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Hypercoordinated organotin triflates

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Recent advances in the chemistry of organotin triflates and related organotin cations are reviewed. Applications in synthesis and catalysis are briefly discussed. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

Hydrated triorganotin cations, $[R_3Sn(H_2O)_2]^+$ (R = alkyl), possessing pentacoordinated tin atoms have been known since the 1960s (type **I**; Scheme 1).[1,2] They are accessible upon addition of proton acids, HX (X = ClO_4, NO_3, etc.) to triorganotin oxides, $(R_3Sn)_2O$, when the conjugated base X^- is a weakly coordinating donor, or, alternatively, by the metathesis reaction of a triorganotin chloride, R_3SnCl, with an appropriate silver salt, AgX. Hydrated triorganotin cations are stable both in water and in the solid state, and a small number of fully characterized examples have been described over the years, e.g. $[Bu_3Sn(H_2O)_2][C_5(CO_2Me)_5]$[3,4] and $[Me_3Sn(H_2O)_2]X$ (X = $N(SO_2Me)_2$,[5] $N(SO_2CF_3)_2$).[6] The first unsolvated (three-coordinated) triorganotin cation, $[R_3Sn][B(C_6F_5)_4]$ (R = 2,4,6-triisopropylphenyl), has been reported only recently (type **II**; Scheme 1).[7,8] The preparation of unsolvated triorganotin cations requires kinetic stabilization by very bulky organic substituents, a non-coordinating counterion[9] and the rigorous exclusion of moisture. The chemistry of hydrated and free triorganotin cations is of fundamental interest, as they are tin homologues of (solvated) carbocations, with the latter playing an important role as intermediates in organic chemistry.[10]

Hydrated diorganotin dications, $[R_2Sn(H_2O)_4]^{2+}$ (R = alkyl), can be prepared in water by the reaction of diorganotin oxides, R_2SnO, with proton acids, HX (X = ClO_4, NO_3 etc.), or, alternatively, by reaction of diorganotin dichlorides, R_2SnCl_2, with silver salts, AgX (type **III**, Scheme 1).[1] However, only two hydrated diorganotin dications, $[Me_2Sn(H_2O)_4]X_2$ (X = 1,1,3,3-tetraoxo-1,3,2-benzodithiazolide)[11] and $[Bu_2Sn(H_2O)_4]X_2$ (X = 2,5-dimethyl benzene sulfonate),[12] have been isolated in the solid state and fully characterized by X-ray crystallography. The stabilization of these compounds is based on the steric bulk of the counterions X^- and is presumably also facilitated by hydrogen bonding between the water molecules and donor atoms of the counterions. Most attempts to isolate hydrated diorganotin dications, e.g. upon slow evaporation of aqueous solutions or extraction with organic solvents, have failed, due to condensation and coordination with the counterions, and eventual formation of olgionuclear organotin oxo clusters containing hydroxy and/or oxo groups.[13–15]

Organotin triflates were first reported by Schmeisser *et al.*[16] in 1970, and over the years a number of examples, such as $R_3SnO_3SCF_3$ (R = Me,[16] $(Me_3Si)_2CH$,[17] Ph[16]) and $R_2Sn(O_3SCF_3)_2$ (R = Me,[16] Bu,[16,18] Ph[16,19]) have been described. Tin triflate linkages, $Sn{-}O_3SCF_3$, are accessible upon reaction of Sn–O,[18] Sn–C,[16,19] and Sn–H[17] bonds with HO_3SCF_3, or, alternatively, by metathesis of Sn–Cl bonds with AgO_3SCF_3.[16,20] As a result of the poor donor strength of the triflate anion, the $Sn{-}O_3SCF_3$ linkage is susceptible to hydrolytic cleavage. The triorganotin triflate $RMe_2SnO_3SCF_3$ (R = 2,6-dimesityl-4-*tert*-butylphenyl) reacts with water to from the hydrate $[RMe_2Sn(H_2O)](O_3SCF_3)$ featuring a pentacoordinated tin atom.[21] Hydrolysis products of the diorganotin triflates $R_2Sn(O_3SCF_3)_2$ (R = Bu, t-Bu) are surprisingly diverse and include the fully characterized examples $[Bu_2Sn(OH)(H_2O)(O_3SCF_3)]_2$,[22] $[Bu_2Sn(OH)(O_3SCF_3)_2]_2$,[23] $[t\text{-}Bu_2Sn(OH)(H_2O)]_2(O_3SCF_3)_2$,[20] and $[Bu_2(HO)SnOSn(O_3SCF_3)Bu_2]_2$.[18]

