

Syntheses, Structures, and Complexation Studies of Tris(organostannyl)methane Derivatives

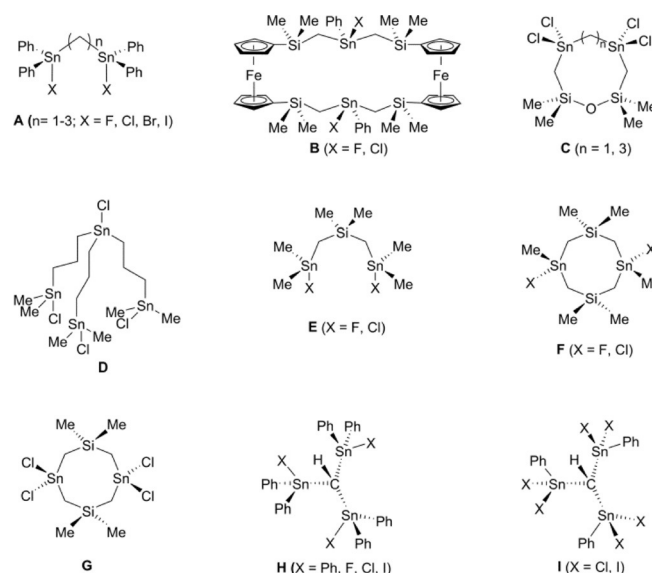
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The syntheses of tris(organostannyl)methanes $\text{HC}(\text{SnX}_n\text{Ph}_{(3-n)})_3$ (**1**, $n=0$; **2**, $n=1$, $\text{X}=\text{I}$; **3**, $n=1$, $\text{X}=\text{F}$; **4**, $n=1$, $\text{X}=\text{Cl}$; **5**, $n=1$, $\text{X}=\text{OAc}$; **6**, $n=2$, $\text{X}=\text{I}$; **7**, $n=2$, $\text{X}=\text{Cl}$) and the organostannate complexes $\text{Et}_4\text{N}[\text{HC}(\text{SnIPh}_2)_3\text{F}]$ (**8**), $\text{Ph}_4\text{P}[\text{HC}(\text{SnClPh}_2)_3\text{Cl}]$ (**9**), and $[\text{Ph}_4\text{P}]_2[\text{HC}(\text{SnCl}_2\text{Ph})_3\text{Cl}]$ (**10**) are reported. The compounds were characterized by ^1H , ^{13}C , ^{19}F , and ^{119}Sn NMR spectroscopy,

IR spectroscopy, electrospray mass spectrometry, and (with the exception of **3**) single-crystal X-ray diffraction analysis. From the reaction between **2** and AgClO_4 resulted the unprecedented hexanuclear organotin oxocluster $[\text{HC}(\text{Sn}(\text{ClO}_4)_2\text{Ph}_2)_2\text{Sn}(\text{OH})_2\text{Ph}]_2$ (**11**), the molecular structure of which was elucidated by using X-ray crystallography.

1. Introduction

The design and synthesis of molecular hosts for the selective recognition of anions continue to attract considerable attention in the field of supramolecular host-guest chemistry.^[1–19] The growing interest in such compounds is stimulated by their potential applications in biological processes including anion transport, in chemical catalysis, as well as in environmental and health issues.^[20–23] Examples of anion receptors that make use of the Lewis acidity of organoelement/organometallic moieties or metal cations have been reported to be efficient in coordinating anions and neutral Lewis bases,^[24–30] as well as in anion sensing,^[16–18,30–46] small molecule activation,^[47–51] and organometallic catalysis.^[52–54] An alternative strategy used to increase the anion affinity of such systems involves two Lewis acids in a bicentric motif that support anion chelation.^[16,35,37,40,55–74] As part of our contribution to this field of research, we have investigated bicentric^[28h,k–l] and multicentric^[28m] Lewis acids of type **A**, **B**, **C**, and **D** (Scheme 1) containing two and three tin atoms, respectively, and have proven their ability to complex halide anions in dichloromethane solution and to selectively recognize the phosphate anion. Recently, we reported the open-chain and cyclic compounds of types **E–G**, containing both silicon and tin atoms and the corresponding salts containing the complex anions.^[75] Notably, among these compounds the simple methylene-bridged repre-



Scheme 1. Selected bi- and multicentric tin- and silicon-based Lewis acids holding potential for anion complexation.

sentative $\text{CH}_2(\text{SnFR}_2)_2$ ($\text{R}=\text{Ph}$, n -octyl) is among the most efficient host for fluoride anion.^[28n–o] In this context, it is surprising that, although reported as early as 1933,^[76,77a] the reactivity/derivatization of tris(triphenylstannyl)methane, $\text{HC}(\text{SnPh}_3)_3$, was not investigated to date. On the other hand, there is one report describing the synthesis and reactivity of tris(trimethylstannyl)methane, $\text{HC}(\text{SnMe}_3)_3$,^[77b] and one report discussing the molecular structure of tris(trimethylstannyl) acetonitrile, $(\text{Me}_3\text{Sn})_3\text{CCN}$.^[77c] With this in mind and in continuation of our previous work mentioned above, we have synthesized and structurally characterized the organotin compounds of type **H** and **I** (Scheme 1). Herein, we show that the iodine- and chlorine-substituted representatives of **H**- and **I**-type compounds are capable of binding fluoride and chloride anions, respectively. Also reported is the reaction of the iodine-substituted repre-

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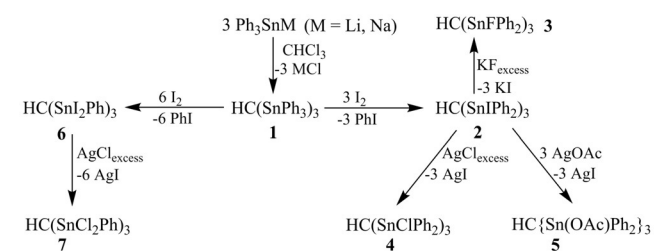
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sentative of H-type compounds with silver acetate and silver perchlorate.

2. Results and Discussion

2.1. Synthetic Aspects

According to the procedure reported in the literature,^[76] the reaction of lithium triphenylstannide, Ph_3SnLi , with trichloromethane, CHCl_3 , provides the methine-bridged tritin compound $\text{HC}(\text{SnPh}_3)_3$, **1**. In a modified procedure using sodium triphenylstannide, Ph_3SnNa , the yield of **1** was similar. The separation of compound **1** from the unavoidable by-product hexaphenyldistannane, $\text{Ph}_3\text{SnSnPh}_3$, by both re-crystallization and chromatography proved to be tedious. Consequently, the content of $\text{Ph}_3\text{SnSnPh}_3$ was estimated from a ^{119}Sn NMR spectrum of the crude reaction mixture. Then, the reaction mixture was treated with an equimolar quantity of elemental iodine (I_2) per $\text{Ph}_3\text{SnSnPh}_3$, exclusively giving Ph_3SnI , which in turn was transferred into poorly soluble triphenyltin fluoride, Ph_3SnF , by stirring the reaction mixture with aqueous potassium fluoride, KF . The Ph_3SnF was filtered, leaving a solution exclusively containing compound **1**. The reaction of the latter with 3 molar equivalents of I_2 afforded tris(diphenyliodostannyl)methane, $\text{HC}(\text{SnIPh}_2)_3$, **2**. This compound was reacted with an excess of potassium fluoride, KF , in a biphasic mixture $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ for 3 days to give the corresponding fluorine-substituted derivative $\text{HC}(\text{SnFPh}_2)_3$, **3**. The corresponding organotin chloride derivative $\text{HC}(\text{SnClPh}_2)_3$, **4**, was obtained through the reaction of compound **2** with an excess of silver chloride, AgCl . The treatment of **2** with silver acetate, AgOAc , gave the corresponding organotin acetate $\text{HC}\{\text{Sn}(\text{OAc})\text{Ph}_2\}_3$, **5**. The reaction of compound **1** with 6 molar equivalents of elemental iodine provided tris(phenyldiiodostannyl)methane $\text{HC}(\text{SnI}_2\text{Ph})_3$, **6** (Scheme 2). In



Scheme 2. Synthesis of compounds 1–7.

a similar manner as described for the synthesis of **4**, compound **6** was converted through a reaction with AgCl into the corresponding organotin chloride $\text{HC}(\text{SnCl}_2\text{Ph})_3$, **7**. The compounds are colorless (**1**, **4**, **5**, and **7**), slightly yellow (**2**), or deep yellow (**6**) crystalline materials that are soluble in organic solvents such as CH_2Cl_2 , CHCl_3 , and THF. Compound **3** is an amorphous solid that is almost insoluble in common organic solvents.

2.2. Molecular Structures in the Solid State

Compound **1** has already been reported,^[76,77] but its crystal structure is unknown. The molecular structures of compounds **1**, **2**, and **4–7** have been determined by single-crystal X-ray diffraction analysis and are shown in Figures 1–6, respectively. Selected interatomic distances and angles are given in the figure captions. Compound **1** crystallized in the triclinic space group $P\bar{1}$. The unit cell of **1** contains two crystallographic independent molecules **A** and **B**, for which the interatomic distances and angles differ only slightly. Consequently, only molecule **A** is shown and a selection of its parameters is

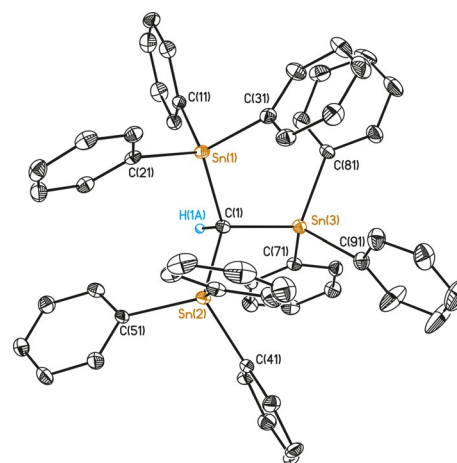


Figure 1. General view (SHELXTL) of a molecule of compound **1** showing 30% probability displacement ellipsoids. Hydrogen atoms at the phenyl rings are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.160(4), Sn(1)–C(11) 2.153(4), Sn(1)–C(21) 2.156(4), Sn(1)–C(31) 2.147(4). Selected interatomic angles ($^\circ$): Sn(1)–C(1)–Sn(2) 114.49(17), Sn(1)–C(1)–Sn(3) 113.34(18), Sn(2)–C(1)–Sn(3) 114.53(19), C(1)–Sn(1)–C(11) 107.00(16), C(1)–Sn(1)–C(21) 112.77(15), C(1)–Sn(1)–C(31) 112.36(16), C(11)–Sn(1)–C(21) 107.98(15), C(11)–Sn(1)–C(31) 111.00(16), C(21)–Sn(1)–C(31) 105.71(16).

