are assigned to OH stretching vibrations of hydroxy groups not involved in hydrogen bonding. The $^{119}Sn$ MAS NMR spectra of **1**−**3** reveal signals at $\delta_{iso}$ −177.0, −187.3, −194.5, and −205.5 for **1** (integral ratio 37:48:10:5), at −224.0 and −238.7 for **2** (integral ratio 90:10), and at −189.9, −196.1, and −239.8 for **3** (integral ratio 13:14:73), consistent with the presence of different oligomers possessing pentacoordinated tin atoms.

**$[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (4−6; $n = 1-3$).** The reaction of $[Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2]$ (**1** − **3**; $n = 1-3$) with 1 equiv of $HO_3SCF_3$ provided the crystalline, air-stable materials $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**4**−**6**; $n = 1-3$) in high yields (eq 2). Notably,

$$\underset{\mathbf{1-3};\ n = 1-3}{Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2} \xrightarrow[-H_2O]{HO_3SCF_3} [Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3) \quad (2)$$
$$\mathbf{4-6};\ n = 1-3$$

the same reaction with more than 1 equiv of $HO_3SCF_3$ led to cleavage of phenyl groups and afforded only ill-defined products.

The solid-state structures of **4** and **5**, established by X-ray crystallography, are shown in Figures 1 and 2; crystal data and selected bond parameters are collected in Tables 1−3. The structure of $[Ph_2SnCH_2SnPh_2(OH)](O_3SCF_3)$ (**4**) consists of a central eight-membered ring, cyclo-$[Ph_2SnCH_2SnPh_2(\mu\text{-}OH)]_2$, which lies across a crystallographic center of inversion. The Sn atoms are additionally coordinated by two bidentate triflate anions, giving rise to a tricyclic arrangement (Figure 1).

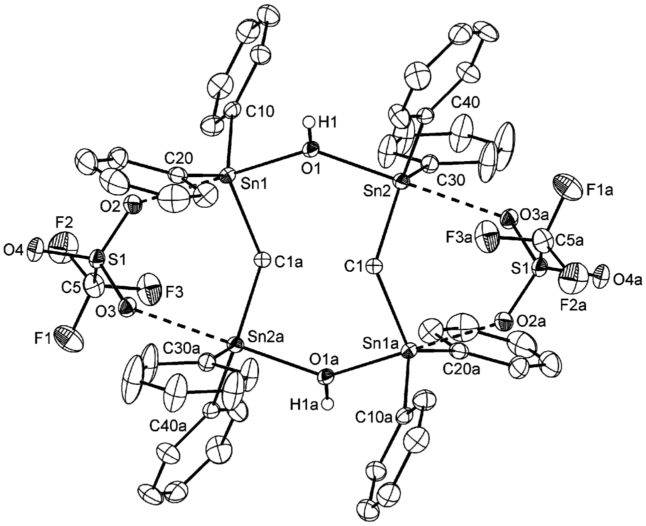

**Figure 1.** General view of **4** showing 20% probability displacement ellipsoids and the atom-numbering scheme (symmetry operation used to generate equivalent atoms: (a) $1 - x$, $1 - y$, $-z$).

The geometry of the two crystallographically independent Sn atoms features distorted trigonal bipyramids (geometrical goodness $\Delta\Sigma(\theta)$[16] 74.7 for Sn1 and 72.2 for Sn2), in which three carbon atoms occupy the equatorial plane and two oxygen atoms are situated in the axial positions. The distortion of the tin atoms is marked by two sets of distinctively different Sn−O bond distances at 2.152(2) and 2.443(2) Å for Sn1 and at 2.138(2) and 2.560(2) Å for Sn2, which originate from the strong coordination of the hydroxy group and the weak association of the triflate group. These differences result in Pauling bond orders (BOs)[17] of 0.61 and 0.24 for Sn1 (Σ(BO) 0.85) and 0.64 and 0.16 for Sn2 (Σ(BO) 0.80). The geometry of the Sn atoms (4 + 1 coordination) lies on the pathway between a tetrahedron and a trigonal bipyramid.[18] It is worthwhile comparing the different Sn−O bond lengths and Pauling bond orders of **4** with those of some reference compounds, namely the polymeric $Ph_3SnOH$ having pentacoordinated Sn atoms (Sn−O, 2.197(5)/2.255(5) Å; BO, 0.52/0.44, Σ(BO), 0.96),[19] the monomeric $Mes_3SnOH$ having tetracoordinated Sn atoms (Sn−O, 1.999(6) Å; BO, 1.00),[20] and the monomeric $[(Me_3Si)_2CH]_3SnO_3SCF_3$ (2.139(4) Å; BO, 0.64).[21] Thus, it appears that the coordination of the hydroxy groups in **4** resembles that in the polymeric $Ph_3SnOH$. The fact that the Sn−O bond orders associated with the coordination of the triflate group in **4** are small and that the sums of the Sn−O bond orders in **4** and $[(Me_3Si)_2CH]_3SnO_3SCF_3$[21] are considerably smaller than 1 may be attributed to the ionic character of these bonds. Accordingly, the structure of **4** may be interpreted in

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(17) Definition: $\log BO = -c(d - d_{st})$ with $c = 1.41$ and $d_{st} = 2.00$ Å. (a) Pauling L. *The Nature of the Chemical Bond,* 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7. (b) Zickgraf, A.; Beuter, M.; Kolb, U.; Dräger, M.; Tozer, R.; Dakternieks, D.; Jurkschat, K. *Inorg. Chim. Acta* **1998**, *275–276*, 203.

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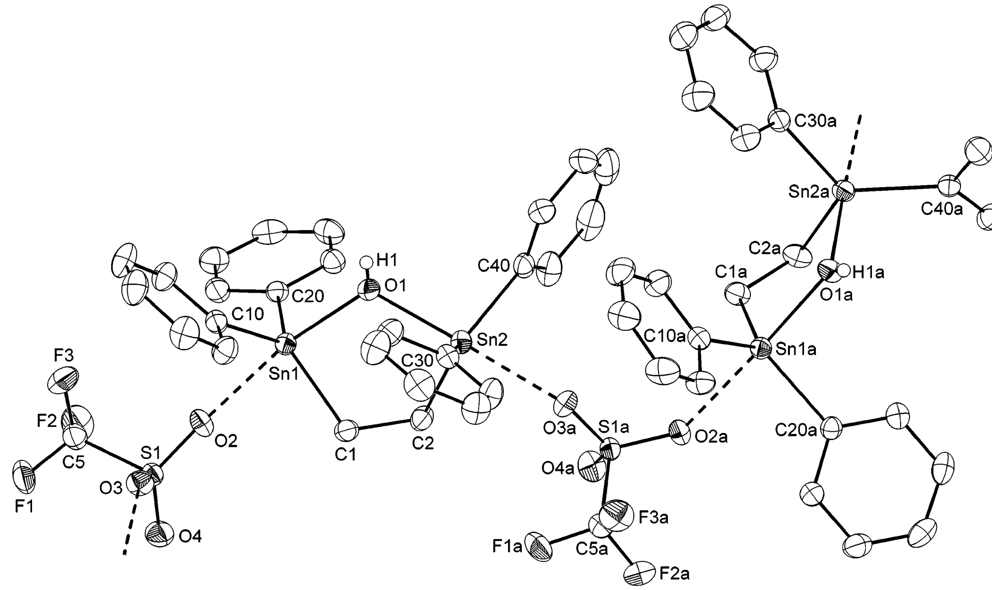

**Figure 2.** General view of **5** showing 20% probability displacement ellipsoids and the atom-numbering scheme (symmetry operation used to generate equivalent atoms: (a) $0.5 + x$, $0.5 - y$, $0.5 + z$).