The hydrolysis of oligomethylene-bridged dinuclear organotin triflates $R(F_3CSO_3)_2Sn(CH_2)_nSn(O_3SCF_3)R$ (R = CH_2SiMe_3; n = 3, 4, 8, 10) afforded hydrated organotin–oxo cluster cations $\{[R(H_2O)Sn(CH_2)_3Sn(OH)R]O\}_4(O_3SCF_3)_4$

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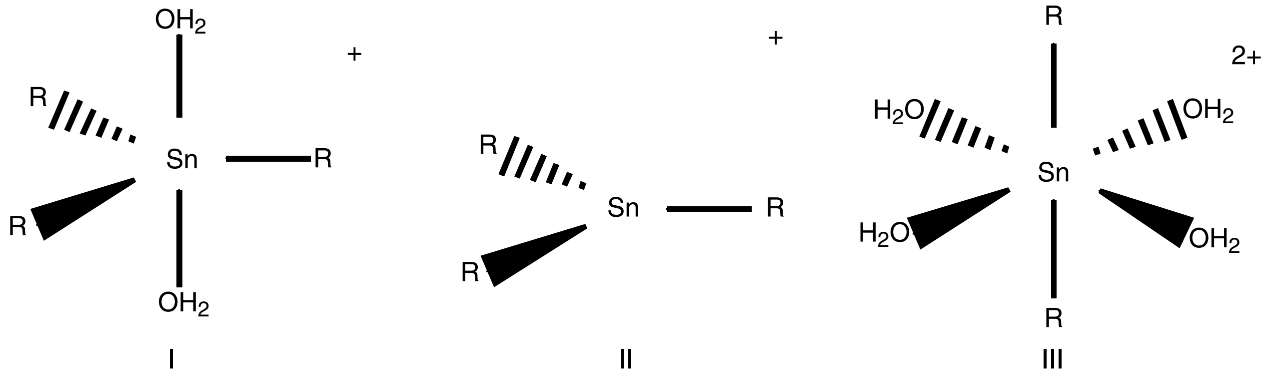
[‡] Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.



Scheme 1.

and $\{R(H_2O)(HO)Sn(CH_2)_nSn(OH)(H_2O)R](O_3SCF_3)_2\}_\infty$ ($n = 4, 8, 10$).[24] The presence of intramolecularly coordinated ligands in diorganotin triflates may prevent the condensation and formation of species having hydroxy and/or oxo groups. This was recently demonstrated for a series of bis(lactamo-*N*-methyl)tin ditriflates $[C(O)(CH_2)_nNCH_2]_2Sn(O_3SCF_3)$ ($n = 3$–5), which in some cases form mono- or di-cationic water adducts.[25]

Owing to their tendency to undergo electrolytic dissociation in polar solvents, organotin triflates are excellent Lewis-acid catalysts for a variety of organic reactions. For instance, $Bu_2Sn(O_3SCF_3)_2$ catalyses the Mukaiyama aldol reaction, in which aldehydes, ketones and their acetals are completely discriminated.[26,27] The same compound also effectively mediates Robinson annulations.[28] The dinuclear organotin species $[Bu_2Sn(OH)(H_2O)(O_3SCF_3)]_2$ and $[t\text{-}Bu_2Sn(OH)(H_2O)]_2(O_3SCF_3)_2$ are potent catalysts for the acetylation of alcohols,[22] whereas anhydrous $[Bu_2Sn(OH)(O_3SCF_3)]_2$ catalyses the transesterification of dimethyl carbonate with phenols.[23]

RESULTS AND DISCUSSION

The reaction of diorganotin oxides, R_2SnO ($R = Me$, Bu), with two equivalents of HO_3SCF_3 in MeCN afforded clear solutions consisting of solvated diorganotin cations and triflate anions.[18] The addition of two equivalents of Ph_3PO and exposure to atmospheric moisture provided $[R_2Sn(H_2O)_2(OPPh_3)_2](O_3SCF_3)_2$ (**1**, $R = Me$; **2**, $R = Bu$) as air-stable crystalline solids:[29]

$$R_2SnO + 2HO_3SCF_3 + 2OPPh_3 \xrightarrow{\text{moist air}} [R_2Sn(H_2O)_2(OPPh_3)_2](O_3SCF_3)_2 \quad \mathbf{1}, R = Me \quad \mathbf{2}, R = Bu \tag{1}$$