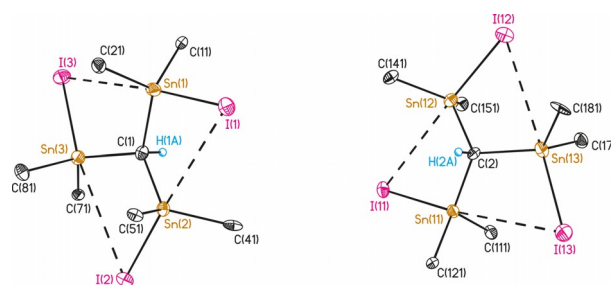


Figure 2. General view (SHELXTL) of the two independent propeller-type molecules of compound **2** showing 30% probability displacement ellipsoids and clockwise (left) and anti-clockwise (right) orientation. Of the phenyl substituents only the C_{ipso} -carbon atoms are shown. Selected interatomic distances (Å): Sn(1)–C(1) 2.176(9), Sn(1)–C(11) 2.136(5), Sn(1)–C(21) 2.150(4), Sn(1)–I(1) 2.7708(11), Sn(1)–I(3) 4.0301(11), Sn(2)–C(1) 2.131(9), Sn(2)–C(41) 2.141(5), Sn(2)–C(51) 2.139(4), Sn(2)–I(1) 3.8287(10), Sn(2)–I(2) 2.7534(10), Sn(3)–C(1) 2.158(10), Sn(3)–C(71) 2.146(5), Sn(3)–C(81) 2.141(5), Sn(3)–I(2) 4.0623(10), Sn(3)–I(3) 2.7352(10). Selected interatomic angles ($^\circ$): Sn(1)–C(1)–Sn(2) 110.9(4), Sn(1)–C(1)–Sn(3) 113.4(4), Sn(2)–C(1)–Sn(3) 116.1(4), C(1)–Sn(1)–C(11) 112.7(3), C(1)–Sn(1)–C(21) 115.7(3), C(11)–Sn(1)–C(21) 117.5(2), I(1)–Sn(1)–I(3) 174.17(3), I(1)–Sn(2)–I(2) 176.97(3), I(2)–Sn(3)–I(3) 168.84(3).

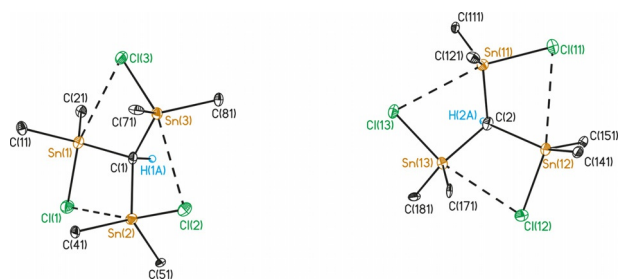


Figure 3. General view (SHELXTL) of the two independent propeller-type molecules of compound **4** showing 30% probability displacement ellipsoids and clockwise (right) and anti-clockwise (left) orientation. Of the phenyl substituents only the C_{ipso} -carbon atoms are shown. Selected interatomic distances (Å): Sn(1)–C(1) 2.120(7), Sn(1)–C(11) 2.146(4), Sn(1)–C(21) 2.120(4), Sn(1)–Cl(1) 2.4205(19), Sn(1)–Cl(3) 3.418(2), Sn(2)–C(1) 2.152(6), Sn(2)–C(41) 2.135(4), Sn(2)–C(51) 2.144(3), Sn(2)–Cl(1) 3.386(2), Sn(2)–Cl(2) 2.414(2), Sn(3)–C(1) 2.138(6), Sn(3)–C(71) 2.135(4), Sn(3)–C(81) 2.139(3), Sn(3)–Cl(2) 3.3871(19), Sn(3)–Cl(3) 2.4059(19), Sn(12)–Cl(11) 3.4639(19), Sn(13)–Cl(12) 3.3125(19). Selected interatomic angles (°): Sn(1)–C(1)–Sn(2) 112.0(3), Sn(1)–C(1)–Sn(3) 114.7(3), Sn(2)–C(1)–Sn(3) 114.2(3), C(1)–Sn(1)–C(11) 124.3(2), C(1)–Sn(1)–C(21) 119.4(2), C(11)–Sn(1)–C(21) 108.83(19), Cl(1)–Sn(1)–Cl(3) 164.11(6), Cl(1)–Sn(2)–Cl(2) 165.18(6), Cl(2)–Sn(3)–Cl(3) 164.45(6).

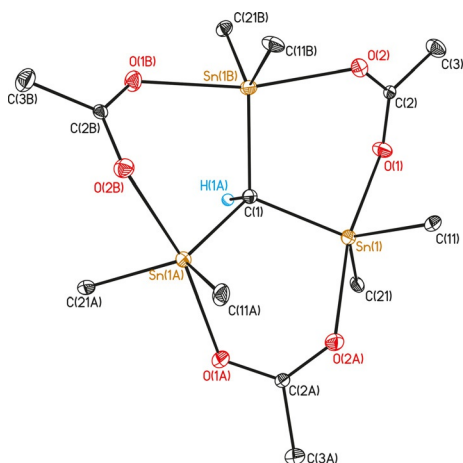


Figure 4. General view (SHELXTL) of a molecule of compound **5**·3CH₂Cl₂ showing 30% probability displacement ellipsoids. Of the phenyl substituents only the C_{ipso} -carbon atoms are shown. The CH₃ hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.1445(14), Sn(1)–C(11) 2.135(3), Sn(1)–C(21) 2.143(3), Sn(1)–O(1) 2.235(2), Sn(1)–O(2A) 2.246(2), C(2)–O(1) 1.262(3), C(2)–O(2) 1.255(4). Selected interatomic angles (°): Sn(1)–C(1)–Sn(1 A) 114.26(11), O(1)–Sn(1)–O(2A) 167.02(8), O(1)–C(2)–O(2) 124.5(3).

discussed. Figure S1 shows both molecules **A** and **B**. The Sn(1) atom exhibits a distorted tetrahedral environment with angles ranging between 105.71(16) [C(21)–Sn(1)–C(31)] and 112.77(15)° [C(1)–Sn(1)–C(21)]. The environments about the Sn(2) and Sn(3) atoms are similar and not discussed in detail. As a result of steric constraint, the central C(1) atom shows an even more distorted tetrahedral environment with Sn–C–Sn angles ranging between 114.53(19) [Sn(2)–C(1)–Sn(3)] and 113.34(18)° [Sn(1)–C(1)–Sn(3)].

Compound **2** crystallized in the orthorhombic space group *Pbca* containing two crystallographically independent molecules **C** and **D** per asymmetric unit. Each of the independent tin atoms in **2** (molecule **C**) is [4+1]-coordinated by one iodine

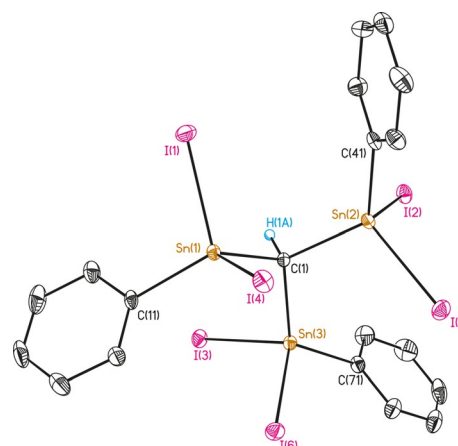


Figure 5. General view (SHELXTL) of a molecule of compound **6** showing 30% probability displacement ellipsoids. The hydrogen atoms of the phenyl substituents are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.145(5), Sn(1)–C(11) 2.125(5), Sn(1)–I(1) 2.6699(4), Sn(1)–I(4) 2.6670(5). Selected interatomic angles (°): Sn(1)–C(1)–Sn(2) 114.7(2), Sn(1)–C(1)–Sn(3) 114.02(19), Sn(2)–C(1)–Sn(3) 114.0(2), C(1)–Sn(1)–C(11) 119.48(17), C(1)–Sn(1)–I(1) 104.13(11), C(1)–Sn(1)–I(4) 107.48(13), I(1)–Sn(1)–I(4) 107.581(16), I(1)–Sn(1)–C(11) 106.65(13), I(4)–Sn(1)–C(11) 110.78(14).

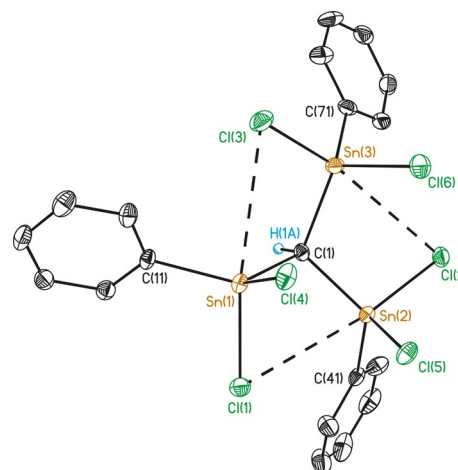


Figure 6. General view (SHELXTL) of a molecule of compound **7** showing 30% probability displacement ellipsoids. The hydrogen atoms of the phenyl substituents are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.128(4), Sn(1)–C(11) 2.104(4), Sn(1)–Cl(1) 2.3468(13), Sn(1)–Cl(3) 3.5950(14), Sn(1)–Cl(4) 2.3357(11). Selected interatomic angles (°): Sn(1)–C(1)–Sn(2) 113.04(19), Sn(1)–C(1)–Sn(3) 113.73(19), Sn(2)–C(1)–Sn(3) 114.05(19), C(1)–Sn(1)–C(11) 129.83(16), C(1)–Sn(1)–Cl(4) 108.12(11), C(11)–Sn(1)–Cl(4) 105.39(12), Cl(1)–Sn(1)–Cl(3) 171.38(4).

and three carbon atoms, forming a distorted tetrahedron. A second iodine atom approaches the central tin atom via a tetrahedral face at Sn–I, distances ranging between 4.0623(10) [Sn(3)–I(2)] and 3.8287(10) Å [Sn(2)–I(1)] being slightly shorter than the sum of the van der Waals radii^[78a] of tin (2.20 Å) and iodine (1.95–2.12 Å), and all fall in the range of the corresponding Sn–I distance found in {[SnBr(C₆H₅)₂(C₂₈H₂₀I)]}, 3.8835(5)^[79a]. These interactions cause, in part, a slight lengthening, as compared with the sum of the covalent radii^[78b] of tin and iodine (2.73 Å), with the other Sn–I distances ranging from 2.7352(10)

[Sn(3)–I(3)] to 2.7708(11) Å [Sn(1)–I(1)]. They fall in the range of the Sn–I distances for tetra- and [4+1]-coordinated triorganotin iodides such as $f(\text{SiMe}_2\text{CH}_2)_2\text{Sn}(\text{I})\text{CH}_2\text{CH}(\text{CH}_2\text{OC}_2\text{H}_4\text{OCH}_2)_2$ (2.7309(4) Å),^[80] $\text{Ph}_2\text{ISnCHCHCMe}(\text{tBu})\text{OH}$ [2.7710(8), 2.763(1) Å],^[81] and $\text{Ph}_2\text{ISnCH}_2\text{CH}_2\text{CO}_2\text{Me}$ [2.811(2) Å].^[82] The position of the experimentally determined geometry for each tin atom along the path tetrahedron→trigonal bipyramid can be quantified by the geometrical goodness $\Delta\Sigma(\theta)$.^[79b] For compound **2**, the values fall in the range between 29.8 (Sn3) and 41.7° (Sn12), showing these to be closer to the tetrahedron (ideal value 0°) than to the trigonal bipyramid (ideal value 90°).

