Organometallics **2006,** *25,* 148−153

Structure and Solution Study of Molecular Triorganotin Compounds Containing an N,C,N Ligand

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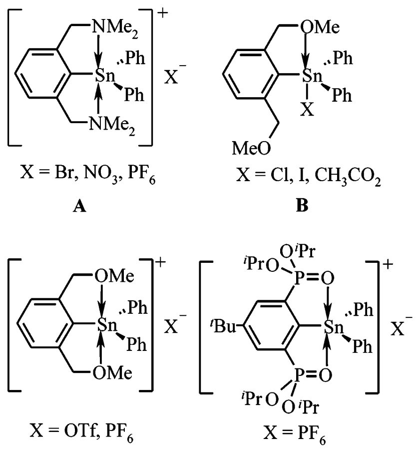
Received June 30, 2005

The triorganotin compounds $R_2(NCN)SnX$ ($NCN = C_6H_3(Me_2NCH_2)_2$-2,6$^-$) containing different polar groups X or substituents R were prepared. The set of organotin compounds $Ph_2(NCN)SnX$ (X = I (**2**), CF_3CO_2 (**3**), CH_3CO_2 (**4**), Et_2NCS_2 (**5**)) was prepared to study the influence of the polar group X on the character of the Sn−X bond. The effect of substituents R on the character of the Sn−X bond was studied in two additional sets of organotin compounds, $R_2(NCN)SnCl$ (R = Ph (**6**), Bu (**7**), Me (**8**)) and $R_2(NCN)SnO_2CCH_3$ (R = Ph (**4**), Bu (**9**), Me (**10**)). The influence of different solvents and temperatures on the presence or absence of covalent Sn−X bonds was studied as well. ^1H and ^{119}Sn NMR spectroscopy showed the occurrence of dissociation of the $Sn-O_2CCH_3$ covalent bond in CD_2Cl_2 solutions of **4**, **9**, and **10** at various temperatures (range 300−200 K). The crystal structures of **8** and **10** were studied by X-ray crystallography.

Introduction

The accommodation of more than eight electrons in the valence shell of the tin atom, the so-called hypercoordination, expands its coordination number to 5, 6, or 7.[1] One possible way to gain such coordination numbers uses Y,C,Y chelating ligands in organotin compounds, where two Sn−Y intramolecular interactions are possible. In general, a key feature of Y,C,Y ligands is that we can change the strength of Sn−Y coordination by changing the donor atoms Y (Y = N, O).[2,3] The result is that the different Y,C,Y ligands differ in their preferred arrangement in the coordination polyhedra of organotin compounds. In early work on organotin compounds containing such so-called pincer ligands van Koten introduced the N,C,N ligand ($C_6H_4(Me_2NCH_2)_2$-2,6).[2] The latest studies have dealt with organotin compounds containing an aryldiphosphonic ester ($C_6H_3[P(O)(OEt)_2]_2$-1,3-*t*-Bu-5) as the O,C,O chelating ligand.[3]

Chart 1



X = Br, NO_3, PF_6
A

X = Cl, I, CH_3CO_2
B

X = OTf, PF_6
C

X = PF_6
D

Previous papers dealing with the structures of triorganotin compounds of the type $R_2(YCY)SnX$ (Chart 1) showed that the mutual position of donor atoms in the tin coordination polyhedra depend on the type of donor atom Y (Y = N, O), the nature of the polar group X, and R.

Triorganotin compounds with N,C,N ligands prepared to date have existed as ionic pairs containing the triorganotin cations with trans trigonal-bipyramidal geometry having the nitrogen donor atoms in trans positions and the polar group X as the compensating anion (**A** in Chart 1).[4] The triorganotin compounds containing a similar O,C,O chelating ligand ($C_6H_4(MeOCH_2)_2$-2,6) contain a covalent Sn−X bond (X = Cl, I, CH_3CO_2; **B** in Chart 1) with both donor oxygen atoms in cis positions, in

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(1) (a) *Chemistry of Tin*; Smith, P. J., Ed.; Blackie Academic & Professional: Glasgow, U.K., 1998. (b) *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: Weinheim, Germany, 1999, and references therein.

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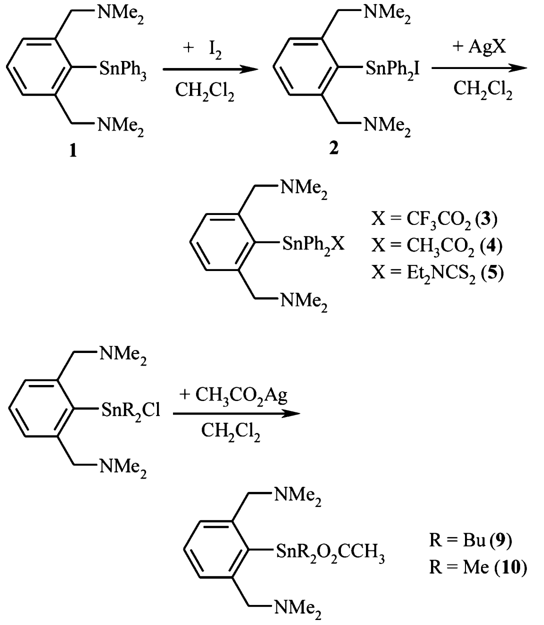
Scheme 1. Preparation and Numbering of Compounds



contrast to the N,C,N analogues.[5] However, the latest papers have reported that the presence of a less nucleophilic polar group X (X = CF_3SO_3, PF_6) results in the formation of triorganotin cations with two strong Sn−O interactions in both of the O,C,O chelate ligands (**C** and **D** in Chart 1),[6] giving the same geometry as that found for N,C,N analogues: i.e., both donor oxygen atoms in trans positions.

