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Triorganotin Compounds $SnXMe_2$-1,4-Cyclohexadiene-COOMe: Intra- and Intermolecular Unfolding of an Inner Tetrahedron to Distorted Trigonal Bipyramids (X = Cl, Br, I) and a Distorted Octahedron (X = F)

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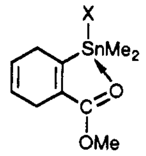
A series of (2-carbomethoxy-1,4-cyclohexadien-1-yl)dimethyltin halides ($SnXMe_2$-CHD-COOMe with X = F, Cl, Br, I (**1b**–**e**)) has been synthesized by halodemetalation of the related trimethyltin derivative X = Me (**1a**). The structure determination of compound **1b** gave the monoclinic space group $C2$ (a = 16.255 (2), b = 7.488 (3), c = 9.946 (1) Å; β = 100.53 (1)°; V = 1190 (1) Å^3; Z = 4; R = 0.0443). The isostructural compounds **1c** and **1d** have the triclinic space group $P\bar{1}$ (a = 7.465 (2); b = 8.896 (1); c = 9.615 (1) Å; α = 85.27 (1), β = 88.56 (1), γ = 77.56 (2)°; V = 621 (2) Å^3; Z = 2; R = 0.0340 and a = 7.49 (1), b = 8.89 (1), c = 9.88 (2) Å; α = 85.4 (2), β = 89.2 (1), γ = 77.8 (1)°; V = 642 (2) Å^3; Z = 2; R = 0.0825). Compound **1e** crystallizes in the monoclinic space group $P2_1/c$ (a = 7.988 (3), b = 15.016 (2), c = 11.470 (1) Å; β = 95.81 (1)°; V = 1369 (1) Å^3; Z = 4; R = 0.0502). **1c**–**e** exhibit five-coordination around tin, and **1b** reveals six-coordinated dimers with Sn···O contacts and an additional Sn···F contact in the latter case. Hence, **1b** forms the first hexacoordinated triorganotin compound with a coordinative tin–oxygen bond. The lengthening of Sn–X in relation to the single bond distances increases in the order F ≪ Cl < Br < I. The coordinating Sn···O distances run in the order F > Cl = Br > I with the shortest Sn···O distance of 2.39 Å in the case of X = I (**1e**). This behavior is contrary to the decreasing electronegativity of the halides and is discussed in analogy to the series of the halides of boron.

Introduction

(2-Carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin ($SnMe_3$-CHD-COOMe, **1a**) was introduced as the first pentacoordinated tetraorganotin compound with a coordinative tin–oxygen bond.[1] Only substances with the more nucleophilic nitrogen as a fifth ligand such as the stannatrane $MeSn(CH_2CH_2CH_2)_3N$[2] and [3-(2-pyridyl)-2-thienyl-*C*,*N*]tri-*p*-tolyltin[3] were known before. The recent structure determination of the tetraorganotin compound (*Z*)-17-[2-(triphenylstannyl)vinyl]-4-estren-17-ol exhibits a Sn···O coordination as well.[4] In contrast to the sp^2 hybridization of the oxygen atom in **1a** the latter compound involves sp^3-hybridized oxygen. In spite of this difference the coordinative Sn···O distances are equal in both compounds (2.781 (3)[1] and 2.77 (1) Å[4]).

A carbonyl group in an acid, ester, amide, or ketone is considered as a weak coordinating ligand when compared to an amine or a sulfoxide. Its low nucleophilicity does not allow the formation of strong coordination bonds. To our knowledge no structure of a monohalogenated compound, where the metal is intermolecularly or intramolecularly coordinated to a carbonyl, has been reported up to now. Such a coordination has been demonstrated in the liquid or solid state by ^1H or ^{13}C NMR spectroscopy or IR spectroscopy for trialkyltin halides and dialkyltin dihalides able to form a 5- or 6-membered ring by intramolecular chelation.[5] As demonstrated by one of us[6] and by other authors,[7] the introduction of a ligand in the γ-position in an organotin derivative has a dramatic effect on the reactivity of the compounds, particularly toward electrophilic substitution. To estimate the possible range of secondary Sn···O bond lengths in compounds similar to **1a**, we substituted one methyl group of **1a** by a halogen atom (Scheme I) and determined the crystal structures of the four compounds.

Scheme I



X	$SnXMe_2$—CHD—COOMe
Me	**1a**
F	**1b**
Cl	**1c**
Br	**1d**
I	**1e**

Table I. ^{119}Sn NMR Data

compd	1a	1b	1c	1d	1e
$\delta^{a,b}$	−47.9^c	−41.9	−31.5	−44.6	−79.6

^{a} $CDCl_3$ solution. ^{b} Shifts relative to Me_4Sn. ^{c} Taken from ref 1.