Compound **4** crystallized in the triclinic space group $P\bar{1}$, containing two crystallographic independent molecules **E** and **F** per asymmetric unit. Like in **2**, each of the independent tin atoms in **4** is [4+1]-coordinated [range of geometrical goodness $\Delta\Sigma(\theta)$ ^[79b] 49.0 (Sn11)–54.6° (Sn1)] by one chlorine and three carbon atoms, forming a distorted tetrahedron. A second chlorine atom approaches the central tin atom via a tetrahedral face at Sn–Cl distances ranging between 3.4639(19) [Sn(12)–Cl(11)] and 3.3125(19) Å [Sn(13)–Cl(12)]. These distances are shorter than the sum of the van der Waals radii^[78a] of tin (2.17 Å) and chlorine (1.75 Å) and are comparable with the corresponding Sn–Cl distances found in $\text{Me}_3\text{SiCH}_2(\text{Cl}_2)\text{Sn}(\text{CH}_2)_3\text{Sn}(\text{Cl}_2)\text{CH}_2\text{SiMe}_3$ [3.319(5) and 3.510(5) Å].^[83] As a result of these weak intramolecular Cl⋯Sn interactions (long distances), the other Sn–Cl distances ranging between 2.4205(19) Å [Sn(1)–Cl(1)] and 2.4059(19) Å [Sn(3)–Cl(3), Sn(4)–Cl(4)] are slightly longer than the corresponding distances in tetra-coordinated triorganotin chlorides such as $[\text{PhC}(\text{CH}_3)_2\text{CH}_2]_3\text{SnCl}$ [2.395(4) Å].^[84] For both organotin halides **2** and **4**, we deal with pairs of enantiomers of propeller-type molecules, showing clockwise and anti-clockwise orientation originating from weak intramolecular halogen–tin interactions at distances just below the sums of the van der Waals radii of the corresponding atoms. The effect is more pronounced for organotin chloride **4** than organotin iodide **2**. The interatomic distances and angles differ slightly within the pairs of enantiomers. With caution, this can be traced to some ionic character of the tin–halogen bonds, which in turn allows interpretation of these structures by a ligand close-packing model.^[85]

The triorganotin acetate **5**, as its dichloromethane solvate $5 \cdot 3\text{CH}_2\text{Cl}_2$, crystallized in the trigonal space group $R\bar{3}$ containing six molecules in the unit cell. The one crystallographic independent Sn(1) atom is penta-coordinated by O(1) and O(2A) occupying the axial and C(1), C(11), and C(21) occupying the equatorial positions of a distorted trigonal bipyramid [geometrical goodness $\Delta\Sigma(\theta)$ ^[79b] = 88.9°]. The distortion is best reflected by the O(1)–Sn(1)–O(2A) angle of 167.02(8)°, which deviates by 12.98° from the ideal angle of 180°. The acetate anion coordinates two neighboring tin atoms in an almost perfect isobidentate mode at Sn(1)–O(1) and Sn(1)–O(2A) distances of 2.235(2) and 2.246(2) Å, respectively. To some extent, the structure resembles that of the motif reported for $[\{\text{Me}_2\text{Sn}(\text{O}_2\text{CMe})\}_2\text{O}]_2$.^[87] However, the latter is a diorganotin dicarboxylate derivative and the acetate anions coordinate unisobidentate with Sn–O distances between 2.24(1) and 2.38(2) Å. Triorganotin carboxylates are usually coordination

polymers, in which the carboxylate anions coordinate the tin centers unisobidentate as well.^[88]

The diorganotin dihalides **6** and **7** both crystallized in the monoclinic space group $P2_1/c$, containing four molecules in the unit cell. The structures resemble those of the triorganotin halides **2** and **4** in that they are pairs of enantiomers of propeller-type molecules. However, in contrast to the latter, the geometric parameters within each pair of enantiomers are identical. Each of the three crystallographically independent tin atoms in both **6** and **7** is [4+1]-coordinated by two iodine and two carbon (compound **6**) or two chlorine and two carbon (compound **7**) atoms, forming distorted tetrahedra. A third iodine (compound **6**) or chlorine (compound **7**) atom approaches the corresponding tin center via a tetrahedral face at distances ranging between 4.1665(5) (Sn3–I5) and 4.2288(5) (Sn2–I4), and 3.5950(14) (Sn1–Cl3) and 3.6476(13) (Sn2–Cl1), respectively. These distances are shorter than the sums of the van der Waals radii of the corresponding atoms.

2.3. Structures in Solution

The ¹¹⁹Sn NMR spectra of compounds **1**, **2**, **4**, and **7** in CDCl₃ show resonances at δ –78, –70, –10, and –3, respectively, which are comparable to those measured for the tetra-coordinated tetraorganotin compounds $(\text{Ph}_3\text{Sn})_2\text{CH}_2$ (δ –79),^[89] $(\text{Ph}_2\text{ISn})_2\text{CH}_2$ (δ –68),^[89] $(\text{Ph}_2\text{ClSnCH}_2)_2$ (δ 2),^[28k] and $(\text{PhCl}_2\text{Sn})_2\text{CH}_2$ (δ 8),^[89] respectively. This is evidence that the tin atoms in compounds **1**, **2**, **4**, and **7** are four-coordinated with distorted tetrahedral geometries, as observed in the solid state. A ¹¹⁹Sn NMR spectrum of the organotin acetate **5** displayed a single resonance at δ –206, indicating penta-coordination. A ¹¹⁹Sn NMR spectrum of compound **6** in CDCl₃ displayed a resonance at δ –262, which is low-frequency shifted with respect to the ¹¹⁹Sn chemical shifts of analogous compounds, having similar substituent patterns about the tin atoms, such as $(\text{PhI}_2\text{SnCH}_2)_2$ (δ –169),^[28k] and Me_2SnI_2 (δ –159).^[90] The former resonance (δ –262) is close to the ¹¹⁹Sn chemical shifts reported for the hyper-coordinated organotin compounds $\text{PhI}_2\text{SnCH}_2$ -[13]-crown-4 (δ –275)^[91] and $\text{PhI}_2\text{SnCH}_2\text{SnI}_2$ -[13]-crown-4 [δ –272, Sn(1)].^[91] This observation suggests that the tin atoms in **6** are penta-coordinated in solution.

The solubility of compound **3** is too low in common organic solvents to allow the measurement of its ¹¹⁹Sn, ¹⁹F, ¹³C, and ¹H NMR spectra.

The ¹H NMR spectra of compounds **1**, **2**, **4**–**7** show the expected singlets and coupling constants for the CH protons at δ 1.46 [² J (¹H–^{117/119}Sn) = 69 Hz, **1**], 2.87 [² J (¹H–^{117/119}Sn) = 72 Hz, **2**], 3.15 [² J (¹H–^{117/119}Sn) = 81 Hz, **4**], 3.57 [² J (¹H–^{117/119}Sn) = 66 Hz, **6**], and 3.04 [² J (¹H–¹¹⁷Sn) = 68 Hz, ² J (¹H–¹¹⁹Sn) = 76 Hz, **7**].

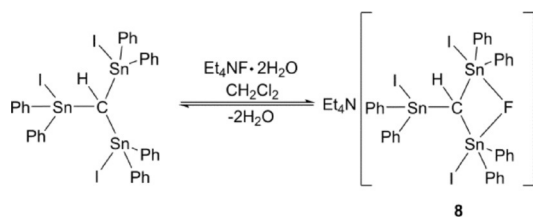
The nonequivalence of the phenyl substituents in the organotin acetate **5** is reflected by a ¹³C{¹H} NMR spectrum showing two resonances (δ 142.0, 143.8 ppm) for the C_i and two resonances (δ 135.5, 136.0 ppm) for the C_o carbon atoms.

An ESI–MS spectrum (negative mode) of compound **2** showed a major mass cluster centered at m/z 1338.4 assigned to $[\text{HC}(\text{SnI}(\text{Ph})_2)_3]^-$.

2.4. Complexation Studies

The ability of compounds **2**, **4**, and **7** to complex anions was studied. Thus, a ^{119}Sn NMR spectrum (223.85 MHz) of compound **2** in CD_2Cl_2 at room temperature, to which 1 molar equivalent of tetraethylammonium fluoride ($\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$) had been added, showed a single resonance at $\delta -72$ [$^2J(^{119}\text{Sn}-^{117}\text{Sn})=230$ Hz]. At $T=193$ K (149.26 MHz), two doublet resonances are observed at $\delta -55$ [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})=367$ Hz, $^3J(^{119}\text{Sn}-^{19}\text{F})=35$ Hz, integral 30, SnIPh_2] and $\delta -163$ [$^1J(^{119}\text{Sn}-^{19}\text{F})=844$ Hz, integral 60, $\nu_{1/2}=95$ Hz, $\text{HC}(\text{SnIPh}_2)_2\text{F}$]. Also present is a singlet resonance at $\delta -77$ (integral 10, **2**). A ^{19}F NMR spectrum (564.84 MHz) of the same sample at room temperature displayed a broad singlet resonance at $\delta -103$ ($\nu_{1/2}=2018$ Hz). At $T=193$ K (376.61 MHz), a doublet resonance flanked with unresolved satellites was observed at $\delta -104$ [$^1J(^{19}\text{F}-^{117/119}\text{Sn})=824$ Hz, $^3J(^{19}\text{F}-^1\text{H})=11$ Hz]. The satellite-to-signal-to-satellite integral ratio is approximately 14:72:14, unambiguously proving the fluoride anion to be complexed by two tin atoms. The $^1J(^{119}\text{Sn}-^{19}\text{F})$ and $^1J(^{19}\text{F}-^{117/119}\text{Sn})$ coupling constants are comparable to the corresponding values reported for $[(\text{Ph}_2\text{Sn})_2\text{CH}_2\cdot\text{F}]$ (780 Hz).^[28 h]

The NMR data indicate Sn–F exchange processes (Scheme 3) to be fast at room temperature and slow at low temperature on the corresponding NMR timescales.