Compounds **1** and **2** were characterized by X-ray crystallography and feature hydrated diorganotin dications $[R_2Sn(H_2O)_2(OPPh_3)_2]^{2+}$ (**1a**, $R = Me$; **2a**, $R = Bu$) and triflate anions associated via hydrogen bonding. The molecular structure of $[Bu_2Sn(H_2O)_2(OPPh_3)_2]^{2+}$ (**2a**) is shown in Fig. 1. The geometry of the tin atom is octahedral, and the ligands are situated in mutual trans-positions.[29] The diorganotin dications $[R_2Sn(H_2O)_2(OPPh_3)_2]^{2+}$ (**1a**, $R = Me$; **2a**, $R = Bu$) may be regarded as derivatives of the parent hydrated diorganotin dications $[R_2Sn(H_2O)_4]^{2+}$ ($R = Me$,[11] Bu[12]) in which two of the water molecules are formally replaced by two Ph_3PO ligands.

Conductivity measurements suggest that $[R_2Sn(H_2O)_2(OPPh_3)_2](O_3SCF_3)_2$ (**1**, $R = Me$; **2**, $R = Bu$) undergo electrolytic dissociation when dissolved in MeCN. The ^{119}Sn NMR spectra of these solutions are consistent with octahedral tin geometries. The broadness of the ^{119}Sn NMR signals suggests that ligand exchange processes occur that are fast on the NMR time scale. Electrospray mass spectrometry agrees with this conjecture by revealing a number of doubly and singly charged mass clusters indicative for the presence of the following organotin cations: $[R_2Sn(OPPh_3)_n]^{2+}$ ($R = Me$; $n = 2$–4), $[R_2Sn(OPPh_3)_nCl]^+$ ($R = Me$, Bu; $n = 1$–2), $[R_2Sn(OPPh_3)_n(O_3SCF_3)]^+$ ($R = Me$, Bu; $n = 1$–3).[29]

The consecutive equimolar reaction of the diorganotin oxides, R_2SnO ($R = Me$, t-Bu), with HO_3SCF_3 and HO_2PPh_2

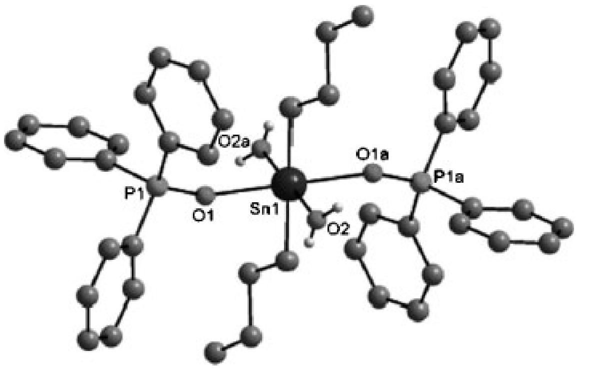


Figure 1. X-ray structure of **2a**.

produced $[R_2Sn(OPPh_2O)_2SnR_2](O_3SCF_3)_2$ (**3**, $R = Me$; **4**, $R = t\text{-}Bu$) as air-stable crystalline solids:[30]

$$\begin{gathered}2R_2SnO + 2HO_2SCF_3 + 2HO_2PPh_2 \xrightarrow[-2H_2O]{} \\ [R_2Sn(OPPh_2O)_2SnR_2](O_3SCF_3)_2 \\ \mathbf{3}, R = Me \\ \mathbf{4}, R = t\text{-}Bu\end{gathered} \tag{2}$$

Compounds **3** and **4** were fully characterized and consist of eight-membered dicationic heterocycles $[R_2Sn(OPPh_2O)_2SnR_2]^{2+}$ and two triflate anions, which are weakly coordinated to the tin atoms via ion pairing. The X-ray structure of **4** is shown in Fig. 2. The coordination of the diphenylphosphinate anion and the triflate anion to the tin atoms may be rationalized in terms of a competition between two donors of different strength. Being the stronger donor, the diphenylphosphinate groups are involved in strong coordination to two tin atoms, whereas each triflate anion is only weakly associated to a single tin atom. The geometry of the tin atoms in **4** can be described as distorted trigonal bipyramidal (4 + 1 coordination).[30]

