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Role of Y,C,Y-Chelating Ligands in Control Hydrolysis of Diorganotin Compounds[†]

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The potential use of Y,C,Y-chelating ligands in control hydrolysis of diorganotin(IV) compounds of general formula $L^{1,2}SnPhX_2$ (L^1 = 2,6-$(Me_2NCH_2)_2C_6H_3$, L^2 = 2,6-$(MeOCH_2)_2C_6H_3$, and X = Cl, CF_3SO_3, and [1-$CB_{11}H_{12}$]) is reported. The hydrolysis of moisture-sensitive compounds $L^1SnPh(OTf)_2$ (**3**) and $L^2SnPh(OTf)_2$ (**4**) gave organotin(IV) cations $\{[L^1SnPh(OH_2)(OTf)]^+[OTf]^-\}$ (**5**) and $\{[L^2SnPh(OH_2)(OTf)]^+[OTf]^-\}$ (**6**). Reported is also the preparation of diorganotin(IV) cations $\{[L^1SnPhCl]^+ [1\text{-}CB_{11}H_{12}]^-\}$ (**7**) and $\{[L^2SnPhCl]^+ [1\text{-}CB_{11}H_{12}]^-\}$ (**8**) and the isolation of $[PhL^2Sn\text{-}\mu\text{-}(OH)_2\text{-}SnL^2Ph]^{2+}$ 2*$[1\text{-}CB_{11}H_{12}]^-$ (**9**), the final hydrolytic product of **8**. The products were characterized by ^1H, ^{11}B, ^{13}C, and ^{119}Sn NMR and IR spectroscopy, ESI/MS, and elemental analyses, and the structures of compounds **3** and **6** were determined by X-ray diffraction studies.

Introduction

The long history investigation of organotin cations showed a relatively large number of triorganotin cations[1] (the trimethyltin cation hydrates and ammoniates have been known since 1960s),[2] while the preparation of diorganotin dications stabilized by coordination with alkynylborates and phosphine oxide was reported recently.[3] One of the most promising areas of organotin cations is the chemistry of cationic clusters. The Sn_{12} dications $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ have received attention in view of nanobuilding blocks for sol–gel-derived hybrid materials,[4] and recently prepared Sn_2 dications $[R_2(H_2O)Sn\text{-}\mu\text{-}(OH)_2\text{-}Sn(H_2O)R_2]^{2+}$ $2Y^-$ (Y = CF_3SO_3, $C_8F_{17}SO_3$) were shown to be very efficient alcohol acetylation and C–C coupling bond catalysts.[5]

In general, organotin cations are well-known as species with pronounced Lewis acidic character of the central tin atom and are important intermediates in hydrolysis of organotin halides, a key step in the preparation of stannoxanes.[6] However, this hydrolysis process is usually complicated to some extent, leading to a variety of the hydrolysis products like organotin oxides, hydroxides, and oxide–hydroxides. The hydrolysis of organotin halides has been discussed to occur through the intermediacy of hydrated organotin cations such as $[R_2Sn(OH_2)_4]^{2+}$ or analogous organotin compounds.[7] Recent reports showed the preparation and structural characterization of such species $\{[n\text{-}Bu_2Sn(OH_2)_4]^{2+}[2,5\text{-}Me_2C_6H_3\text{–}SO_3^-]_2\}$,[8a] $\{[n\text{-}Bu_2Sn(OH_2)_3\text{-}[\mu\text{-}L]\text{-}n\text{-}Bu_2Sn(OH_2)_3]^{2+}\text{-}[L]^{2-}\}$ (L = 1,5-$C_6H_{10}(SO_3^-)_2$),[8b] $\{[Me_2Sn(OH_2)_4]^{2+}[X^-]_2\}$ (X = 1,1,3,3-tetraoxo-1,3,2-benzodithiazide),[8c] and $\{[R_2Sn(OH_2)_2(OPPh_3)_2]^{2+}[CF_3SO_3^-]_2\}$ (R = Me, *n*-Bu).[8d] These compounds can act as the precursors of hydrolysis to effort the products containing Sn–OH or Sn–O bonds.

Recently, we have noted the simple preparation of tetraorganodistannoxane $[\{2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3\}_2Sn(OH)]_2O$ containing O,C,O-chelating ligand.[9] To explore the field of potential use of Y,C,Y-chelating ligands in control hydrolysis of organotin(IV) compounds, diorganotin(IV) compounds of general

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[†] Dedicated to Professor Jaroslav Holeček on the occasion of his 75th birthday.

