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Solvent-Controlled Ring Size in Double C,N-Chelated Stannoxanes[⊥]

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The stannylene $(L^{CN})_2Sn$ where L^{CN} is a chelating ligand (2-(*N*,*N*-dimethylaminomethyl)phenyl−) was oxidized by an excess of oxygen, nitrous oxide, or TEMPO free radical, giving dimeric stannoxane $[(L^{CN})_2Sn]_2(\mu\text{-O})_2$ in dynamic equilibrium with its monomeric form in solution. In the solid state, an unusual tetraoxatetrastannacycle cyclo-$[(L^{CN})_2SnO]_4$ can be crystallized from diethyl ether and the trioxatristannacyclic complex of formula cyclo-$[(L^{CN})_2SnO]_3$ from the hexane solution. The same result has been obtained when C,N-chelated organotin(IV) dihalides ($(L^{CN})_2SnX_2$, where X = Cl or Br) were hydrolyzed with an excess of sodium hydroxide and than dehydrated by azeotropic distillation. The oxo-bridged dihydroxide $[(L^{CN})_2Sn(OH)]_2(\mu\text{-O})$ has been isolated during the course of this hydrolysis.

Introduction

The chemistry of organotin(IV) oxides and/or hydroxides is well established.[1] This class of compounds, mainly diorganotin(IV) or cationic species, found its use as homogeneous catalysts in various types of transesterification and transcarbamoylation processes.[2]

These compounds were structurally investigated mainly with the help of NMR techniques in solution[3] and XRD techniques in the solid state.[1] The structures are polymeric[4] in the case of small substituents on the tin atom and oligomeric in the case of compounds having sterically demanding groups.[1] In the case of sterically hindered diorganotin(IV) species, the compounds with cyclic structures were found. The dimeric dioxa-,[5] diperoxa,[6] oxa-peroxa-,[7] or 1-oxa-3-thia-[8]bridged distannanes were obtained via oxidation of lower oxidation states of tin by dioxygen or Me_3NO with hetero ring size from four to six. The trimeric ($[R_2SnO]_3$) complexes either with planar or twisted six-membered ring geometry were generally proposed and studied as well-defined complexes.[9] The cluster-like or alkanyl, sulfonyl, heteroatom, hydroxo, and carbonyl bridge stabilized structures with the main motif of Sn_2O_2 appeared in recent years as well.[10] The reaction of a dimethylaminomethyl ferrocenyl-substituted stannylene with water/oxygen gave the first structurally determined diorganotin dihydroxide of formula $(C_5H_5FeC_5H_3\text{-}2\text{-}CH_2NMe_2)_2Sn(OH)$.[11]

We found recently that the use of C,N-chelating ligands ({2-[dimethylaminomethyl]phenyl}−) can monomerize tri- and diorganotin(IV) systems and increase their reactivity, especially in the case of fluorination reactions.[12] In this paper, we

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[⊥] Dedicated to Prof. Dr. Marcel Gielen on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic chemistry.

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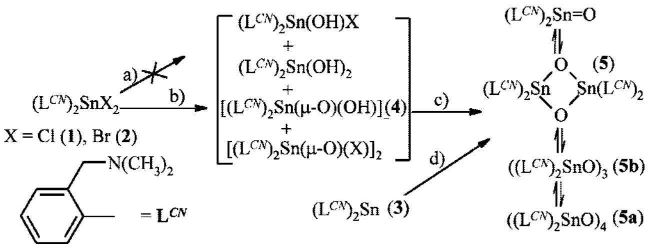

Figure 1. Studied reactivity: (a) water, (b) NaOH, (c) no water, (d) oxygen, N_2O, or TEMPO. **5** is observed in solution. **5a** crystallizes from polar and **5b** from nonpolar solvents.

communicate on the oxidation of C,N-chelated stannylene and hydrolysis of C,N-chelated stannane containing such a ligand.