On the basis of these findings, we decided to focus on the preparation of triorganotin compounds R_2(NCN)SnX containing different polar groups X or substituents R. The set of organotin compounds Ph_2(NCN)SnX (X = I (**2**), CF_3CO_2 (**3**), CH_3CO_2 (**4**), Et_2NCS_2 (**5**)) with the same substituent R = Ph was prepared to study the influence of the polar group X on the character of the Sn−X bond and on the shape of the coordination polyhedra. The effect of substituents R on the character of the Sn−X bond was studied in the two sets of organotin compounds R_2(NCN)SnCl (R = Ph (**6**),[7] Bu (**7**),[12] Me (**8**)) and R_2(NCN)SnO_2CCH_3 (R = Ph (**4**), Bu (**9**), Me (**10**)). The influence of different solvents and temperatures on the presence or absence of a covalent Sn−X bond was studied as well.

Results and Discussion

Synthetic Aspects. Recently, we have reported on the low stability of the triorganotin chloride Ph_2(NCN)SnCl, which readily decomposes in solution at ambient temperature.[7] We have prepared the stable triorganotin halide Ph_2(NCN)SnI (**2**) by reacting Ph_3(NCN)Sn (**1**) with I_2 (Scheme 1). The reaction of the silver salts of the corresponding anions with Ph_2(NCN)SnI (**2**), Bu_2(NCN)SnCl (**7**), and Me_2(NCN)SnCl (**8**) has been used for the preparation of the remaining compounds.

NMR Study. The NMR parameters ($\delta(^{119}Sn)$, $^1J(^{119}Sn, ^{13}C)$) were shown to be very sensitive indicators of the influence of increasing nucleophilicity of polar groups on the structure of triorganotin derivatives.[8] In particular, the value of $\delta(^{119}Sn)$ is very informative for the determination of the ionic or covalent character of the triorganotin compounds. The range of $\delta(^{119}Sn)$ values from −140 to −260 ppm is typical for 5- or [4 + 2]-coordinated triphenyltin compounds containing a covalent bond Sn−X (X = polar group).[9] The presence of [3 + 2]-coordinated organotin cations resulted in a downfield shift $\Delta\delta(^{119}Sn)$ of about 100 ppm (the range of $\delta(^{119}Sn)$ is from −50 to −100 ppm).[10]

Table 1. Selected ^1H, ^{13}C, and ^{119}Sn NMR Data[a] for the Newly Prepared Compounds 2−5, 9, and 10

compd	$\delta(^{119}Sn)$	$\delta(^1H(NCH_2))$	$\delta(^{13}C(1))$[c] ($^nJ(^{119}Sn,^{13}C(1))$)	$\delta(^{13}C(1'))$[d] ($^nJ(^{119}Sn,^{13}C(1'))$)
2	−64.7	4.10	133.4 (*b*)	133.2 (*b*)
3	−72.3	3.92	137.6 (*b*)	134.5 (*b*)
4	−229.1	3.60	143.4 (724.0)	134.6 (572.9)
5	−257.7	3.89	134.4 (720.1)	134.7 (550.5)
9	−103.2	3.46	142.4 (*b*)	18.1 (501.7)
10	−105.1	3.60	142.6 (*b*)	0.98 (550.0)

[a] Measured in $CDCl_3$. All δ values are given in ppm and all *J* values in Hz. [b] Not found. [c] Refers to the tin-bound ipso carbon of the N,C,N pincer ligand. [d] Refers to the tin-bound carbon of the phenyl groups.

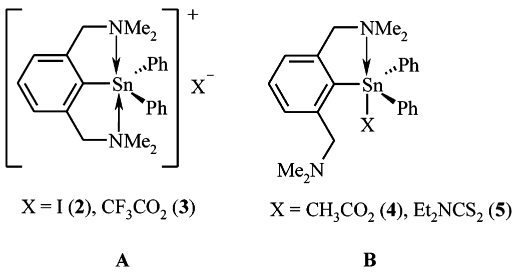


Figure 1. Proposed structures of prepared triorganotin compounds **2**−**5**.

(a) Influence of the Polar Group X. The values of $\delta(^{119}Sn)$ (−64.7 ppm in the ^{119}Sn NMR spectrum of Ph_2(NCN)SnI (**2**) and −72.3 ppm for Ph_2(NCN)SnO_2CCF_3 (**3**), respectively; see Table 1) indicate the existence of [3 + 2]-coordinated organotin cations[6a,7,10] with the polar groups outside of the primary tin coordination sphere in these compounds.

^1H NMR spectroscopy at various temperatures showed no decoalescence of signals of the CH_2 and CH_3 groups, indicating the symmetrical arrangement of the tin coordination sphere (**A** in Figure 1).