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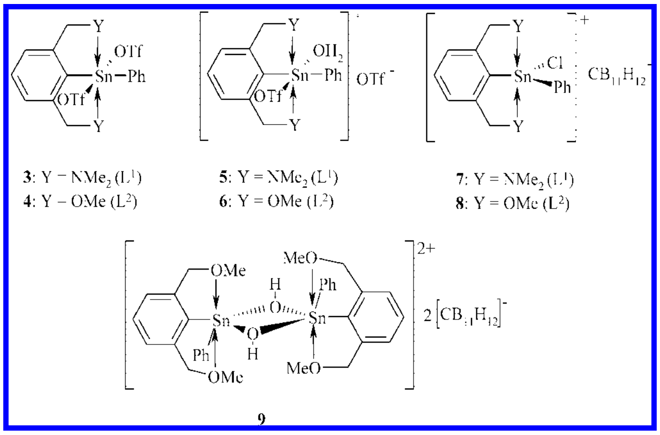
Chart 1



formula $L^{1,2}SnPhX_2$, where $L^1 = 2,6\text{-}(Me_2NCH_2)_2C_6H_3$, $L^2 = 2,6\text{-}(MeOCH_2)_2C_6H_3$, and X = Cl, CF_3SO_3 (hereafter OTf), and $[1\text{-}CB_{11}H_{12}]$ were prepared (Chart 1). The central tin(IV) atom in these compounds possess different Lewis acidity depending on group X. As the result of these variances, the isolation of hydrated organotin(IV) cations $\{[L^{1,2}SnPh(OH_2)(OTf)]^+ [OTf]^-\}$ as well as $[PhL^2Sn\text{-}\mu\text{-}(OH)_2\text{-}SnL^2Ph]^{2+}\ 2{*}[1\text{-}CB_{11}H_{12}]^-$ as the final hydrolytic product is reported.

Results and Discussion

The treatment of $L^{1,2}SnPhCl_2$ (L^1 (**1**) and L^2 (**2**)) with 2 equiv of AgOTf led to the preparation of moisture-sensitive compounds $L^1SnPh(OTf)_2$ (**3**) and $L^2SnPh(OTf)_2$ (**4**) (eq 1).

$$L^{1,2}PhSnCl_2 + 2AgOTf \rightarrow \underset{L^1(\mathbf{3}),\,L^2(\mathbf{4})}{L^{1,2}PhSn(OTf)_2} + 2AgCl \quad (1)$$

The values of $\delta(^{119}Sn)$ found for **3** (−320.1 ppm) and **4** (−401.3 ppm) indicate the presence of a six-coordinated central tin atom.[10] The upfield shift of $\delta(^{119}Sn)$ compared to the starting **1** (−212.8 ppm) and **2** (−208.8 ppm) suggests an important increase of Sn−Y bond strength in **3** and **4**. The ^1H NMR spectroscopy at various temperatures (range of 300−170 K) revealed the presence of one set of sharp signals of CH_2 and CH_3 protons indicating that both CH_2Y groups are coordinated mutually in trans positions giving thus a symmetrical octahedral arrangement at the central tin atom in **3** and **4** having also both C atoms and O atoms of both OTf groups mutually in trans positions. The IR spectrum showed the presence of covalently bound OTf groups in monodentate fashion.[11]

The X-ray structure analysis of **3** proved these assumptions, and the structure is shown in Figure 1 together with selected bond lengths and angles. The structure of compound **3** showed a distorted octahedral arrangement comprising two nitrogen atoms (N1 and N2) of the L^1 ligand, two oxygen atoms of OTf groups (O11 and O21), and two carbon atoms from the L^1 ligand C(21) and phenyl group C(11) arranged in trans positions with respect to each other (Figure 1). Both nitrogen atoms are coordinated to the tin atom by strong intramolecular interactions Sn−N (Sn(1)−N(1) 2.3850(16) Å and Sn(1)−N(2) 2.4020(17)Å). The Sn1−O11 and Sn1−O21 distances 2.2187(14)Å and 2.2368(15)Å (involving OTf groups) being longer than Σ_{cov}Sn−O (2.13Å)[12] indicate the presence of strong intramolecular interactions Sn−O rather than a covalent bond. Both OTf groups are, however, bound more tightly to the tin than in $[n\text{-}Bu_2Sn(\mu\text{-}OH)\text{-}(OH_2)(O_3SCF_3)]_2$ (Sn−O 2.622(4) Å).[13]

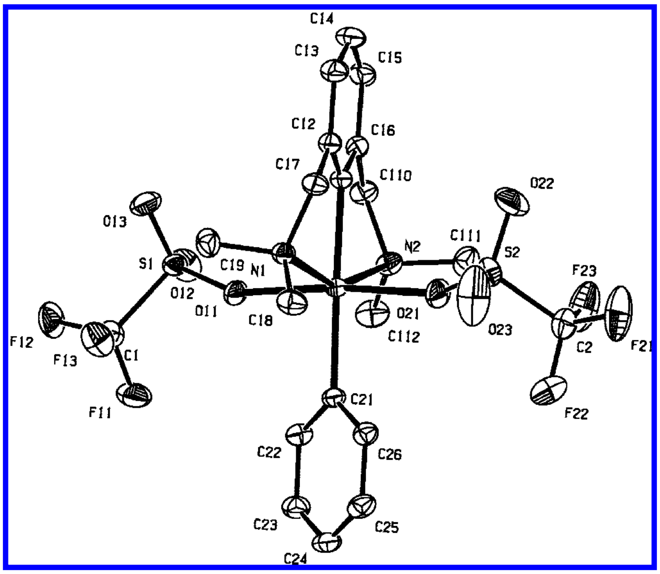


Figure 1. General view (ORTEP) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **3**. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angels (deg): Sn(1)−O(11) 2.2187(14); Sn(1)−O(21) 2.2368(15); Sn(1)−C(11) 2.0745(18); Sn(1)−C(21) 2.1265(18); Sn(1)−N(1) 2.3850(16); Sn(1)−N(2) 2.4020(17); N(2)−Sn(1)−N(2) 153.35(5); O(11)−Sn(1)−O(21) 174.49; N(2)−Sn(1)−O(21) 94.41(6); N(2)−Sn(1)−O(11) 86.48(6); C(11)−Sn(1)−C(21) 178.64(8).