Results and Discussion

The reactivity of diorganotin(IV) dihalides **1** and **2** (Figure 1) with several agents was studied (water, an excess of aqueous ammonia, a 1 M triethyl amine in water/benzene mixture,[12b,13] 1 to 10 molar equiv of sodium hydroxide in water/benzene biphasic system) in order to characterize products of hydrolysis of these compounds. At the same time, the investigation of oxidation of stannylene **3** was started to explain the presence of seven different signals in the ^{119}Sn NMR spectrum of the product of oxidation of Lappert's stannylene[14] by TEMPO free radical in analogy with Kira's results on silylene, germylene, and stannylene oxidation[15] on a more simple system where tin atoms are prevented from making higher oligomers by C,N-chelating ligands. The stannylene **3** was treated by O_2, N_2O, and TEMPO, respectively.

Compounds **1** and **2** did not react with water at ambient conditions, but they reacted with aqueous ammonia, triethyl amine/water, and sodium hydroxide to give similar results. In all of these reactions an equilibrium is suggested between mononuclear $(L^{CN})_2Sn(OH)X$ and $(L^{CN})_2Sn(OH)_2$ and dinuclear $(L^{CN})_2SnX(\mu\text{-}O)SnX(L^{CN})_2$ and $(L^{CN})_2Sn(OH)(\mu\text{-}O)Sn(OH)(L^{CN})_2$ (**4**) complexes. This suggestion is based on previous reports[16] and also on continuous ^{119}Sn NMR screening of the reaction mixtures (signals at −196.5 (broad), −254.3, −263.5, −275.3, −282.9 in benzene-d_6). Unfortunately, only the last compound has been isolated pure, and its structure was determined by diffraction techniques on single crystals. The structure is very close to the first oxo-bridged dihydroxo compound published by Lappert[5] and of chelated compounds that appeared during the course of completing this paper[17] (for a structure comparison see the Supporting Information).

When **4** is refluxed in benzene or toluene in a Dean-Stark apparatus, the new broad signal at −222.0 ppm (in C_6D_6 and is also very close to the signal found in THF-d_8) appeared in the ^{119}Sn NMR spectrum, and in 2 h of continuous distillation it was preserved as the sole one (Figure 2). Also the signals in the ^{1}H NMR spectrum in toluene-d_8 are a bit broadened at room temperature, but the coupling of tin nuclei to the benzyl ortho proton is still visible. When the temperature is increased to 320 K, the signals in both types of NMR spectra become much sharper and the $^3J(^{119}Sn{-}O{-}^{117}Sn)$ coupling is visible at 408 Hz, which indicated a distanoxane-like structure.[3] At 250 K, the signal in the ^{119}Sn NMR becomes much broader and is shifted to higher field, and also signals in the ^{1}H NMR spectrum are very broad. All these signals started to decoalesce into four sets of new signals at 220 K. Further lowering of the temperature to 180 K gave four sets of signals with the center of gravity at the same values as was found at 250 K. On the basis of these values and patterns we calculated the possible geometry of the tin centers and suggested the structure of this molecule (**5**) as well. Unfortunately, it is not possible to prepare suitable single crystals for diffraction experiments by this reaction sequence, probably due to very small amounts of inorganic impurities.

All reactions of stannylene **3**[18] gave exactly the same NMR spectra as observed for **5** after very short reaction times. The reaction with TEMPO led to the same compound after less than 10 min, but inseparable and unidentified intermediates containing a tin atom were observed in both NMR and EPR spectra during this time. The signal in the ^{119}Sn NMR was observed immediately after mixing of **3** with TEMPO at −146.2 ppm, and some broad signals in the ^{1}H NMR were observed as well. In the EPR spectrum, the main band centered at $g = 2.0074$, which is very close to that of unreacted TEMPO, with two relatively low intensity satellite doublets (altogether approximately 10% of main band) with hyperfine splitting of 24.1 and 20.4 G was found. The observed hyperfine splitting arose from weak dipolar interactions of unpaired electrons of TEMPO with the Sn nucleus as the first step of oxidation, similar to that proposed by Kira.[15] An unidentified signal without any resolved pattern and a similar g value was observed as well.