**Table 1. Crystal Data and Structure Refinement Details for 4, 5, 7, and 12**

| | **4** | **5** | **7** | **12** |
|---|---|---|---|---|
| formula | $C_{26}H_{23}F_3O_4SSn_2$ | $C_{27}H_{25}F_3O_4SSn_2$ | $C_{38}H_{32}F_3O_5PSSn_2$ | $C_{51}H_{46}O_4P_2Sn_2$ |
| formula wt | 725.88 | 739.91 | 926.05 | 1022.20 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic |
| cryst size, mm | 0.15 × 0.30 × 0.40 | 0.10 × 0.10 × 0.35 | 0.30 × 0.40 × 0.40 | 0.10 × 0.10 × 0.14 |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 11.3508(7) | 10.7603(5) | 12.2152(7) | 9.7842(6) |
| $b$, Å | 14.2659(8) | 19.7598(9) | 20.2426(11) | 16.3885(11) |
| $c$, Å | 17.8781(10) | 13.2294(6) | 16.6242(9) | 28.9285(18) |
| $\alpha$, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 107.8260(10) | 94.8060(10) | 110.7180(10) | 96.1990(10) |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| $V$, Å$^3$ | 2756.0(3) | 2803.0(2) | 3844.8(4) | 4611.5(5) |
| $Z$ | 4 | 4 | 4 | 4 |
| $\rho_{calcd}$, Mg m$^{-3}$ | 1.749 | 1.753 | 1.600 | 1.472 |
| $T$, K | 293(2) | 293(2) | 293(2) | 293(2) |
| $\mu$, mm$^{-1}$ | 1.938 | 1.907 | 1.450 | 1.196 |
| $F(000)$ | 1416 | 1448 | 1832 | 2056 |
| $\theta$ range, deg | 1.86−27.52 | 1.86−25.00 | 1.65−27.52 | 1.42−25.00 |
| index ranges | $-14 \le h \le 14$ | $-13 \le h \le 13$ | $-15 \le h \le 14$ | $-11 \le h \le 11$ |
| | $-18 \le k \le 8$ | $-25 \le k \le 25$ | $-26 \le k \le 25$ | $-19 \le k \le 17$ |
| | $-22 \le l \le 23$ | $-16 \le l \le 17$ | $-15 \le l \le 21$ | $-31 \le l \le 34$ |
| no. of rflns collcd | 17 020 | 24 105 | 24 399 | 24 063 |
| completeness to $\theta_{max}$, % | 98.6 | 99.3 | 98.7 | 99.9 |
| no. of indep rflns/$R_{int}$ | 6265 | 6375 | 8728 | 8130 |
| no. of rflns obsd with ($I > 2\sigma(I)$) | 5877 | 5443 | 7433 | 6644 |
| no. of refined params | 330 | 338 | 451 | 532 |
| GOF ($F^2$) | 1.073 | 1.044 | 1.068 | 1.192 |
| R1($F$) ($I > 2\sigma(I)$) | 0.029 | 0.031 | 0.030 | 0.063 |
| wR2($F^2$) (all data) | 0.069 | 0.077 | 0.073 | 0.127 |
| $(\Delta/\sigma)_{max}$ | 0.0014(1) | <0.0001 | <0.0001 | <0.0001 |
| largest diff peak/hole, e Å$^{-3}$ | 0.563/−0.427 | 0.672/−0.274 | 0.798/−0.256 | 1.249 (near Sn)/−0.882 |

terms of ion pairing between a dicationic eight-membered ring, cyclo-$[Ph_2SnCH_2SnPh_2(\mu\text{-}OH)]_2^{2+}$, and two triflate anions. The dication cyclo-$[Ph_2SnCH_2SnPh_2(\mu\text{-}OH)]_2^{2+}$ may be regarded as a diprotonated form of the neutral parent ring, cyclo-$(Ph_2SnCH_2SnPh_2O)_2$, whose presence has been claimed on the basis of $^{119}$Sn NMR spectroscopy for solutions of partially condensed $[Ph_2(OH)SnCH_2Sn(OH)Ph_2]$ (**1**).[15] The hydroxy group of **4** is involved in weak hydrogen bonding to a triflate group of an adjacent molecule (hydrogen bond parameters (Å, deg): O1−H1, 0.691(28); H1···O4b, 2.296(28); O1···O4b, 2.915(3); O1−H1···O4, 150.0(33); symmetry operation labeled b is $1.5 - x$, $-0.5 + y$, $0.5 - z$).[22] In addition to the solvent-free modification of $[Ph_2SnCH_2SnPh_2(OH)](O_3SCF_3)$ (**4**), a pseudo-polymorph, namely the acetonitrile solvate **4**·MeCN, was investigated by X-ray crystallography.[23] Unlike the situation in c-$Hex_3Sn(MeCN)_2](SbF_6)$[9] and $[t\text{-}Bu_3Sn(MeCN)_2](BPh_4)$,[10] the MeCN is not coordinated to the Sn atoms but associated via hydrogen bonding to the hydroxy group. This is somewhat surprising, as the triflate anion is generally a rather weak

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[23] The structure of **4**·MeCN is presented in the Supporting Information.

**Table 2. Selected Bond Parameters (Å, deg) for 4**[a]

| | | | |
|---|---|---|---|
| Sn1−O1 | 2.152(2) | Sn1−O2 | 2.443(2) |
| Sn1−C1a | 2.136(3) | Sn1−C10 | 2.139(4) |
| Sn1−C20 | 2.129(3) | Sn2−O1 | 2.138(2) |
| Sn2−O3a | 2.560(2) | Sn2−C1 | 2.124(3) |
| Sn2−C30 | 2.123(4) | Sn2−C40 | 2.117(3) |
| O1−Sn1−O2 | 179.48(8) | O1−Sn1−C1a | 93.65(10) |
| O1−Sn1−C10 | 95.64(10) | O1−Sn1−C20 | 94.1(1) |
| O2−Sn1−C1a | 86.49(9) | O2−Sn1−C10 | 83.84(9) |
| O2−Sn1−C20 | 86.27(10) | C1a−Sn1−C10 | 109.13(11) |
| C1a−Sn1−C20 | 118.04(13) | C10−Sn1−C20 | 130.96(13) |
| O1−Sn2−O3a | 177.53(8) | O1−Sn2−C1 | 93.73(10) |
| O1−Sn2−C30 | 96.99(10) | O1−Sn2−C40 | 94.7(1) |
| O3a−Sn2−C1 | 85.58(9) | O3a−Sn2−C30 | 85.31(10) |
| O3a−Sn2−C40 | 83.45(10) | C1−Sn2−C30 | 126.40(12) |
| C1−Sn2−C40 | 114.72(11) | C30−Sn2−C40 | 116.45(13) |
| Sn1−O1−Sn2 | 139.74(11) | Sn1−C1a−Sn2a | 123.07(13) |

[a] Symmetry operation used to generate equivalent atoms: (a) $1 - x$, $1 - y$, $-z$.

**Table 3. Selected Bond Parameters (Å, deg) for 5**[a]

| | | | |
|---|---|---|---|
| Sn1−O1 | 2.130(3) | Sn1−O2 | 2.517(2) |
| Sn1−C1 | 2.126(3) | Sn1−C10 | 2.120(3) |
| Sn1−C20 | 2.133(3) | Sn2−O1 | 2.161(2) |
| Sn2−O3a | 2.428(2) | Sn2−C2 | 2.135(3) |
| Sn2−C30 | 2.136(3) | Sn2−C40 | 2.123(3) |
| O1−Sn1−O2 | 170.50(8) | O1−Sn1−C1 | 86.97(10) |
| O1−Sn1−C10 | 97.90(9) | O1−Sn1−C20 | 97.2(1) |
| O2−Sn1−C1 | 83.99(9) | O2−Sn1−C10 | 89.13(9) |
| O2−Sn1−C20 | 84.93(9) | C1−Sn1−C10 | 119.61(12) |
| C1−Sn1−C20 | 120.52(10) | C10−Sn1−C20 | 118.42(12) |
| O1−Sn2−O3a | 174.89(8) | O1−Sn2−C2 | 86.14(11) |
| O1−Sn2−C30 | 97.03(10) | O1−Sn2−C40 | 95.28(10) |
| O3a−Sn2−C2 | 90.09(10) | O3a−Sn2−C30 | 87.72(9) |
| O3a−Sn2−C40 | 83.76(9) | C2−Sn2−C30 | 116.00(11) |
| C2−Sn2−C40 | 121.72(10) | C30−Sn2−C40 | 121.53(12) |
| Sn1−O1−Sn2 | 118.58(11) | | |

[a] Symmetry operation used to generate equivalent atoms: (a) $0.5 + x$, $0.5 - y$, $0.5 + z$.

donor toward Sn, as seen in the organotin complexes $[t\text{-Bu}_2\text{Sn(OH)(H}_2\text{O)}]_2(\text{O}_3\text{SCF}_3)$,[24] $[\text{Me}_2\text{Sn(H}_2\text{O)}_2(\text{OPPh}_3)_2](\text{O}_3\text{SCF}_3)_2$,[25] and $[\text{Ph}_2\text{P(OSn}t\text{-Bu}_2)_2\text{O}\cdot t\text{-Bu}_2\text{Sn(OH)}_2](\text{O}_3\text{SCF}_3)$,[26] respectively. However, in **4**·MeCN the bidentate coordination mode of the triflate anion apparently outweighs the donor strength of MeCN.[27] On the basis of the close similarity with **4**, the solid-state structure of $[\text{Ph}_2\text{Sn(CH}_2)_2\text{SnPh}_2(\text{OH})](\text{O}_3\text{SCF}_3)$ (**5**) may be described as an alternating sequence of loosely associated five-membered cationic rings, cyclo-$[\text{Ph}_2\text{Sn(CH}_2)_2\text{SnPh}_2(\mu\text{-OH})]^+$, and bidentate triflate anions (Figure 2), whose symmetry translation gives rise to the formation of a coordination polymer (symmetry operation labeled a is $0.5 + x$, $0.5 - y$, $0.5 + z$). The geometry of the two crystallographically independent Sn atoms is again best described as 4 + 1 coordination (geometrical goodness $\Delta\Sigma(\theta)$[16] 76.1 for Sn1 and 80.8 for Sn2), in which the strongly coordinating hydroxy groups and the weakly associated triflate anions account for the distortion. The two sets of different axial Sn−O bond distances, at 2.130(3) and 2.517(2) Å for Sn1 and at 2.161(2) and 2.428(2) Å for Sn2, account for the Pauling bond orders[17] of 0.65 and 0.19 for Sn1 ($\Sigma$(BO) 0.84) and 0.59 and 0.25 for Sn2 ($\Sigma$(BO) 0.84).