Scheme 3. Reaction of **2** with $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$.

An ESI–MS spectrum in the positive mode of compound **2** in CD_3CN , to which 1 molar equivalent of $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$ had been added, showed a mass cluster centered at m/z 865.1 that is assigned to $\{[(\text{Ph}_2\text{SnOH})_2(\text{Ph}_2\text{Sn})]\text{CH}\}^+$. In addition, there was a less intense mass cluster centered at m/z 907.1, which corresponds to $\{[(\text{Ph}_2\text{SnOH})_2(\text{Ph}_2\text{SnF})]\text{CH}\cdot\text{Na}\}^+$. In the negative mode, no tin-containing mass cluster was observed.

The formation of the organostannate complex $\text{NEt}_4[\text{HC}(\text{SnIPh}_2)_3\text{F}]$ (**8**) was confirmed by X-ray diffraction analysis. The molecular structure of the anion of **8** is shown in Figure 7. Selected interatomic distances and angles are given in the figure caption. The molecular structure of **8** shows that the fluoride anion is chelated by two tin atoms to form a four-membered CSn_2F ring. The Sn(1) and Sn(2) atoms in compound **8** are pentacoordinated and each exhibit a distorted trigonal bipyramidal environment [geometrical goodness $\Delta\Sigma(\theta)^{[79b]}=67.4^\circ$ (Sn1) and 76.1° (Sn2)] with C(1), C(11), and C(21) (Sn1) and C(1), C(41), and C(51) (Sn2) occupying the equatorial positions and F(10) and I(1) (Sn1), and F(10) and I(2) (Sn2) occupying the axial positions. The distortion is expressed by the F(10)–Sn(1)–I(1) (Sn1) and F(10)–Sn(2)–I(2) (Sn2) angles

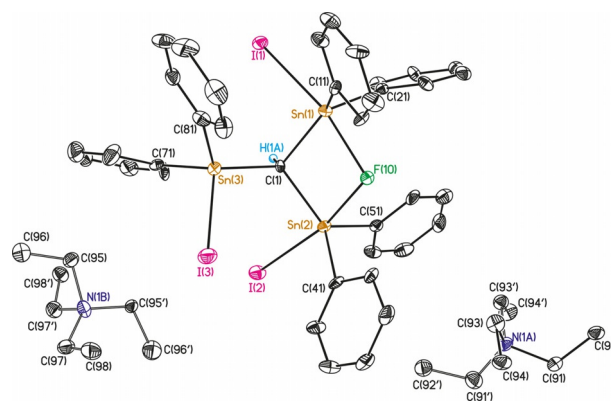


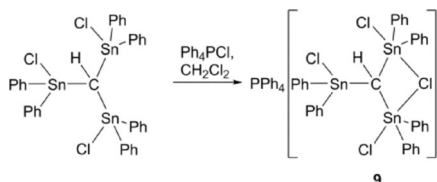
Figure 7. General view (SHELXTL) of the anion and cations of compound **8** showing 30% probability displacement ellipsoids. The hydrogen atoms of the phenyl and ethyl substituents are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.160(10), Sn(1)–C(11) 2.169(6), Sn(1)–C(21) 2.141(6), Sn(1)–I(1) 2.8856(12), Sn(1)–F(10) 2.270(6), Sn(2)–I(2) 2.9150(12), Sn(2)–F(10) 2.205(6), Sn(2)–I(3) 4.1206(14), Sn(3)–I(1) 4.0390(12), Sn(3)–I(3) 2.7360(12). Selected interatomic angles ($^\circ$): Sn(1)–C(1)–Sn(2) 104.4(4), Sn(1)–C(1)–Sn(3) 112.4(6), Sn(2)–C(1)–Sn(3) 120.5(5), Sn(1)–F(10)–Sn(2) 99.5(2), C(1)–Sn(1)–C(11) 124.6(4), C(1)–Sn(1)–C(21) 121.6(4), C(11)–Sn(1)–C(21) 110.3(3), I(1)–Sn(1)–F(10) 165.95(15), C(1)–Sn(2)–C(41) 128.2(4), C(1)–Sn(2)–C(51) 118.1(4), C(41)–Sn(2)–C(51) 111.4(3), I(2)–Sn(2)–F(10) 168.41(18), C(1)–Sn(3)–C(71) 114.8(4), C(1)–Sn(3)–C(81) 117.2(4), C(1)–Sn(3)–I(3) 107.6(3), C(71)–Sn(3)–C(81) 109.0(4), C(71)–Sn(3)–I(3) 106.9(2), C(81)–Sn(3)–I(3) 99.7(2), I(1)–Sn(3)–I(3) 161.31(4).

of $165.95(15)^\circ$ (Sn1) and $168.41(18)^\circ$ (Sn2), deviating from the ideal angle of 180° . The tin atoms are displaced by $0.2325(8)$ Å (Sn1) and $0.1898(8)$ Å (Sn2) from the trigonal planes defined by C(1), C(11), C(21) (Sn1)/C(1), C(41), C(51) (Sn2) in the direction of I(1) (Sn1) and I(2) (Sn2).

The Sn(3) atom is four-coordinated and shows a distorted tetrahedral environment, with angles varying between $99.7(2)^\circ$ (C81–Sn3–I3) and $117.2(4)^\circ$ (C1–Sn3–C81). The distortion of the tetrahedral environment is brought about by the I(1) and I(2) atoms intramolecularly approaching the Sn(3) atoms via the tetrahedral faces defined by C(1), C(71), C(81), and C(1), C(71), I(3) at distances of $4.0390(12)$ and $4.1206(14)$ Å, respectively. These distances are slightly shorter than the sum of the van der Waals radii^[78a] of tin (2.17 Å) and iodine (1.98 Å).

The coordination of the fluoride anion to the Sn(1) and Sn(2) influences the Sn(1)–I(1) [$2.8856(12)$] and Sn(2)–I(2) [$2.9150(12)$] bonds, which are lengthened in comparison with the corresponding Sn(3)–I(3) bond [$2.7360(12)$] involving a tetracoordinated tin atom. It exceeds the sum of the covalent radii of Sn (1.40 Å) and I (1.33 Å).^[78b]

The ^{119}Sn NMR spectrum of compound **4** in CDCl_3 to which 1 molar equivalent of tetraphenylphosphonium chloride, $\text{Ph}_4\text{P}\text{Cl}$, had been added, showed a single resonance at $\delta -98$, which is displaced by 88 ppm to low frequency with respect to the chemical shift of the parent compound **4** ($\delta -10$). This result is interpreted in terms of the formation of the organochloridostannate complex $\text{Ph}_4\text{P}[\text{HC}(\text{SnClPh}_2)_3\text{Cl}]$ (**9**), in which all three tin atoms are equivalent on the ^{119}Sn NMR timescale. The complex was isolated from the reaction mixture as its dichloromethane solvate $\mathbf{9}\cdot 1/3\text{CH}_2\text{Cl}_2$, as colorless crystalline material



Scheme 4. Reaction of **4** with Ph_4PCl .

(Scheme 4). The formation of complex **9** is further supported by ^1H NMR spectroscopy and ESI-MS. The ^1H NMR spectrum of a solution of compound **9** in CDCl_3 showed that the signal of the methine (CH) proton is shifted to low frequency by 0.35 ppm. An ESI-MS mass spectrum of compound **9** in the negative mode showed a mass cluster centered at m/z 729.9, which is assigned to $[\text{HC}(\text{SnClPh}_2)_3\text{Cl}]^-$. No tin-containing mass cluster was observed in an ESI-MS in the positive mode.

The molecular structure of the anion of $\mathbf{9}\cdot\frac{1}{3}\text{CH}_2\text{Cl}_2$ is shown in Figure 8. Selected interatomic distances and angles are collected in the figure caption. The molecular structure of **9** shows that the chloride anion bridges the Sn(2) and Sn(3) atoms non-symmetrically at Sn(2)–Cl(3) and Sn(3)–Cl(3) distances of 2.9397(14) and 2.6307(14) Å, respectively. The Sn(3) atom is pentacoordinated and exhibits a distorted trigonal bipyramidal environment [geometrical goodness $\Delta\Sigma(\theta)^{[79b]} = 88.4^\circ$] with C(1), C(71), and C(81) occupying the equatorial po-

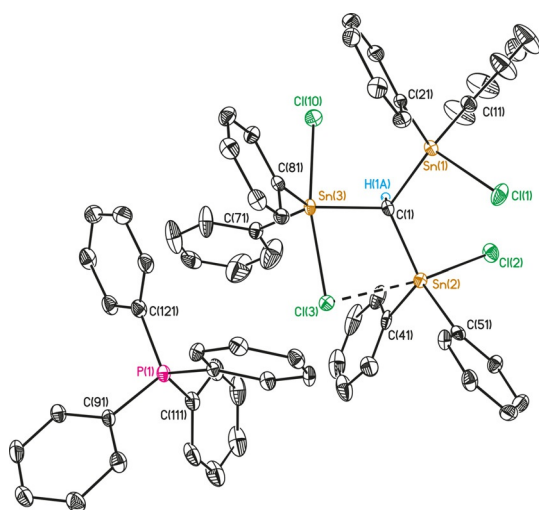
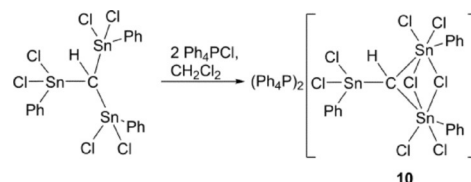


