# **ORGANOMETALLICS**

# Unusual Reactivity of a C,N-Chelated Stannylene with Siloxanes and Silanols

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# **Supporting Information**

**ABSTRACT:** The reactivity of stannylene  $(L^{CN})_2$ Sn (1), where  $L^{CN}$  is the 2-(*N*,*N*-dimethylaminomethyl)phenyl substituent, toward (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), silicon grease, and triphenylsilanol was explored. The reaction of 1 with one equivalent of TEMPO and silicon grease yielded *cyclo*- $[(L^{CN})_2$ SnOSn $(L^{CN})_2$ OSiMe<sub>2</sub>O] (**6a**), whereas the addition of two equivalents of TEMPO afforded *cyclo*- $[(L^{CN})(L^{CN} - O)$ SnOSiMe<sub>2</sub>OSiMe<sub>2</sub>O] (**6b**), in which the amine nitrogen atom of one of the L<sup>CN</sup> ligands is oxidized to N-oxide. The reaction of 1 with one equivalent of TEMPO and subsequent addition of triphenylsilanol gave  $(L^{CN})_2$ Sn(OSiPh<sub>3</sub>)<sub>2</sub> (**5**), which further reacted with air in a chloroform solution to provide  $[(L^{CN})(L^{CN} = O)$ Sn(OSiPh<sub>3</sub>)Cl] (7), containing one of the chelating L<sup>CN</sup> ligands in the corresponding N-oxide form. In contrast, the direct reactions of 1 with one or two equivalents of triphenylsilanol gave rise to the adduct [Sn-(OSiPh<sub>3</sub>)<sub>2</sub>]·C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NMe<sub>2</sub> (**8a**) and the salt  $[C_6H_5CH_2N(H)Me_2]^+[Sn(OSiPh_3)_3]^-$  (**8b**), respectively. All compounds were characterized by NMR spectroscopy and by X-ray



diffraction. Analogous reactions of 1 with activated silica were shown to yield tin-doped silica, which was characterized by powder X-ray diffraction and various spectroscopic and microscopic techniques.

# 1. INTRODUCTION

The cyclic heterometallic oxides attract considerable attention mostly because of growing interest in special, mainly ceramic, materials and their applications.<sup>1</sup> In the case of the siloxane cycles, some unexpected and fortuitous results<sup>2</sup> have been obtained by the reactions of strongly polar reagents with silicon grease, which is generally granted to be a nonreactive material. In the field of organotin(IV) siloxanes, the tricyclic species t-Bu<sub>4</sub>Sn(Me<sub>2</sub>Si)O<sub>3</sub>·t-Bu<sub>2</sub>Sn(OH)<sub>2</sub> was reported by Pannell and co-workers.<sup>3</sup> Structurally related but branched systems containing electronegative (halogen or oxygen atoms) substituents were prepared by substitution<sup>4</sup> or condensation<sup>5</sup> reactions of tin and silicon oxides and/or hydroxides and, in some cases, were isolated as byproducts of polymerization reactions. They revealed high structural differences, featuring for example six-membered rings with one or two tin atoms, different eight-membered rings in either chair- or boat-like conformation with one to three tin atoms, and, last but not least, oligocyclic structures.

Recently, we have isolated an unusual product from the metathesis of silicon grease and organotin oxide  $[(L^{CN})_2Sn]_2(\mu$ -

 $\begin{array}{l} O)_2 \ (\textbf{2},^6 \ L^{CN} = 2\text{-}[(CH_3)_2 NCH_2] C_6 H_4; \text{ Scheme 1}), \text{ viz., cyclo-} \\ [(L^{CN})_2 SnO(Me)_2 SiO)]_2 \ (\textbf{4}).^7 \ An \ alternative \ approach \ to \ the \ synthesis \ of \ this \ eight-membered \ cyclic \ disilastannoxane \ from \ \end{array}$ 