The observation of one signal in the ^{119}Sn NMR spectrum with satellites at 320 K and four equivalent signals at 180 K in toluene-d_8 solution suggested dimeric species with average structure at higher temperature and the possibility of formation of different isomers of this arrangement or a tetranuclear species at lower temperature. On the other hand, only an isotopic pattern corresponding to dimeric arrangement (positive-ion MS: m/z 809 $[M + H]^+$, 100%) has been observed in the ESI/MS spectra in acetonitrile, and a molecular mass value of 550.6, which can be taken as a value of 63:37 for monomer:dimer equilibrium, was determined by cryoscopy in benzene. The broad signals around −260 ppm were found in the CP/MAS NMR spectra for **5** crystallized from both coordinating and noncoordinating solvents (hexane, diethyl ether).

To rationalize experimental results, we performed DFT calculations of structure, energetic parameters, and chemical shifts of monomer to tetramer of $[(L^{CN})_2SnO]_x$. Dimeric, trimeric, and tetrameric structures are close in energies (Table S2). The differences, both in H^0 and G^0, do not exceed 3 kcal/mol. Thus solvent and crystal-packing effects would strongly affect the structure of oligomers both in solution and in the solid state. In the gas phase, in terms of H^0, the tetramer is 0.7 kcal/mol (all energies are with respect to one subunit) more stable

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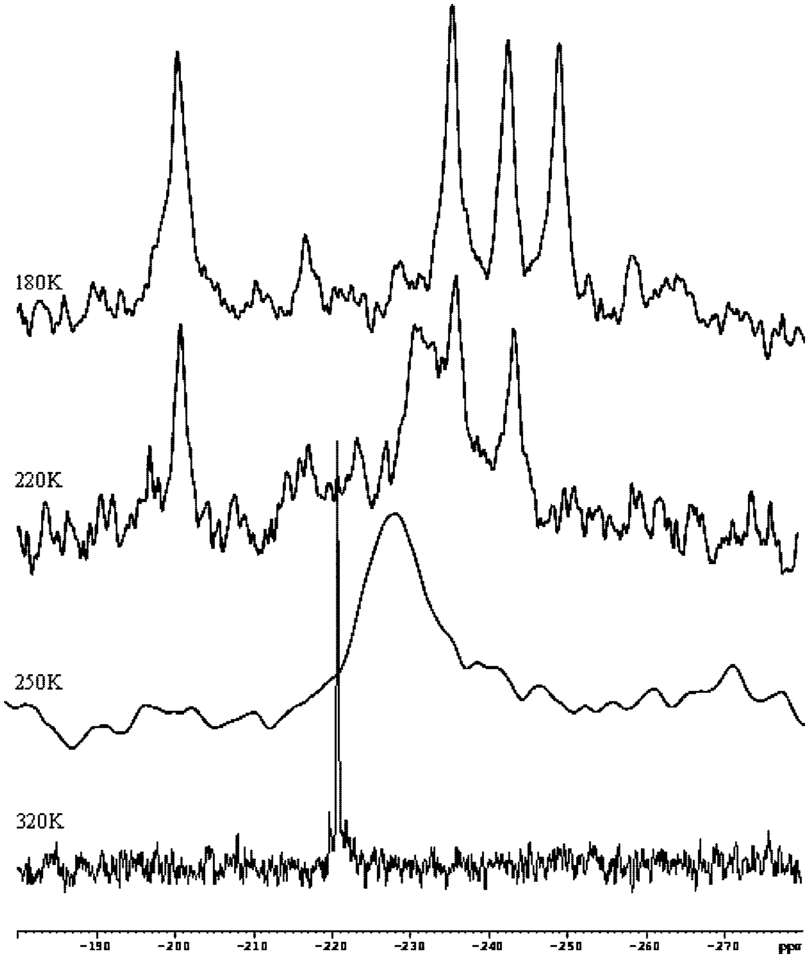

Figure 2. Temperature-dependent ^{119}Sn NMR spectra of **5** in toluene-d_8.