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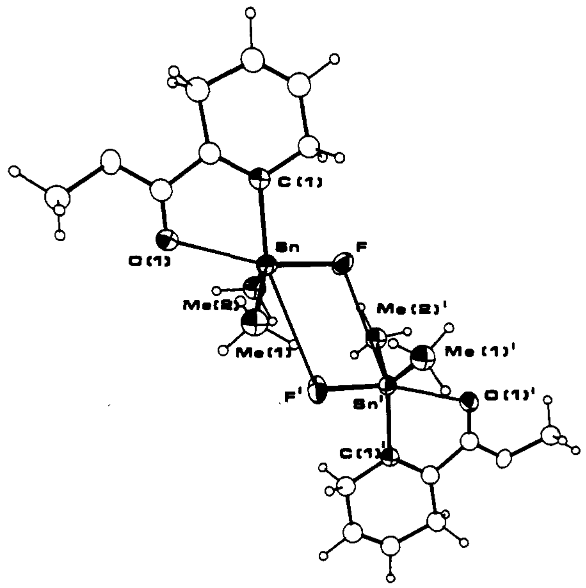
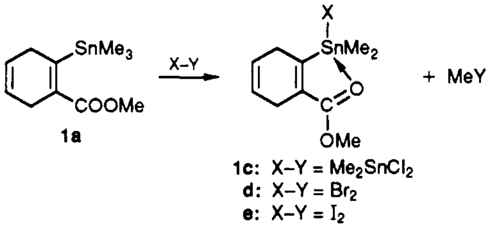


Figure 1. Intra- and intermolecular coordination in the C_2 symmetric dimer of $SnFMe_2$-CHD-COOMe (**1b**). Labels of atoms and groups as given in Table VI. ORTEP drawing: thermal ellipsoids are at the 30% probability level, H atoms are isotropic spheres with radii 0.1 Å.

Results

1d and **1e** were prepared as mentioned earlier for **1e**,[6] by electrophilic cleavage of **1a** with the corresponding halogen. This method led to a poor yield of **1c**. It was better obtained by a redistribution reaction from **1a** and dimethyltin dichloride in carbon tetrachloride. A reversal of the known selectivity occurred also in this case: a tin-methyl bond was cleaved instead of the tin-vinyl bond. Treatment of **1e** with potassium fluoride in acetone afforded **1b**. The ^{119}Sn NMR spectral characteristics of



compounds **1b–e** (Table I) are diagnostic for a coordination number higher than four. The tin resonances exhibit an upfield shift of about 100 ppm with regard to the expected values for uncoordinated halides, indicating pentacoordination of the metal in solution.[8]

In the solid state, $SnFMe_2$-CHD-COOMe **1b** forms the first hexacoordinated triorganotin compound with a coordinative tin–oxygen bond. The only other example of a triorganotin compound with six bonded ligand sites, trimethyltin tris(pyrazolyl)borate, includes three bonds to nitrogen.[9] The hexacoordinated tetraorganotin species bis[3-(2-pyridyl)-2-thienyl-*C,N*]diphenyltin[3] exhibits two bonds to nitrogen.[10] All other compounds with hexacoordinated tin have more than three electronegative substituents on tin.[11] The structure determinations of **1c**, **1d**, and **1e** reveal pentacoordinated tin.

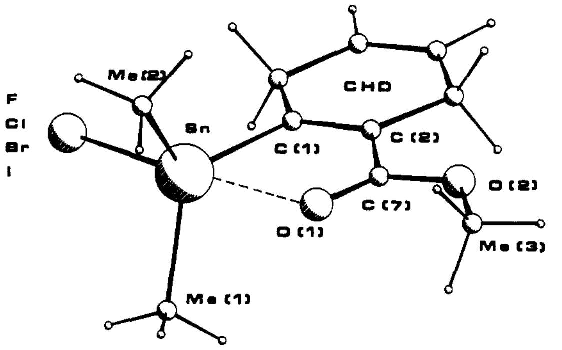


Figure 2. Intramolecular coordination in the compounds $SnXMe_2$-CHD-COOMe, X = F (**1b**), Cl (**1c**), Br (**1d**), and I (**1e**). Labels of atoms and groups as given in Table VI (CHD, C(1)–C(6), Me(1,2,3), C(8)–C(10)) (PLUTO-78 drawing).

The hexacoordination of compound **1b** in the crystalline state results in dimeric units with two intermolecular Sn···F bonds. Figure 1 shows such a dimer containing a 2-fold axis in its center. In contrast, **1c–e** form monomers which, in a rough overview, differ not much from one compound to the other and also are similar to both halves of dimeric **1b**. Figure 2 represents a mean monomeric unit for all four halogenated compounds. This figure gives an idea of the very planar structure: only the two methyl groups are situated over and under the plane and the methoxy group has a smaller or bigger torsion angle. For **1b**, the planarity expands over the whole dimer.

Table II contains the relevant data of the four synthesized compounds in detail. The data of **1a** are given for comparison. The first part of Table II shows bond lengths and bond angles for the second structural feature of the compound series: a central tetrahedron of ligands around tin (substituents: 2 × Me, CHD, and halide) extends by a nucleophilic attack of C=O trans to the halide atom into a distorted trigonal bipyramid. In **1b**, a second nucleophilic attack intermolecular concerted of two fluoride atoms trans to the CHD group extends the trigonal bipyramid furthermore into two edge-connected distorted octahedra. The coordinative Sn···F bond length amounts to 3.64 Å. This length is 1.7 Å longer than the covalent distance found in **1b** and is placed near the borderline to a van der Waals Sn···F contact (3.63 Å[12]); it stretches the concept of a coordination "bond". More convincing for a true hexacoordination of tin in **1b** are the geometric conditions of the two edge-connected distorted octahedra: two trans positions of ligands (O(1)···Sn–F 165° and F···Sn–C(1) 162°) and two equatorial planes with good merits of planarity:[13] five units for the eight atoms O(1)···SnC(1)-FF′C(1)′Sn′···O(1)′ (maximum deviation from the least-squares plane including both edge-connected octahedra: +0.06 (5) Å for O(1)′ and −0.04 (4) Å for C(1)′) and a little poorer 203 units for the five atoms SnMe(1)Me(2)C(1)F′ (mean deviation from the second least-squares plane of the two octahedra: ±0.12 (2) Å). Only the angle Me(1)–Sn–Me(2) with 119° resists a true octahedral coordination.