The values of $\delta(^{119}Sn)$ (−229.1 ppm for **4** and −257.7 ppm for **5** in $CDCl_3$) are typical for 5-coordinated triphenyltin compounds[7,9] and indicate the existence of a molecular (non-ionic) form of Ph_2(NCN)SnO_2CCH_3 (**4**) and Ph_2(NCN)SnS_2CNEt_2 (**5**). These represent rare examples of triorganotin derivates of N,C,N chelating ligands containing a covalent Sn−X bond (X = CH_3CO_2 (**4**), Et_2NCS_2 (**5**)). The values of $^1J(^{119}Sn,^{13}C(1'))$ are rather different from values of $^1J(^{119}Sn,^{13}C(1))$ in **4** and **5** (calculated values of bonding angles being 111 (**4**) and 109° (**5**) for C(1′)−Sn−C(1′) and 122 (**4**) and 120° (**5**) for C(1)−Sn−C(1′)).[11] These observations indicate that

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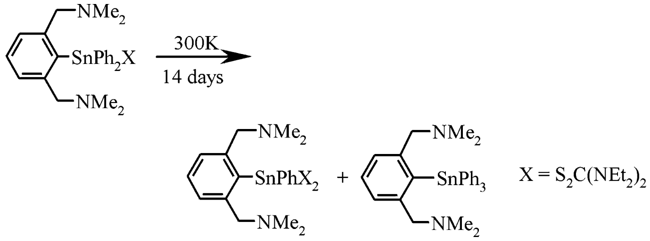
Scheme 2. Detected Disproportionation of 5 in $CDCl_3$ Solution



the shape of the tin coordination polyhedron is a distorted trans trigonal bipyramid in **4** and **5** (**B** in Figure 1). The first nitrogen atom of the N,C,N chelate ligand occupies one of the axial positions (the second nitrogen atom is noncoordinated), while the polar group X is placed on the second one (vide infra).

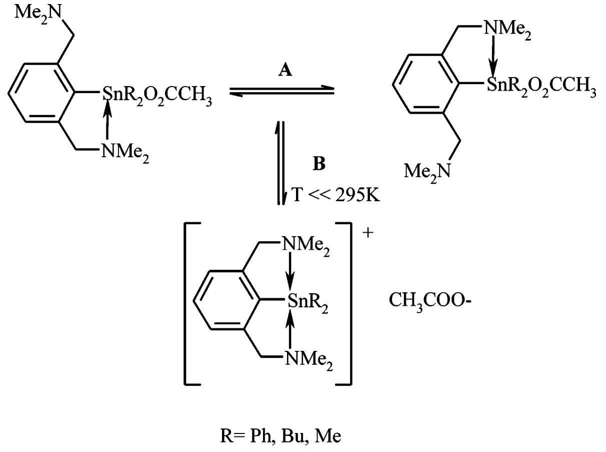
The compound **5** is unstable and disproportionates. ^{119}Sn NMR spectroscopy revealed two new signals at −193 (20%) and −383.8 ppm (20%) after standing for 14 days in $CDCl_3$ solution, in addition to the original signal (100%). The signal at −193 ppm was assigned to the tetraorganotin compounds **1**,[7] while the −383 ppm signal was assigned to the diorganotin compound $Ph(NCN)Sn(Et_2NCS_2)_2$ on the basis of ESI-MS (Figure 1 in the Supporting Information; the *m*/*z* 536 ion corresponds to $[Ph(NCN)Sn(Et_2NCS_2)]^+$). Similar disproportionation to tetraorgano- and diorganotin compounds (Scheme 2) also was reported in the case of $Ph_2(NCN)SnCl$.[7]

(b) Influence of the Substituent R. The triorganotin chlorides $R_2(NCN)SnCl$ (R = Ph (**6**), Bu (**7**), Me (**8**)) enable us to follow the structure of organotin N,C,N chelates depending on the substituent R. The phenyl-substituted compound **6** and its butyl-substituted analogue **7** contain a covalent Sn−Cl bond (δ(^{119}Sn) −191.4 and −35.1 ppm),[7,12] while the methyl-substituted representative **8** forms a triorganotin cation in $CDCl_3$ solution (δ(^{119}Sn) +14.5 ppm) as well as in the solid state (Figure 2).[13] A detailed study and comparison of these compounds is not possible, due to the low stability of the phenyl analogue **6**.[7] However, the stability of **4** allowed us to prepare the set of triorganotin compounds $R_2(NCN)SnO_2CCH_3$, in which the dependence of the Sn−O bond character on the substituent R (R = Ph (**4**), Bu (**9**), Me (**10**)) could be investigated.

The value of δ(^{119}Sn) (−103.2 ppm) indicates the presence of a covalent Sn−X bond (X = O_2CCH_3) in the butyl-substituted analogue **9**. The value of δ(^{119}Sn) of −105.1 ppm in $Me_2(NCN)SnO_2CCH_3$ (**10**) is shifted upfield ($\Delta\delta(^{119}\mathrm{Sn})_{\mathbf{10-8}}$ = −119.9 ppm) compared to that of $Me_2(NCN)SnCl$ (**8**) and indicates a change on going from the ionic **8** to the covalent **10**.

(c) Dynamic Behavior of 4, 9, and 10 in Solution. The compounds $R_2(NCN)SnO_2CCH_3$ (R = Ph (**4**), Bu (**9**), Me (**10**)) are representative triorganotin compounds containing covalent Sn−O bonds. Because of the coordination of one nitrogen donor atom of the N,C,N chelate ligand, the second one being noncoordinated, the dynamic behavior has been studied by ^{1}H and ^{119}Sn NMR spectroscopy at various temperatures in CD_2Cl_2 (range 300−200 K). Two different dynamic processes in **4**, **9,** and **10** were found to occur.

Scheme 3. Dynamic Processes of 4, 9, and 10 in CD_2Cl_2 Solutions: (A) Dissociation−Association; (B) Dissociation of the Acetate Ligand



The dissociation−association of both donor nitrogen atoms is the first expected process[14] (path A in Scheme 3), and indeed, ^{1}H NMR spectroscopy revealed a broadening of the signals due to the CH_2 and CH_3 groups, resulting in decoalescence at 215 K for **4**, 230 K for **9**, and 240 K for **10** ($\Delta G^\ddagger$ = 41.5 kJ mol^{-1} for **4**, 44.9 kJ mol^{-1} for **9**, and 45.2 kJ mol^{-1} for **10**).[15]

The second process was observed by both ^{1}H and ^{119}Sn NMR spectroscopy, and the latter seems to be a very sensitive and useful tool for investigation of this process. A decrease in the temperature resulted in the observation of new signals in the ^{119}Sn NMR spectra of phenyl- (**4**), butyl- (**9**), and methyl-substituted (**10**) compounds at 230 K. While the intensity of the original signals decreased in the ^{119}Sn NMR spectra of **4**, **9**, and **10**, the intensity of the new signals increased during a further decrease in temperature (see Figure 2 in the Supporting Information).