**Table 4. Selected Solid-State $^{119}$Sn and $^{31}$P NMR Parameters of 4−12**[a]

| | $^{119}$Sn | | | | | | | $^{31}$P | |
|---|---|---|---|---|---|---|---|---|---|
| | $\delta_{iso}$ | integral | $\zeta$ | $\eta$ | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ | $\delta_{iso}$ | integral |
| **4** | −83.9 | 48 | −234 | 0.80 | 295 | 107 | −150 | | |
| | −137.8 | 52 | −252 | 0.25 | 295 | 232 | −114 | | |
| **5** | −120.4 | 55 | −271 | 0.40 | 310 | 202 | −151 | | |
| | −129.6 | 45 | −309 | 0.40 | 346 | 222 | −179 | | |
| **6** | −69.6 | 27 | −218 | 0.95 | 282 | 75 | −148 | | |
| | −74.3 | 31 | −218 | 0.95 | 287 | 80 | −144 | | |
| | −77.1 | 42 | −205 | 1.00 | 282 | 77 | −128 | | |
| **7** | −78.2 | 52 | −277 | 0.40 | 272 | 161 | −198 | 32.4 | 100 |
| | −149.4 | 48 | −300 | 0.45 | 367 | 232 | −151 | | |
| **8** | −82.1 | 54 | −254 | 0.75 | 304 | 114 | −172 | 32.9 | 100 |
| | −131.3 | 46 | −254 | 0.60 | 334 | 182 | −123 | | |
| **9** | −120.4 | 49 | −273 | 0.85 | 373 | 141 | −153 | 26.1 | 100 |
| | −138.8 | 51 | −233 | 0.85 | 354 | 156 | −94 | | |
| **10** | −193.1 | 49 | −359 | 0.45 | 453 | 292 | −166 | 25.1 | 50 |
| | −219.2 | 51 | −390 | 0.40 | 492 | 336 | −170 | 19.6 | 50 |
| **11** | −204.7 | 54 | −361 | 0.55 | 484 | 286 | −156 | 25.1 | 50 |
| | −240.1 | 46 | −355 | 0.45 | 497 | 338 | −115 | 19.6 | 50 |
| **12** | −215.5 | 100 | −354 | 0.60 | 499 | 286 | −139 | 20.0 | 100 |

[a] $\delta_{iso}$ (ppm) $= -\sigma_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, $\zeta$ (ppm) $= \sigma_{33} - \sigma_{iso}$, and $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$, where $\sigma_{11}$, $\sigma_{22}$, and $\sigma_{33}$ (ppm) are the principal tensor components of the shielding anisotropy (SA), sorted as follows: $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$.

$^{119}$Sn NMR spectroscopy provides a very sensitive tool for the elucidation of relative coordination numbers in organotin compounds, particularly of free and solvated triorganotin cations.[1,28] Compounds **4**−**6** were investigated by $^{119}$Sn MAS NMR spectroscopy, and the results are collected in Table 4. For compounds **4** and **5**, the number of signals is consistent with the number of crystallographically independent Sn sites. For compound **6**, three signals are found, which were tentatively attributed to the presence of more than one crystal form in the bulk material. The $^{119}$Sn MAS NMR chemical shifts for **4**−**6** cover a rather wide range, extending from $\delta_{iso}$ −69.6 to −137.8, and are essentially in good agreement with the 4 + 1 coordination geometry of the Sn atoms. For compound **4** the two signals differ considerably ($\delta_{iso}$ −83.9 and −137.8), which is probably a reflection of the different $\text{C}_{\text{Ph}}$−Sn−$\text{C}_{\text{Ph}}$ angles (C10−Sn1−C20, 130.96(13)°; C30−Sn2−C40, 116.45(13)°) and the additional intermolecular Sn1···O4b contact of 3.625(3) Å (symmetry operation labeled b is $1.5 - x$, $-0.5 + y$, $0.5 - z$), which increases the coordination number of Sn1 to 4 + 1 + 1. The isotropic chemical shifts were accompanied by sets of spinning sidebands indicative of large shielding anisotropies (SA), which were used to perform tensor analyses according to the method of Herzfeld and Berger (Table 4).[29] The magnitudes of the anisotropies ($\zeta$) of **4**−**6** fall in the relatively narrow range between 205 and 309 ppm. In contrast, the asymmetries ($\eta$) for **4**−**6** are between 0.25 and 1.00 and cover almost the whole defined range. The IR spectra (KBr) of **4**−**6** show reasonably sharp signals at 3587, 3564, and 3567 cm$^{-1}$, which are assigned to OH stretching vibrations. In view of the established molecular structures and the presence (**4**) and absence (**5**) of

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(24) Sakamoto, K.; Hamada, Y.; Akashi, H.; Orita, A.; Otera, J. *Organometallics* **1999**, *18*, 3555.

(25) Beckmann, J.; Dakternieks, D.; Duthie, A.; Mitchell, C. *Dalton* **2003**, 3258.

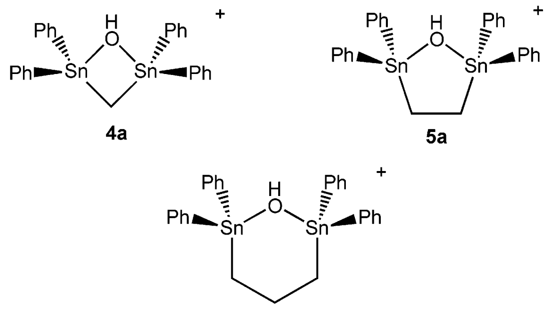
(26) Beckmann, J.; Dakternieks, D.; Duthie, A.; Jurkschat, K.; Mehring, M.; Mitchell, C.; Schürmann, M. *Eur. J. Inorg. Chem.* **2003**, 4356.

(27) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(28) (a) Edlund, U.; Arshadi, M.; Johnels, D. *J. Organomet. Chem.* **1993**, *456*, 57. (b) Kira, M.; Oyamada, T.; Sakurai, H. *J. Organomet. Chem.* **1994**, *471*, C4. (c) Arshadi, M.; Johnels, D.; Edlund, U. *Chem. Commun.* **1996**, 1279.

(29) (a) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021. (b) Herzfeld, J.; Chen, X. In *Encyclopedia of Nuclear Magnetic Resonance*; Wiley: New York, 1996; Vol. 7, p 6021.

**Chart 1**



hydrogen bonding, the slight blue shift of 23 cm$^{-1}$ by going from **4** to **5** is rather unexpected. Similar blue shifts have been discussed in the literature under the keyword of improper hydrogen bonding.[22] Compounds $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**4**−**6**; $n$ = 1−3) are readily soluble in polar solvents. The $^{119}$Sn NMR spectra ($d_3$-MeCN) of **4**−**6** ($n$ = 1−3) give rise to singlets at $\delta$ −116.0, −139.7, and −102.7, respectively. The molar conductivities ($\Lambda$) of **4**−**6** in MeCN (88, 111, and 113 S cm$^2$ mol$^{-1}$, respectively) are consistent with substantial electrolytic dissociations to form solvated organotin cations and triflate anions.[30] To further determine the degree of association of cations and ions in solution, osmometric molecular weight determinations were performed in MeCN, which somewhat contradict the results of the conductivity measurements. The measured molecular weights for **4**−**6** (60 °C, $c$ = 13.0 mmol L$^{-1}$ MeCN) of 705, 789, and 774 are in good agreement with theoretical values (726, 740, 754) expected for complete ion pairing.