The dimeric structure of **1b** is found only in the solid state. The NMR data of **1b** in solution (Table I) show no marked difference in comparison to **1a** and **1c–e**.

The second part of Table II describes the planarity of the molecules **1a–e** quantitatively. The merit of the least-squares planes,[13] averaging CHD, 5-membered che-

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[13] For a definition of the merit of planarity, see: Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*, 2nd ed.; John Wiley & Sons: New York, 1989; Chapter 18.7.

Table II. Bond Lengths and Bond Angles of the Coordination Polyedra at the Central Tin Atom in SnFMe$_2$-CHD-COOMe (1b), SnClMe$_2$-CHD-COOMe (1c), SnBrMe$_2$-CHD-COOMe (1d), and SnIMe$_2$-CHD-COOMe (1e), and in SnMe$_3$-CHD-COOMe (1a) for Comparison, Least-Squares Planes Averaging the "Central Cores" of the Molecules, and Torsion Angles of the Methoxy Groups

	1b (X = F)	**1c** (X = Cl)	**1d** (X = Br)	**1e** (X = I)	**1a** (X = Me)
Bond Lengths, Å					
Sn–X	1.974 (8)	2.432 (1)	2.588 (1)	2.830 (7)	2.150 (5)
Sn···O(1)	2.52 (1)	2.470 (3)	2.470 (6)	2.391 (5)	2.781 (3)
Sn···F′[a]	3.641 (7)	*b*	*b*	*b*	*b*
Sn–Me(1)	2.12 (2)	2.129 (5)	2.125 (9)	2.123 (8)	2.146 (5)
Sn–Me(2)	2.14 (2)	2.112 (6)	2.136 (1)	2.115 (7)	2.127 (6)
Sn–C(1) (CHD)	2.15 (1)	2.151 (3)	2.158 (7)	2.155 (5)	2.177 (3)
Bond Angles, deg					
X–Sn–Me(1)	103 (1)	98.6 (2)	98.5 (3)	98.1 (2)	106.3 (2)
X–Sn–Me(2)	94 (1)	99.2 (2)	99.5 (3)	99.4 (2)	106.0 (2)
X–Sn–C(1)	93.3 (4)	98.6 (1)	99.7 (2)	99.3 (1)	103.7 (2)
C(1)–Sn–Me(1)	124 (2)	117.4 (2)	117.9 (3)	117.7 (3)	111.0 (2)
C(1)–Sn–Me(2)	113 (2)	118.0 (2)	118.0 (4)	116.4 (3)	115.7 (2)
Me(1)–Sn–Me(2)	119.1 (8)	117.6 (2)	116.5 (4)	118.8 (3)	113.1 (2)
O(1)···Sn–X	165.4 (4)	172.12 (8)	173.4 (1)	172.5 (1)	172.4 (2)
O(1)···Sn–Me(1)	87 (1)	85.2 (2)	85.3 (3)	81.3 (3)	77.8 (2)
O(1)···Sn–Me(2)	91 (1)	84.9 (2)	83.4 (4)	87.4 (3)	77.6 (2)
O(1)···Sn–C(1)	72.2 (4)	73.5 (1)	73.8 (2)	74.6 (2)	68.8 (1)
F′···Sn–X[a]	69.0 (3)				
F′···Sn···O(1)[a]	125.4 (2)				
F′···Sn–Me(1)[a]	64.2 (8)				
F′···Sn–Me(2)[a]	68.5 (9)				
F′···Sn–C(1)[a]	162.3 (4)				
Least-Squares Planes Averaging the 10 Atoms XSn-CHD-CO, Deviations, Å					
figure of merit	12	182	61	772	1849
max deviation (+)	0.07 (5)	0.024 (8)	0.032 (9)	0.0770 (4)	0.064 (4)
max deviation (–)	–0.05 (7)	–0.051 (6)	–0.05 (1)	–0.0804 (5)	–0.093 (4)
deviation of O(2)	–0.00 (3)	–0.007 (4)	0.0353 (8)	–0.264 (5)	0.231 (4)
deviation of Me(3)	0.57 (2)	0.009 (7)	–0.02 (1)	–0.366 (9)	0.312 (9)
Torsion Angles, deg					
C(1)C(2)–C(7)O(2)	–170 (4)	+179.8 (4)	–179.1 (8)	+173.3 (5)	–172.9 (3)
C(2)C(7)–O(2)Me(3)	–151 (3)	+178.8 (4)	–177.4 (7)	–178.5 (6)	+176.8 (5)

[a] F′ by $-x, y, -z$ from F. [b] Shortest intermolecular distances Sn···X > 4.3 Å.