Figure 8. General view (SHELXTL) of the anion and cation of $\mathbf{9}\cdot\frac{1}{3}\text{CH}_2\text{Cl}_2$ showing 30% probability displacement ellipsoids. The hydrogen atoms at the phenyl substituents are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.136(5), Sn(1)–C(11) 2.126(3), Sn(1)–C(21) 2.143(2), Sn(1)–Cl(1) 2.3962(16), Sn(1)–Cl(10) 3.4644(16), Sn(2)–Cl(2) 2.4473(15), Sn(2)–Cl(3) 2.9397(14), Sn(3)–Cl(3) 2.6307(14), Sn(3)–Cl(10) 2.5860(15). Selected interatomic angles ($^\circ$): Sn(1)–C(1)–Sn(2) 118.9(3), Sn(1)–C(1)–Sn(3) 111.2(2), Sn(2)–C(1)–Sn(3) 115.2(2), Sn(2)–Cl(3)–Sn(3) 80.63(4), C(1)–Sn(1)–C(11) 113.73(18), C(1)–Sn(1)–C(21) 120.80(17), C(1)–Sn(1)–Cl(1) 101.99(16), C(11)–Sn(1)–C(21) 112.35(15), C(11)–Sn(1)–Cl(1) 105.37(14), C(21)–Sn(1)–Cl(1) 99.52(10), Cl(1)–Sn(1)–Cl(10) 159.83(5), C(1)–Sn(2)–C(41) 112.24(18), C(1)–Sn(2)–C(51) 133.00(17), C(41)–Sn(2)–C(51) 109.52(14), Cl(2)–Sn(2)–Cl(3) 173.57(5), C(1)–Sn(3)–C(71) 119.38(18), C(1)–Sn(3)–C(81) 126.11(17), C(1)–Sn(3)–Cl(3) 84.29(15), C(1)–Sn(3)–Cl(10) 83.16(15), C(71)–Sn(3)–C(81) 114.50(15), C(71)–Sn(3)–Cl(3) 90.89(13), C(71)–Sn(3)–Cl(10) 93.51(13), C(81)–Sn(3)–Cl(3) 94.05(9), C(81)–Sn(3)–Cl(10) 94.96(9), Cl(3)–Sn(3)–Cl(10) 167.29(5).

sitions and Cl(3) and Cl(10) occupying the axial positions. The distortion is best reflected in the Cl(3)–Sn(3)–Cl(10) angle of $167.29(5)^\circ$, which deviates from the ideal angle of 180° . The Sn(3) atom is displaced by 0.0138(4) Å from the trigonal plane in the direction of Cl(10). The Sn(1) and Sn(2) atoms each exhibit a distorted tetrahedral environment, with angles varying between $99.52(10)^\circ$ (C21–Sn1–Cl1) and $120.80(17)^\circ$ (C1–Sn1–C21) (Sn1), and $96.14(11)^\circ$ (C41–Sn2–Cl2) and $133.00(17)^\circ$ (C1–Sn2–C51) (Sn2). The distortion from the ideal geometry is mainly the result of the Cl(3) and Cl(10) atoms intramolecularly approaching the Sn(2) and Sn(1) atoms at distances of 2.9397(14) and 3.4637(16) Å, respectively. These distances are shorter than the sum of the van der Waals radii^[78a] of tin (2.17 Å) and Cl (1.75 Å), and render the corresponding tin atoms [4+1]-coordinated. The Sn(2)–Cl(2) [2.4473(15) Å] and Sn(1)–Cl(1) [2.3962(16) Å] distances reflect the different extent of these [4+1]-coordinations, as do the geometrical goodness $\Delta\Sigma(\theta)^{[79b]}$ values of 40.0° for Sn(1) and 62.5° for Sn(2). The latter distance is close to the corresponding distances in tetra-coordinated triorganotin chlorides such as *cyclo*-MeClSn(CH₂SiMe₂CH₂)₂SnClMe [Sn(1)–Cl(1) 2.3841(11) Å].^[75] They exceed the sum of the covalent radii^[78b] of tin and chlorine by 0.2407 and 0.196 Å, respectively.

The ^{119}Sn NMR spectrum of a solution of compound **7** in CD_2Cl_2 , to which 2 molar equivalents of Ph_4PCl had been added, showed a single resonance at δ –248 that is shifted by 245 ppm to lower frequency as compared to **7**, and that refers to the formation of the organochloridostannate complex $(\text{Ph}_4\text{P})_2[\text{HC}(\text{SnCl}_2\text{Ph})_3\cdot 2\text{Cl}]$ (**10**) (Scheme 5). The latter was isolat-



Scheme 5. Reaction of **7** with Ph_4PCl .

ed from the reaction mixture as colorless crystalline material. Further experimental support for the formation of **10** stems from the ^1H NMR spectroscopy and ESI-MS. A ^1H NMR spectrum of a solution of compound **10** in CD_2Cl_2 showed that the signal of the methine (CH) proton is shifted to a higher frequency by 1.31 ppm. The displacement of the chemical shift of the methine proton in **10** to higher frequency contrasts well with the low-frequency chemical shift observed for **9**. An ESI-MS mass spectrum of compound **10** in the negative mode showed a mass cluster centered at m/z 848.6 that is assigned to the anion of **10**.

Compound **10** crystallized in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The molecular structure of the anion of **10** is shown in Figure 9. Selected interatomic distances and angles are collected in the figure caption. It consists of a centrosymmetric doubly intramolecularly chlorido-bridged organostannate anion and two tetraphenylphos-

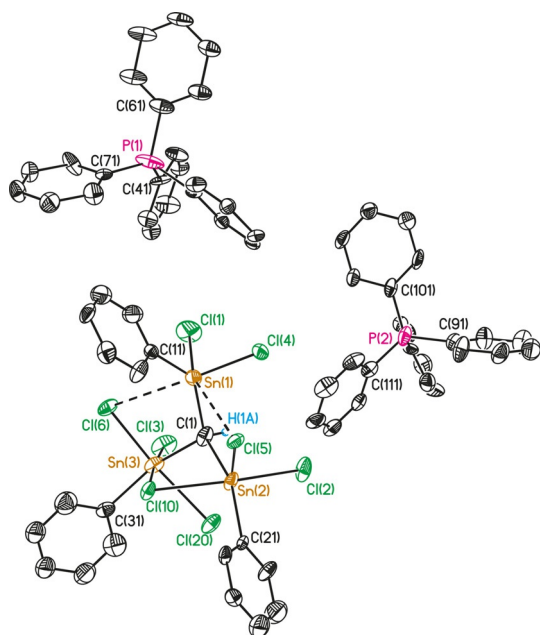


Figure 9. General view (SHELXTL) of the anion and cations of compound **10** showing 30% probability displacement ellipsoids. The hydrogen atoms at the phenyl substituents are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.114(14), Sn(1)–C(11) 1.982(13), Sn(1)–Cl(1) 2.366(4), Sn(1)–Cl(4) 2.382(3), Sn(1)–Cl(5) 3.536(3), Sn(1)–Cl(6) 3.218(3), Sn(2)–C(1) 2.149(11), Sn(2)–C(21) 2.124(6), Sn(2)–Cl(2) 2.453(3), Sn(2)–Cl(5) 2.435(3), Sn(2)–Cl(10) 2.686(3), Sn(2)–Cl(20) 2.894(3), Sn(3)–C(1) 2.111(14), Sn(3)–C(31) 2.198(8), Sn(3)–Cl(3) 2.408(3), Sn(3)–Cl(6) 2.481(3), Sn(3)–Cl(10) 2.868(3), Sn(3)–Cl(20) 2.713(3). Selected interatomic angles (°): Sn(1)–C(1)–Sn(2) 113.6(5), Sn(1)–C(1)–Sn(3) 115.7(6), Sn(2)–C(1)–Sn(3) 106.2(6), C(1)–Sn(1)–Cl(1) 108.2(3), C(1)–Sn(1)–Cl(11) 136.7(6), C(1)–Sn(1)–Cl(4) 105.2(4), Cl(1)–Sn(1)–Cl(4) 92.60(15), Cl(1)–Sn(1)–Cl(11) 98.9(5), Cl(4)–Sn(1)–Cl(11) 106.6(5), C(1)–Sn(2)–C(21) 156.8(4), Cl(2)–Sn(2)–Cl(10) 175.47(10), Cl(5)–Sn(2)–Cl(20) 169.96(10), C(1)–Sn(3)–C(31) 157.1(4), Cl(3)–Sn(3)–Cl(10) 175.91(14), Cl(6)–Sn(3)–Cl(20) 170.06(10).

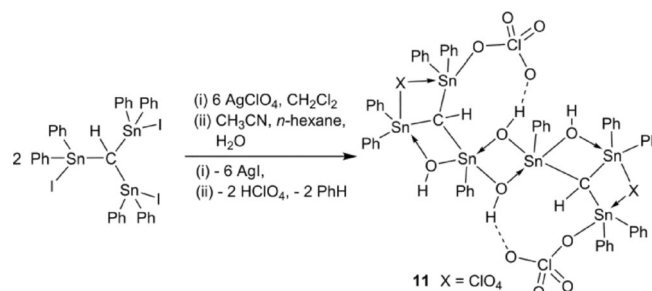
phonium cations, and resembles that of $(\text{Et}_4\text{N})_2[\text{cyclo-Cl}_2\text{Sn}(\text{CH}_2\text{SiMe}_2\text{CH}_2)_2\text{SnCl}_2\cdot 2\text{Cl}]$.^[75]

The Sn(2) and Sn(3) tin atoms are hexa-coordinated and exhibit each a distorted octahedral all-*trans* SnC_2Cl_4 environment with C(1)–Sn(2)–C(21), Cl(2)–Sn(2)–Cl(10), Cl(5)–Sn(2)–Cl(20), C(1)–Sn(3)–C(31), Cl(3)–Sn(3)–Cl(10), and Cl(6)–Sn(3)–Cl(20) angles of 156.8(4), 175.47(10), 169.96(10), 157.1(4), 175.91(14), and 170.06(10)°, respectively. The chlorido bridges are unsymmetrical with Sn(2)–Cl(10), Sn(2)–Cl(20), Sn(3)–Cl(10), and Sn(3)–Cl(20) distances of 2.686(3), 2.894(3), 2.868(3), and 2.713(3) Å, respectively. The Sn(2)–Cl(2), Sn(2)–Cl(5), Sn(3)–Cl(3), and Sn(3)–Cl(6) distances of 2.453(3), 2.435(3), 2.408(3), and 2.481(3) are comparable with the corresponding distances in $(\text{Et}_4\text{N})_2[\text{cyclo-Cl}_2\text{Sn}(\text{CH}_2\text{SiMe}_2\text{CH}_2)_2\text{SnCl}_2\cdot 2\text{Cl}]$ [2.4735(6), 2.4906(5) Å].^[75] The situation at Sn(2) and Sn(3) can be seen as a model for $\text{S}_\text{N}3$ substitution pathways at SnC_2Cl_2 moieties, as reported by Britton and Dunitz.^[86] The Sn(1) atom is four-coordinated and shows a distorted tetrahedral environment, with angles varying between 98.9(5)° [Cl(1)–Sn(1)–C(11)] and 136.7(6)° [C(1)–Sn(1)–C(11)]. The distortion is expressed by the Cl(5) and Cl(6) atoms intramolecularly approaching the Sn(1) atom at distances of 3.536(3) and 3.218(3) Å, respectively. The

Sn(1)–Cl(1) [2.366(4) Å] and Sn(1)–Cl(4) [2.382(3) Å] distances are almost the same and slightly shorter than the Sn(1)–Cl(1) and Sn(2)–Cl(2) distances in **9**.