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 $(L^{CN})_2 \text{SnBr}_2$ , Me<sub>2</sub>SiCl<sub>2</sub>, and four equivalents of NaOH or from  $[(L^{CN})_2 \text{SnO}]_n$  (2) and cyclic siloxanes D<sub>3</sub> or D<sub>4</sub> (i.e., (Me<sub>2</sub>SiO)<sub>3</sub> or (Me<sub>2</sub>SiO)<sub>4</sub>) in refluxing xylene has been reported also.<sup>7</sup> Oxide 2 reacts with carbon dioxide to give carbonate 3 and also condensates with triphenylsilanol to produce acyclic compound 5 (Scheme 1).<sup>7</sup> All compounds mentioned in our previous work as well as in the present study contain a C,N-chelating ligand, which is, according to the work done by Jurkschat et al.<sup>8</sup> probably responsible for a higher reactivity of organotin species and formation of cyclic structures. These compounds are also relevant to the nowadays popular area of mimicking heterogeneous catalysts immobilized over silica supports or zeolites by molecular models represented by silanols and polyhedral oligomeric silsesquioxanes.<sup>9</sup>

The complex reactivity suggested by our previous studies led us to further explore the reactivity of C,N-chelated tin(II/IV) species with simple siloxanes (silicone grease), triphenylsilanol, and silica. The results of this study are presented in this paper.

# 2. RESULTS AND DISCUSSION

The present study started with an oxidation reaction of stannylene  $1^{10}$  using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) according to an approach of Kira,<sup>11</sup> who oxidized his low-valent group 14 species with this reagent essentially quantitatively. After the oxidation, we isolated **6a** as a very minor species and characterized it by X-ray diffraction analysis (Scheme 2). The yield of **6a** improved when the same amount

Scheme 2. Reactivity of 1 toward TEMPO and Silicon Grease (2: n = 1-4)



of Wacker silicon grease or one molar equivalent of freshly prepared  $Me_2Si(OH)_2$  was added to the system directly after oxidation. Surprisingly, the same product was obtained in a nearly quantitative yield when two equivalents of lithium metal, 12-crown-4, and silicon grease were mixed in diethyl ether for three weeks.

It should be noted that the course of the reaction between 1, TEMPO, and silicon grease depends on the order of addition and the amount of reagents (Scheme 2). For instance, increasing the amount of TEMPO to two or more equivalents results in the formation of disilastannoxane **6b**, in which one of the chelating  $L^{CN}$  ligands is oxidized to the corresponding N-oxide. Similar results of nitrogen oxidation were observed for other tin and also bismuth species in which, however, harsh reaction conditions had to be applied to complete the oxidation.<sup>12</sup>

The <sup>1</sup>H NMR spectrum of **6a**, which is quite insoluble in all common deuterated solvents, is rather complex due to mutual nonequivalence of the organic ligands connected to the tin atom, similarly to that described in the literature.<sup>13</sup> One broad and one doublet resonance is observed for the H6 protons (for

numbering see Scheme 1). Signals of the benzylic CH<sub>2</sub> protons coalesce into an unresolved hump, and a single signal for the Me<sub>2</sub>SiO group is found at  $\delta_{\rm H}$  –0.4 ppm. The <sup>119</sup>Sn NMR spectra of **6a** were recorded in two different solvents (toluene- $d_8$  and THF- $d_8$ ) in order to explore a possible dependence of chemical shift on the solvent. The <sup>119</sup>Sn chemical shifts are very close to each other ( $\delta_{\rm Sn}$  –292 ppm in THF- $d_8$ , and –288 ppm in toluene- $d_8$ ), comparable to values found for other pseudo-octahedrally coordinated tin atoms in **2** and **3**.<sup>6,7</sup> The <sup>119</sup>Sn signal observed in toluene- $d_8$  displays coupling satellites of 458 Hz, typical for two-bond <sup>119</sup>Sn–<sup>117</sup>Sn couplings in stannoxanes.<sup>14</sup> When the solution of **6a** is allowed to stand for a longer period (ca. 2 months), the formation of stannoxane **2** is detected by <sup>119</sup>Sn NMR.