Table III. Transition from a Tetrahedron to a Trigonal Bipyramid in the Compound series 1a–e ($\sum\vartheta_{eq}$ and $\sum\vartheta_{ax}$, deg, Δ_{Sn}(plane), Å)

X	$\sum\vartheta_{eq}$	$\sum\vartheta_{ax}$	$\sum\vartheta_{eq} - \sum\vartheta_{ax}$	Δ_{Sn}(plane)
tetrahedron	328.5	328.5	0	0.71
Me (**1a**)	339.8 (6)	316.0 (6)	24 (1)	0.57
I (**1e**)	353 (1)	296.8 (5)	56 (2)	0.33
Br (**1d**)	352 (1)	298 (1)	55 (2)	0.34
Cl (**1c**)	353.0 (6)	296.4 (5)	57 (1)	0.33
F (**1b**)	356 (1)	290 (1)	66 (2)	0.25
trigonal bipyramid	360	270	90	0.00

Table IV. Compilation of Sn–X Distances (Å) in the Solid State (X-ray Diffraction) and in the Gas Phase (Electron Diffraction (el diffr))

compd	F	Cl	Br	I
Monohalides				
Me$_3$SnX (el diffr)		2.37[18]	2.49[18]	2.72[18]
Me$_3$SnX	2.15/2.45[19]			
Ph$_3$SnX		2.32[20]	2.49[21]	
Mes$_3$SnX	1.96[22]			
(c-Hex)$_3$SnX	2.45[23]	2.41[23]	2.52[23]	2.54[23]
Dihalides				
Me$_2$SnX$_2$ (el diffr)		2.34[18]	2.48[18]	2.69[18]
Me$_2$SnX$_2$	2.12[11a]	2.41[24]		
Et$_2$SnX$_2$		2.39[25]	2.50[25]	2.72[25]
Ph$_2$SnX$_2$		2.35[26]		
(c-Hex)$_2$SnX$_2$		2.39, 2.41[27]	2.49, 2.52[27]	
Tri- and Tetrahalides				
MeSnX$_3$ (el diffr)		2.32[18]	2.45[18]	2.68[18]
SnX$_4$ (el diffr)		2.28[28]	2.44[29]	2.64[29]
SnX$_4$	1.88/2.02[30]			
Conclusion				
Sn–X (single)	1.96	2.345	2.49	2.72
Sn–X (**1b**–**1e**)	1.97	2.43	2.59	2.83
Δ (Sn–X)	0.01	0.085	0.10	0.11
EN(X)[a]	3.98	3.16	2.96	2.66
Sn···O (**1b**–**e**)	2.52	2.47	2.47	2.39

[a] Electronegativity of the halides.[32]

late, and trans ligands together, runs better in the order X = Me, I, Cl, Br, F. Especially in **1b**, these 10 atoms exhibit nearly ideal planarity. In contrast, the methoxy group is noticeably turned out of this plane only in **1b** and not in the other four compounds.

Discussion

As set out above, the compound series **1a–e** marks a path from an inner tetrahedron to a trigonal bipyramid and further to an octahedron for **1b**. Such a nucleophilic reaction path can be described quantitatively in a complicated manner by a structure–correlation method original given by Bürgi[14] and elaborated for tin compounds by Britton and Dunitz.[15] To describe the transition range, we introduced alternatively a rather simple procedure which uses only the six bond angles of the inner tetrahedron.[16] By approaching a trigonal bipyramid, three of

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Table V. Crystallographic Data for SnFMe$_2$-CHD-COOMe (1b), SnClMe$_2$-CHD-COOMe (1c), SnBrMe$_2$-CHD-COOMe (1d), and SnIMe$_2$-CHD-COOMe (1e) and Structure Determination Details