The values of the new signals are shifted downfield ($\Delta\delta(^{119}\mathrm{Sn})_{\mathrm{new-original}}$ = 169.6 (**4**), 178.6 (**9**), 164.9 ppm (**10**)) and are comparable to those found in the ionic triorganotin N,C,N analogues (see Table 2).[10]

On the basis of the previous results, the ionization of compounds **4**, **9**, and **10** can be proposed to occur in CD_2Cl_2 solution at lower temperatures (path B in Scheme 3). The original covalent compounds dissociate to their ionic forms at low temperatures. The concentration of the ionic forms increased with decreasing temperature. The equilibrium constants K = [Ionic]/[Covalent] were evaluated directly from ^{119}Sn NMR spectra,[16] when the signals for both species were observed. The K values for [Covalent] ↔ [Ionic] equilibrium have been evaluated at a number of temperatures and used for a ln K vs T^{-1} plot (Figure 3 in the Supporting Information). From the linear relation the reaction enthalpy and entropy have been extracted: $\Delta H°$ = −5.54 (**4**), −5.65 (**9**) ,and −6.78 (**10**) kcal mol^{-1} and $\Delta S°$ = −28.40 (**4**), −29.16 (**9**), −34.60 (**10**) cal mol^{-1} K^{-1}.[17] A similar ionic dissociation was found in the organosilicon compounds.[18]

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[15] Eyring equation: $\Delta G^\ddagger = -RT_c \ln\,[2\pi h(\Delta\upsilon)/kT_c\sqrt{3}]$, with $\Delta G^\ddagger$ = free energy of activation (J), T_c = coalescence temperature (K), and $\Delta\upsilon$ = chemical shift difference (Hz); the other symbols have their usual meanings.

[16] The ^{119}Sn NMR was used, despite the potential superiority of ^{1}H NMR signal integration, because at low temperatures the two species were well resolved only in the ^{119}Sn spectra, due to the huge chemical shift differences.

Table 2. Temperature Dependence of Selected ^{1}H and ^{119}Sn NMR Parameters (ppm)[a]

		CD$_2$Cl$_2$		toluene-d_8		acetone-d_6	
compd	T (K)	δ(^{119}Sn)	CH_2N	δ(^{119}Sn)	CH_2N	δ(^{119}Sn)	CH_2N
4	300	−233.3	3.61	−227.6	3.38	−235.1	3.57
	200	−72.7/−242.3	3.90; 3.55/3.35	−234.2	3.75/3.15	−73.3/−236.9	4.20; 3.82/3.61
9	300	−103.2	3.46	−106.4	3.39	−109.9	3.62
	200	65.4/−113.2	3.89; 3.65/3.49	−115.1	3.64/3.10	49.7/−110.9	4.03; 4.24/3.06
10	300	−105.1	3.60	−110.1	3.31	−109.9	3.80
	200	49.8/−115.1	4.06; 3.60/3.20	−113.9	3.72/3.59	40.5/−117.2	4.06; 4.24/3.17

[a] Range of 200−300 K for toluene-d_8, acetone-d_6, and CD$_2$Cl$_2$.

To discuss the effect of the substituent R, we compare the equilibrium reactions in CD$_2$Cl$_2$ solutions for these compounds: **10** (R = Me), **9** (R = Bu), **4** (R = Ph). The list is ordered from the most electron-releasing substituent R to the least. The data for this series show that both enthalpies and the corresponding entropies increase along the series. This can be rationalized by noting that the more strongly electron releasing substituent R = Me causes the tin atom to have a greater electron density, resulting in an easier dissociation of the acetate ligand: i.e., to a more negative reaction enthalpy.

The dynamic behavior of **4**, **9**, and **10** was studied in toluene-d_8 and acetone-d_6 to determine the solvent effect. In toluene-d_8, ^{1}H NMR spectroscopy revealed decoalescence of the signals of the CH$_2$ and CH$_3$ groups at 200 K for **4**, at 210 K for **9**, and at 220 K for **10** ($\Delta G^\ddagger = 36.7$ kJ mol^{-1} for **4**, 38.8 kJ mol^{-1} for **9**, and 43.3 kJ mol^{-1} for **10**). The values of δ(^{119}Sn) NMR signals are −227.6 (**4**), −106.4 (**9**), and −105.1 ppm (**10**), proving the presence of their covalent forms, and they are shifted slightly upfield with decreasing temperature (Table 2). New signals were not observed in the ^{119}Sn NMR spectra of **4**, **9**, and **10** at 170 K, indicating the absence of ionization processes of **4**, **9**, and **10** in toluene-d_8.

The values of δ(^{119}Sn) in the acetone-d_6 solutions of **4**, **9**, and **10** (300 K) fall in the region typical for covalent triorganotin N,C,N chelates (decoalescence of the signals of the CH$_2$ and CH$_3$ groups in acetone-d_6: 200 K for **4**, 215 K for **9**, and 220 K for **10** ($\Delta G^\ddagger = 38.4$ kJ mol^{-1} for **4**, 38.4 kJ mol^{-1} for **9**, and 39.4 kJ mol^{-1} for **10**)). Formation of new signals typical for ionic forms of **4**, **9**, and **10** was observed at temperatures as high as 200 K, in contrast to the case for CD$_2$Cl$_2$ solutions (see Table 2), and hence no equilibrium constant could be evaluated.