The speciation of the organotin cations associated with **4**−**6** was achieved by electrospray mass spectrometry (ESMS),[31] which enables the detection of preformed ions from solution. The spectra of **4**−**6** (MeCN, cone voltage 40 V, positive mode) show highly intense mass clusters at $m/z$ 577.3 (for **4**), 591.4 (for **5**), and 605.4 (for **6**), respectively, which are unambiguously assigned to the organotin cations $[(Ph_2Sn)_2(CH_2)_n(OH)]^+$ (**4a**−**6a**; $n$ = 1−3); proposed structures are shown in Chart 1. Thus, it appears that the dicationic eight-membered ring cyclo-$[Ph_2SnCH_2SnPh_2(\mu\text{-}OH)]_2^{2+}$ observed in the solid-state structure of **4** undergoes a reversible rearrangement in solution into the monocationic species cyclo-$[(Ph_2Sn)_2(CH_2)_n(OH)]^+$ (**4a**). It is noteworthy that small solvent molecules, such as MeCN and water, often dissociate from solvate complexes under electrospray conditions.[31]

**$[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)$ (7−9; $n$ = 1−3).** The reaction of $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**4**−**6**; $n$ = 1−3) with 1 equiv of $HO_2PPh_2$ proceeded with condensation of water to give good yields of the air-stable crystalline solids $[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)$ (**7**−**9**; $n$ = 1−3) as the main products (eq 3). From

$$\underset{\mathbf{4-6};\ n = 1-3}{[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)} \xrightarrow[-H_2O]{HO_2PPh_2} \underset{\mathbf{7-9};\ n = 1-3}{[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)} \quad (3)$$

the crude reaction mixtures of **8** and **9**, small amounts of very poorly soluble byproducts, namely $[Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (**11**, **12**; $n$ = 2, 3), were isolated. A similar observation was made during the synthesis of cyclo-$[Ph_2P(OSnMe_2O)_2PPh_2](O_3SCF_3)_2$ from $Me_2SnO$, $HO_3SCF_3$, and $HO_2PPh_2$, whereby polymeric $Me_2Sn(O_2PPh_2)_2$ was obtained as the byproduct.[32] Compounds **11** and **12** were subsequently prepared from the more rational, high-yielding syntheses given below.

**Table 5. Selected Bond Parameters (Å, deg) for 7**[a]

| | | | |
|---|---|---|---|
| Sn1−O1 | 2.155(2) | Sn1−O3a | 2.497(2) |
| Sn1−C1 | 2.120(2) | Sn1−C10 | 2.113(2) |
| Sn1−C20 | 2.131(3) | Sn2−O2 | 2.147(2) |
| Sn2−O4 | 2.425(2) | Sn2−C1 | 2.120(3) |
| Sn2−C30 | 2.127(3) | Sn2−C40 | 2.112(3) |
| P1−O1 | 1.524(2) | P1−O2 | 1.517(2) |
| P1−C50 | 1.796(3) | P1−C60 | 1.795(3) |
| O1−Sn1−O3a | 175.82(7) | O1−Sn1−C1 | 98.44(9) |
| O1−Sn1−C10 | 91.48(8) | O1−Sn1−C20 | 92.35(9) |
| O3a−Sn1−C1 | 85.66(9) | O3a−Sn1−C10 | 85.59(8) |
| O3a−Sn1−C20 | 86.32(9) | C1−Sn1−C10 | 122.68(11) |
| C1−Sn1−C20 | 116.59(10) | C10−Sn1−C20 | 119.17(10) |
| O2−Sn2−O4 | 171.94(7) | O2−Sn2−C1 | 98.83(9) |
| O2−Sn2−C30 | 90.66(10) | O2−Sn2−C40 | 90.68(9) |
| O4−Sn2−C1 | 89.23(9) | O4−Sn2−C30 | 85.76(10) |
| O4−Sn2−C40 | 85.85(10) | C1−Sn2−C30 | 114.68(11) |
| C1−Sn2−C40 | 116.57(12) | C30−Sn2−C40 | 127.84(12) |
| O1−P1−O2 | 113.94(12) | O1−P1−C50 | 111.98(12) |
| O1−P1−C60 | 106.79(13) | O2−P1−C50 | 105.94(13) |
| O2−P1−C60 | 111.09(13) | C50−P1−C60 | 106.94(14) |
| Sn1−C1−Sn2 | 121.00(13) | Sn1−O1−P1 | 129.31(11) |
| Sn2−O2−P1 | 128.44(11) | | |

[a] Symmetry operation used to generate equivalent atoms: (a) $1 - x$, $2 - y$, $2 - z$.

The crystal structure of $[Ph_2SnCH_2SnPh_2(O_2PPh_2)](O_3SCF_3)$ (**7**) is shown in Figure 3. Crystal data and selected bond parameters are collected in Tables 1 and 5, respectively. The structure may be described as two symmetry-related six-membered cationic rings, cyclo-$[Ph_2P(OSnPh_2)_2CH_2]^+$, that are weakly associated with two related bidentate triflate anions, rendering the Sn atoms pentacoordinated. It is interesting to note that these six-membered cationic rings are isoelectronic with the recently reported metastable stannasiloxane ring, cyclo-$Ph_2Si(OSnPh_2)_2CH_2$.[33] Similar to compounds **4** and **5**, the geometry of the two crystallographically independent Sn atoms of **7** is distorted trigonal bipyramidal (geometrical goodness $\Delta\Sigma(\theta)$[16] 76.2 for Sn1 and 78.9 for Sn2). Once again, the distortion is created by the different Sn−O bond lengths, this time from the strongly coordinating diphenylphosphinate group and the weakly associated triflate group. At 2.155(2) and 2.497(2) Å for Sn1 and 2.147(2) and 2.425(2) Å for Sn2, these bonds give rise to Pauling bond orders[17] of 0.60 and 0.20 for Sn1 ($\Sigma$(BO) 0.80) and 0.62 and 0.25 for Sn2 ($\Sigma$(BO) 0.87). The P−O bond lengths of **7** are almost equal at 1.524(2) and 1.517(2) Å. $^{119}$Sn MAS NMR spectroscopy of **7** − **9** reveals in both cases two signals in the range $\delta_{iso}$ −78.2 to −149.4, indicative of two crystallographically independent Sn sites (Table 4). Interestingly, this range essentially overlaps with that of compounds **4**−**6**, which suggests that the relative coordination numbers (4 + 1

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[31] (a) Henderson, W.; Taylor, M. J. *Polyhedron* **1996**, *15*, 1957. (b) Dakternieks, D.; Lim, A. E. K.; Lim, K. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *150−151*, 339.

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[33] Beckmann, J.; Jurkschat, K.; Rabe, S.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **2000**, *19*, 3272.

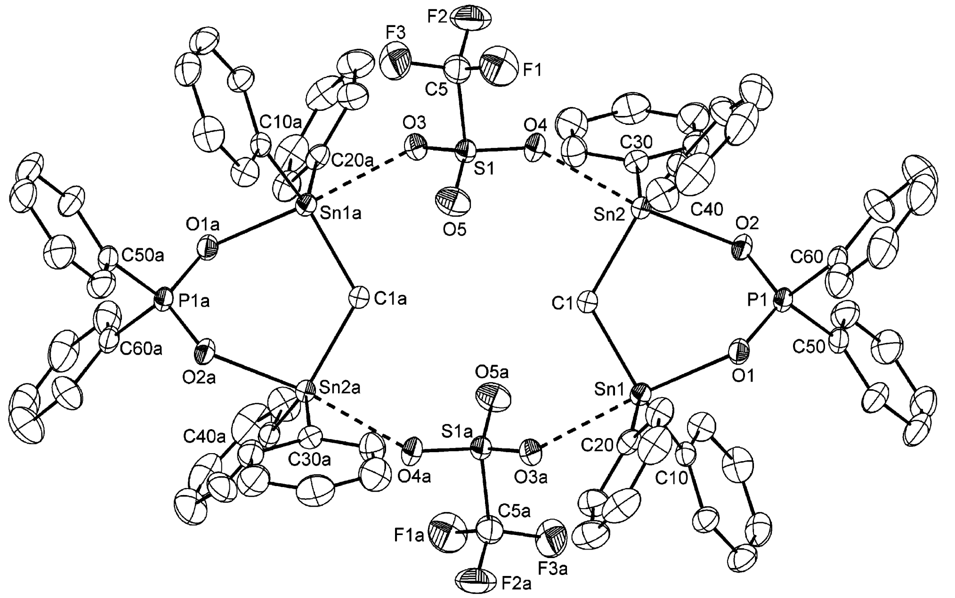


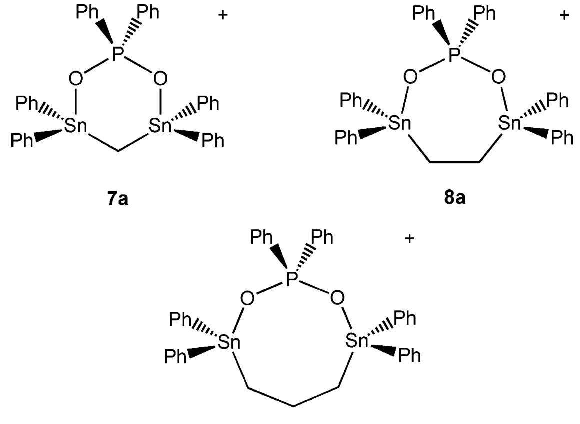
**Figure 3.** General view of **7** showing 20% probability displacement ellipsoids and the atom-numbering scheme (symmetry operation used to generate equivalent atoms: (a) $1 - x$, $2 - y$, $2 - z$).

coordination) are very similar. The magnitude of the anisotropies ($\zeta$) and the asymmetries ($\eta$) vary between 232 and 300 ppm and between 0.40 and 0.85, respectively, and hence, the latter of the parameters is less useful for the characterization of this class of compounds. The $^{31}$P MAS NMR spectra of **7**−**9** show one signal each at $\delta_{\mathrm{iso}}$ 32.4, 32.9, and 26.1, respectively (Table 4).