Consistent with the results of conductivity measurements, $[R_2Sn(OPPh_2O)_2SnR_2](O_3SCF_3)_2$ (**3**, $R = Me$; **4**, $R = t\text{-}Bu$) undergoes electrolytic dissociation in MeCN into organotin cations and triflate anions. However, ^{119}Sn and ^{31}P NMR spectroscopy show that the initially formed dicationic $[R_2Sn(OPPh_2O)_2SnR_2]^{2+}$ heterocycles lack configurational stability and rearrange into other organotin species in solution. This observation is supported by electrospray mass spectrometry, which indicates mass clusters that were assigned to the following cyclic organotin cations: *cyclo*-$[R_2SnOPPh_2O]^+$, *cyclo*-$[Ph_2P(OSnR_2)_2O]^+$ and *cyclo*-$[R_2Sn(OPPh_2O)_2SnR_2X]^+$ ($R = Me$, t-Bu; $X = O_3SCF_3$, O_2PPh_2).

In addition, a mass cluster was observed for compound **4**, which was indicative for the trinuclear organotin–oxo cluster cation $[Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]^+$ (**5a**). The preparation of the related neutral compound $[Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2](O_3SCF_3)$ (**5**) was achieved by the consecutive reaction of three equivalents of $t\text{-}Bu_2SnO$ with HO_3SCF_3 and HO_2PPh_2 (Eqn (3)). Compound **5** was obtained as an air-stable crystalline solid.[31]

$$\begin{gathered}3t\text{-}Bu_2SnO + HO_3SCF_3 + HO_2PPh_2 \longrightarrow \\ [Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2](O_3SCF_3) \\ \mathbf{5}\end{gathered} \tag{3}$$

In the solid state, **5** exists as essentially isolated $[Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]^+$ cations (**5a**) and triflate anions, which are associated via hydrogen bonding. The molecular structure of the cation **5a** is shown Fig. 3; it features an almost planar PSn_3O_5 inorganic core and pentacoordinated tin atoms.

The $[Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]^+$ cation (**5a**) is the first charged member of a well-established class of organotin–oxo clusters $[E(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]$, in which the ESn_3O_5 structural motif is apparently tolerant to variation by a number of substituted main group elements, e.g. $E = Ph_2Si$,[32] MesB,[33] OC.[34] In MeCN and $CHCl_3$ solutions, the $[Ph_2P(OSn\text{-}t\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2]^+$ cation (**5a**) is configurationally stable, as evidenced by ^{119}Sn and ^{31}P NMR spectroscopy.[31]

The equimolar reaction of $Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$ ($n = 1–3$) with HO_3SCF_3 proceeded under condensation and formation of $[Ph_2Sn(CH_2)_nSn(OH)Ph_2](O_3SCF_3)$ (**6**, $n = 1$; **7**, $n = 2$; **8**, $n = 3$), which were isolated as air-stable crystalline solids:[35]

$$\begin{gathered}Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2 \xrightarrow[-H_2O]{HO_3SCF_3} \\ [Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3) \\ \mathbf{6}\text{–}\mathbf{8};\ n = 1–3\end{gathered} \tag{4}$$

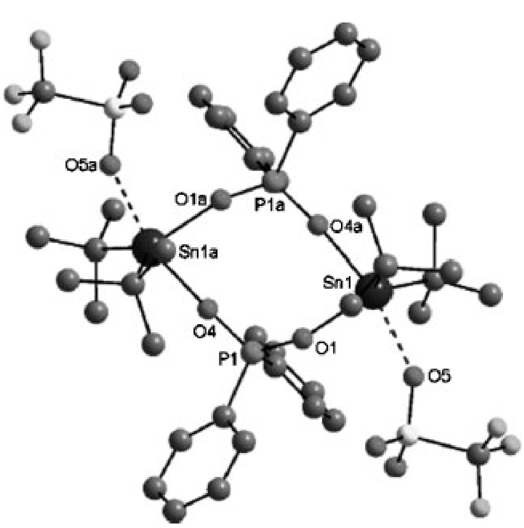


Figure 2. X-ray structure of **4**.

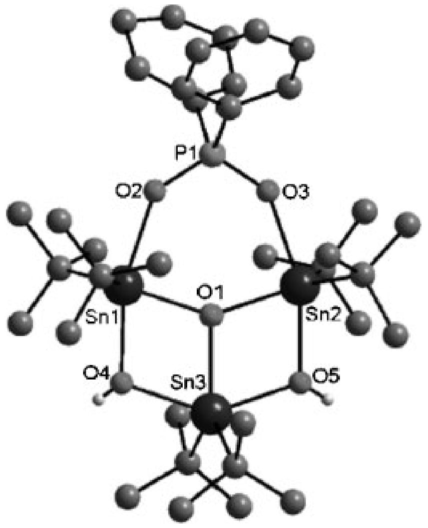


Figure 3. X-ray structure of **5a**.