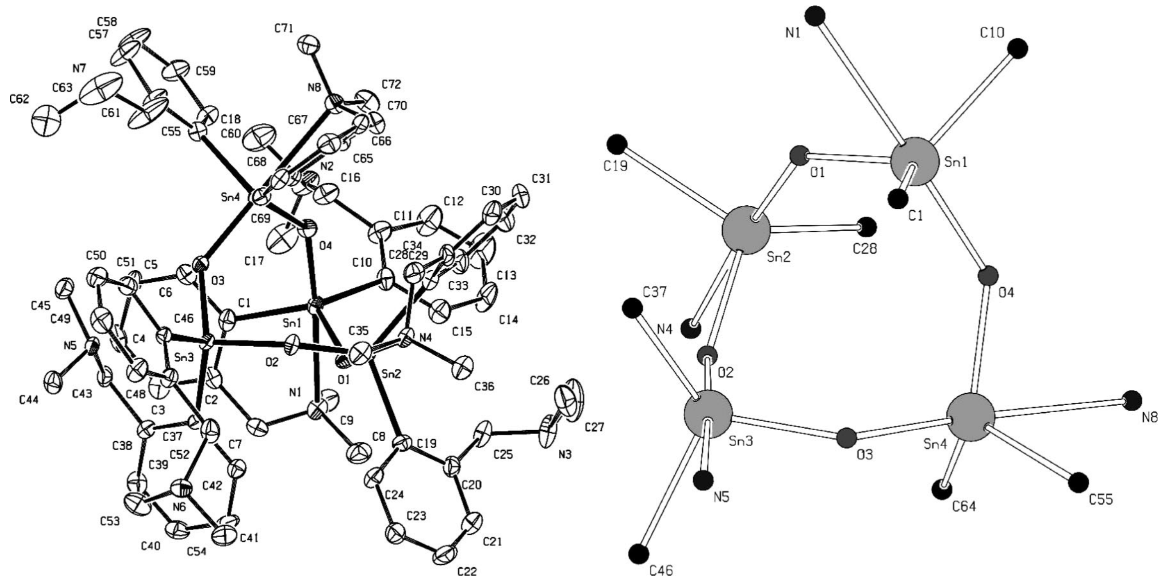

Figure 3. ORTEP view (30% probability level, hydrogen atoms are omitted for clarity) and the detail of the structure of Sn_4O_4 ring of **5a** together with atoms found in the tin atoms' primary coordination spheres. Selected bond lengths (Å) and angles (deg) (for different ORTEP view see Figure S3): Sn1−O1 1.933(6), Sn1−O4 1.986(6), Sn1−C10 2.144(9), Sn1−C1 2.156(9), Sn1−N1 2.671(8), Sn1−N2 4.569(8), Sn2−O2 1.946(5), Sn2−O1 1.996(6), Sn2−C19 2.156(9), Sn2−C28 2.159(10), Sn2−N3 4.587(8), Sn1−N4 2.716(7), Sn4−O4 1.936(6), Sn4−O3 1.996(6), Sn4−C64 2.143(8), Sn4−C55 2.156(9), Sn4−N7 4.717(8), Sn4−N8 2.729(7), Sn3−O3 1.936(5), Sn3−O2 1.991(5), Sn3−C37 2.132(9), Sn3−C46 2.160(8), Sn3−N5 2.731(7), Sn3−N6 4.613(8), Sn2−O2 Sn3 135.3(3), Sn3−O3−Sn4 135.4(3), Sn4−O4−Sn1 136.5(3), Sn1−O1−Sn2 137.0(3).

than the dimer, while in terms of G^0 the dimer is 2.3 kcal/mol more favorable than the tetramer. Thus it can be supposed that the choice of solvent can strongly affect the equilibrium between dimeric, trimeric, and tetrameric structures.