The exposition of **3** and **4** to air resulted in the isolation of air- and moisture-stable organotin(IV) cations $\{[L^1SnPh(OH_2)(OTf)]^+ [OTf]^-\}$ (**5**) and $\{[L^2SnPh(OH_2)(OTf)]^+ [OTf]^-\}$ (**6**) (eq 2).

$$\underset{L^1(\mathbf{3}),\,L^2(\mathbf{4})}{L^{1,2}SnPh(OTf)_2} \xrightarrow{\text{air moisture}} \underset{L^1(\mathbf{5}),\,L^2(\mathbf{6})}{[L^{1,2}SnPh(OH_2)OTf]^+[OTf]^-} \quad (2)$$

The ionic nature of **5** and **6** has been mainly established by solution ^{119}Sn NMR spectroscopy and solution IR spectroscopy. The values of $\delta(^{119}Sn)$ (−303.6 ppm for **5**, − 356.4 ppm for **6**) are shifted downfield compared to those found in molecular compounds **3** (−320.1 ppm) and **4** (−401.3 ppm) and indicate the presence of a six-coordinated central tin atom.[10] The downfield shift of $\delta(^{119}Sn)$ in **5** and **6** is characteristic of the ionization process in organotin compounds.[14] The values of

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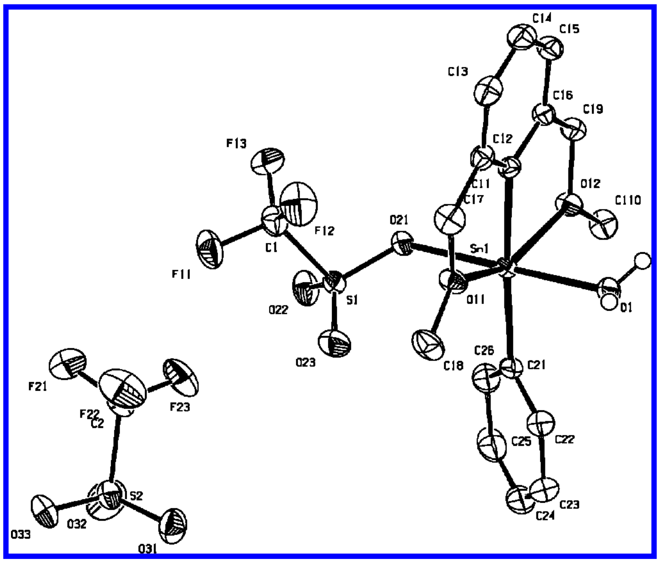


Figure 2. General view (ORTEP) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **6**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Sn(1)−O(1) 2.2363(17); Sn(1)−O(11) 2.2305(16); Sn(1)−O(12) 2.2561(16); Sn(1)−O(31) 8.015(19); Sn(1)−O(21) 2.2281(16), Sn(1)−C(21) 2.094(2); Sn(1)−C(11) 2.062(2); O(12)−Sn(1)−O(11) 152.74(5); O(1)−Sn(1)−O(21) 177.91(6); O(11)−Sn(1)−O(1) 86.53(6); O(21)−Sn(1)−O(11) 91.49(6); C(11)−Sn(1)−C(21) 175.82(9).

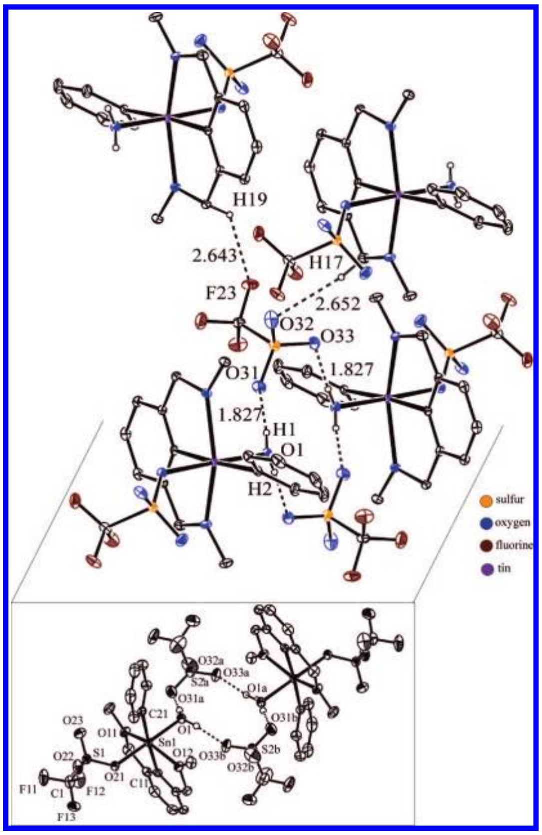


Figure 3. Polymeric structure of **6** mediated by hydrogen-bonding interactions. Hydrogen atoms have been omitted for clarity.