Compounds $[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)$ (**7**−**9**; $n = 1-3$) are readily soluble in most polar solvents. The $^{119}$Sn NMR spectra ($d_3$-MeCN) of **7**−**9** ($n = 1-3$) show doublets centered at $\delta$ −120.9, −125.7, and −136.9, with $^2J(^{119}\mathrm{Sn-O-}^{31}\mathrm{P})$ couplings of 69, 90, and 120 Hz, respectively. The $^{31}$P NMR spectra of the same samples reveal singlets at $\delta$ 34.6, 31.2, and 30.6 with unresolved $^{117/119}$Sn satellites indicating $^2J(^{31}\mathrm{P-O-}^{117/119}\mathrm{Sn})$ couplings of 66, 91, and 119 Hz, respectively. The observed signals and coupling patterns suggest that the cyclic core structures of **7**−**9** are retained in solution, which is in contrast with the dissociative behavior of the recently reported cyclo-$[R_2Sn(OPPh_2O)_2SnR_2](O_3SCF_3)_2$ (R = Me, *t*-Bu).[32] The molar conductivities ($\Lambda$) of **7**−**9** in MeCN (103, 101, 89 S cm$^2$ mol$^{-1}$ respectively) confirm the electrolytic dissociation into solvated organotin cations and triflate anions.[30] However, osmometric molecular weight determinations performed on **7** and **8** (60 °C, $c$ = 10.0 mmol L$^{-1}$ MeCN) gave somewhat contradictory results with regard to the degree of dissociation in MeCN. The molecular weights of **7** and **8**, being 902 and 942, are in excellent agreement with the theoretical values of 926 and 940 for complete ion pairing.

Electrospray mass spectrometry was used to identify the organotin cations associated with **7**−**9** in solution.[31] The ESMS spectra of **7**−**9** (MeCN, cone voltage 40 V, positive mode) show highly intense mass clusters at $m/z$ 777.4 (for **7**), 791.5 (for **8**), and 805.4 (for **9**), respectively, which were unambiguously assigned to the organotin cations $[(Ph_2Sn)_2(CH_2)_n(O_2PPh_2)]^+$ (**7a**−**9a**; $n = 1-3$); proposed structures are shown in Chart 2.

**Chart 2**



**7a** **8a** **9a**

**$[Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (10−12; $n$ = 1−3).** The reaction of $[Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2]$ (**1**−**3**; $n = 1-3$) with 2 equiv of $HO_2PPh_2$ proceeded under condensation of water to give $[Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2]$ (**10**−**12**, $n = 1-3$) as amorphous or microcrystalline products in high yields (eq 4). The

$$\underset{\mathbf{1-3};\ n = 1-3}{[Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2]} \xrightarrow[-2H_2O]{2HO_2PPh_2} \underset{\mathbf{10-12};\ n = 1-3}{Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2} \quad (4)$$

solid-state structure of $[Ph_2(O_2PPh_2)Sn(CH_2)_3Sn(O_2PPh_2)Ph_2]$ (**12**) is shown in Figure 4. Crystal data and selected bond parameters are collected in Tables 1 and 6, respectively. The structure may be rationalized as a 16-membered macrocycle that lies across a crystallographic center of inversion and therefore contains two independent Sn and P atoms. In this way it closely resembles the structure of the tetramer cyclo-$[Me_3SnOPPh_2O]_4$ reported by Haiduc et al.[34] Bearing in mind that the Sn atoms are also linked via propylene bridges, the overall structure is effectively tricyclic. The two crystallographically independent Sn atoms feature

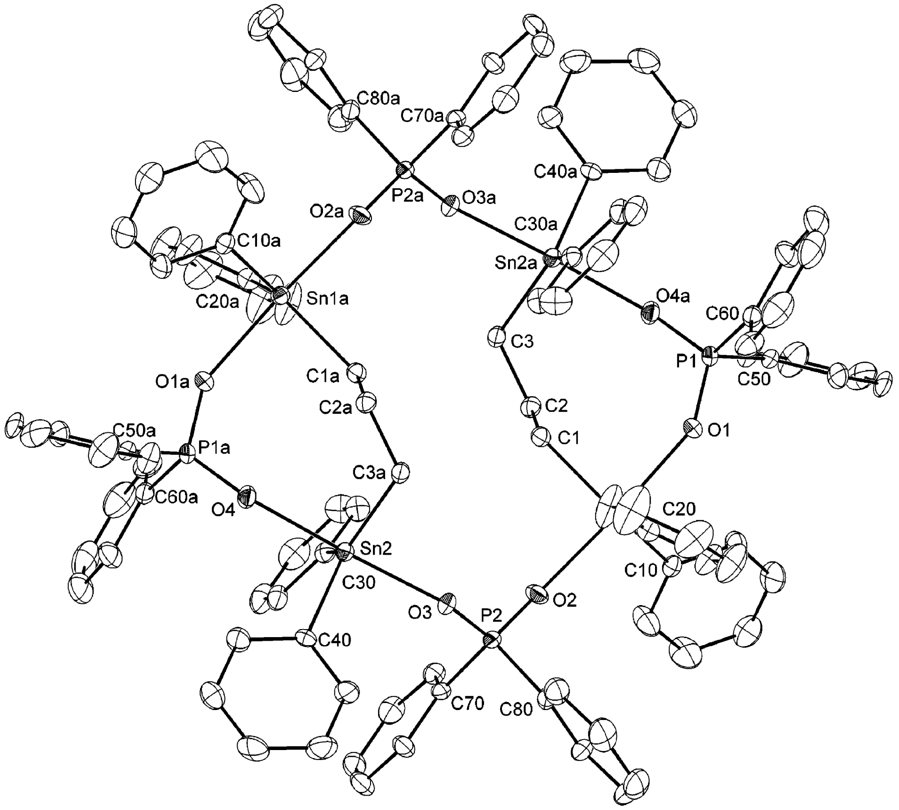


**Figure 4.** General view of **12** showing 20% probability displacement ellipsoids and the atom-numbering scheme (symmetry operation used to generate equivalent atoms: (a) $2 - x$, $1 - y$, $1 - z$).

**Table 6. Selected Bond Parameters (Å, deg) for 12**[a]

| | | | |
|---|---|---|---|
| Sn1−O1 | 2.237(4) | Sn1−O2 | 2.205(4) |
| Sn1−C1 | 2.123(6) | Sn1−C10 | 2.136(6) |
| Sn1−C20 | 2.127(7) | Sn2−O3 | 2.246(3) |
| Sn2−O4 | 2.215(3) | Sn2−C3a | 2.132(6) |
| Sn2−C30 | 2.128(6) | Sn2−C40 | 2.153(6) |
| P1−O1 | 1.504(5) | P1−O4a | 1.503(4) |
| P1−C50 | 1.794(7) | P1−C60 | 1.783(6) |
| P2−O2 | 1.512(5) | P2−O3 | 1.503(4) |
| P2−C70 | 1.804(6) | P2−C80 | 1.811(7) |
| O1−Sn1−O2 | 175.18(15) | O1−Sn1−C1 | 85.69(20) |
| O1−Sn1−C10 | 90.15(20) | O1−Sn1−C20 | 87.1(2) |
| O2−Sn1−C1 | 90.68(20) | O2−Sn1−C10 | 89.64(20) |
| O2−Sn1−C20 | 97.26(19) | C1−Sn1−C10 | 128.75(24) |
| C1−Sn1−C20 | 113.11(24) | C10−Sn1−C20 | 117.66(24) |
| O3−Sn2−O4 | 176.26(12) | O3−Sn2−C3a | 85.92(20) |
| O3−Sn2−C30 | 92.74(20) | O3−Sn2−C40 | 90.74(20) |
| O4−Sn2−C3a | 90.69(21) | O4−Sn2−C30 | 90.45(20) |
| O4−Sn2−C40 | 89.61(21) | C3a−Sn2−C30 | 123.62(22) |
| C3a−Sn2−C40 | 120.35(22) | C30−Sn2−C40 | 116.03(22) |
| O1−P1−O4a | 115.93(26) | O1−P1−C50 | 108.45(28) |
| O1−P1−C60 | 107.78(27) | O4a−P1−C50 | 107.33(26) |
| O4a−P1−C60 | 109.81(28) | C50−P1−C60 | 107.21(31) |
| O2−P2−O3 | 116.33(24) | O2−P2−C70 | 106.91(26) |
| O2−P2−C80 | 108.62(27) | O3−P2−C70 | 110.44(27) |
| O3−P2−C80 | 107.59(26) | C70−P2−C80 | 106.54(31) |
| Sn1−O1−P1 | 149.01(26) | Sn1−O2−P2 | 143.59(26) |
| Sn2−O4−P1a | 152.76(22) | Sn2−O3−P2 | 143.18(21) |

[a] Symmetry operation used to generate equivalent atoms: (a) $2 - x$, $1 - y$, $1 - z$.