	1b	**1c**	**1d**	**1e**
Crystal Data (Mo $K_{\alpha 1}$, λ = 0.709 26 Å)				
formula, M	$C_{10}H_{15}FO_2Sn$, 304.92	$C_{10}H_{15}ClO_2Sn$, 321.37	$C_{10}H_{15}BrO_2Sn$, 365.83	$C_{10}H_{15}IO_2Sn$, 412.82
cryst habit	thin unregular platelet	flat needle	big plate	unregular square
face indices (dist from a common origin inside the crystal, mm)	100, −1,0,0 (0.01); 010, 0–1,0 (0.20); 001, 0,0–1 (0.08)	100, −1,0,0 (0.50); 0,−1,1, 0, 1,−1 (0.14); 0 11, 0,−1,−1 (0.08); −1,−1,1 (0.37); 1,−1,1 (0.35)	100, −1,0,0 (0.77); 001, 0,0,−1 (0.49); 010 0,−1,0 (0.11); 101, −1,0–1 (0.625)	100, −1,0,0 (0.35); 010 (0.125); 0,0,−1 (0.20); 0,−1,1 (0.10); 0,−1,−1 (0.10)
cryst color	yellow	colorless, light dim	colorless	colorless
cryst syst, space group	monoclinic, $C2$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
unit cell dimens				
a, α	16.255 (2) Å	7.465 (2) Å, 85.27 (1)°	7.49 (1) Å, 85.4 (2)°	7.988 (3) Å
b, β	7.488 (3) Å, 100.53 (1)°	8.896 (1) Å, 88.56 (1)°	8.89 (1) Å, 89.2 (1)°	15.016 (2) Å, 95.81 (1)°
c, γ	9.946 (1) Å	9.615 (1) Å, 77.56 (2)°	9.88 (2) Å, 77.8 (1)°	11.470 (1) Å
least-squares fit	60 refl θ = 17–21°	50 refl θ = 23–27°	15 refl θ = 13–14°	50 refl θ = 24–27°
packing: V, Z, F (000)	1190 (1) Å^3, 4, 600	621 (1) Å^3, 2, 316	642 (2) Å^3, 2, 352	1369 (1) Å^3, 4, 776
D_{calcd}, D_{exptl}	1.699, 1.700 g cm^{-3}	1.717, 1.694 g cm^{-3}	1.892, 1.845 g cm^{-3}	2.003, 2.000 g cm^{-3}
Intensity Data Collection (Mo $K\bar{\alpha}$, λ = 0.710 69 Å, graphite monochromator)				
temp, θ range	22 °C, 1.5–30.0°	22 °C, 1.5–30.0°	22 °C, 1.5–30.0°	22 °C, 1.5–30.0°
$(\sin \theta_{max})/\lambda$, Å^{-1}	0.7035	0.7035	0.7035	0.7035
range of h,k,l	+22,+10,±14	+10,±12,±13	+10,±12,±13	+11,+21,±16
reference rflns	3, every 3000 s	3, every 4000 s	3, every 4000 s	3, every 4000 s
loss of intens (time)	57% (5 days)	10% (5 days)	15% (5 days)	20% (5 days)
correction	linear	direct fit	direct fit	linear
no. of reflns: meas, indep (int R)	1911, 1850 (0.0273)	3864, 3606 (0.0225)	4030, 3766 (0.0508)	4386, 3973 (0.0392)
no. of reflns used, limit	788 with $I > 1\sigma(I)$	3228 with $I > 2\sigma(I)$	2951 with $I > 2\sigma(I)$	2939 with $I > 2\sigma(I)$
μ, cm^{-1}, abs cor	19.70, by face indices	20.73, by face indices	48.70, by face indices	38.17, by face indices
range of transmissn	0.9601–0.7151	0.7303–0.5538	0.3514–0.0294	0.4944–0.3565
Refinement				
choice of thermal params	Sn, F, O anisotropic, C isotropic, H isotropic fixed	Sn, Cl, O, C anisotropic, H isotropic fixed	Sn, Br, O, C anisotropic, H isotropic fixed	Sn, I, O, C anisotropic, H isotropic fixed
variables, ratio refl var	79, 10	130, 24.8	129, 22.9	130, 22.6
last shifts	mostly $<0.5\sigma$	$<0.003\sigma$	$<0.04\sigma$	$<0.02\sigma$
final R, R_w	0.0443, 0.0545	0.0340, 0.0675	0.0825, 0.1192	0.0502, 0.0851
weighting scheme, w^{-1}	$\sigma^2(F) + 0.025F^2$	$\sigma^2(F) + 0.032F^2$	$\sigma^2(F) + 0.032F^2$	$\sigma^2(F) + 0.010F^2$
final diff Fourier maxima	1 e/Å^3 near Sn	1 e/Å^3 near Sn	2.8 e/Å^3 near Sn	0.7 e/Å^3 near Sn

these angles become equatorial and their sum $\sum\vartheta_{eq}$ runs from 328.5 to 360°; the three other angles become axial and their sum $\sum\vartheta_{ax}$ runs from 328.5 to 270°. The border values of the difference of the two sums are 0° for a tetrahedron and 90° for a trigonal bipyramid. Yet simpler a procedure to follow the transition from a tetrahedron to a trigonal bipyramid is to measure the deviation Δ_{Sn}(plane) of the tin atom from the plane of the three ligands which become equatorial. In case of three carbon atoms, these values range from 0.71 to 0.0 Å. Table III lists the actual values.

Both techniques give equivalent results. For compound **1a** (X = Me) the geometry around the tin atom is not yet far from a tetrahedron. Between the three compounds **1c–e** (X = Cl, Br, I) there exists no geometrical difference: all three coordination polyhedra are midway between a tetrahedron and a trigonal bipyramid. The geometry inside compound **1b** (X = F) approaches nearest to a trigonal bipyramid: in case of the assumed octahedron five of the six angles should come close to 90° and one angle should meet 180°. Hexacoordinated silicon species described recently[17] exhibit similar differences to true octahedra as in **1b**.

In order to discuss the four tin–halide distances of the compounds **1b–e**, we first need an idea of the usual tin–halide distances in the literature. We consider this to be a better way than to rely on conventional covalent radii. Table IV gives a compilation for some simple compounds.

For the most simple compounds Me_3SnX, Me_2SnX_2, $MeSnX_3$, and SnX_4 electron diffraction data in the gas phase are shown. The Sn–X bond shortens from iodide to chloride and to a smaller amount with increasing halide content; no such data are available for X = F.