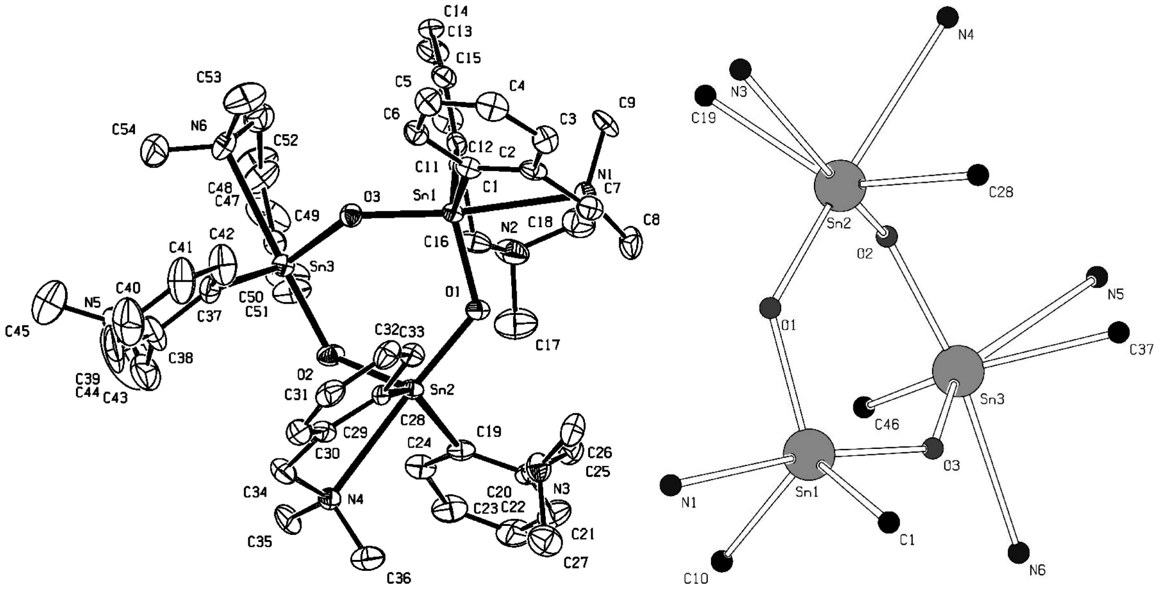

Figure 4. ORTEP view (30% probability level, hydrogen atoms are omitted for clarity) and the detail of the structure of the Sn_3O_3 ring of **5b** together with atoms found in the tin atoms' primary coordination spheres. Selected bond lengths (Å) and angles (deg) (for a different ORTEP view see Figure S5): Sn1−O1 1.951(4), Sn1−O3 1.984(4), Sn1−C1 2.151(6), Sn1−C10 2.159(7), Sn2−O2 1.971(5), Sn2−O1 2.013(4), Sn2−C28 2.132(6), Sn2−C19 2.144(6), Sn3−O3 1.951(4), Sn3−O2 1.991(5), Sn3−C37 2.123(7), Sn3−C46 2.143(7), Sn1−N1 2.621(5), Sn1−N2 4.771(7), Sn2−N3 3.076(6), Sn2−N4 2.675(6), Sn3−N5 3.432(11), Sn3−N6 2.614(15), Sn3−O3−Sn1 131.6(2), Sn2−O2−Sn3 126.9(2), Sn1−O1−Sn2 125.9(2).

There were three conformers of a monomer found. ^{119}Sn chemical shifts of these conformers are significantly different: −178, −195, and −230 ppm. These conformers lie within only ~3 kcal/mol in energy. It can be supposed that in solution these conformers are in equilibrium; the mean value of the ^{119}Sn chemical shift is −201 ppm. Formation of a monomeric $L^{CN}{}_2SnO$, containing a Sn═O double bond, is energetically strongly unfavorable (Table S2). Thus formation of monomers can take place only at higher temperatures or in the presence of solvation molecules. This phenomenon has been theoretically studied previously with the same result.[19]