slightly distorted trigonal bipyramidal geometries (geometrical goodness $\Delta\Sigma(\theta)$[16] 81.9 for Sn1 and 89.3 for Sn2). The axial Sn−O bond lengths are only slightly different at 2.205(4) and 2.237(4) Å for Sn1 and 2.215(3) and 2.246(3) Å for Sn2 and account for Pauling bond orders[17] of 0.51 and 0.46 for Sn1 (sum 0.97) and 0.49 and 0.45 for Sn2 (sum 0.92). Compounds **10**−**12** were also studied by $^{119}$Sn MAS NMR spectroscopy, which shows two signals for **10** and **11**, presumably due to two independent Sn sites. Although two independent Sn sites have been confirmed also by X-ray crystallography for compound **12**, $^{119}$Sn MAS NMR spectroscopy fails to resolve the putative magnetic inequivalence. The limited number of signals suggests that the bulk material of compounds **10**−**12** is homogeneous and presumably consists of only one oligomeric form. In contrast, $^{119}$Sn and $^{31}$P MAS NMR spectroscopy of $Ph_3SnO_2PPh_2$, also prepared by the condensation of $Ph_3SnOH$ with $HO_2PPh_2$,[35] reveals several signals that are indicative of magnetically inequivalent Sn and P sites, which presumably arise from the presence of different oligomeric or crystalline forms.[36] The observation that the structures of **12** and cyclo-[$Me_3SnOPPh_2O$]$_4$ have only a small void within their structures suggests that a 16-membered ring for $Ph_3SnO_2PPh_2$ is not feasible on steric grounds.[37] The $^{119}$Sn MAS NMR chemical shifts of **10**−**12** fall in the narrow range from $\delta_{iso}$ −193.1 to −240.1 and are consistent with pentacoordinated Sn sites (Table 4). Interestingly, the magnitudes of the anisotropies ($\zeta$) and the asymmetries ($\eta$) are also found within very narrow ranges: between 354 and 390 ppm and

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between 0.40 and 0.60, respectively (Table 4). The $^{31}P$ MAS NMR chemical shifts of **10**−**12** lie between $\delta_{iso}$ 19.6 and 25.1 (Table 4).

**[$Ph_2(OH)Sn(CH_2)_nSnPh_2(O_2PPh_2)$] (13**−**15; *n* = 1**−**3).** The reaction of [$Ph_2Sn(CH_2)_nSnPh_2(OH)$]($O_3SCF_3$) (**4**−**6**; $n = 1-3$) with 1 equiv of $NaO_2PPh_2$ provided [$Ph_2(OH)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**13**−**15**, $n = 1-3$) as amorphous solids in high yields (eq 5). Attempts to

$$\underset{\mathbf{4-6};\ n = 1-3}{[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)} \xrightarrow[-NaO_3SCF_3]{NaO_2PPh_2} \underset{\mathbf{13-15};\ n = 1-3}{[Ph_2(OH)Sn(CH_2)_nSnPh_2(O_2PPh_2)]} \quad (4)$$

obtain the same materials by the selective condensation of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (**1**−**3**; $n = 1-3$) with 1 equiv of $HO_2PPh_2$ failed.

Compounds **13**−**15** show broad IR bands (KBr) at 3436, 3432, and 3404 $cm^{-1}$, respectively, which are assigned to OH stretching vibrations of hydroxy groups involved in hydrogen bonding. The $^{119}Sn$ MAS NMR spectra of **13**−**15** reveal signals at $\delta_{iso}$ −189.1, −199.7, −200.4, and −203.6 for **13** (integral 18:58:18:6), −226.2, −235.5, −237.0, −239.4, and −263.2 for **14** (integral 19:28:28:19:6), and approximately −200 for **15** (very broad), consistent with the presence of magnetically inequivalent Sn sites. The $^{119}Sn$ MAS NMR chemical shifts of **13**−**15** fall in the same range as those of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (**1**−**3**; $n = 1-3$) and [$Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**10**−**12**, $n = 1-3$). No attempts were made to perform tensor analyses. The $^{31}P$ MAS NMR spectra of **13**−**15** show signals at $\delta_{iso}$ 26.6 and 25.3 for **13** (integral 50:50), 22.5 and 13.3 for **14** (integral 40:60), and 22.3 and 18.8 for **15** (integral 35:65).

In contrast to [$Ph_2Sn(CH_2)_nSnPh_2X$]($O_3SCF_3$) (**4**−**9**, X = OH, $O_2PPh_2$; $n = 1-3$), the compounds [$Ph_2XSn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**10**−**15**, X = OH, $O_2PPh_2$; $n = 1-3$) possess no noticeable solubility in common organic solvents at room temperature.

## Conclusion

The reaction of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (**1**−**3**, $n = 1-3$) with 1 equiv of the strong acid $HO_3SCF_3$ affords [$Ph_2Sn(CH_2)_nSnPh_2(OH)$]($O_3SCF_3$) (**4**−**6**; $n = 1-3$), whereas use of larger amounts of $HO_3SCF_3$ leads to phenyl group cleavage and formation of ill-defined products. On the other hand, the reaction of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (**1**−**3**, $n = 1-3$) with 2 equiv of the substantially weaker acid $HO_2PPh_2$ produces [$Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**10**−**12**, $n = 1-3$) without any evidence for the cleavage of phenyl groups. Apparently, the same reaction with only 1 equiv of $HO_2PPh_2$ is unselective and fails to provide [$Ph_2(OH)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**13**−**15**, $n = 1-3$). The reaction of [$Ph_2Sn(CH_2)_nSnPh_2(OH)$]($O_3SCF_3$) (**4**−**6**; $n = 1-3$) with $HO_2PPh_2$ and $NaO_2PPh_2$ gives rise to the formation of [$Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)$]($O_3SCF_3$) (**7**−**9**; $n = 1-3$) and [$Ph_2(OH)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (**13**−**15**, $n = 1-3$), respectively. Thus, the mildly acidic $HO_2PPh_2$ reacts with the basic sites of **4**−**6**, namely the hydroxy groups, while the conjugate base $NaO_2PPh_2$ undergoes a nucleophilic displacement reaction of the triflate group.

## Experimental Section

**General Considerations.** All solvents were distilled prior to use. $HO_3SCF_3$ and $HO_2PPh_2$ were purchased from Aldrich, whereas $Ph_2(I)Sn(CH)_nSn(I)Ph_2$ ($n = 1-3$)[15,38] and $NaO_2PPh_2$[39] were prepared according to a literature procedure. The solution NMR spectra were measured using a JEOL Eclipse Plus 400 spectrometer (at 399.78 ($^1H$), 100.54 ($^{13}C$), 161.84 ($^{31}P$), and 149.05 MHz ($^{119}Sn$)) and were referenced against $SiMe_4$, aqueous $H_3PO_4$ (90%), and $SnMe_4$. The solid-state NMR spectra were measured using the same instrument equipped with a 6 mm MAS probe. Crystalline $NH_4H_2PO_4$ ($\delta$ 0.95) and c-$Hex_4Sn$ ($\delta$ −97.35) were used as secondary references. The $^{119}Sn$ MAS NMR spectra were obtained using cross polarization (contact time 5 ms, recycle delay 10 s). The tensor analyses were performed using the computer program DM Fit 2002.[40] The ESMS spectra were obtained with a Platform II single-quadrupole mass spectrometer (Micromass, Altrincham, U.K.) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 $\mu$L loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 $\mu L\ min^{-1}$. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 and 20 mL $min^{-1}$, respectively. Pressure in the mass analyzer region was usually about $4 \times 10^{-5}$ mbar. Typically 10 signal-averaged spectra were collected at a cone voltage of 40 V in the positive detection mode. The IR spectra were recorded using a BioRad FTIR spectrometer. Microanalyses were carried out by CMAS, Belmont, Australia. The thermogravimetric analysis was carried out under air using a Perkin-Elmer TGA 7 thermogravimetric analyzer with TAC 7/DX controller and gas selector. The conductivity measurements were performed using a CDM80 conductivity meter equipped with a CDC104 conductivity cell (Radiometer, Copenhagen, Denmark) at 25 °C. Molecular weight determinations were carried out at 60 °C in acetonitrile using a a Gonotec Osmomat 070 osmometer.

**Synthesis of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (1**−**3; *n* = 1**−**3).** A solution of NaOH (796 mg, 20.0 mmol) in water (50 mL) was added to a stirred solution of $Ph_2(I)Sn(CH)_nSn(I)Ph_2$ (8.14 g for **1** ($n = 1$), 8.27 g for **2** ($n = 2$), and 8.42 g for **3** ($n = 3$); 10.0 mmol) in methanol (100 mL), generating a white precipitate immediately. The reaction mixture was stirred at room temperature for 1 h. The white precipitate was collected by filtration, washed with water (150 mL) and methanol (50 mL), and left to dry overnight.