Crystal Structures of 8 and 10. The compounds Me$_2$(NCN)SnCl (**8**) and Me$_2$(NCN)SnO$_2$CCH$_3$ (**10**) were selected for crystal structure determination to provide examples of both the ionic and covalent characters and the different coordinations of both nitrogen donor atoms. The molecular structures of **8** and **10** are depicted in Figures 2 and 3. Crystallographic data are given in Table 3.

Compound **8** contains an organotin cation, while the chloride anion is outside of the primary tin coordination sphere (the shortest Sn−Cl distance is 4.9298(2) Å; see Figure 2). The central tin atom is coordinated by a carbon atom and two nitrogen atoms of the N,C,N ligand in a tridentate fashion and by two methyl carbon atoms. The resulting geometry is pseudo trans trigonal bipyramidal, formed by three carbon atoms in the equatorial plane and two trans nitrogen atoms, and is comparable to that found in organotin compounds containing [Me$_2$(NCN)Sn]$^+$ and {[Me$_2$N(CH$_2$)$_3$]$_2$SnPh}$^+$ ions.[13,19] The C$_3$Sn girdle is almost planar ($\sum$C−Sn−C = 360.01(7)° for **8**). The equivalent

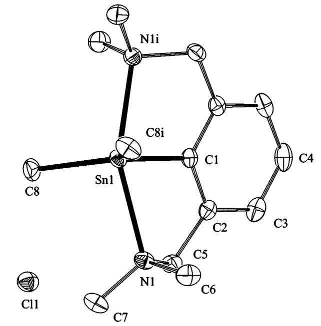

Figure 2. General view (ORTEP) of a molecule of **8** showing 50% probability displacement ellipsoids and the atom-numbering scheme. The molecule is placed on a crystallographic 2-fold axis passing through the Sn1, C1, and C4 atoms. The hydrogen atoms are omitted for clarity. Selected values of bond lengths (Å) and angles (deg): Sn1−C1 = 2.094(2), Sn1−C8 = 2.1279(16), Sn1−C8^i = 2.1279(16), Sn1−N1 = 2.4273(13), Sn1−N1^i = 2.4273(13); C1−Sn1−C8 = 121.55(5), C1−Sn1−C8^i = 121.55(5), C8−Sn1−C8^i = 116.91(10), N1−Sn1−N1^i = 151.52(7). Symmetry code: (i) 1 − x, y, 0.5 − z.

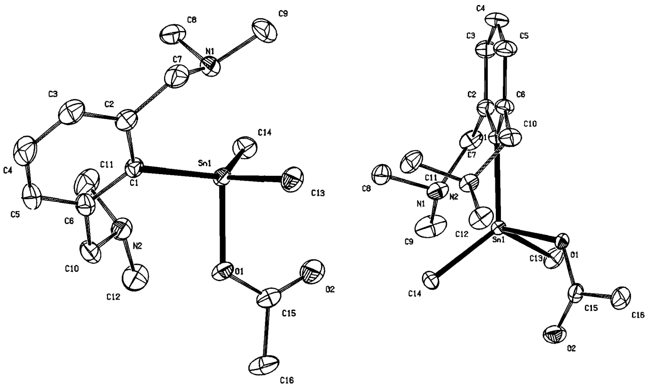

Figure 3. General view (ORTEP) of a molecule of **10** showing 50% probability displacement ellipsoids and the atom-numbering scheme. The hydrogen atoms are omitted for clarity. Selected values of bond lengths (Å) and angles (deg): Sn1−O1 = 2.1088(14), Sn1−C14 = 2.119(2), Sn1−C13 = 2.140(2), Sn1−C1 = 2.150(2), Sn1−N1 = 2.5957(18); O1−Sn1−C14 = 105.31(7), O1−Sn1−C13 = 90.02(8), C14−Sn1−C13 = 117.22(10), O1−Sn1−C1 = 97.16(7), C14−Sn1−C1 = 123.76(9), C13−Sn1−C1 = 113.53(9), O1−Sn1−N1 = 165.50(6), N1−Sn1−N2 = 116.37(6).

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Table 3. Crystal Data and Structure Refinement Details for 8 and 10

	8	**10**
empirical formula	$C_{14}H_{25}N_2SnCl$	$C_{16}H_{28}N_2O_2Sn$
color	colorless	colorless
cryst syst	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$P2_1/c$
a (Å)	9.8090(3)	9.4320(2)
b (Å)	16.3150(5)	11.1520(2)
c (Å)	10.8910(4)	17.7050(4)
β (deg)	113.9471(17)	99.1520(13)
Z	4	4
μ (mm^{-1})	1.759	1.396
D_{exptl} (Mg m^{-3})	1.566	1.442
cryst size (mm)	0.3 × 0.2 × 0.175	0.3 × 0.3 × 0.22
cryst shape	plate	irregular
θ range, deg	1.0−27.5	1.0−27.5
T_{min}, T_{max}	0.669, 0.736^a	0.684, 0.735^a
no. of rflns measd	12 503	28 894
no. of unique rflns; $R_{int}{}^d$	1833; 0.037	4211; 0.035
no. of obsd rflns ($I > 2\sigma(I)$)	1808	3661
no. of params	87	198
S^b (all data)	1.084	1.059
final R^b indices ($I > 2\sigma(I)$)	0.018	0.024
wR2^b indices (all data)	0.044	0.058
$w_1/w_2{}^c$	0.0224, 1.375	0.0264, 1.1586
max, min $\Delta\rho$ (e Å^{-3})	0.838, −0.691	1.026, −0.581