There are 32 conformeres of the dimer with four coordination N→Sn bonds possible. It was found that these conformers lie within ~4 kcal/mol in energy. Breaking of one coordination bond requires only 1−3 kcal/mol. Calculated ^{119}Sn chemical shifts of tin atoms in dimers with four coordination bonds lie in the range −228 to −234 ppm. Breaking of one coordination bond leads to a downfield shift to −180 to −190 ppm for signals of tin atoms with one coordination bond and a slight upfield shift to −234 to −237 ppm for signals of tin atoms with four coordination bonds. Calculated ^{119}Sn chemical shifts in the dimers are close to those found experimentally. It can be supposed that at elevated temperatures the process of breaking/formation of Sn−N coordination bonds is fast. Thus only one ^{119}Sn signal is observed. At lower temperatures two types of signals were found. According to calculated chemical shifts, one signal at −200 ppm corresponds to a tin atom with one coordination bond. Three signals between −236 and −243 ppm correspond to doubly coordinated tin atoms. Thus it can be supposed that at lower temperatures at least two 4-fold and one 3-fold coordinated isomers of a dimer coexist in solution. This is also supported by the observation of a $^3J(^{119}Sn{-}O{-}^{117}Sn)$ coupling of 408 Hz, which is indicative for a distannoxane structure.

Calculated ^{119}Sn chemical shifts of the tetramer do not agree with experimental values. In the tetramer with four coordination bonds chemical shifts are −256 ppm for the tin atom with a longer Sn−N bond and −264 ppm for the other three tin atoms. The calculated energy of breaking of one coordination bond is only 1 kcal/mol. The calculated chemical shift of the noncoordinated tin atom is −185 ppm. Signals corresponding to monocoordinated tin atoms fall in a narrow range between −260 and −263 ppm. Calculated chemical shifts of the tetramer differ from experimental values significantly. Additionally, the difference between non- and monocoordinated tin atoms is about 80 ppm, while in experiment it is only 35−50 ppm.

On the basis of these findings, we suggest the presence of a dimer in solutions of different solvents with average structure at higher temperatures and conformers with variable coordination of donor groups at lower temperatures. The monomer/dimer equilibrium can be present under special conditions, for example close to crystallization temperature in nonpolar solvents.

Finally we obtained two exclusive and different single crystals from diethyl ether and hexane solution. The single crystals of **5a** (mp 232−234 °C) (Figure 3) suitable for X-ray analysis grew from diethyl ether solution as the first tetranuclear monocyclic organotin compound (the structure of the tricyclic one was determined by X-ray techniques[10e] and the monocyclic one was suggested on the basis of NMR parameters by Jurkschat[10j]). The structure of this compound can be described as a rather symmetrical boat-like eight-membered ring containing four $(L^{CN})_2SnO$ monomeric units. Each tin atom is located between two oxygen atoms with disparate distances of approximately 1.93 and 1.99 Å, respectively, where the first distance corresponds to equatorially bonded oxygen atoms and the longer one to axial oxygen atoms in trans position to one of the nitrogen atoms in trigonal bipyramidal coordination vicinities of four tin atoms. Coordination polyhedra are completed by two carbon atoms in equatorial positions. The remaining four nitrogen donor atoms are out of the tin atoms' primary coordination spheres.

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Single crystals of **5b** (mp 263−266 °C) (Figure 4) suitable for X-ray analysis grew from a hexane solution. The six-membered ring $(Sn-O)_3$ (for similar structures see ref 9) is more symmetrical than that of **5a** and also the degree of planarity of this ring is higher. The Sn−O distances (1.95 to 2.01 Å) in **5b** as well as the appropriate Sn−O−Sn angles differ significantly from corresponding values found for **5a**. The major difference was found in the coordination vicinity of Sn1, which is trigonal bipyramidal with only one nitrogen coordinated similarly to that in **5a**, and both tin atoms Sn2 and Sn3, where both nitrogen atoms are located in the primary coordination spheres; thus the geometries are more closely related to distorted octahedra.