Solid-state ^{119}Sn NMR spectroscopy provides conclusive evidence that the tin atoms of **6**–**8** are pentacoordinated, which in the case of **6** and **7** was confirmed by X-ray crystallography. The molecular structure of **6** as an MeCN solvate is shown in Fig. 4; it consists of a central eight-membered dicationic $[(Ph_2Sn)_2(CH_2)(OH)]_2^{2+}$ heterocycle and two triflate anions that are loosely coordinated to the tin atoms on either side of the ring (ion pairing). The two MeCN molecules are associated with the hydroxy groups via hydrogen bonding.[35]

In MeCN solution, compounds **6**–**8** undergo electrolytic dissociation into configurationally stable cyclic $[(Ph_2Sn)_2(CH_2)_n(OH)]^+$ cations (**6a**, $n = 1$; **7a**, $n = 2$; **8a**, $n = 3$) and triflate anions, indicated by ^{119}Sn NMR spectroscopy, conductivity measurements and electrospray mass spectrometry.[35] Attempts to prepare $[Ph_2Sn(CH_2)_nSnPh_2]$ $(O_3SCF_3)_2$ by the reaction of $Ph_2(OH)Sn(CH_2)_nSn(OH)Ph_2$ ($n =$ 1–3) with two equivalents of HO_3SCF_3 was complicated by substantial phenyl group cleavage and provided only ill-defined intractable products.

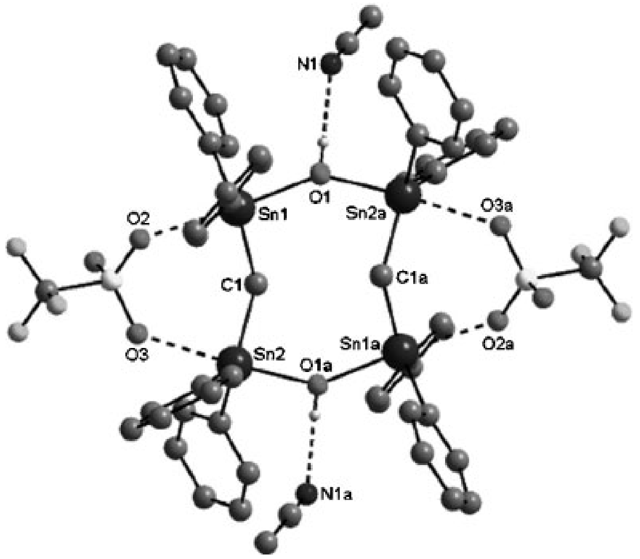


Figure 4. X-ray structure of **6**·MeCN.

The equimolar reaction of $[Ph_2Sn(CH_2)_nSn\,Ph_2(OH)](O_3SCF_3)$ (**6**, $n = 1$; **7**, $n = 2$; **8**, $n = 3$) with HO_2PPh_2 proceeded under condensation and formation of $[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)$ (**9**, $n = 1$; **10**, $n = 2$; **11**, $n = 3$), which were isolated as air-stable crystalline solids:

$$\underset{\mathbf{6}\text{–}\mathbf{8};\, n = 1\text{–}3}{[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)} \xrightarrow[-H_2O]{HO_2PPh_2} \underset{\mathbf{9}\text{–}\mathbf{11};\, n = 1\text{–}3}{[Ph_2Sn(CH_2)_nSnPh_2(O_2PPh_2)](O_3SCF_3)} \quad (5)$$

For compounds **9**–**11**, ^{119}Sn MAS NMR spectroscopy unambiguously shows that the tin atoms are pentacoordinated, a fact that was confirmed by X-ray crystallography for compound **9**. The molecular structure of **9** is shown in Fig. 5; it contains two six-membered cationic $[(Ph_2Sn)_2(CH_2)(O_2PPh_2)]^+$ heterocycles linked by two triflate anions, giving rise to a tricyclic arrangement in which the tin atoms are pentacoordinated.