[a] Correction by SORTAV program. [b] Definitions: $R(F) = \sum||F_o| - ||F_c||/\sum|F_o|$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2]^{1/2}$; $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{rflns} - N_{params})]^{1/2}$. [c] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$, $P = [\max(F_o^2,0) + 2F_c^2]/3$. [d] $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

Sn−N bond distances (Sn−N(1) = Sn−N(1^i) = 2.4273(13) Å) indicate strong Sn−N interactions in the cation. The main deformation from the ideal trigonal-bipyramidal geometry is seen for the N(1)−Sn−N(1^i) angle (151.52(7)°). Comparable deviations in pseudo trans trigonal bipyramidal structures also have been found in other triorganotin cations bearing both N,C,N[13,19] and O,C,O chelating ligands[6] (the range of Y−Sn−Y bonding angles is 150.28(7)−159.01(9)°).

The value of the Sn−N(1) bond length in **10** (2.5957(18) Å) indicates that the presence of the CH_3COO^- group results in a decrease of the Sn−N bond strength in this compound compared to **8** (Figure 3). The shape of the coordination polyhedron is a trans trigonal bipyramid formed by three C atoms in the equatorial plane and one nitrogen and one oxygen donor atom in axial positions (the bonding angle N(1)−Sn−O(1) is 165.50(6)°). The different bond lengths of Sn−O(1) (2.1088(14) Å) and Sn−O(2) (3.1152(17) Å) clearly indicate monodentate bonding of the CH_3COO^- group to tin.[20] The C(15)−O(2) distance (1.217(3) Å), typical for the carbonyl part of monodentate carboxylic groups, confirms this coordination mode of the CH_3COO^- group (compare with C(15)−O(1) = 1.305(3) Å).[21] While the value of the Sn−N(1) bond length indicates a medium to strong interaction, the second nitrogen donor atom from the N,C,N pincer ligand is bound very weakly (Sn−N(2) = 3.0372(14) Å).[22] The C_3Sn girdle is almost planar ($\sum$C−Sn−C = 354.51(9)°). The value of the N(1)−Sn−N(2) bond angle (116.37(6)°) clearly demonstrates the cis position of both nitrogen donor atoms of the N,C,N chelating ligand. This is in contrast with the trans coordination of both nitrogen atoms in **8**.

Experimental Section

General Methods. The starting compounds **1**, **6**, and **7** were prepared according to previous literature reports.[7,12] All moisture- and air-sensitive reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The synthesis of **2** was performed in air with commercially available solvents. The reactions with silver salts were light protected. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were acquired on Bruker AMX360 and Avance500 spectrometers at 300 K in $CDCl_3$ or in toluene-d_8 and acetone-d_6 for temperatures in the range 300−170 K. Appropriate chemical shifts were calibrated on the ^{1}H residual peak of $CHCl_3$ (δ 7.27 ppm), toluene (δ 2.09 ppm), and acetone (δ 2.05 ppm), the ^{13}C residual peak of $CHCl_3$ (δ 77.23 ppm), and the ^{119}Sn peak of external tetramethylstannane (δ 0.00 ppm). Chemical shift data are provided in ppm, with coupling constants in Hz. Abbreviations used are as follows: s = singlet; d = doublet; q = quartet; m = complex multiplet. Electrospray ionization (ESI) mass spectra (MS) were measured using an Esquire3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany). Mass spectra were recorded in the range *m/z* 50−800 in both negative ion and positive ion modes. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1−5 μL/min. The ion trap was tuned to give an optimum response for *m/z* 500 or 150. The ion source temperature was 300 °C, and the flow rate and pressure of nitrogen were 4 L/min and 10 psi, respectively. The IR spectra (cm^{-1}) were recorded on Perkin-Elmer 684 equipment as Nujol suspensions or $CHCl_3$ solutions.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]diphenyltin Iodide (2). Iodine (1.4 g, 5.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of **1** (3.1 g, 5.7 mmol) in CH_2Cl_2 (20 mL) and stirred for 1 day. The solvent was evaporated in vacuo, and the residue was washed with pentane to give **2** as an orange solid. Yield: 2.90 g (86%). Mp: 251−253 °C. Anal. Calcd for $C_{24}H_{29}IN_2Sn$ (mol wt 591.11): C, 48.77; H, 4.95. Found: C, 48.55; H, 5.05. Monoisotopic mol wt: 592. Positive-ion ESI-MS: *m/z* 465, $[M - I]^+$, 100%. Negative-ion ESI-MS: *m/z* 127, $[I]^-$, 85%; *m/z* 381, $[I_3]^-$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.28 (s, 12H, NCH_3), 4.10 (s, 4H, CH_2N), 7.30−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 47.3 (NCH_3), 64.7 (CH_2, $^nJ(^{119}Sn,^{13}C) = 36.0$ Hz); $SnPh_2$, 133.2 (C(1′)), 130.7, 127.4, 136.7; SnC_6H_3, 133.4 (C(1)), 128.5, 132.2, 143.5. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −64.7.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]diphenyltin Trifluoroacetate (3). CF_3COOAg (0.18 g, 0.83 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **2** (0.49 g, 0.83 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred at room temperature for 5 days, and the solid was filtered. The solvent was evaporated in vacuo, and the residue was washed with pentane to afford **3** as a white solid. Yield: 0.34 g (71%). Mp: 126−129 °C. Anal. Calcd for $C_{26}H_{29}F_3N_2O_2Sn$ (mol wt 577.22): C, 54.10; H, 5.06. Found: C, 54.01; H, 4.98. Monoisotopic mol wt: 578. Positive-ion ESI-MS: *m/z* 465, $[M - CF_3COO]^+$, 100%. Negative-ion ESI-MS: *m/z* 113, $[CF_3COO]^-$, 28%; *m/z* 249, $[(CF_3COO)_2Na]^-$, 100%; *m/z* 385, $[(CF_3COO)_3Na_2]^-$, 29%; *m/z* 521, $[(CF_3COO)_4Na_3]^-$, 41%. ^{1}H