For comparison with the compound series **1b–e** we searched for compounds which were measured in the solid state and which have no coordinative bonds. The molecule chosen for Sn–I is Et_2SnI_2[25] with a distance of 2.72 Å. In this structure there exists no remarkable autoassociation in contrast to the comparable compounds Et_2SnCl_2 and Et_2SnBr_2. The value chosen for Sn–Br is 2.49 Å from Ph_3SnBr.[21] Difficulties were encountered in the case of Sn–Cl. We chose 2.345 Å as the average between the gas-phase value for Me_3SnCl[18] and the X-ray value for Ph_3SnCl;[20] the aromatic phenyl groups shorten the Sn–Cl bond and the gas-phase measurements usually give a bond length that is too long. The most electronegative halogen F exhibits polymeric structures in nearly all of its compounds with tin: SnF_4[30] (hexacoordinated) is a network, Me_2SnF_2[11a] (hexacoordinated) builds layers, and Me_3SnF[19] (pentacoordinated) forms chains. Only in cases of bulky substituents can monomeric units be found: Mes_3SnF[22]

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(Sn–F 1.957 and 1.965 Å), (PhMe$_2$Si)$_3$CSnMe$_2$F[31] (1.965 Å), and (Me$_3$Si)$_3$CSnPh$_2$F[31] (1.965 Å). From these figures we chose 1.96 Å as a Sn–F single-bond distance.

The first two lines of the conclusion part of Table IV summarize the selected single-bond distances Sn–X (single) and the distances Sn–X (**1b–e**) found in the concerned compound series. The difference

$$\Delta(\text{Sn–X}) = \text{Sn–X (single)} - \text{Sn–X } (\mathbf{1b–e}) = f(\text{EN}(X))$$

increases in the series F ≪ Cl = Br < I and shows a rough correlation with decreasing electronegativity EN(X)[32] of the halides. In contrast, the only other compound series investigated includig all four halides, (c-Hex)$_3$Sn–X,[23] exhibits a reversed order of Δ(Sn–X): F ≫ Cl > Br > I (0.49 ≫ 0.065 > 0.03 > −0.18 Å).

The last line of Table IV summarizes the distances of the carbonyl oxygen to the tin atom trans to the halide atoms: Sn···O (**1b–e**). It reveals just the reversed order (F > Cl > Br > I) as would be assumed from the electronegativity order of the halides: the more electronegative halide should render the tin atom more acidic and this enhanced acidity of tin should enhance the nucleophilic attack of oxygen. In the case of X = F (**1b**), the long Sn···O distance follows from the octahedral hexacoordination: the enhanced acidity of tin is spread over two coordination sites Sn···O and Sn···F. Not obvious is the short distance of only 2.39 Å in the case of X = I (**1e**). Such meaningless terms as "heavy-atom effect" or more scientifically "polarizability" as often used in spectroscopic discussions seem to be of little utility in this context. A possible explanation could be given in analogy to the series of the boron halides: a decreasing p_π–d_π overlap from Sn–F to Sn–I contrary to the decreasing electronegativity effect would cause a higher Lewis acidity at tin for X = Br and even higher for X = I.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen by using Schlenk tube techniques. **1a** was obtained as described earlier.[33] ^{1}H NMR spectra were recorded on a Perkin-Elmer R 24 spectrometer in CDCl$_3$ as solvent and Me$_4$Si as internal reference. ^{119}Sn NMR spectra were recorded on a Bruker AC 200 instrument in CDCl$_3$ with Me$_4$Sn as internal reference.

Preparation of 1b. A solution of **1e** (1.65 g, 4 mmol) in acetone (50 mL) was stirred with 20 mL of a saturated solution of KF for 24 h. After extraction with pentane (3 × 50 mL) the solvents were evaporated and the residue recrystallized from hexane: yield 0.62 g, 51%; mp 118 °C. ^{1}H NMR δ 0.65 (s, 6 H), 3–3.5 (m, 4 H), 3.95 (s, 3 H), 5.81 (bs, 2 H). Anal. Calcd. for C$_{10}$H$_{15}$O$_2$FSn: C, 39.39; H, 4.95. Found: C, 39.13; H, 4.85.

Preparation of 1c. To a solution of **1a** (1.5 g, 5 mmol) in 50 mL of dry CCl$_4$ was added Me$_2$SnCl$_2$ (1.1 g, 5 mmol). The solution was stirred at 80 °C for 2 h. After evaporation of the solvent, the residue was chromatographed on silica (eluent petroleum ether–diethyl ether 90/10) and recrystallized from pentane: yield 1.03 g, 64%; mp 97 °C. MS (^{120}Sn, m/z) 307 (100, M − CH$_3$), 285 (53, M − Cl). ^{1}H NMR δ 0.72 (s, 6 H), 2.9–3.4 (m, 4 H), 3.91 (s, 3 H), 5.85 (bs, 2 H). Anal. Calcd. for C$_{10}$H$_{15}$O$_2$ClSn: C, 37.37; H, 4.70. Found: C, 37.31; H, 4.65.