$\delta(^1H(CH_2))$ (4.60 ppm for **5**, 5.30 ppm for **6**) are shifted downfield in comparison to **3** (4.12 ppm) and **4** (5.00 ppm) and show further forcing of Sn−Y intramolecular interactions as the result of an increase of Lewis acidity of the central tin atom in the ionic compounds **5** and **6**. The ^1H NMR spectra also revealed broad signals at 3.42 ppm (**5**) and 4.11 (**6**) proving the coordination of water to the central tin atom. The ^1H NMR spectroscopy at various temperatures (range of 300−170 K) revealed the presence of one set of sharp signals of CH_2 and CH_3 protons, indicating that both CH_2Y groups are coordinated mutually in trans positions giving in **5** and **6**. The IR spectra proved the presence of both covalently bound and ionic OTf groups in **5** and **6** as well as the presence of coordinated water molecule (ν(OH) at 3064 for **3** and at 3695 for **4**).[11] The positive modes of the ESI/MS spectra of **5** and **6** showed the presence of intensive peak at *m/z* = 405 and 379 assigned to $[L^1SnPh(OH)]^+$ and $[L^2SnPh(OH)]^+$, fragments of starting ionic organotin(IV) cations $[L^1SnPh(OH_2)OTf]^+$ and $[L^2SnPh(OH_2)OTf]^+$.

The X-ray structure analysis of **6** proved these assumptions. Compound **6** is formed by the diorganotin(IV) cation $[L^2SnPh(OH_2)OTf]^+$ compensated by OTf anion. The structure of diorganotin(IV) cation $[L^2SnPh(OH_2)OTf]^+$ shows the central tin atom (Sn1) with an octahedral coordination environment comprising two oxygen atoms (O11 and O12) of the L^2 ligand, two oxygen atoms from water (O1) and OTf group (O21), and two carbon atoms from the L^2 ligand C(21) and phenyl group C(11) arranged in trans geometry with respect to each other (Figure 2). The bond angles O(12)−Sn(1)−O(11) = 152.74(5)°, O(1)−Sn(1)−O(21) = 177.91(6)°, and C(11)−Sn(1)−C(21) = 175.82(9)°, respectively, indicate the distortion from an ideal octahedral geometry (Figure 2). All four oxygen atoms are coordinated to the tin atom by a strong intramolecular interaction Sn−O (the range of Sn−O is 2.2281(16)−2.2561(16) Å). The Sn1−O1 distance (involving the coordinated water molecule) is 2.2363(17) Å and is similar to that found in $\{[n\text{-}Bu_2Sn(OH_2)_4]^{2+}[2,5\text{-}Me_2C_6H_3{-}SO_3^-]_2\}$ (average Sn−Ow 2.271(3) Å),[8a] $\{[n\text{-}Bu_2Sn(OH_2)(Phen)(O_3SC_6H_3\text{-}2,5\text{-}Me_2)]^+[2,5\text{-}Me_2C_6H_3SO_3]^-\}$ (Sn-Ow 2.273(3) Å), and in $\{[R_2Sn(OH_2)_2(OPPh_3)_2]^{2+}[CF_3SO_3^-]_2\}$ (Sn−O = 2.254(2)Å for R (*n*-Bu) and 2.237(3) Å for R(Me).[8d] The Sn1−O21 distance (involving the OTf group) is 2.2281(16) Å and indicates that in the current instance tin is bound more tightly to the OTf group than in $[n\text{-}Bu_2Sn(\mu\text{-}OH)\text{-}(OH_2)(O_3SCF_3)]_2$ (Sn−O 2.622(4) Å).[13]

The *free* OTf counteranion in **6** is involved in an O−H- - -O hydrogen bonding with one of the coordinated water molecules (H2- - -O33) (Figure 3) bringing thus two molecules of **6** together to form a centrosymmetric dimer as a result of the hydrogen bonding (O−H- - -O) between the coordinated water and the OTf counteranions. Two of the oxygen atoms (O33 and O31) of each OTf anion and both the hydrogen atoms (H1 and H2) of the water (O1) molecule are involved in this hydrogen-bonding interaction to form a 12-membered hydrogen-bonded ring (Figure 3). The bond parameters involved in this interaction [O- - -O31 2.658(53) Å, O1−H- - -O31 174.24(47)°, O1- - -O33 2.655(5) Å, and O1−H2- - -O33 174.96(61)°] indicate that the hydrogen bonds formed are quite strong (see Table 1, Supporting Information). These parameters are comparable to those found in $\{[n\text{-}Bu_2Sn(OH_2)_4]^{2+}[2,5\text{-}Me_2C_6H_3{-}SO_3^-]_2\}$[8a] and in $\{[n\text{-}Bu_2Sn(OH_2)_3\text{-}[\mu\text{-}L]\text{-}n\text{-}Bu_2Sn(OH_2)_3]^{2+}[L]^{2-}\}$ (L = 1,5-C_6H_{10}-$(SO_3^-)_2$).[8b] The remaining oxygen atom (O32) of *free* OTf counteranion of **6** is involved in intermolecular C−H- - -O hydrogen bonding between the dimmers to give polymeric tape (Figure 3). The hydrogen atom involved in this interaction belongs to the methylene group (H17) of L^2 ligand. These dimensional tapes are together connected by an additional intermolecular C−H- - -F interaction involving the second methylene group (H19) of L^2 ligand and fluorine atom (F23) of *free* OTf anion to afford a three-dimensional network (see the Supporting Information).