2.5. Reaction of $\text{HC}(\text{SnPh}_2)_3$ with AgClO_4

The reaction under non-inert conditions of the triorganotin iodide derivative **2** with silver perchlorate in a 1:3 molar ratio gave a crude reaction mixture, a ^{119}Sn NMR spectrum of which showed five resonances at $\delta -69$ [$^2J(^{119}\text{Sn}-^{117}\text{Sn})=236$ Hz, integral 2.0, **2**], -76 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})=297/310$ Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn})=232$ Hz, $^1J(^{119}\text{Sn}-^{13}\text{C})=591$ Hz, $^2J(^{119}\text{Sn}-^{13}\text{C}_o)=52$ Hz, $^3J(^{119}\text{Sn}-^{13}\text{C}_m)=69$ Hz, integral 10.2, signal *a*], -83 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})=270/283$ Hz, integral 1.0, signal *b*], -228 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})=297/310$ Hz, integral 5.7, signal *c*], and -244 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})=271/283$ Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn})=370$ Hz, integral 2.9, signal *d*]. From the $^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$ coupling constants and integral ratio, we conclude that signals *a* and *c* belong to one compound that contains three tin atoms, two of which are chemically identical. The identity of this compound was, however, not established. Signals *b* and *d* seem also to belong to one compound (from coupling arguments), but the integral ratio of almost 1:3 disfavors this view. From the reaction mixture, the partially hydrolyzed organotin(IV) perchlorate derivative **11** was obtained as a colorless crystalline material (Scheme 6) that, once crystallized, showed rather poor solubility. Consequently, no NMR spectra were recorded.



Scheme 6. Reaction of **2** with AgClO_4 .

The formation of **11** under the experimental conditions employed can, with caution, be rationalized by hydrolysis of a tin perchlorate function giving perchloric acid, which in turn cleaves a $\text{Sn}-\text{C}_{\text{phenyl}}$ bond.

The molecular structure of compound **11** is shown in Figure 10. Selected interatomic distances and angles are collected in the figure caption.

Compound **11** crystallized in the orthorhombic space group $Pbca$ with four molecules in the unit cell. It is a centrosymmetric dimer consisting of two CSn_3 moieties. The Sn(2) and Sn(3) atoms are pentacoordinated and each exhibits a distorted trigonal bipyramidal environment [geometrical goodness $\Delta\Sigma(\theta)^{[79b]}=79.9^\circ$ (Sn2) and 85.8° (Sn3) with C(1), C(21), and C(31) (Sn2)] with C(1), C(41), and C(51) (Sn3) occupying the equatorial positions and O(1) and O(11) (Sn2), and O(12) and O(15) (Sn3) occupying the axial positions. The Sn(2) and Sn(3)

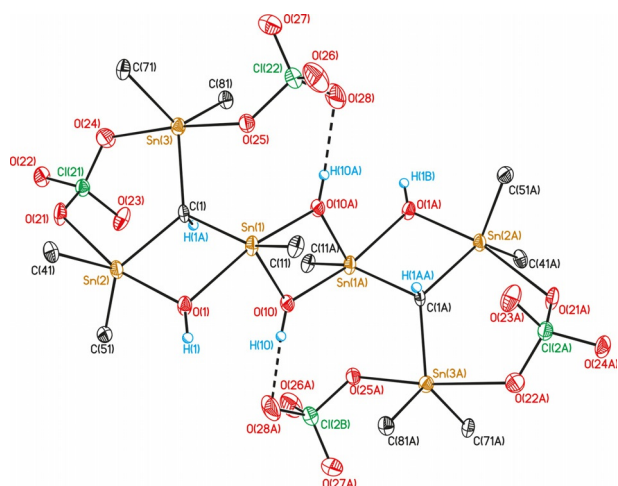


Figure 10. General view (SHELXTL) of a molecule of **11** showing 30% probability displacement ellipsoids. Of the phenyl substituents only the C_{ortho} carbon atoms are shown. Selected interatomic distances (Å): Sn(1)–C(1) 2.122(7), Sn(1)–C(11) 2.123(8), Sn(1)–O(1) 2.155(5), Sn(1)–O(10) 2.042(5), Sn(1)–O(10 A) 2.181(5), Sn(2)–C(1) 2.153(7), Sn(2)–C(41) 2.134(7), Sn(2)–C(51) 2.114(9), Sn(2)–O(1) 2.124(5), Sn(2)–O(21) 2.503(5), Sn(3)–C(1) 2.125(7), Sn(3)–C(71) 2.112(8), Sn(3)–C(81) 2.124(7), Sn(3)–O(22) 2.440(6), Sn(3)–O(25) 2.304(5), O(1)⋯O(24B) 2.931(7), O(10)⋯O(28 A) 2.789(9). Selected interatomic angles (°): Sn(1)–C(1)–Sn(2) 100.9(3), Sn(1)–C(1)–Sn(3) 116.4(3), Sn(1)–O(1)–Sn(2) 100.8(2), Sn(1)–O(10)–Sn(1 A) 109.4(2), Sn(2)–C(1)–Sn(3) 126.1(3), C(1)–Sn(1)–C(11) 144.6(3), C(1)–Sn(1)–O(10) 106.2(3), C(11)–Sn(1)–O(10) 108.8(3), O(1)–Sn(1)–O(10 A) 159.7(2), C(1)–Sn(2)–C(41) 122.8(3), C(1)–Sn(2)–C(51) 116.9(3), C(41)–Sn(2)–C(51) 119.4(3), O(1)–Sn(2)–O(21) 165.64(18), C(1)–Sn(3)–C(71) 126.1(3), C(1)–Sn(3)–C(81) 112.7(3), C(71)–Sn(3)–C(81) 121.1(3), O(22)–Sn(3)–O(25) 172.86(18). Symmetry codes: A) $-x+1, -y+2, -z+1$; B) $-x+1/2, y+1/2, z$.

atoms are displaced by 0.1161(5) and 0.0461(6) Å from the trigonal plane in the direction of O(2) and O(15), respectively. The Sn(1) atom is pentacoordinated as well, but its geometry is best seen as a square pyramid with C(1), C(11), O(1), and O(10A) occupying the equatorial positions and O(10) occupying the apical position. The structure is stabilized by a non-symmetric intramolecular O(10)–H(10)⋯O(28A) hydrogen bridge at an O(10)⋯O(28A) distance of 2.789(9) Å. In addition, there is an intermolecular O(1)–H(1)⋯O(24B) hydrogen bridge at an O(1)⋯O(24B) distance of 2.931(7) Å.

3. Conclusions

A series of tris(organostannyl)methanes and their chloride and fluoride complexes has been synthesized and completely characterized. In the solid state, the halogen-substituted derivatives $\text{HC}(\text{SnXPh}_2)_3$ ($\text{X}=\text{Cl}, \text{I}$) show propeller-type structures with clockwise and anti-clockwise orientation of the $\text{X}\rightarrow\text{Sn}$ coordination. These compounds give 1:1-complexes with chloride and fluoride anions, respectively. No 1:2 or 1:3 complexes were obtained, however. On the other hand, the hexachlorido-substituted derivative $\text{HC}(\text{SnCl}_2\text{Ph})_3$ complexes two chloride anions. All of these compounds [$\text{HC}(\text{SnXPh}_2)_3$ ($\text{X}=\text{Cl}, \text{I}$) and $\text{HC}(\text{SnCl}_2\text{Ph})_3$] have in common that they act as bicentric rather than tricentric Lewis acids. The third tin atoms in each of these derivatives appear to be satisfied by either steric protection

and/or intramolecular interaction with the remaining halogen substituents. As it is nicely shown for the chloridostannate complex **9**, as compared with the corresponding host compound **4**, the strength of the intramolecular Sn–Cl \rightarrow Sn interaction is enhanced by the incoming chloride anion (guest). The acetate-substituted derivative $\text{HC}(\text{Sn}(\text{OAc})\text{Ph})_3$ shows a highly symmetric structure in the solid state that is retained in solution. The replacement of the acetate moiety by other potentially bridging substituents such diorganophosphinate is in progress. The isolation of $[\text{HC}(\text{Sn}(\text{ClO}_4)_2\text{Ph}_2)_2\text{Sn}(\text{OH})_2\text{Ph}]_2$, although achieved by serendipity only, illustrates the potential of the tris(organostannyl)methane derivatives for the synthesis of unprecedented organotin oxoclusters. Examples for this have been presented at the 14th International Symposium on Inorganic Ring Systems (IRIS14, Book of Abstracts A27) and details will be reported in a forthcoming paper.

Experimental Section

General Methods

Where necessary, reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. The solvents were dried by standard methods and freshly distilled before use. $\text{Et}_4\text{NF}\cdot 2\text{H}_2\text{O}$, Ph_4PCl , AgCl , and KF were commercially available.

The NMR spectra were, unless otherwise stated, recorded at ambient temperature on Bruker DPX 300, DRX 400, DRX 500, AVANCE III HD-400, AVANCE III HD-600 and AVANCE III HD-700 spectrometers. The chemical shifts δ are given in ppm and referenced to tetramethylstannane (^{119}Sn), trichlorofluoromethane (^{19}F) and tetramethylsilane (^1H , ^{13}C). Electrospray mass spectroscopy (ESI-MS) was recorded on a Thermoquest–Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as solution in CH_3CN through a syringe pump operating at $0.5\ \mu\text{L}\text{min}^{-1}$. The capillary voltage was 4.5 kV, whereas the cone skimmer voltage was varied between 50 and 250 kV. Identification of the expected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The m/z values reported correspond to those of the most intense peak in the corresponding isotope pattern. Elemental analyses were performed on a LECO-CHNS-932 analyzer. Melting points were determined using a Büchi Melting Point M-560. IR spectra were recorded on a PerkinElmer FTIR spectrometer.

Crystallography

Intensity data for all crystals were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) using $\text{Mo K}\alpha$ radiation at 173 K. The structures were solved with direct methods using SHELXS-2014/7,^[92] and refinements were carried out against F^2 by using SHELXL-2014/7.^[92] The C–H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters.

The nitrogen atoms N1A and N1B in compound **8** are half occupied for symmetry reasons. The associated ethyl groups C91 to C98 are affected by disorder and refined by a split model over two positions (occupancy values 50/50).

The disordered electron density of a non-coordinating solvent molecule of compound **9** was modelled by the SQUEEZE routine of the program Platon^[93] to improve the main part of the structure.