In MeCN solution, compounds **9**–**11** undergo electrolytic dissociation into configurationally stable $[(Ph_2Sn)_2(CH_2)_n(O_2PPh_2)]^+$ cations (**9a**, $n = 1$; **10a**, $n = 2$; **11a**, $n = 3$) and triflate anions, indicated by ^{119}Sn and ^{31}P NMR spectroscopy, conductivity measurements and electrospray mass spectrometry.[35]

The equimolar reaction of $[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)$ (**6**, $n = 1$; **7**, $n = 2$; **8**, $n = 3$) with NaO_2PPh_2, the conjugated base of HO_2PPh_2, led to substitution of the triflate anion and produced $[Ph_2(OH)Sn(CH_2)_nSnPh_2(O_2PPh_2)]$ (**12**,

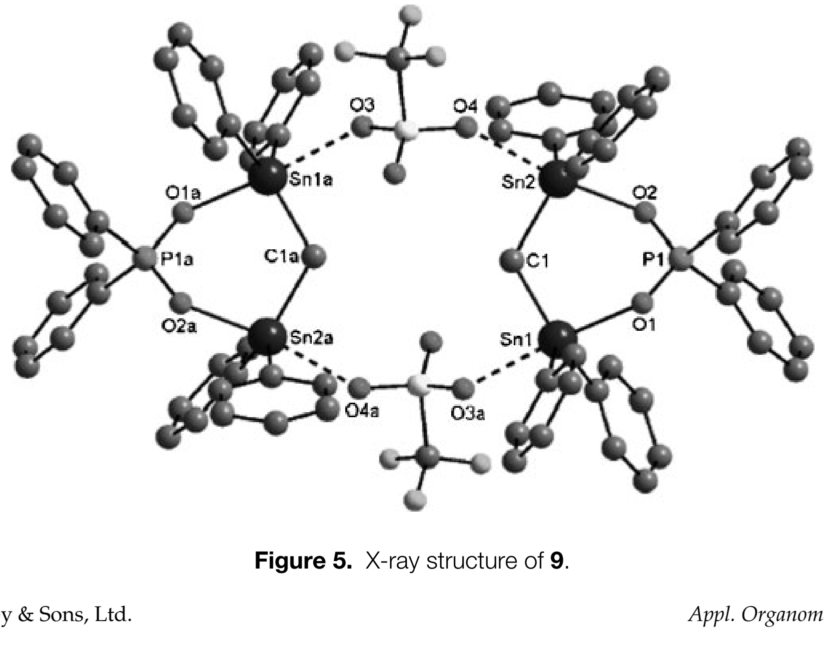


Figure 5. X-ray structure of **9**.

$n = 1$; **13**, $n = 2$; **14**, $n = 3$), which were isolated as air-stable microcrystalline solids:

$$\underset{\textbf{9–11};\ n = 1–3}{[Ph_2Sn(CH_2)_nSnPh_2(OH)](O_3SCF_3)} \xrightarrow[-NaO_3SCF_3]{NaO_2PPh_2} \underset{\textbf{12–14};\ n = 1–3}{[Ph_2(OH)Sn(CH_2)_nSnPh_2(O_2PPh_2)]} \quad (6)$$

The reaction of $Ph_3SnOSnPh_3$ (or two equivalents of Ph_3SnOH) with HO_3SCF_3 apparently provided a solution of $[Ph_3SnOHSnPh_3](O_3SCF_3)$ (**15**). However, attempts to isolate this material by evaporation of the solvent led to partial phenyl group cleavage and formation of the dimeric tetraorganodistannoxane $[Ph_2(OH)SnOSn(O_3SCF_3)Ph_2]_2$ (**16**).[36] The molecular structure of **16** is shown in Fig. 6; it comprises an almost planar inorganic Sn_4O_6 structural motif and four pentacoordinated tin atoms.

The reaction of $[Ph_3SnOHSnPh_3](O_3SCF_3)$ (**15**) prepared *in situ*, with one equivalent of HO_2PPh_2, produced $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**17**) as an air-stable crystalline solid:

$$Ph_3SnOSnPh_3 + HO_3SCF_3 + HO_2PPh_2 \xrightarrow[-H_2O]{MeCN} \underset{\textbf{17}}{[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)} \quad (7)$$

The crystal structure of **17** was investigated by X-ray crystallography and is shown in Fig. 7; it features associated pairs of $[Ph_3SnOPPh_2OSnPh_3]^+$ cations and triflate anions, which give rise to a coordination polymer rendering the geometry of the tin atoms pentacoordinated.[36]