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[20] The values of Sn−O(1) and Sn−O(2) are similar to those of (OCO)-$Ph_2SnO_2CCF_3$, where the covalent Sn−O bond was observed (Sn−O(1) = 2.1546(13) Å, Sn−O(2) = 3.2096(15) Å).[6a]

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[22] However, if this weak bond of Sn(1)−N(2) is taken in account, then the geometry of **10** is an example of [5 + 1] coordination where the C_3N_2Sn trigonal bipyramid is attacked by the second nitrogen donor atom from a pincer ligand.

NMR ($CDCl_3$): δ (ppm) 2.18 (s, 12H, NCH_3), 3.92 (s, 4H, CH_2N), 7.28−7.65 (complex pattern, 13H, $SnPh_2$, SnC_6H_3).^{13}C NMR ($CDCl_3$): δ (ppm) 46.7 (N*C*H_3), 64.2 (*C*H_2), 117.1 (q, *C*F_3, $^nJ(^{19}F,^{13}C) = 294.3$ Hz), 175.7 (*C*OO); $SnPh_2$, 134.5 (C(1′)), 130.4, 131.8, 136.5; SnC_6H_3, 137.6 (C(1)), 127.3, 132.8, 143.9. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −72.3.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]diphenyltin Acetate (4). The procedure was similar to that used for **3**. The reaction of **2** (0.50 g, 0.84 mmol) in CH_2Cl_2 (10 mL) and CH_3COOAg (0.14 g, 0.84 mmol) resulted in **4** as a white powder. Yield: 0.35 g (80%). Mp 85−88 °C. Anal. Calcd for $C_{26}H_{32}N_2O_2Sn$ (mol wt 523.25): C, 59.68; H, 6.16. Found: C, 59.90; H, 6.05. Monoisotopic mol wt: 524. Positive-ion ESI-MS: *m/z* 465, $[M - CH_3COO]^+$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.98 (s, 12H, NCH_3), 2.25 (s, 3H, CCH_3), 3.60 (s, 4H, CH_2N), 7.24 (d, 2H, SnC_6H_3), 7.40−7.50 (m, 7H, $SnPh_2$, SnC_6H_3), 7.81 (d, 4H, $SnPh_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 45.3 (N*C*H_3), 63.8 (*C*CH_3), 64.5 (*C*H_2, $^nJ(^{119}Sn,^{13}C) = 27.7$ Hz), 175.7 (*C*OO); $SnPh_2$, 134.6 (C(1′), $^1J(^{119}Sn,^{13}C) = 572.9$ Hz), 127.9, 128.6, 136.3; SnC_6H_3, 143.4 (C(1), $^1J(^{119}Sn,^{13}C) = 724.0$ Hz), 128.2, 128.5, 146.5. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −229.1. IR (suspension in Nujol): ν_{as}(CO) 1643 cm^{-1}, ν_s(CO) 1456 cm^{-1}. IR (solution in $CHCl_3$): ν_{as}(CO) 1709 cm^{-1}, ν_s(CO) 1455 cm^{-1}.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]diphenyltin Diethyldithiocarbamate (5). The procedure was similar to that used for **3**. Reaction of **2** (0.57 g, 0.96 mmol) and $AgS_2CN(C_2H_5)_2$ (0.24 g, 0.96 mmol) resulted in **5** as a white solid. Yield: 0.49 g (83%). Mp: 145−148 °C. Anal. Calcd for $C_{29}H_{39}N_3S_2Sn$ (mol wt 612.47): C 56.87; H, 6.42. Found: C, 56.71; H, 6.53. Monoisotopic mol wt: 613. Positive-ion ESI-MS: *m/z* 465, $[M - S_2CN(C_2H_5)_2]^+$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.30 (q, 6H, CH_3), 2.15 (s, 12H, NCH_3), 3.89 (s, 4H, CH_2N), 4.01 (t, 4H, CH_2), 7.14 (d, 2H, SnC_6H_3), 7.20−7.50 (m, 7H, $SnPh_2$, SnC_6H_3,), 7.80 (d, 4H, $SnPh_2$). ^{13}C NMR ($CDCl_3$): δ (ppm) 46.6 (N*C*H_3), 47.6 (CH_2*C*H_3), 63.1 (*C*H_2CH_3), 64.3 (*C*H_2, $^nJ(^{119}Sn,^{13}C) = 32.9$ Hz), 192.8 (*C*S_2); $SnPh_2$, 134.7 (C(1′)), 130.1, 131.1, 136.3; SnC_6H_3, 134.4 (C(1)), 127.6, 132.2, 143.9. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −257.7. IR (suspension in Nujol): ν_{as}(CS) 1270 cm^{-1}, ν_s(CS) 850 cm^{-1}. IR (solution in $CHCl_3$): ν_{as}(CS) 1260 cm^{-1}, ν_s(CS) 840 cm^{-1}.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]dimethyltin Chloride (8). A 1.6 M hexane solution of *n*-BuLi (1.6 mL, 5.8 mmol) was added dropwise to a stirred hexane (20 mL) solution of 1,3-bis((dimethylamino)methyl)benzene (1.1 g, 5.8 mmol) and the mixture was stirred for 24 h. The resulting solution was added to a stirred benzene solution (20 mL) of Me_2SnCl_2 (1.3 g, 5.8 mmol). The reaction mixture was stirred for a further 48 h. The solid was filtered and washed with hexane (10 mL), and the filtrate was evaporated in vacuo. The residue was washed with pentane to afford **8** as a white solid. Yield: 1.88 g (86%). Mp: 92−93 °C. Anal. Calcd for $C_{14}H_{25}ClN_2Sn$ (mol wt 375.51): C, 44.78; H, 6.71. Found: C, 44.73; H, 6.69. Monoisotopic mol wt: 376. Positive-ion ESI-MS: *m/z* 341, $[M - Cl]^+$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.83 (s, 6H, $SnCH_3$, $^2J(^{119}Sn,^1H) = 65.9$ Hz), 2.31 (s, 12H, NCH_3), 3.76 (s, 4H, CH_2N), 7.10 (d, 2H, SnC_6H_3), 7.27 (t, 1H, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 1.1 (Sn*C*H_3, $^1J(^{119}Sn,^{13}C) = 516$ Hz), 45.3 (N*C*H_3), 64.6 (N*C*H_2); SnC_6H_3, 141.0 (C(1)), 127.5, 129.7, 145.5. ^{119}Sn NMR ($CDCl_3$): δ (ppm) +14.5 (br s).