The use of carborane anion $[1\text{-}CB_{11}H_{12}]^-$ as a less nucleophilic polar group instead of OTf^- group was another step that should result to the preparation of more Lewis acidic tin centers. The reaction of **1** and **2** with 1 equiv of $AgCB_{11}H_{12}$ in CH_2Cl_2 yielded to diorganotin(IV) cations $\{[L^1SnPhCl]^+ [1\text{-}CB_{11}H_{12}]^-\}$ (**7**) and $\{[L^2SnPhCl]^+ [1\text{-}CB_{11}H_{12}]^-\}$ (**8**) (eq 3).

$$\begin{gathered} \underset{L^1(\mathbf{1}),\,L^2(\mathbf{2})}{L^{1,2}SnPhCl_2} + Ag^+[1\text{-}CB_{11}H_{12}]^- \xrightarrow{CH_2Cl_2} \\ \underset{L^1(\mathbf{7}),\,L^2(\mathbf{8})}{[L^{1,2}SnPhCl]^+[1\text{-}CB_{11}H_{12}]^-} + AgCl \qquad (3) \end{gathered}$$

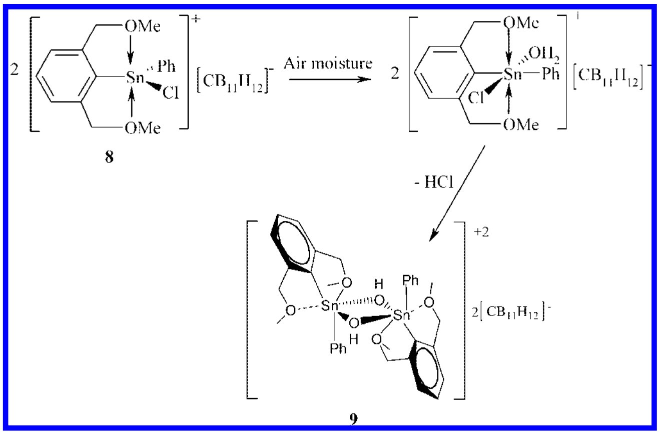
The values of $\delta(^{119}Sn)$ in compounds **7** (−73.33 ppm) and **8** (−88.1 ppm) are shifted downfield compared with **1** (−212.8 ppm) and **2** (−208.8 ppm) and fall to the region typical for [3 + 2] coordinated organotin cations.[14,16] The ^{11}B NMR spectra of **7** and **8** showed three distinct signals in a 1:5:5 ratio that is typical for noncoordinated $CB_{11}H_{12}$ anion.[17] The ^1H NMR spectra of compounds **7** and **8** exhibit an AB system of CH_2Y groups indicating their diastereotopic character and two signals of NMe_2 groups in **7** proving the presence of prochiral central tin atom in **7** and **8**. The geometry of the diorganotin cation in both compounds **7** and **8** can be thus described as the trans-trigonal bipyramid with CH_2Y groups in axial positions and two carbon atoms (one involved in Ph group and second one in L^1 or L^2 ligand) and chlorine atom in the equatorial plane. The presence of two strong Sn−Y interactions is also corroborated by a downfield shift of CH_2Y units in **7** (4.03 ppm) and **8** (5.19 ppm) in comparison to the values found in **1** (3.96 ppm) and **2** (4.68 ppm). The positive part of the ESI/MS showed the most intense peak at $m/z = 423$ for **7** ($m/z = 397$ for **8**) assignable to cations $[L^1SnPhCl]^+$ and $[L^2SnPhCl]^+$.

Compound **8** underwent facile hydrolysis resulting in Sn_2 dication $\{[PhL^2Sn\text{-}\mu\text{-}(OH)_2\text{-}SnL^2Ph]^{2+}\ 2{*}(1\text{-}CB_{11}H_{12})^-\}$ (**9**).[18] Thus, the formation of compound **9** can be explained by the coordination of water molecule to the tin atom of **8** in the first step (similarly to **5** or **6**). However, the use of low nucleophilic $1\text{-}CB_{11}H_{12}$anion increases Lewis acidity of the tin(IV) center in **8** leading to the polarization of O−H bond in the coordinated water. This polarization can lead to easy elimination of HCl followed by the formation of the dimeric compound **10** (Scheme 1).