**1**. Yield: 5.76 g, 97%. Anal. Calcd for $C_{25}H_{23}O_2Sn_2$ (593.93): C, 50.64; H, 3.88. Found: C, 50.55; H, 3.79.

**2**. Yield: 5.17 g, 85%. IR (KBr): $\nu$ 3600 s, 3043 s, 3011 s, 2988 w, 2892 m, 2808 m, 1638 w, 1573 w, 1478 m, 1423 s, 1331 w, 1302 m, 1257 m, 1189 m, 1155 w, 1072 s, 1034 s, 997 m, 906 m, 852 w, 814 w, 766 w, 728 s, 697 s, 658 m, 532 m, 502 w, 450 m $cm^{-1}$. Anal. Calcd for $C_{26}H_{25}O_2Sn_2$ (607.86): C, 51.30; H, 4.30. Found: C, 50.90; H, 4.40.

**3**. Yield: 3.79 g, 61%. IR (KBr): $\nu$ 3606 s, 3046 s, 3008 w, 2944 m, 2904 m, 2850 w, 1635 br, 1579 m, 1477 m, 1426 s, 1330 w, 1300 w, 1260 m, 1165 m, 1107 w, 1076 s, 1022 s, 998 m, 922 s, 903 s, 884 m, 725 s, 696 s, 673 m, 659 sh, 643 sh, 516 w, 451 m $cm^{-1}$. Anal. Calcd for $C_{27}H_{27}O_2Sn_2$ (621.99): C, 52.14; H, 4.54. Found: C, 52.10; H, 4.54.

**Synthesis of [$Ph_2Sn(CH_2)_nSnPh_2(OH)$]($O_3SCF_3$) (4**−**6; *n* = 1**−**3).** To a suspension of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (2.37 g for **4** ($n = 1$), 2.43 g for **5** ($n = 2$), and 2.49 g for **6** ($n =$

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3); 4.0 mmol) in MeCN (20 mL) was added $HO_3SCF_3$ (600 mg, 4.0 mmol) via syringe. The mixture was stirred for 15 min to give a clear solution. Solvent was removed in vacuo, and the residue was recrystallized from hexane/$CH_2Cl_2$ (**4** and **5**) and pentane/$CH_2Cl_2$ (**6**).

**4**. Yield: 2.64 g, 91%. Mp: 152 °C dec. IR (KBr): $\nu$ 3587 s, 3065 m, 3052 m, 3017 w, 2994 w, 2959 w, 2904 w, 1641 br, 1578 m, 1483 m, 1431 s, 1334 w, 1292 s, 1218 s, 1175 s, 1072 m, 1026 s, 994 m, 911 w, 849 w, 803 w, 764 w, 727 s, 695 s, 660 m, 633 s, 586 w, 568 w, 513 w, 489 m, 467 m, 444 m cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.3−7.0 (20H), 4.9 (1H), 2.1 (2H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 142.7 ($^1J(^{13}C-^{119}Sn)$ = 740 Hz), 137.3, 131.4, 130.2, 121.9 ($CF_3$), 23.0 ($^1J(^{13}C-^{119}Sn)$ = 459 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −116.0. Conductivity ($c$ = 3.33 mmol L$^{-1}$ MeCN): 290 $\mu$S. Anal. Calcd for $C_{26}H_{23}O_4F_3SSn_2$ (726.00): C, 43.02; H, 3.19. Found: C, 43.07; H, 3.15. Mol wt ($c$ = 13.0 mmol L$^{-1}$ MeCN): 705.

**5**. Yield: 2.52 g, 85%. Mp: 143 °C dec. IR (KBr): $\nu$ 3564 s, 3064 m, 3048 m, 3020 w, 2992 w, 2944 w, 2904 w, 1635 br, 1578 w, 1481 m, 1427 s, 1404 w, 1300 s, 1262 w, 1215 s, 1182 s, 1072 m, 1029 s, 997 m, 913 w, 886 m, 864 w, 773 sh, 735 s, 694 s, 660 w, 628 s, 574 w, 539 w, 513 w, 507 sh, 447 m, 421 m cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.6−7.0 (20H), 3.3 (1H), 2.1 (4H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 142.9 ($^1J(^{13}C-^{119}Sn)$ = 687 Hz), 137.1, 130.8, 129.7, 121.3 ($CF_3$), 14.6 ($^1J(^{13}C-^{119}Sn)$ = 599 Hz, $_2J(^{13}C-^{119}Sn)$ = 30 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −139.7. Conductivity (MeCN, $c$ = 3.33 mmol L$^{-1}$): 369 $\mu$S. Anal. Calcd for $C_{27}H_{25}O_4F_3SSn_2$ (740.02): C, 43.82; H, 3.41. Found: C, 43.65; H, 3.34. Mol wt ($c$ = 13.0 mmol L$^{-1}$ MeCN): 789.

**6**. Yield: 2.44 g, 81%. Mp: 149−152 °C dec. IR (KBr): $\nu$ 3567 s, 3065 m, 3052 m, 3017 w, 2994 w, 2959 w, 2904 w, 1641 br, 1578 m, 1483 m, 1431 s, 1334 w, 1292 s, 1218 s, 1175 s, 1072 m, 1026 s, 994 m, 911 w, 849 w, 803 w, 764 w, 727 s, 695 s, 660 m, 633 s, 586 w, 568 w, 513 w, 489 m, 467 m, 444 m cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.5−7.0 (20H), 3.9 (1H), 1.9 (4H), 0.8 (2H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 142.5 ($^1J(^{13}C-^{119}Sn)$ = 676 Hz), 137.0, 130.7, 129.6, 121.3 ($CF_3$), 23.2 ($^2J(^{13}C-^{119}Sn)$ = 36 Hz), 21.9 ($^1J(^{13}C-^{119}Sn)$ = 554 Hz, $^3J(^{13}C-^{119}Sn)$ = 14 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −102.7. Conductivity ($c$ = 3.33 mmol L$^{-1}$ MeCN): 377 $\mu$S. Anal. Calcd for $C_{28}H_{27}O_4F_3SSn_2$ (754.05): C, 44.60; H, 3.61. Found: C, 43.75; H, 3.66. Mol wt ($c$ = 13.0 mmol L$^{-1}$ MeCN): 774.

**Synthesis of [$Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)$]($O_3SCF_3$) (7−9; $n$ = 1−3).** To a suspension of [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (1.19 g for **7** ($n$ = 1), 1.21 g for **8** ($n$ = 2), 1.24 g for **9** ($n$ = 3); 2.0 mmol) in MeCN (20 mL) was added $HO_3SCF_3$ (300 mg, 2.00 mmol) via syringe to give a clear solution after 5 min of stirring at room temperature. Then, $HO_2PPh_2$ (0.436 g, 2.00 mmol) was added and the mixture stirred at 80 °C for 1 h. The solvent was removed in vacuo. The residue was recrystallized from hexane/$CH_2Cl_2$. The byproducts of **8** (323 mg, 0.32 mmol; 16%) and **9** (218 mg, 0.21 mmol; 11%) were filtered off as insoluble solids after 2 days. The solvent was removed in vacuo and the recrystallization repeated.

**7**. Yield: 1.04 g, 56%. Mp: 201−205 °C. IR (KBr): $\nu$ 3057 s, 1651 m, 1617 w, 1482 m, 1431 s, 1296 m, 1232 s, 1184 m, 1129 s, 1117 s, 1070 m, 1026 s, 1019 s, 995 m, 852 w, 751 sh, 730 s, 695 s, 659 w, 628 m, 605 w, 541 m, 502 w, 447 m, 401 w cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.8−7.0 (30H), 1.5 (2H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 140.9, 135.8, 133.6, 131.9, 131.9, 131.7, 131.0, 130.8, 129.5, 128.3, 128.1, 119.3 ($CF_3$), 5.2 ($^1J(^{13}C-^{119}Sn)$ = 455 Hz). $^{31}$P NMR ($d_3$-MeCN): $\delta$ 34.6 ($^2J(^{31}P-O-^{117/119}Sn)$ = 66 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −120.9 ($^2J(^{119}Sn-O-^{31}P)$ = 69 Hz). Conductivity ($c$ = 3.33 mmol L$^{-1}$ MeCN): 344 $\mu$S. Anal. Calcd for $C_{38}H_{32}O_5F_3PSSn_2$ (926.11): C, 49.28; H, 3.48. Found: C, 49.06; H, 3.68. Mol wt ($c$ = 10.0 mmol L$^{-1}$ MeCN): 902.

**8**. Yield: 1.18 g, 63%. Mp: 169−171 °C dec. IR (KBr): $\nu$ 3066 s, 3051 sh, 1643 m, 1629 w, 1592 w, 1482 m, 1432 s, 1265 s, 1251 s, 1238 s, 1175 m, 1130 s, 1072 m, 1031 s, 993 m, 853 w, 753 sh, 729 s, 694 s, 636 m, 502 w, 447 m, 401 w cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.8−7.0 (30H), 2.3 (4H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 140.9, 137.0, 136.0, 134.4, 133.4, 131.7, 131.0, 130.9, 129.2, 128.8, 128.5, 128.3, 128.1, 119.4 ($CF_3$), 16.1 ($^1J(^{13}C-^{119}Sn)$ = 561 Hz, $^2J(^{13}C-^{119}Sn)$ = 32 Hz). $^{31}$P NMR ($d_3$-MeCN): $\delta$ 31.2 ($^2J(^{119}Sn-O-^{31}P)$ = 91 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −125.7 ($^2J(^{119}Sn-O-^{31}P)$ = 90 Hz). Conductivity ($c$ = 3.33 mmol L$^{-1}$ MeCN): 335 $\mu$S. Anal. Calcd for $C_{39}H_{34}O_5F_3PSSn_2$ (940.20): C, 49.82; H, 3.64. Found: C, 49.89; H, 3.54. Mol wt ($c$ = 10.0 mmol L$^{-1}$ MeCN): 942.