Preparation of 1d. To a solution of **1a** (1.5 g, 5 mmol) in 50 mL of dry CHCl$_3$ at 50 °C was slowly added a solution of bromine (800 mg, 5 mmol) in 50 mL of CHCl$_3$. The solvent was then evaporated and the residue recrystallized from hexane: yield 1.3 g, 72%; mp 81 °C. MS (^{120}Sn, m/z) 351 (100, M − CH$_3$), 285 (90, M − Br); ^{1}H NMR δ 0.75 (s, 6 H), 2.9–3.4 (m, 4 H), 3.90 (s, 3 H), 5.85 (m, 2 H). Anal. Calcd. for C$_{10}$H$_{15}$O$_2$BrSn: C, 32.83; H, 4.13. Found: C, 32.75; H, 4.08.

Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for SnFMe$_2$-CHD-COOMe (1b), SnClMe$_2$-CHD-COOMe (1c), SnBrMe$_2$-CHD-COOMe (1d), and SnIMe$_2$-CHD-COOMe (1e) (Esd's in Parentheses)

group	atom	x/a	y/b	z/c	U(eq),[a] Å^2
			1b		
	Sn(1)	0.12603 (5)	0.25000	0.16149 (8)	0.0518 (5)
	F(1)	0.0065 (4)	0.2526 (60)	0.1758 (7)	0.079 (6)
	O(1)	0.2838 (5)	0.2366 (71)	0.2081 (8)	0.060 (7)
	O(2)	0.3877 (5)	0.2183 (25)	0.3895 (9)	0.040 (7)
CHD	C(1)	0.1673 (7)	0.2414 (77)	0.3791 (10)	0.045 (2)*
	C(2)	0.2494 (6)	0.2554 (77)	0.4311 (10)	0.045 (2)*
	C(3)	0.2866 (7)	0.2581 (79)	0.5783 (11)	0.053 (3)*
	C(4)	0.2181 (8)	0.2287 (37)	0.6650 (12)	0.054 (3)*
	C(5)	0.1407 (8)	0.2272 (38)	0.6180 (12)	0.055 (3)*
	C(6)	0.1041 (7)	0.2333 (43)	0.4696 (10)	0.049 (3)*
	C(7)	0.3077 (7)	0.2326 (42)	0.3309 (10)	0.047 (3)*
Me(1)	C(8)	0.1367 (13)	0.4786 (31)	0.0394 (20)	0.069 (6)*
Me(2)	C(9)	0.1194 (13)	−0.0090 (30)	0.0688 (21)	0.065 (5)*
Me(3)	C(10)	0.4483 (8)	0.2909 (25)	0.2972 (12)	0.052 (3)*
			1c		
	Sn(1)	0.20004 (3)	0.19468 (2)	0.14205 (2)	0.0411 (1)
	Cl(1)	0.2405 (2)	0.0602 (1)	0.9295 (1)	0.0636 (6)
	O(1)	0.1681 (5)	0.2956 (3)	0.3751 (3)	0.056 (1)
	O(2)	0.1928 (5)	0.2007 (3)	0.5978 (3)	0.061 (1)
CHD	C(1)	0.2526 (4)	−0.0032 (3)	0.2914 (3)	0.039 (1)
	C(2)	0.2448 (4)	0.0238 (3)	0.4262 (3)	0.040 (1)
	C(3)	0.2808 (6)	−0.0998 (4)	0.5467 (4)	0.052 (1)
	C(4)	0.3277 (9)	−0.2588 (4)	0.4950 (6)	0.069 (2)
	C(5)	0.3335 (9)	−0.2853 (5)	0.3602 (5)	0.066 (2)
	C(6)	0.2920 (7)	−0.1628 (4)	0.2445 (5)	0.056 (2)
	C(7)	0.1972 (5)	0.1866 (3)	0.4627 (3)	0.042 (1)
Me(1)	C(8)	−0.0777 (6)	0.3138 (6)	0.1134 (5)	0.060 (2)
Me(2)	C(9)	0.4056 (7)	0.3241 (6)	0.1086 (6)	0.063 (2)
Me(3)	C(10)	0.1514 (9)	0.3543 (5)	0.6421 (5)	0.072 (3)
			1d		
	Sn(1)	0.19856 (7)	0.19967 (5)	0.14421 (4)	0.0439 (3)
	Br(1)	0.2381 (1)	0.0623 (1)	−0.07879 (8)	0.0641 (5)
	O(1)	0.1713 (10)	0.3010 (6)	0.3707 (5)	0.062 (3)
	O(2)	0.2021 (10)	0.2026 (6)	0.5867 (5)	0.068 (3)
CHD	C(1)	0.2471 (10)	0.0009 (8)	0.2897 (6)	0.044 (3)
	C(2)	0.2426 (10)	0.0274 (8)	0.4177 (6)	0.046 (3)
	C(3)	0.2798 (11)	−0.0958 (8)	0.5378 (6)	0.051 (3)
	C(4)	0.3173 (17)	−0.2509 (10)	0.4897 (10)	0.071 (5)
	C(5)	0.3249 (16)	−0.2802 (9)	0.3586 (9)	0.072 (5)
	C(6)	0.2859 (14)	−0.1591 (8)	0.2463 (8)	0.060 (4)
	C(7)	0.2003 (11)	0.1898 (8)	0.4534 (7)	0.050 (3)
Me(1)	C(8)	−0.0748 (13)	0.3240 (11)	0.1141 (10)	0.066 (5)
Me(2)	C(9)	0.4070 (14)	0.3301 (11)	0.1168 (12)	0.076 (6)
Me(3)	C(10)	0.1552 (17)	0.3553 (11)	0.6356 (9)	0.074 (5)
			1e		
	Sn(1)	0.14891 (5)	0.11805 (3)	0.22415 (3)	0.0489 (2)
	I(1)	0.03989 (7)	0.27914 (3)	0.32000 (5)	0.0770 (3)
	O(1)	0.2672 (6)	−0.0191 (3)	0.1655 (3)	0.059 (2)
	O(2)	0.3997 (6)	−0.1369 (3)	0.2499 (4)	0.065 (2)
CHD	C(1)	0.2107 (7)	0.0444 (3)	0.3841 (4)	0.044 (2)
	C(2)	0.2811 (6)	−0.0345 (3)	0.3733 (4)	0.046 (2)
	C(3)	0.3301 (8)	−0.0982 (4)	0.4740 (5)	0.056 (3)
	C(4)	0.2993 (9)	−0.0593 (5)	0.5873 (5)	0.062 (3)
	C(5)	0.2319 (8)	0.0206 (5)	0.5998 (4)	0.059 (3)
	C(6)	0.1779 (8)	0.0808 (4)	0.5008 (4)	0.054 (3)
	C(7)	0.3143 (7)	−0.0626 (4)	0.2532 (5)	0.051 (2)
Me(1)	C(8)	0.3507 (9)	0.1704 (5)	0.1383 (6)	0.070 (4)
Me(2)	C(9)	−0.0756 (9)	0.0809 (6)	0.1219 (6)	0.072 (4)
Me(3)	C(10)	0.1533 (18)	0.3556 (12)	0.6365 (10)	0.073 (6)