Conclusion

In conclusion, an important role of Y,C,Y-ligands in controlled hydrolysis pathway was showed. The presence of Y,C,Y ligands in diorganotin(IV) compounds resulted to stabilization of highly Lewis acidic tin atoms in air and moisture sensitive compounds **3** and **4**. Their exposition to air led to the isolation of the hydrated forms **5** and **6**. Substitution of $[OTf]^-$ by $[1\text{-}CB_{11}H_{12}]^-$ group resulted to the stabilization of diorganotin(IV) cations **7** and **8**. Thanks to the presence of highly Lewis acidic tin center, however, the hydrated form of **8** could not be isolated and the Sn_2 dication **9** was obtained as the final hydrolytic product.

Scheme 1. Formation of Sn_2 Dication $[PhL^2Sn\text{-}\mu\text{-}(OH)_2\text{-}SnL^2\text{-}Ph]^{2+}\ 2{*}(1\text{-}CB_{11}H_{12})^-$ (9), the Final Hydrolytic Product of 8



Experimental Section

General Methods. The starting compounds $(L^{1,2})SnPhCl_2$ (**1** and **2**) were prepared according to the literature. The preparation, characterization, and X-ray structure of Sn_2 dication $\{[PhL^2Sn\text{-}\mu\text{-}(OH)_2\text{-}SnL^2Ph]^{2+}\ 2\cdot(1\text{-}CB_{11}H_{12})^-\}$ (**9**) was published previously,[18] but a new procedure described here gives better yields. All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use, and operations with silver salts were light protected. The ^1H,^{11}B, ^{13}C, and^{119}Sn NMR spectra were recorded on a Bruker AMX360 spectrometer at 300 K in $CDCl_3$. Appropriate chemical shifts were calibrated on: ^1H-residual peak of $CHCl_3$ ($\delta = 7.27$ ppm), ^{11}B-external $BF_3\cdot OEt_2$ ($\delta = 0.00$ ppm), ^{13}C-residual peak of $CHCl_3$ ($\delta = 77.23$ ppm), ^{119}Sn-external tetramethylstannane ($\delta = 0.00$ ppm). Chemical shifts data are given in ppm and coupling constants in hertz. Electrospray mass spectra (ESI/MS) were recorded in the positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) (range 100−600 *m/z*) and in the negative mode on the Platform quadrupole analyzer (range 100−800 *m/z*). The samples were dissolved in acetonitrile and analyzed by direct infusion (flow rate 1−10 μL/min). For the detection of negative ions of $m/z < 60$, a quadropole analyzer had to be used in place of the ion trap. The IR spectra were recorded on a Perkin-Elmer 684 equipment.

Preparation of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnPh(OTf)_2]$ (3). $L^1PhSnCl_2$ (0.69 g, 1.5 mmol) in CH_2Cl_2 (40 mL) was stirred with AgOTf (0.8 g, 3 mmol) for 2 h. The AgCl was removed by filtration, the filtrate evaporated, and the solid residue washed with pentane (2 × 5 mL) to give **3** (yield 0.98 g, 95%). Mp: 253−255 °C. Anal. Calcd for $C_{20}H_{24}F_6N_2O_6S_2Sn$ (MW 685.23): C, 35.06; H, 3.53. Found: C, 35.00; H, 3.50. MW = 685. MS: *m/z* 149, 100% $[OTf]^-$; *m/z* 537, 100% $[M - OTf]^+$. ^1H NMR ($CDCl_3$): δ (ppm); 2.68 (s, 12H, $N(CH_3)_2$); 4.12 (s, 4H, CH_2); 7.29−7.99 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 47.29 (CH_3); 62.42 (CH_2, $^nJ(^{119}Sn,^{13}C) = 68.9$ Hz); 119.56 (q-CF_3, $^nJ(^{19}F,^{13}C) = 316.85$ Hz); SnC_6H_3: 129.10 (C(1)), 138.46, 127.10, 133.14; $SnPh_2$: 134.31 (C′(1)), 135.69, 130.42, 132.59. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −320.10. IR (solution in $CHCl_3$): (cm $^{-1}$) ν_s $(SO_3) = 1040$s; ν_{as} $(SO_3) = 1264$s, 1188s.

Preparation of $[\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPh(OTf)_2]$ (4). Similar procedure to that for **3**. $L^2PhSnCl_2$ (0.86 g, 2 mmol) and AgOTf (1 g, 4 mmol) resulted to **4** (yield 1.25 g, 95%). **4**. Mp: 256−260 °C. Anal. Calcd for $C_{18}H_{18}F_6O_8S_2Sn$ (MW 659.15): C, 32.80; H, 2.75. Found: C, 32.70; H, 2.73. MW = 659. MS: *m/z* 149, 100% $[OTf]^-$; *m/z* 511, 100% $[M - OTf]^+$. ^1H NMR ($CDCl_3$): δ (ppm) 3.74 (s, 6H, CH_3); 5.00 (s, 4H, CH_2,$^nJ(^{119}Sn,\ ^1H) = 10.38$ Hz);

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7.15 (d, 2H, $H_{2',6'}$); 7.45 (t, 1H, $H_{4'}$); 7.58 (complex pattern, 4H, $H_{3,5}$, $H_{3',5'}$); 8.03 (t, 1H, H_4). ^{13}C NMR ($CDCl_3$): δ (ppm) 61.23 (CH_3); 73.66 (CH_2, $^{n}J(^{119}Sn, ^{13}C) = 46.5$ Hz); 119.81 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 318.3$ Hz); SnC_6H_3: 128.75 (C(1),$^{n}J(^{119}Sn, ^{13}C) = 348.64$ Hz), 138.44, 124.08, 132.38; $SnPh_2$: 134.33 (C′(1), $^{n}J(^{119}Sn, ^{13}C) = 405.69$ Hz), 136.92, 131.05, 134.33. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −401.34. IR (solution in $CHCl_3$): (cm $^{-1}$) $\nu_s(SO_3) = 1033$ s; $\nu(SO_3) = 1258$ s, 1177 s.