It has been shown previously that triflate anions in organotin triflates may be subject to nucleophilic substitution reactions.[19] $[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3)$ (**17**) reacts with $Bu_3N[Ph_3SnF_2]$, resulting in the formation of the coordination polymer $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**18**) and $Bu_4N(O_3SCF_3)$:[37]

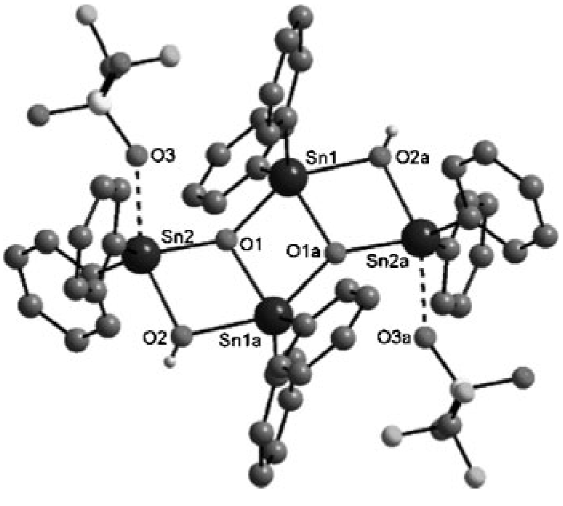


Figure 6. X-ray structure of **16**.

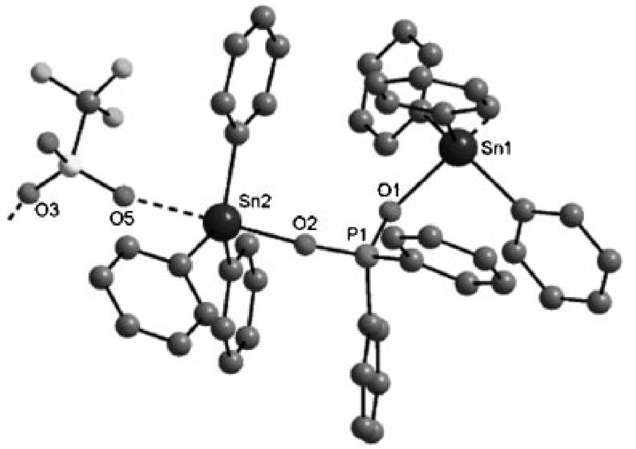


Figure 7. X-ray structure of **17**.

$$\underset{\textbf{17}}{[Ph_3SnOPPh_2OSnPh_3](O_3SCF_3) + Bu_4N[Ph_3SnF_2]} \xrightarrow[-Bu_4N(O_3SCF_3)]{THF} \underset{\textbf{18}}{[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]} \quad (8)$$

Owing to its amorphous nature and the apparent lack of periodic order, the structure of $[(Ph_3SnF)_2(Ph_3SnO_2PPh_2)]$ (**18**) was investigated by a combination of ^{119}Sn, ^{31}P and ^{19}F MAS NMR spectroscopy, which suggest a sequential arrangement of the fluorine atoms and diphenylphosphinate groups rather than a random structure.[37]

In summary, a number of organotin triflates featuring hypercoordinated tin atoms has been prepared and structurally characterized. In the solid state, the triflate groups are either weakly coordinated to the tin atoms (ion pairing) or associated with water molecules or hydroxy groups via hydrogen bonding. In polar solvents, the organotin triflates undergo electrolytic dissociation in solvated (hypercoordinated) organotin cations and triflate anions. Owing to the weak donor capacity, the triflate group is an excellent leaving group in nucleophilic substitution reactions at the tin atoms and may be replaced by a number of nucleophiles (e.g. Cl^-,[19] $Ph_2PO_2^-$[35] and $Ph_3SnF_2^-$[37]).

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REFERENCES

1. Tobias RS. *Organometal. Chem. Rev.* 1966; **1**: 93 and references cited therein.
2. Wada M, Okawara R. *J. Organometal. Chem.* 1965; **4**: 487.
3. Davies AG, Goddard JP, Hursthouse MB, Walker NPC. *J. Chem. Soc. Chem. Commun.* 1983; 597.