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]dibutyltin Acetate (9). The procedure was similar to that used for **3**. Reaction of **7** (0.49 g, 1.41 mmol) in CH_2Cl_2 (10 mL) and CH_3COOAg (0.24 g, 1.41 mmol) resulted in formation of **9** as an oily product. Yield: 0.41 g (80%); Anal. Calcd for $C_{22}H_{40}N_2O_2Sn$ (mol wt 483.27): C, 54.68; H, 8.34. Found: C, 54.88; H, 8.45. Monoisotopic mol wt: 484. Positive-ion ESI-MS: *m/z* 425, $[M - CH_3COO]^+$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.78 (t, 6H, $C(4)H_3$), 1.21 (m, 4H, CH_2), 1.25 (m, 4H, CH_2), 1.53 (t, 4H, CH_2), 1.88 (s, 3H, CCH_3), 2.04 (s, 12H, NCH_3), 3.46 (s, 4H, CH_2N), 6.91−7.05 (m, 3H, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 23.0 (*C*CH_3), 44.9 (N*C*H_3), 64.9 (N*C*H_2, $^nJ(^{119}Sn,^{13}C) = 20.2$ Hz), 175.5 (*C*OO); SnBu, 18.1 (C(1′), $^1J(^{119}Sn,^{13}C) = 501.7$ Hz), 13.6, 27.1, 28.2; SnC_6H_3, 142.4 (C(1)), 127.3, 128.4, 145.3. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −103.2.

Synthesis of [2,6-Bis((dimethylamino)methyl)phenyl]dimethyltin Acetate (10). The procedure was similar to that used for **3**. Reaction of **8** (0.52 g, 1.38 mmol) in CH_2Cl_2 (10 mL) and CH_3COOAg (0.23 g, 1,38 mmol) resulted in formation of **10** as a white solid. Yield: 0.42 g (75%). Mp: 85−88 °C. Anal. Calcd for $C_{16}H_{28}N_2O_2Sn$ (mol wt 399.10): C, 48.15; H, 7.07. Found: C, 48.39; H, 6.91. Monoisotopic mol wt: 400. Positive-ion ESI-MS: *m/z* 341, $[M - CH_3COO]^+$, 100%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.61 (s, 6H, $SnCH_3$, $^2J(^{119}Sn,^1H) = 68.5$ Hz), 1.99 (s, 3H, CCH_3), 2.14 (s, 12H, NCH_3), 3.60 (s, 4H, CH_2N), 7.03−7.27 (m, 3H, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 0.98 (Sn*C*H_3, $^1J(^{119}Sn,^{13}C) = 550$ Hz), 22.8 (*C*CH_3), 44.6 (N*C*H_3), 64.6 (N*C*H_2, $^nJ(^{119}Sn,^{13}C) = 24.4$ Hz), 175.9 (*C*OO), SnC_6H_3, 142.6 (C(1)), 127.9, 127.3, 145.9. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −105.1.

Crystallography Studies. Colorless crystals were obtained from layering of *n*-hexane onto a dichloromethane solution of the compound. The crystals of compounds of **8** and **10** were mounted on glass fibers with epoxy cement and measured on a KappaCCD four-circle diffractometer with CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, and empirical absorption corrections[23] were applied (multiscan from symmetry-related measurements). The structures were solved by direct methods (SIR97[24]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97[25]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2[U_{eq}(\text{pivot atom})]$; for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance. Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 274080 and 274081 for **8** and **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Acknowledgment. We thank the Grant Agency of the Czech Republic (Grant No. 203/04/0223) and the Ministry of Education of the Czech Republic (Project No. VZ0021627501) for financial support.

Supporting Information Available: Figures giving the ESI mass spectrum of partial disproportionation of compound **5**, the ^{119}Sn NMR spectra of **4** in CD_2Cl_2 solution at various temperatures, and a plot of ln *K* vs 1/*T* for the equilibrium dissociation of **4**, **9,** and **10** and CIF files giving further details of the structure determination of compounds **8** and **10**, including atomic coordinates, anisotropic displacement parameters and geometric data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050549C

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