**9**. Yield: 1.35 g, 71%. Mp: 216−218 °C. IR (KBr): $\nu$ 3065 m, 3051 m, 2950 w, 2912 w, 2858 w, 1481 w, 1458 w, 1432 m, 1383 w, 1334 w, 1299 s, 1277 sh, 1229 s, 1188 m, 1164 w, 1130 s, 1068 m, 1045 m, 1025 s, 997 w, 892 w, 853 w, 730 s, 695 s, 628 m, 577 w, 547 s, 513 w, 449 m cm$^{-1}$. $^1$H NMR ($d_3$-MeCN): $\delta$ 7.8−7.0 (30H), 0.8 (4H), 0.7 (2H). $^{13}$C NMR ($d_3$-MeCN): $\delta$ 142.2, 137.0, 133.1, 131.9, 131.8, 130.9, 129.8, 129.5, 129.3, 119.5 ($CF_3$), 26.9 ($^1J(^{13}C-^{119}Sn)$ = 574 Hz, $^3J(^{13}C-^{119}Sn)$ = 42 Hz), 22.5 ($^2J(^{13}C-^{119}Sn)$ = 38 Hz). $^{31}$P NMR ($d_3$-MeCN): $\delta$ 30.6 ($^2J(^{119}Sn-O-^{31}P)$ = 119 Hz). $^{119}$Sn NMR ($d_3$-MeCN): $\delta$ −136.9 ($^2J(^{119}Sn-O-^{31}P)$ = 120 Hz). Conductivity ($c$ = 3.33 mmol L$^{-1}$ MeCN): 298 $\mu$S. Anal. Calcd for $C_{40}H_{36}O_5F_3PSSn_2$ (954.23): C, 50.35; H, 3.80. Found: C, 50.97; H, 3.86. Mol wt: not measured due to poor solubility.

**Synthesis of [$Ph_2(O_2PPh_2)Sn(CH_2)_nSn(O_2PPh_2)Ph_2$] (10−12; $n$ = 1−3).** [$Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$] (1.19 mg for **10** ($n$ = 1), 1.21 g for **11** ($n$ = 2), 1.24 g for **12** ($n$ = 3); 2.00 mmol) and $HO_2PPh_2$ (0.873 g, 4.00 mmol) in MeCN (20 mL) were stirred at 80 °C for 18 h. The insoluble white precipitate was isolated by filtration and dried under high vacuum.

**10**. Yield: 1.59 g, 80%. Mp: 257−259 °C. IR (KBr): $\nu$ 3046 m, 3012 w, 2990 w, 2898 w, 2850 w, 1480 w, 1432 m, 1330 w, 1303 w, 1259 w, 1178 sh, 1150 s, 1127 s, 1070 m, 1039 s, 1014 s, 995 m, 972 sh, 922 w, 846 w, 749 m, 727 s, 693 s, 664 m, 648 w, 610 w, 554 s, 544 s, 482 w, 451 m cm$^{-1}$. Anal. Calcd for $C_{49}H_{42}O_4P_2Sn_2$ (994.29): C, 59.19; H, 4.26. Found: C, 59.21; H, 4.33.

**11**. Yield: 1.69 g, 84%. Mp: 240−244 °C. IR (KBr): $\nu$ 3065 m, 3046 m, 3012 w, 2990 w, 2906 w, 1480 w, 1431 m, 1330 w, 1303 w, 1256 w, 1144 s, 1127 s, 1079 w, 1067 w, 1041 s, 1018 s, 998 m, 919 w, 751 w, 725 s, 693 s, 618 w, 551 s, 537 s, 451 m cm$^{-1}$. Anal. Calcd for $C_{50}H_{44}O_4P_2Sn_2$ (1008.32): C, 59.56; H, 4.40. Found: C, 59.60; H, 4.37.

**12**. Yield: 1.74 g, 85%. Mp: 216−218 °C. IR (KBr): $\nu$ 3053 m, 3014 w, 2989 w, 2961 w, 2944 w, 2894 w, 2850 w, 1480 w, 1432 m, 1331 w, 1300 w, 1260 w, 1179 sh, 1146 s, 1128 s, 1068 m, 1043 s, 1021 s, 998 m, 929 w, 891 w, 848 w, 748 m, 728 s, 694 s, 672 m, 618 w, 551 s, 538 sh, 510 w, 451 m cm$^{-1}$. Anal. Calcd for $C_{51}H_{46}O_4P_2Sn_2$ (1022.34): C, 59.92; H, 4.54. Found: C, 59.95; H, 4.61.

**Synthesis of [$Ph_2(OH)Sn(CH_2)_nSnPh_2(O_2PPh_2)$] (13−15; $n$ = 1−3).** [$Ph_2Sn(CH_2)_nSnPh_2(OH)$]($O_3SCF_3$) (594 mg for **13** ($n$ = 1), 608 mg for **14** ($n$ = 2), 622 mg for **15** ($n$ = 3); 1.00 mmol) and $NaO_2PPh_2$ (0.240 g, 1.00 mmol) were stirred in MeCN (50 mL) at 80 °C for 18 h. An insoluble white precipitate was isolated and washed with MeCN to remove any soluble residue. The solid was dried under high vacuum.

**13**. Yield: 0.706 g, 89%. Mp: 192−196 °C. IR (KBr): $\nu$ 3436 vbr, 3052 m, 3016 w, 2988 w, 2964 w, 2923 w, 2853 w, 1629 br, 1581 w, 1544 w, 1511 w, 1479 w, 1429 w, 1305 w, 1261 w, 1215 w, 1132 s, 1071 w, 1038 s, 1016 m, 997 m, 967 w, 946 w, 909 w, 848 w, 806 w, 752 w, 727 s, 696 s, 660 w, 617 w, 551 m, 537 m, 480 w cm$^{-1}$. Anal. Calcd for $C_{37}H_{33}O_3PSn_2$ (793.72): C, 55.90; H, 4.10. Found: C, 55.98; H, 4.14. Mol wt: not measured due to poor solubility.

**14**. Yield: 0.614 g, 76%. Mp: 188−191 °C. IR (KBr): $\nu$ 3432 vbr, 3062 w, 3047 w, 3014 w, 2989 w, 2929 w, 2901 w, 2854 w, 1479 w, 1428 m, 1377 w, 1331 w, 1304 w, 1257 w, 1157 s, 1129 s, 1073 w, 1045 s, 1022 m, 997 w, 923 w, 851 w, 828 w, 811 w, 753 m, 726 s, 694 s, 660 w, 618 w, 547 s, 499 w, 452 m

$cm^{-1}$. Anal. Calcd for $C_{38}H_{35}O_3PSn_2$ (807.73): C, 56.50; H, 4.30. Found: C, 56.62; H, 4.26. Mol wt: not measured due to poor solubility.

**15**. Yield: 0.485 g, 59%. Mp: 225−229 °C. IR (KBr): $\nu$ 3404 vbr, 3048 w, 3015 w, 2988 w, 2943 w, 2905 w, 2849 w, 1479 w, 1430 m, 1331 w, 1302 w, 1280 w, 1261 w, 1153 s, 1127 s, 1071 w, 1044 s, 1021 m, 997 m, 931 w, 891 w, 853 w, 749 w, 726 s, 695 s, 619 w, 547 s, 505 w, 453 w $cm^{-1}$. Anal. Calcd for $C_{39}H_{37}O_3PSn_2$ (821.74): C, 56.90; H, 4.50. Found: C, 57.25; H, 4.52. Mol wt: not measured due to poor solubility.

**X-ray Crystallography.** Intensity data for **4**, **4**·MeCN, **5**, **7**, and **12** were collected on a Bruker SMART Apex CCD diffractometer fitted with Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\ 73$ Å) to $\theta_{max}$ via $\omega$ scans. Data were reduced and corrected for absorption using the programs SAINT and SADABS.[41] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.[42] Full-matrix least-squares refinement on $F^2$, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically.

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**Supporting Information Available:** Table of crystal data and selected bond parameters for **4**·MeCN, as well as a figure of **4**·MeCN, and tables of all coordinates, anisotropic displacement parameters, and geometric data for **4**, **4**·MeCN, **5**, **7**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 234571 for **4**, 234572 for **4**·MeCN, 234573 for **5**, 234574 for **7**, and 234575 for **12**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk; web http://www.ccdc.cam.ac.uk).

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