In compound **10**, there are short non-bonding inter H...H contacts (H14B...H36A, 1.60 Å; H32A...H95B, 1.36 Å), which can be explained by packing effects. Several phenyl groups of compound **10** are affected by disorder and refined by a split model over two positions (C11 to C16, 50/50; C41 to C46, 60/40; C51 to C56, 60/40; C71 to C76, 50/50; C81 to C86, 60/40; C91 to C96, 65/35).^[94]

For decimal rounding of numerical parameters and standard uncertainty (su) values, the rules of IUCr have been employed.^[95]

Synthesis of Tris(triphenylstannyl)methane HC(SnPh₃)₃ (**1**)

Method A

To a solution of Ph₃SnCl (3 g, 7.8 mmol) in THF (100 mL) was added lithium (0.54 g, 78 mmol), and the mixture was stirred overnight. After filtration of the excess of lithium, chloroform (21 mL, 26 mmol) was added dropwise at room temperature. The mixture was stirred for 3 h. The solvent was evaporated and the residue was heated at reflux in hexane. The mixture was hot filtered and allowed to stand overnight at room temperature. The solid material that had been deposited was separated and recrystallized several times from hexane to afford 0.53 g (19%) of pure **1** as colorless crystals, mp 139 °C.

Method B

To a solution of Ph₃SnCl (3.00 g, 7.78 mmol, 3.0 equiv) in THF (150 mL) were added metallic sodium (0.43 g, 18.68 mmol, 7.2 equiv) and a catalytic amount of naphthalene. The mixture was stirred at room temperature for 5 days, during which its color changed to deep black. Activation by ultrasound (45 min) and addition of a further catalytic amount of naphthalene accelerated the process. After the solution had been separated from non-reacted sodium, CHCl₃ (0.21 mL, 2.59 mmol, 1.0 equiv) was added dropwise at -70 °C under magnetic stirring. Overnight, the reaction mixture was warmed to room temperature followed by evaporation of the solvent in vacuo. To the residue thus obtained, diethyl ether (100 mL) was added and it was washed with distilled water (3 × 50 mL) in order to remove the sodium chloride. The organic phase was dried over MgSO₄. The latter was separated by filtration and the solvent of the filtrate was removed in vacuo, giving an amorphous solid material that was recrystallized from *iso*-hexane to give a crystalline solid. A ¹¹⁹Sn NMR spectrum of a solution of this material in CDCl₃ revealed two resonances at δ -78 (integral 85, 1) and δ -144 (integral 15, Ph₃SnSnPh₃). To remove the by-product Ph₃SnSnPh₃, elemental iodine (0.042 g, 0.166 mmol, 1.1 equiv with respect to Ph₃SnSnPh₃) was added in small portions to a magnetically stirred solution of the crystalline solid (0.73 g) in CH₂Cl₂ (20 mL) at -20 °C. The reaction mixture was slowly warmed to room temperature, which was followed by addition of an aqueous solution of KF. Stirring this two-phase mixture for 3 h caused precipitation of Ph₃SnF, which was separated by filtration. The organic layer was separated, washed with distilled water, dried over MgSO₄, and then filtrated. Evaporation of the solvent in vacuo gave compound **1** (0.49 g, 0.46 mmol, 18%) as a crystalline material.

¹H NMR (CDCl₃, 400.25 MHz, 294 K): δ 1.48 [s, 1H, ²J(¹H-^{117/119}Sn) = 67/70 Hz, ¹J(¹H-¹³C) = 138 Hz, CH], 6.93–7.50 (complex pattern, 45H, Ph). ¹³C{¹H} NMR (CDCl₃, 150.94 MHz, 294 K): δ: -21.2 [¹J(¹³C-^{117/119}Sn) = 183/190 Hz, CH], 128.1 [³J(¹³C-^{117/119}Sn) = 51 Hz, C_m], 128.5 [⁴J(¹³C-^{117/119}Sn) = 11 Hz, C_p], 137.2 [²J(¹³C-^{117/119}Sn) = 38 Hz, C_o], 140.2 [¹J(¹³C-^{117/119}Sn) = 486/511 Hz, ³J(¹³C-^{117/119}Sn) = 11 Hz, C_j]. ¹¹⁹Sn{¹H} NMR (CDCl₃, 149.26 MHz, 298 K): δ -78 [²J(¹¹⁹Sn-¹¹⁷Sn) =

278 Hz, ¹J(¹¹⁹Sn-¹³C) 509 Hz, ²J(¹¹⁹Sn-¹³C) 38 Hz, ³J(¹¹⁹Sn-¹³C) 51 Hz]. Anal. calcd for C₅₅H₄₆Sn₃ (1062.99): C 62.1; H 4.4. Found: C 62.0; H 4.6.

Synthesis of Tris(iodidodiphenylstannyl)methane HC(SnIPh₂)₃ (**2**)

Over a period of 3 h, elemental iodine (96 mg, 0.378 mmol) was added in small portions at 0 °C to a stirred solution of **1** (134 mg, 0.126 mmol) in CH₂Cl₂. Stirring was continued and the reaction mixture was warmed to room temperature overnight. Dichloromethane and iodobenzene were removed in vacuo (10⁻³ mmHg) to afford a slightly yellow solid. Recrystallization from CH₂Cl₂/hexane or ethanol gave 125 mg (82%) of pure **2** as colorless crystals, mp 107 °C.

¹H NMR (CDCl₃, 400.25 MHz, 294 K): δ 2.87 [s, ¹H, ²J(¹H-^{117/119}Sn) = 70/72 Hz, ¹J(¹H-¹³C) = 141 Hz, CH], 7.29–7.54 (complex pattern, 30H, Ph). ¹³C{¹H} NMR (CDCl₃, 100.64 MHz, 294 K): δ: -0.3 [¹J(¹³C-^{117/119}Sn) = 154/161 Hz, CH], 128.7 [³J(¹³C-^{117/119}Sn) = 65/67 Hz, C_m], 130.0 [⁴J(¹³C-^{117/119}Sn) = 14 Hz, C_p], 136.6 [²J(¹³C-^{117/119}Sn) = 51 Hz, C_o], 138.2 [¹J(¹³C-^{117/119}Sn) = 564/590 Hz, ³J(¹³C-^{117/119}Sn) = 7 Hz, C_j]. ¹¹⁹Sn{¹H} NMR (CHCl₃, 111.92 MHz, 298 K): δ -70 [²J(¹¹⁹Sn-¹¹⁷Sn) = 234 Hz]. Anal. calcd for C₃₇H₃₁I₃Sn₃ (1212.5): C 36.7; H 2.6. Found: C 36.6; H 2.7.

Synthesis of Tris(fluoridodiphenylstannyl)methane HC(SnFPh₂)₃ (**3**)

A solution of **2** (200 mg, 0.165 mmol) in CH₂Cl₂ (25 mL) was mixed with a solution of KF (96 mg, 1.65 mmol) in water (20 mL). The biphasic mixture was stirred at room temperature for 3 days. The organic phase was then separated, dried over MgSO₄, and filtered. Removing the solvent in vacuo afforded 90 mg (61%) of **3** as amorphous solid material of mp 264 °C that was almost insoluble in organic solvents. Consequently, no NMR spectra were recorded.

Anal. calcd for C₃₇H₃₁F₃Sn₃ (888.8): C 50.0; H 3.5. Found: C 48.0; H 3.8.

Synthesis of Tris(chloridodiphenylstannyl)methane HC(SnClPh₂)₃ (**4**)

To a solution of **2** (150 mg, 0.12 mmol) in CH₂Cl₂ (20 mL) an excess of silver chloride (180 mg, 1.24 mmol) was added. The resulting mixture was stirred at room temperature in the dark for 14 days. The AgI that had formed and the non-reacted AgCl were removed by filtration. The solvent of the filtrate was evaporated in vacuo (10⁻³ mmHg) to afford a white solid. Recrystallization of the latter from CH₂Cl₂/*n*-hexane gave 83 mg (74%) of pure **4** as colorless crystals, mp 160 °C.

¹H NMR (CDCl₃, 300.13 MHz, 295 K): δ 3.15 [s, 1H, ²J(¹H-^{117/119}Sn) = 72 Hz, CH], 7.32–7.65 (complex pattern, 30H, Ph). ¹³C{¹H} NMR (CDCl₃, 75.47 MHz, 296 K): δ: 25.3 (CH), 128.9 [³J(¹³C-^{117/119}Sn) = 71/86 Hz, C_m], 130.3 [⁴J(¹³C-^{117/119}Sn) = 16 Hz, C_p], 136.3 [²J(¹³C-^{117/119}Sn) = 54 Hz, C_o], 138.9 (C). No ¹J(¹³C-^{117/119}Sn) coupling constants were obtained. ¹¹⁹Sn{¹H} NMR (CDCl₃, 149.26 MHz, 294 K): δ -9 [²J(¹¹⁹Sn-¹¹⁷Sn) = 203 Hz]. Anal. calcd for C₃₇H₃₁Cl₃Sn₃ (938.13): C 47.4; H 3.3. Found: C 47.5; H 3.7.

Synthesis of HC[Sn(OAc)Ph₂]₃ (5)

3 molar equivalents of silver acetate (41 mg, 0.24 mmol) were added to a solution of **2** (99 mg, 0.08 mmol) in CH₂Cl₂ (15 mL). The resulting mixture was stirred at room temperature in the dark for 2 days. The AgI formed was removed by filtration. The filtrate was kept at -5 °C for several days to give 41 mg (51%) of pure **5** as colorless crystals of its dichloromethane solvate 5·3CH₂Cl₂, mp 166 °C.

¹H NMR (CDCl₃, 700.19 MHz, 298 K): δ 1.71 (s, 9H, CH₃), 2.42 [s, 1H, ²J(H-^{117/119}Sn)=91 Hz], 7.22–7.90 (complex pattern, 30H, Ph). ¹³C{¹H} NMR (CDCl₃, 176.06 MHz, 296 K): δ: 4.3 [¹J(¹³C-^{117/119}Sn)=349/366 Hz, CH], 24.5 (CH₃COO), 128.3 [³J(¹³C-^{117/119}Sn)=76 Hz, C_m], 129.2 (C_p), 135.6 [²J(¹³C-^{117/119}Sn)=63 Hz, C_o], 136.0 [²J(¹³C-^{117/119}Sn)=46 Hz, C_o], 142.0(C_i), 143.8 (C_i), 182.4 (CH₃COO). ¹¹⁹Sn{¹H} NMR (CDCl₃, 223.85 MHz, 294 K): δ -206 [²J(¹¹⁹Sn-^{117/119}Sn)=199 Hz]. Anal. calcd for C₄₆H₄₆Cl₆O₆Sn₃ (1263.70): C 43.7; H 3.7. Found: C 43.8; H 3.8

Synthesis of Tris(diiodidophenylstannyl)methane HC(SnI₂Ph)₃ (6)

Over a period of 3 h, elemental iodine (106 mg, 0.42 mmol) was added in small portions at 0 °C to a stirred solution of **1** (74 mg, 0.07 mmol). Stirring was continued and the reaction mixture was warmed to room temperature overnight. Dichloromethane and iodobenzene were removed in vacuo (10⁻³ mmHg) to afford a yellow solid. Recrystallization of the latter from CH₂Cl₂/hexane gave 59 mg (62%) of pure **6** as yellow crystals, mp 167 °C.