[a] U(eq) = one third of the trace of the orthogonal $U(ij)$ tensor; *, isotropic U.

Preparation of 1e. To a solution of **1a** (1.5 g, 5 mmol) in 50 mL of dry CHCl$_3$ at 0 °C was slowly added crushed iodine (1.3

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g, 5 mmol). After decoloration of the solution, the solvent was evaporated and the solid residue recrystallized from hexane: yield 1.8 g, 88%; mp 78 °C. MS (^{120}Sn, *m/z*) 399 (6, M − CH_3), 287 (100, M − I); ^{1}H NMR δ 0.80 (s, 6 H), 3.0–3.5 (m, 4 H), 3.94 (s, 3 H), 5.6–5.8 (bs, 2 H). Anal. Calcd. for $C_{10}H_{15}O_2ISn$: C, 29.09; H, 3.66. Found: C, 28.98; H, 3.61.

Structure Determination of 1b–e. Crystal data as well as details of intensity data collections and refinements are given in Table V. The densities are obtained from neutral buoyancy (polytungstate solution). The crystals are fixed by gravity and sealed in small glass capillaries. The quality and symmetry of the crystals are examined by Weissenberg exposures; all crystals of **1d** are of low quality. Integrated intensities are measured by means of $\omega/2\theta$ scans on a CAD4 diffractometer (Enraf-Nonius).

The structures are solved by Patterson syntheses (Sn, Cl, I, Br atoms) and completed by Fourier syntheses (F, O, and C atoms). Hydrogen atoms are considered as riding on carbon atoms. The temperature factors are all anisotropic, except the carbon atoms of compound **1b** (X = F) because of the small amount of available reflections. The refinements of the structures of **1c–e** come out with a good convergence and an even distribution of the variances. **1b** crystallizes undoubtedly in the space group *C*2; this is proven experimentally by a separate measurement and refinement with 758 Friedel pairs (R_{w2}/R_{w1} = 0.0797/0.0788). Yet, 10 of the 14 atoms are almost in the same plane (Table II) arranged nearly perpendicular to the *y* axis of the unit cell. Hence, the space group *C*2 comes close to *C*2/*m* with strong correlations between all components (positional and thermal) for the 10 approximately planar atoms. This leads to a bad convergence and high standard deviations for this parameter. Furthermore the space group *C*2 results in a chiral structure. Inverting all coordinates causes no change of *R* or R_w in the main measurement and only a slight difference in the measurement with Friedel pairs (see above: ratio of weighted *R*'s 1.011 is true at a 90% probability level). However, the two formally equivalent Sn–Me distances split to 2.07 and 2.18 Å. Therefore we consider the enantiomer shown in Figure 1 to be the right one. The poor final *R* of 0.0825 and the high difference Fourier residual of 2.8 e/Å^3 near the Sn atom for compound **1d** is a result of the "defective" crystal (poorly chosen for size and shape) used in the measurement; various crystallizations yielded no better material. Besides several local written routines, local versions of SHELX-76 and SHELX-86 are used for the calculations. To prepare the figures shown we used ORTEP and PLUTO-78. The calculations are run at HB-DPS-8/70 equipment at Zentrum für Datenverarbeitung, Universität Mainz. Table VI contains the final parameters.

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Supplementary Material Available: Tables of anisotropic thermal parameters, coordinates of the hydrogen atoms, and bond lengths and bond angles of the cyclohexadiene ring CHD and the carbomethoxy group COOMe (9 pages); a listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.