4. Davies AG, Goddard JP, Hursthouse MB, Walker NPC. *J. Chem. Soc. Dalton Trans.* 1986; 1873.
5. Blaschette A, Schomburg D, Wieland E. *Z. Anorg. Allg. Chem.* 1989; **571**: 75.
6. Vij A, Wilson WW, Vij V, Corley RC, Tham FS, Gerken M, Haiges R, Schneider S, Schroer T, Wagner RI. *Inorg. Chem.* 2004; **43**: 3189.
7. Lambert JB, Lin L, Keinan S, Müller T. *J. Am. Chem. Soc.* 2003; **125**: 6022.
8. Zharov I, Michl J. Free and complexed R_3M^+ cations (M = Ge, Sn, Pb). In *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol. 2, Rappoport Z (ed.). John Wiley: New York, 2003; Chapter 10.
9. Krossing I, Raabe I. *Angew. Chem. Int. Ed.* 2004; **43**: 2066.
10. Olah GA. *J. Org. Chem.* 2001; **66**: 5943.
11. Hippel I, Jones PG, Blaschette A. *J. Organometal. Chem.* 1993; **448**: 63.
12. Chandrasekhar V, Boomishankar R, Singh S, Steiner A, Zacchini S. *Organometallics* 2002; **21**: 4575.
13. Domingos AM, Sheldrick GM. *J. Chem. Soc. Dalton Trans.* 1974; 475.
14. Lambert JB, Kuhlmann B, Stern CL. *Acta Crystallogr. Sect. C* 1993; **49**: 887.
15. Natsume T, Aizawa SI, Hatano K, Funahashi S. *J. Chem. Soc. Dalton Trans.* 1994; 2749.
16. Schmeisser M, Sartori P, Lippsmeier B. *Chem. Ber.* 1970; **103**: 868.
17. Westerhausen M, Schwarz W. *Main Group Met. Chem.* 1997; **20**: 351.
18. Orita A, Xiang J, Sakamoto K, Otera J. *J. Organometal. Chem.* 2001; **624**: 287.
19. Uhlig W. *J. Organometal. Chem.* 1991; **421**: 189.
20. Sakamoto K, Ikeda H, Akashi H, Fukuyama T, Orita A, Otera J. *Organometallics* 2000; **19**: 3242.
21. Mehring M, Nolde C, Reeske G, Schürmann M. In *XIth International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead*, Santa Fe, USA, 27 June–2 July; poster P24.
22. Sakamoto K, Hamada Y, Akashi H, Orita A, Otera J. *Organometallics* 1999; **18**: 3555.
23. Lee H, Bae JY, Kwon OS, Kim SJ, Lee SD, Kim HS. *J. Organometal. Chem.* 2004; **689**: 1816.
24. Beckmann J, Dakternieks D, Duthie A, Kuan FS, Tiekink ERT. *Organometallics* 2003; **22**: 4399.
25. Bylikin SY, Baukov YI, Jurkschat K, Schürmann M. In *XIth International Conference On the Coordination and Organometallic Chemistry Of Germanium, Tin and Lead*, Santa Fe, USA, 27 June–2 July; poster P19.
26. Sato T, Otera J, Nozaki H. *J. Am. Chem. Soc.* 1990; **112**: 901.
27. Sato T, Wakahara Y, Otera J, Nozaki H. *Tetrahedron* 1991; **47**: 9773.
28. Sato T, Wakahara Y, Otera J, Nozaki H. *Tetrahedron Lett.* 1990; **31**: 1581.
29. Beckmann J, Dakternieks D, Duthie A, Mitchell C. *Dalton* 2003; 3258.
30. Beckmann J, Dakternieks D, Duthie A, Mitchell C. *Organometallics* 2003; **22**: 2161.
31. Beckmann J, Dakternieks D, Duthie A, Jurkschat K, Mehring M, Mitchell C, Schürmann M. *Eur. J. Inorg. Chem.* 2003; 4356.
32. Beckmann J, Jurkschat K, Mahieu B, Schürmann M. *Main Group Met. Chem.* 1998; **21**: 113.
33. Brown P, Mahon MF, Molloy KC. *J. Chem. Soc. Dalton Trans.* 1992; 3503.
34. Reuter H. PhD thesis, University of Bonn, 1986.
35. Beckmann J, Dakternieks D, Duthie A, Mitchell C. *Organometallics* 2004; **23**: in press.
36. Beckmann J, Dakternieks D, Duthie A, Mitchell C. *Appl. Organometal. Chem.* 2004; **18**: 51.
37. Beckmann J, Dakternieks D, Duthie A, Ribot F, d'Espinose de la Caillerie JB, Revel B. *Appl. Organometal. Chem.* 2004; **18**: 353.