¹H NMR (CDCl₃, 300.13 MHz, 294 K): δ 3.57 [s, 1H, ²J(H-^{117/119}Sn)=66 Hz, ¹J(H-¹³C)=129 Hz, CH], 7.39 (m, 9H, Ph-H_{m,p}), 7.56 [m, 6H, ²J(H-^{117/119}Sn)=90 Hz, Ph-H_o]. ¹³C{¹H} NMR (CDCl₃, 75.47 MHz, 294 K): δ: 9.2 (CH), 129.0 [³J(¹³C-¹¹⁷Sn)=88 Hz, ³J(¹³C-¹¹⁹Sn)=89 Hz, C_m], 131.4 [⁴J(¹³C-^{117/119}Sn)=19 Hz], C_p], 135.1 [²J(¹³C-^{117/119}Sn)=66 Hz, C_o], 136.3. No ¹J(¹³C-^{117/119}Sn) coupling constants were obtained. ¹¹⁹Sn{¹H} NMR (CDCl₃, 111.92 MHz, 298 K): δ -262 [²J(¹¹⁹Sn-¹¹⁷Sn)=311 Hz]. Anal. calcd for C₁₉H₁₆I₆Sn₃ (1361.8): C 16.8; H 1.2. Found: C 17.0; H 1.2.

Synthesis of Tris(dichloridophenylstannyl)methane HC(SnCl₂Ph)₃ (7)

To a solution of **6** (250 mg, 0.18 mmol) in CH₂Cl₂ (25 mL) was added excess of silver chloride (260 mg, 1.81 mmol). The resulting mixture was stirred at room temperature in the dark for 14 days. The AgI that had formed and the non-reacted AgCl was removed by filtration. The solvent of the filtrate was evaporated in vacuo (10⁻³ mmHg) to afford a white solid. Recrystallization of the latter from CH₂Cl₂/hexane gave 99 mg (66%) of pure **7** as colorless crystals, mp 176 °C.

¹H NMR (CDCl₃, 400.25 MHz, 295 K): δ 3.13 [s, 1H, ²J(H-^{117/119}Sn)=68/76 Hz, CH], 7.56 (m, 9H, Ph-H_{m,p}), -7.79 [m, 6H, ²J(H-^{117/119}Sn)=28 Hz, Ph-H_o]. ¹³C{¹H} NMR (CDCl₃, 100.64 MHz, 297 K): δ: 33.2 (CH), 129.9 [³J(¹³C-^{117/119}Sn)=100/105 Hz, C_m], 132.3 [⁴J(¹³C-^{117/119}Sn)=21 Hz, C_p], 134.9 [²J(¹³C-^{117/119}Sn)=68/73 Hz, C_o], 137.8 (C_i). No ¹J(¹³C-^{117/119}Sn) coupling constants were obtained. ¹¹⁹Sn{¹H} NMR (CDCl₃, 149.26 MHz, 294 K): δ -3 [²J(¹¹⁹Sn-^{117/119}Sn)=279 Hz]. Anal. calcd for C₁₉H₁₆Cl₆Sn₃ (813.09): C 28.1; H 2.0. Found: C 28.1; H 2.4.

Synthesis of Et₄N[(HC(SnPh₂)₃·F] (8)

Tetraethylammonium fluoride dihydrate (8 mg, 0.05 mmol) was added to a solution of **2** (58 mg, 0.05 mmol) in dichloromethane and the mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo to afford a white solid. Recrystallization of the latter from CH₃CN gave 26 mg (40%) of pure **8** as colorless crystals mp=180 °C.

Anal. calcd for C₄₅H₅₁Fl₃Ns₃ (1361.64): C 39.7; H 3.8; N 1.0 Found: C 39.5; H 4.0; N 1.2.

The NMR spectroscopic data given below were obtained from a solution of compound **2**, to which had been added 1 molar equivalent of NEt₄F·2H₂O.

¹⁹F NMR (CD₂Cl₂, 376.61 MHz, 193 K) δ -104 [d, ¹J(¹⁹F-^{117/119}Sn)=824 Hz, ³J(¹⁹F-¹H)=11 Hz]. ¹⁹F NMR (CD₂Cl₂, 564.84 MHz, 298 K) δ -103 (ν_{1/2} 2018 Hz). ¹¹⁹Sn{¹H} NMR (CD₂Cl₂, 149.26 MHz, 193 K): δ -163 [d, ¹J(¹¹⁹Sn-¹⁹F)=844 Hz, **8**], -77 (**2**), -55 [d, ²J(¹¹⁹Sn-^{117/119}Sn)=367 Hz, ³J(¹¹⁹Sn-¹⁹F)=35 Hz, **8**]. ¹¹⁹Sn{¹H} NMR (CD₂Cl₂, 223.85 MHz, 298 K): δ -72 (**2**).

Synthesis of PPh₄[(HC(SnClPh₂)₃·Cl] (9)

Tetraphenylphosphonium chloride (11 mg, 0.03 mmol) was added to a solution of **4** (28 mg, 0.03 mmol) and the mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo to afford a white solid. Recrystallization of the latter from Et₂O/CH₂Cl₂ gave 33 mg (85%) of pure **9**·1CH₂Cl₂ as colorless crystals of mp 228 °C.

¹H NMR (CDCl₃, 400.25 MHz, 299 K): δ 2.80 [s, 1H, ²J(H-^{117/119}Sn)=88 Hz, CH], 6.96–7.90 (complex pattern, 50H, Ph). ¹³C{¹H} NMR (CDCl₃, 75.47 MHz, 296 K): δ: 117.3 [d, ¹J(¹³C-³¹P)=90 Hz, Ci (PPh₄)], 127.6 [³J(¹³C-^{117/119}Sn)=73 Hz, C_m (SnPh)], 128.2 (C_p) (SnPh), 130.8 [d, ²J(¹³C-³¹P)=12 Hz, C_o (PPh₄)], 134.4 [d, ³J(¹³C-³¹P)=10 Hz, C_m (PPh₄)], 135.8 [d, ⁴J(¹³C-³¹P)=3 Hz, C_p (PPh₄)], 136.7 [²J(¹³C-^{117/119}Sn)=52 Hz, C_o (SnPh)], 138.9 (C_i) (SnPh). The signal for the CH carbon atom was not measured. ¹¹⁹Sn{¹H} NMR (CDCl₃, 149.26 MHz, 294 K): δ -97. ESI-MS (negative mode): m/z 972.9 [(Ph₂ClSn)₃CH·Cl]⁻. Anal. calcd for C₆₁H₅₁Cl₄Psn₃ (1312.85): C 55.8; H 3.9. Found: C 55.4; H 4.1.

Synthesis of (PPh₄)₂[(HC(SnClPh₂)₃·2Cl] (10)

Tetraphenylphosphonium chloride (41 mg, 0.11 mmol) was added to a solution of **7** (44 mg, 0.05 mmol) in CH₂Cl₂ and the mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo to afford a white solid. Recrystallization of the latter from CH₂Cl₂/hexane gave 67 mg (85%) of pure **10** as colorless crystals of mp 252 °C.

¹H NMR (CD₂Cl₂, 400.25 MHz, 299 K): δ 4.35 [s, 1H, ²J(H-^{117/119}Sn)=104 Hz, CH], 7.06–8.18 (complex pattern, 55H, Ph). ¹³C{¹H} NMR (CD₂Cl₂, 75.47 MHz, 296 K): δ 117.5 [d, ¹J(¹³C-³¹P)=90 Hz, Ci (PPh₄)], 127.5 [³J(¹³C-^{117/119}Sn)=88 Hz, C_m (SnPh)], 128.3 (C_p) (SnPh), 130.7 [d, ²J(¹³C-³¹P)=13 Hz, C_o (PPh₄)], 134.5 [d, ³J(¹³C-³¹P)=10 Hz, C_m (PPh₄)], 134.9 [C_o (SnPh)], 135.7 [d, ⁴J(¹³C-³¹P)=3 Hz, C_p (PPh₄)], 153.5 (C_i) (SnPh). The signal for the CH carbon atom was not measured. ¹¹⁹Sn{¹H} NMR (CD₂Cl₂, 149.26 MHz, 294 K): δ -248. Anal. calcd for C₆₇H₅₆Cl₈P₂Sn₃ (1562.72): C 51.5; H 3.6. Found: C 51.1; H 3.9.

Synthesis of (11)

To a solution of **2** (300 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) were added 3 molar equivalents of silver perchlorate (155 mg, 0.75 mmol). The resulting mixture was stirred at room temperature in the dark for 22 h. After the AgI that had formed had been removed by filtration, the solvent of the filtrate was reduced in vacuo (10^{-3} mmHg) to a volume of approximately 2 mL. The addition of *iso*-hexane (2 mL) caused precipitation of a small amount of **2** as crystalline material that was separated by filtration. The solvent of the filtrate was completely removed in vacuo, giving an amorphous white solid material. One part of the latter was dissolved in CDCl_3 . An ^{119}Sn NMR spectrum was recorded from this solution (see below). Another part of the solid material was recrystallized from CH_3CN /hexane giving a few crystals of pure **11**, mp 229°C .

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3 , 149.26 MHz, 298 K): δ -69 [$^2J(^{119}\text{Sn}-^{117}\text{Sn})$] = 237 Hz, integral 2.0, **2**], -76 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$] = 297/310 Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ = 232 Hz, $^1J(^{119}\text{Sn}-^{13}\text{C})$ = 592 Hz, $^3J(^{119}\text{Sn}-^{13}\text{C}_m)$ = 69 Hz, $^2J(^{119}\text{Sn}-^{13}\text{C}_o)$ = 52 Hz, integral 10.2], -83 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$] = 270/283 Hz, integral 1.0], -228 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$] = 297/310 Hz, integral 5.7], -244 [$^2J(^{119}\text{Sn}-^{117/119}\text{Sn})$] = 271/283 Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ = 370 Hz, integral 2.9]. IR(ATR): ν = 3394 (OH).

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