The solid-state structure of **6a** consists of a six-membered ring constituted by two tin atoms and one  $SiMe_2$  moiety alternating with three oxygen atoms, displaying an approximate twisted boat conformation (Figure 1). The tin atoms in **6a** are



Figure 1. Molecular structure of 6a (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sn1–O1 1.991(4), Sn1–O2 2.004(4), Sn1–N1 2.736(5), Sn1–N2 2.693(4), Sn1–C1 2.134(4), Sn1–C10 2.132(6), Sn2–O1 1.981(4), Sn2–O3 2.019(3), Sn2–N21 2.674(4), Sn2–N22 2.796(5), Sn2–C201 2.125(5), Sn2–C210 2.160(12); Sn1–O1–Sn2 127.44(17), Sn1–O1–Sn2 127.44(17), O1–Sn1–N1 171.77(16), O2–Sn1–N2 167.90(16), C1–Sn1–C10 147.7(2), O1–Sn2–N22 171.48(15), O3–Sn2–N21 167.84(14), C201–Sn2–C210 142.5(4).

[4+2] coordinated, adopting a heavily distorted octahedral geometry. The interatomic Sn–N distances varying in the range 2.674(4) Å (Sn2–N21) to 2.796(5) Å (Sn2–N22) indicate very weak intramolecular N $\rightarrow$ Sn interactions, affecting nevertheless the coordination of the tin atoms.

The <sup>1</sup>H NMR spectrum of **6b** recorded at room temperature in THF- $d_8$  suggests some dynamic behavior. Similar dynamic behavior has been reported by Jurkschat et al. for the closely related hypercoordinated organotin(IV) species according to NMR spectroscopy measurements performed at variable temperature.<sup>13</sup> The methyl groups at the N-oxide moiety give rise to two singlets, while those in the amino group give rise to a broad singlet, indicating some exchange process. Upon lowering the temperature, the latter signals split into two singlets ( $\delta_{\rm H}$  2.36 and 1.96 ppm at -25 °C), whereas raising the temperature led to a broadening of the N-oxide methyl resonances as well, suggesting that the N-oxide arm likewise undergoes a similar dynamic process at higher temperature (the temperature was limited to 40 °C because of using a sealed NMR tube). The assumed dynamic process averages only the methyl resonances but not the benzyl CH<sub>2</sub> resonances, which remain unaffected. The <sup>29</sup>Si NMR spectrum of **6b** recorded at room temperature revealed two broad signals. Even in this case, the temperature lowering caused the signals to sharpen, while increasing the temperature led to their coalescence into an extremely broad resonance. The dynamic behavior averaging the <sup>29</sup>Si resonances can be due to either ring dynamics or decoordination of the nitrogen atoms and their exchange around the tin center. Methyl group exchange under configuration inversion of the nitrogen atom of the  $\tilde{L}^{CN}$  ligand is another possibility that needs to be taken into consideration. The <sup>119</sup>Sn NMR resonance of **6b** (-456 ppm) appears about 200 ppm upfield when compared to 2, 3, and 6a, which suggests a very strong coordination of the N-oxide group to the tin atom.

Unequivocal confirmation of the structure of **6b** is provided by the X-ray crystallographic analysis (Figure 2). The tin atom



Figure 2. Molecular structure of **6b** (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sn1-O1 2.226(3), Sn1-O2 2.036(3), Sn1-O4 2.055(2), Sn1-N2 2.584(3), Sn1-C1 2.146(5), Sn1-C10 2.141(4), N1-O1 1.403(4), Si1-O2 1.611(3), Si1-O3 1.642(3), Si2-O3 1.640(3), Si2-O4 1.598(3); O1-Sn1-O4 173.81(11), Sn1-O1-N1 125.2(2), O2-Sn1-N2 170.72(10), C1-Sn1-C10 160.13(14), Sn1-O2-Si1 129.87(15), Sn1-O4-Si2 129.29(14), Si1-O3-Si2 134.46(18).

in **6b** is six-coordinated with a distorted octahedral geometry. The unaffected  $L^{CN}$  ligand expectedly binds in C,N-chelating fashion, while the second one forms a C,O-chelate ring, resulting in the formation of a new nonplanar six-membered heteroazaoxastanna cycle with a chairlike conformation. Both intramolecular distances  $N \rightarrow Sn$  (2.584(3) Å) and  $O \rightarrow Sn$  (Sn1–O1 2.226(3) Å) are indicative of medium<sup>6,7</sup> to very strong interactions. Despite the fact that the observed Sn1–O1 interatomic distance is somewhat longer when compared to that reported in the literature for  $Me_2(O)N(CH_2)_3Sn-(OCOCH_2)_3N$  (Sn–(O) = 2.101(6) Å), it still represents very strong intramolecular O $\rightarrow$ Sn interaction.<sup>12b</sup>