A similar equilibrium of trinuclear/tetranuclear rings has been proposed for antimony oxides.[20]

Conclusion

The oxidation of bis-C,N-chelated stannylene gave the same product as the hydrolysis bis-C,N-chelated tin(IV) dihalide followed by dehydratation. The structure of this compound differs significantly from monomer to dimer equilibrium in benzene at cryoscopy conditions: a dimer in toluene at room temperature, a trimer in the solid state when crystallized from noncoordinating solvents such as hexane, and a tetramer in the solid state crystallized from diethyl ether. All these results were rationalized by and compared with theoretical calculations.

Experimental Section

General Methods. NMR Spectroscopy. The NMR spectra were recorded as solutions in toluene-d_8 or benzene-d_6 on a Bruker Avance 500 spectrometer (equipped with a *Z*-gradient 5 mm probe) at 180 to 320 K for ^{1}H (500.13 MHz) and ^{119}Sn{^{1}H} (186.50 MHz). The solutions were obtained by dissolving 40 mg of each compound in 0.5 mL of deuterated solvents.

ESR Spectroscopy. The ESR spectra of solutions were measured at ambient temperature at X-band (ν ~9.5 GHz) using an ERS 221 spectrometer (Magnettech Berlin). A microwave power of 1 mW, sufficiently below the saturation power, was used.

X-ray Crystallography. Data for colorless crystals were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The structures were solved by direct methods (SIR92[21]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97[22]). Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map; however to ensure uniformity of treatment of crystals, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors of $H_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$(pivot atom) or $1.5U_{\text{eq}}$ for the methyl moiety. Absorption corrections were carried out, using Gaussian integration from the crystal shape for **5a**[23] or by SADABS.[24]

A full list of crystallographic data and parameters including fractional coordinates is deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk]. CCDC deposition numbers: 684116−684118 for **4**, **5a**, and **5b**.

ESI Mass Spectrometry. In the mass spectrometry, the positive-ion electrospray ionization ESI mass spectra were measured on an Esquire3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 100−1000, and negative-ion ESI mass spectra were measured on a Platform quadrupole analyzer (Micromass, UK) in the range *m*/*z* 15−600. The ion trap was tuned to give an optimum response for *m*/*z* 500. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1−3 μL/min.

Computations. All calculations were done at the DFT level of theory. Geometry optimizations were carried out using the PBE generalized gradient functional.[25,26] The triple-ζ valence basis set including polarization functions TZ2P {3,1,1/3,1,1/1,1} for Sn, C, N, and O atoms and {3,1,1/1) for H atoms was used. Innermost electrons for Sn, C, N, and O atoms were treated using the ECP-SBKJC relativistic effective core potentials.[27] Total energies *E*, zero-point vibration energies ZPE, $E^0 = E + \text{ZPE}$, H^0, and G^0 were calculated for all stationary points. Vibration frequencies were used to characterize stationary points as minima. Calculations of chemical shifts at GIAO approach[28] were made using the full electron TZ2P basis set. All calculations were performed using the PRIRODA program.[29]

Synthetic Procedures. $(L^{CN})_2SnX_2$ (**1** and **2**)[12d] and $(L^{CN})_2Sn$ (**3**)[18] were prepared according to published procedures. All solvents and starting compounds were obtained from commercial sources (Sigma-Aldrich). Toluene, THF, diethyl ether, benzene, *n*-hexane, and *n*-pentane were dried over and distilled from sodium, degassed, and stored over potassium mirror under argon. The alkaline metal hydroxides were separated from carbonates via Sörensen's method or prepared via addition of alkaline metals into degassed water.