Preparation of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnPh(OH_2)(OTf)]^+$ $[OTf]^-$ (5). Compound **3** (0.5 g) was diluted in nondried CH_2Cl_2 (15 mL) after the solution was exposed to the air and slowly evaporated to obtain an oily residue that was crystallized by addition of hexane (10 mL). White crystalline material was identified as **5** (yield 0.4 g, 77%). Mp: 186−188 °C. Anal. Calcd for $C_{20}H_{26}F_6N_2O_7S_2Sn$ (MW 703.15): C, 34.16; H, 3.73. Found C, 34.00; H, 3.70. MW = 703. MS: *m/z* 149, 100% $[OTf]^-$; *m/z* 405, 100 $[M - 2OTf - H]^+$. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.06 (s, 12H, $N(CH_3)_2$); 3.42 (bs, 2H, OH_2); 4.61 (s, 4H, CH_2); 7.51−7.94 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 43.59 ($N(CH_3)$); 61.64 (s, CH_2); 121.85 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 320.3$ Hz); SnC_6H_3: not found (C(1)), 134.59, 131.04, not found; $SnPh_2$: not found (C′(1)), 133.72, 132.02, not found. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −303.58. IR ($CHCl_3$ solution): (cm $^{-1}$) $\nu_s(SO_3) = 1040$s; $\nu_{as}(SO_3) = 1169$, 1259s, 1301s; $\nu(OH) = 3064$br.

Preparation of $[\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPh(OH_2)(OTf)]^+$ $[OTf]^-$ (6). Similar procedure to **5**; 0.5 g of **4** was used to obtained 0.4 g of **6** (yield 75%). Mp: 191−192 °C. Anal. Calcd for $C_{18}H_{20}F_6O_9S_2Sn$ (MW 677.16): C, 31.93; H, 2.98. Found: C, 31.90; H, 2.94. MW = 677. MS: *m/z* 149, 100% $[OTf]^-$; *m/z* 379, 100% $[M - 2OTf - H]^+$. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.43 (s, 6H, CH_3); 4.10 (s, 2H, OH_2); 4.99 (s, 4H, CH_2); 7.44−7.62 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 59.67 (CH_3); 73.42 (CH_2, $^{n}J(^{119}Sn,^{13}C) =$ Hz); 121.77 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 320.3$ Hz); SnC_6H_3: not found (C(1)), 144.75, 126.76, 132.55; $SnPh_2$: not found (C′(1)), 136.00, 130.71, 132.89. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −356.37. IR (solution in $CHCl_3$): (cm $^{-1}$) $\nu_s(SO_3) = 1032$; $\nu_{as}(SO_3) = 1171$s, 1249s, 1277s; $\nu(OH) = 3695$ wm, 1625 s.

Preparation of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnPhCl]^+$ $[1\text{-}CB_{11}H_{12}]^-$ (7). Similar procedure to **3**. $L^1SnPhCl_2$ (0.55 g, 1.2 mmol) and $AgCB_{11}H_{12}$ (0.39 g, 1.2 mmol) resulted to **7** (yield 0.66 g, 97%). Mp: 87−90 °C. Anal. Calcd for $C_{19}H_{36}B_{11}ClN_2Sn$ (MW 565.59): C, 40.35; H, 6.42. Found: C, 40.30; H, 6.40. MW = 566. MS: *m/z* 423, 100 $[M\text{-}CB_{11}H_{12}]^+$; *m/z* 143, 100 $[CB_{11}H_{12}]^-$. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.41 (s, 6H, $(CH_3')_2$); 2.47 (s, cage C*H*); 2.66 (s, 6H, $N(CH_3)_2$); 4.03 (AB, 4H, CH_2, $^{n}J(^1H,^1H) = 15.0$ Hz); 7.37−7.77 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 46.76 ($N(C'H_3)$); 47.14 ($N(CH_3)$); 54.73 (s, cage *C*H); 63.34 (s, CH_2, $^{n}J(^{119}Sn,^{13}C) =$ Hz); SnC_6H_3: not found (C(1)), 141.47, 127.99, 134.83; SnPh: not found (C′(1)), 135.53, 131.22, 133.54. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −73.33. ^{11}B NMR ($CDCl_3$): δ (ppm) −14.90 (s, 1B, B(12)); −18.23 (s, 10B, B(7−11 and 2−6)). IR (suspension in Nujol): (cm $^{-1}$) $\nu(BH) = 2565$.