An unexpected result was obtained from the already reported condensation reaction<sup>7</sup> leading to compound 5. When 5 was exposed to air in benzene solution, it was converted mainly into carbonate 3 (Scheme 1).<sup>7</sup> Our further reactivity studies of diorganotin(IV) species 5 led to the isolation of novel compound 7, resulting from air oxidation of 5 in chloroform (Scheme 3). During this oxidation, one of the two Sn–





O(SiPh<sub>3</sub>) bonds was cleaved under the action of chloroform (or HCl formed from this solvent), giving rise to a new Sn–Cl bond. Simultaneously, one of the amine nitrogen atoms is oxidized to the corresponding N-oxide with air oxygen. Compound 7 displays two sets of broad signals for the nonequivalent ligands in the <sup>1</sup>H NMR spectrum, similarly to **6b**, but the  $\delta$ (<sup>119</sup>Sn) chemical shift for 7 (–304 ppm) is very close to the value found for carbonate **3** (–319 ppm).

The central tin atom in 7 exhibits distorted octahedral coordination geometry (Figure 3). Similarly to **6b**, one of the



Figure 3. Molecular structure of 7 (ORTEP view, 30% probability level). Hydrogen atoms and the modeled disordered part are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sn1–Cl 2.521(3), Sn1–O1X 2.031(13), Sn1–Cl9X 2.108(17), Sn1–C27X 2.185(14), Sn1–O2X 2.28(2), Sn1–N2X 2.597(19), Si1–O1X 1.619(14); Sn1–O1X-Si1 154.0(8), O1X–Sn1–N2X 173.5(6), Cl–Sn1–O2X 171.4(5), C19X–Sn1–C27X 160.4(7).

organic ligands coordinates as a C,O-chelate donor, thereby forming a six-membered ring with very strong  $O \rightarrow Sn$  interaction (Sn1-O2X = 2.28(2) Å) similarly to those found in **6b** and Me<sub>2</sub>(O)N(CH<sub>2</sub>)<sub>3</sub>Sn(OCOCH<sub>2</sub>)<sub>3</sub>N.<sup>12b</sup> The second, unaffected ligand behaves as a regular C,N-chelating ligand (Sn1-N2X = 2.597(19) Å).

Surprisingly, the reaction of 1 with  $Ph_3SiOH$  in 1:1 molar ratio did not provide the expected product of simple oxidative addition or silanol reduction and further hydrolysis. Instead,

inorganic Sn(II) disiloxane 8a, crystallizing as an adduct with  $HL^{CN}$  formed as a side product by protonolysis, was isolated from the reaction mixture (Scheme 4). The observed reaction





requires two equivalents of silanol, as evidenced by the presence of nonreacted 1 detected by NMR spectroscopy in the reaction mixture. To the best of our knowledge, there is only one report<sup>15</sup> describing the preparation and characterization of a compound resulting from protonolysis of a stannylene with a silanol. The archetypal Lappert's stannylene  $Sn[N(SiMe_3)_2]_2$  was shown to react with two equivalents of triphenylsilanol and further with potassium triphenylsilanolate to give stannate  $K(dme)[Sn(OSiPh_3)_3]$  (dme = 1,2-dimethoxy-ethane).<sup>15</sup>

When 1 was reacted with two equivalents of  $Ph_3SiOH$ , the Sn(II) salt **8b** was obtained (Scheme 4). Similar reactions between 1 and  $Ph_3GeOH$  or  $Ph_3SnOH$  led to oxide 2 and, in the case of triphenylstannol, also to hexaphenyldistannane and hexaphenyldistannoxane, according to the <sup>119</sup>Sn NMR spectra.<sup>16</sup>