Typical Hydrolytic and Oxidation Conditions. The appropriate diorganotin halide **1** or **2** (0.5 g) was stirred overnight at room temperature with sodium hydroxide (or aqueous ammonia or triethyl amine/water; 1 to 4 equiv) in a 20/20 mL mixture of benzene/water under an argon atmosphere. Subsequently the phases were separated and evaporated in vacuo. There was typically no tin-containing species in the water phase. The residue from the benzene layer was extracted with benzene, washed with water, dried with sodium sulfate, and then evaporated, giving typically a mixture of five different tin-containing species (monitored by ^{119}Sn NMR −196.5 (broad), −254.3, −263.5, −275.3, and −282.9 in benzene-d_6; very broad signals were observed in the ^{1}H NMR spectra) as a white solid. When four or more equivalents of sodium hydroxide is added, the formation of **4** as the sole product is observed. The hydroxide/oxide equilibrium can be shifted by heating **4** in vacuo or dehydratation in toluene using a Dean-Stark apparatus for a minimum 2 h for complete formation of **5**.

The oxidation of stannylene **3** to form **5** was done by bubbling synthetic air (N_2/O_2 of 78/21 ratio) for gas chromatography or N_2O through a Schlenck tube with 1 g of **3** in 50 mL of toluene at room temperature for 10 min, giving an essentially quantitative yield of **5**. An alternative procedure is to oxidize **3** by TEMPO free radical. The solution of **3** in toluene was cooled in liquid nitrogen to form

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a glassy solid in NMR or a quartz tube in vacuo. TEMPO was added as a solid and the tube sealed. Afterward the ^{1}H or ^{119}Sn NMR and ESR spectra were measured with a spontaneous increase of temperature.

Bis{hydroxobis[2-(*N*,*N*-dimethylaminomethyl)phenyl]tin(IV)} Oxide (4). White solid, yield 84%. ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.05 (d, 4H, H(6), $^3J(^1H, ^1H) = 6.9$ Hz, $^3J(^1H, ^{119}Sn) = 88$ Hz); 7.34 (m, 8H, H(4, 5)); 7.11 (d, 4H, H(3), $^3J(^1H, ^1H) = 7.2$ Hz); 3.51 (s, 2H, NCH_2); 2.08 (s, 24H, $N(CH_3)_2$); −0.22 (brs, 2H, OH). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −282.9. Anal. (%) Found: C, 52.3; H, 6.1; N, 6.7. Calcd for $C_{36}H_{50}N_4O_3Sn_2$ (824.20): C, 52.46; H, 6.11; N, 6.80. Positive-ion MS: *m*/*z* 809 $[M - OH]^+$, 100%; 522 $[L_3Sn]^+$; 405 $[L_2Sn{=}O + H]^+$. MS/MS of *m*/*z* 809: *m*/*z* 764 $[M + H - (CH_3)_2NH]^+$; 405 $[L_2Sn{=}O + H]^+$; 254 $[LSn]^+$. Mp: 215−217 °C.

Bis[2-(*N*,*N*-dimethylaminomethyl)phenyl]tin(IV)] Oxide (5a and 5b). White solids, yield 82−94%. ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.09 (d, 4H, H(6), $^3J(^1H, ^1H) = 7.0$ Hz, $^3J(^1H, ^{119}Sn) = 72$ Hz); 7.08 (m, 8H, H(4, 5)); 6.96 (d, 4H, H(3), $^3J(^1H, ^1H) = 7.1$ Hz); 3.35 (s, 2H, NCH_2); 1.93 (s, 24H, $N(CH_3)_2$). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 300 K, ppm): −222.4 ($^3J(^{119}Sn-^{119}Sn) = 408$ Hz). Anal. (%) Found: C, 53.7; H, 6.1; N, 7.1. Calcd for $C_{36}H_{48}N_4O_2Sn_2$ (806.19): C, 53.64; H, 6.00; N, 6.95. Positive-ion MS: *m*/*z* 808 $[M + H]^+$, 100%; 522 $[L_3Sn]^+$; 405 $[L_2Sn{=}O + H]^+$. Mp: 232−234 °C and 263−266 °C for **5a** (ether) and **5b** (hexane), respectively.

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Supporting Information Available: The *in silico* generated starting geometries for the geometry optimizations, further insights into the observed trends in Sn−O distances and crystallographic data for **4**, **5a**, and **5b** as well as the computed values of selected geometrical parameters of various compounds are available free of charge via the Internet at http://pubs.acs.org.

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