Preparation of $[\{2,6\text{-}(MeOCH_2)_2C_6H_3\}SnPhCl]^+$ $[1\text{-}CB_{11}H_{12}]^-$ (8). Similar procedure to **1**. $L^2SnPhCl_2$ (0.432 g, 1.0 mmol) and $AgCB_{11}H_{12}$ (0.33 g, 1.0 mmol) resulted in **8** (yield 0.52 g, 96%). Mp: 145−148 °C. Anal. Calcd for $C_{17}H_{30}B_{11}ClO_2Sn$ (MW 539.50): C, 37.85; H, 5.60. Found: C, 37.81; H, 5.39. MW = 540. MS: *m/z* 397, 100% $[M - CB_{11}H_{12}]^+$; *m/z* 143, 100% $[CB_{11}H_{12}]^-$. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.15 (s, cage C*H*); 3.86 (s, 6H, CH_3); 5.19 (AB, 4H, CH_2, $^{n}J(^1H,^1H) = 12.3$ Hz); 7.43−7.87 (complex pattern, 8H, SnPh, SnC_6H_3). ^{13}C NMR ($CDCl_3$): δ (ppm) 42.60 (s, cage *C*H); 61.10 (CH_3), 74.0 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 36.10$ Hz); SnC_6H_3: 131.73 (C(1)), 140.82, 125.08, 121.03; SnPh: 133.88 (C′(1)), 135.74, 131.31, 134.31. ^{119}Sn NMR ($CDCl_3$): δ (ppm) −88.13. ^{11}B NMR ($CDCl_3$): δ (ppm) −10.03 (s, 1B, B(12)); −16.38 (s, 5B, B(7−11); −20.37 (s, 5B, B(2−6)). IR (suspension in Nujol): (cm $^{-1}$) $\nu(BH) = 2569$.

Preparation of $[\{2,6\text{-}(MeOCH_2)_2C_6H_3\}(Ph)Sn\text{-}\mu\text{-}(OH)_2\text{-}Sn\text{-}(Ph)\{2,6\text{-}(MeOCH_2)_2C_6H_3\}]^+$ $2\cdot[1\text{-}CB_{11}H_{12}]^-$ (9). One microliter of H_2O was added to the THF solution of **8** (0.3 g, 0.4 mmol) at 0 °C, and the resulting suspension was stirred for 3 h. Insoluble precipitate was filtered off, and the filtrate was evaporated to dryness. The residue was washed with 15 mL of pentane to precipitate a white solid characterized as **10**. Yield: 0.2 g (75%).

Crystallography Studies. Colorless crystals were obtained by layering *n*-hexane onto a dichloromethane solutions of the compounds. Crystals of compounds of **3** and **6** were mounted on a glass fiber with epoxy cement and measured on a KappaCCD four-circle diffractometer with a CCD area detector by monochromatized Mo K radiation (= 0.71073 Å) at 150(2) K. The details pertaining to the data collection and refinement for crystals are as follows. For **3**: $C_{20}H_{24}F_6N_2S_2Sn$, $M = 685.22$, monoclinic, space group *P*21/c, $a = 13.7458(3)$ Å, $b = 9.3395(10)$ Å, $c = 19.9533(4)$ Å, $\alpha = 90°$, $\beta = 98.0965(9)°$, $\gamma = 90°$, $Z = 4$, $\rho = 1.795$ g·cm^{-3}, $\mu = 1.256$ mm^{-1}, crystal size 0.6 × 0.5 × 0.35 mm, crystal shape prism, θ range 1−27.5°, $T_{min,}$, T_{max} 0.503, 0.653, 27364 reflections collected, of which 5793 were independent [R(int) = 0.0433], no. of observed ref [$I > 2\sigma(I)$] 5464, no. of parameters 339, *S* all data 1.075, final *R* indices [$I > 2\sigma$(I)]: R1 = 0.0243, wR2 = 0.0575.

For **6**: $C_{18}H_{20}F_6O_9S_2Sn$, $M = 677.15$, triclinic, space group *P*-1, $a = 10.0999(3)$ Å, $b = 10.4971(3)$ Å, $c = 11.9202(2)$ Å, $\alpha = 73.1794(16)°$, $\beta = 86.1036(16)°$, $\gamma = 85.1050(11)°$, $Z = 2$, $\rho = 1.868$ g·cm^{-3}, $\mu = 1.328$ mm^{-1}, crystal size 0.3 × 0.3 × 0.15 mm, crystal shape prism, θ range 1−27.5°, $T_{min,}$, T_{max} 0.786, 0.880, 18543 reflections collected, of which 5531 were independent [R(int) = 0.0354], no. of observed ref [$I > 2\sigma(I)$] 5092, no. of parameters 336, *S* all data 1.040, final *R* indices [$I > 2\sigma$(I)]: R1 = 0.0254, wR2 = 0.0601.

The crystal structure of **10** was already published.[18] The empirical absorption corrections[19] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97[20]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97[21]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(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 have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 668524 and 668525 for **3** and **6**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; internet: http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Further details of the structure determination of compounds **3** and **6**, including atomic coordinates, anisotropic displacement parameters and geometric data. This material is available free of charge via the Internet at http://pubs.acs.org.

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