The NMR spectra of **8a** were recorded in a noncoordinating solvent, benzene- $d_{6i}$  in order to avoid alternations of the coordination environment by solvent coordination. The <sup>1</sup>H NMR spectrum reveals a set of narrow signals at predictable chemical shifts. On the other hand, the <sup>119</sup>Sn NMR spectrum reveals a broad signal at -157 ppm consistent with values reported for three-coordinate tin atoms.<sup>16</sup> The <sup>1</sup>H NMR spectrum of **8b** in benzene- $d_6$  is similar to the spectrum of **8a** except that the benzylic proton signal is broadened, and the <sup>119</sup>Sn NMR spectrum shows a signal at -341 ppm comparable to the value observed for K(dme)[Sn(OSiPh\_3)\_3] (-360.5 ppm).<sup>15</sup>

Two polymorphs, **8a** and **8a'**, were isolated and characterized by X-ray crystallography (Table S1). Only hardly significant differences in the interatomic bonds and angles are observed (Figure 4). The central tin atom in **8a** is three-coordinate with trigonal pyramidal geometry. One HL<sup>CN</sup> ligand is coordinated to the tin atom at a distance suggesting a strong intermolecular  $N \rightarrow Sn$  interaction (Sn1-N1 = 2.341(4) and 2.345(2) Å). Two oxygen atoms from the two silanolate moieties complete the primary coordination sphere of the tin atom in **8a**.

The solid-state structure of **8b** (Figure 5) reveals, similarly to **8a**, the central tin atom to be three-coordinate, with trigonal pyramidal geometry. All three Sn–O interatomic distances lie within the range typical for the Sn–O bonds.<sup>17</sup> The negative charge of the  $[(Ph_3SiO)_3Sn]^-$  unit is compensated by the presence of free-protonated ligand  $([H_2L^{CN}]^+)$  interacting with the O1 atom in **8b** via a N–H···O hydrogen bond (N1···O1 = 2.818(2) Å).

In order to prepare an analogous, silica-based material from **1** using a similar protolytic reaction, which could be used, for



Figure 4. Molecular structure of 8a (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg] (corresponding values for the second polymorph are given in parentheses): Sn1–O1 2.012(3) (1.996(2)), Sn1–O2 2.031(3) (2.011(2)), Sn1–N1 2.341(4) (2.345(2)), Si1–O1 1.604(3) (1.606(2)), Si2–O2 1.603(3) (1.617(3)); O1–Sn1–O2 94.84(12) (94.52(10)), O1–Sn1–N1 87.89(14) (87.22(9)), O2–Sn1–N1 84.07(14) (85.18(9)), Sn1–O1–Si1 152.23(19) (146.15(14)), Sn1–O2–Si2 135.04(19) (133.21(14)).



Figure 5. Molecular structure of 8b (ORTEP view, 40% probability level). Hydrogen atoms bound to carbon atoms are omitted for clarity. Selected interatomic distances [Å] and angles [deg]: Sn(1)-O(1) 2.1033(14), Sn(1)-O(2) 2.0601(14), Sn(1)-O(3) 2.0347(14), O(1)-Si(1) 1.6281(15), O(2)-Si(2) 1.6071(15), O(3)-Si(3) 1.5947(15); O(1)-Sn(1)-O(2) 89.42(6), O(1)-Sn(1)-O(3) 91.54(6), O(2)-Sn(1)-O(3) 91.25(6), Sn(1)-O(1)-Si(1) 125.52(8), Sn(1)-O(2)-Si(2) 136.83(9), Sn(1)-O(3)-Si(3) 154.05(9). Hydrogen bonding:  $N(1)-H(1)\cdots O(1)$  2.818(2), 162.6.

example, as a solid-supported tin material for catalytic purposes,<sup>18</sup> the stannylene **1** was reacted with activated silica. The tin-doped silica gel materials **9a** and **9b** were prepared by treatment of freshly calcinated, conventional chromatography grade, silica gel with two different concentrations of toluene solutions of stannylene **1** followed by the removal of nongrafted modifier using air-exposed Soxhlet extraction. The resulting materials were characterized by elemental analysis (conventional combustion and ICP-OES analysis), powder X-ray diffraction, and IR spectra.

The amounts of grafted tin in materials **9a** and **9b** (1.18% and 0.57%, respectively) are practically identical to the values calculated from the mass balance (1.18% and 0.59%), thereby indicating complete grafting of the tin species from the solution. The X-ray diffraction patterns of **9a** and **9b** (see Supporting Information, Figure S1) displayed only a single broad peak at  $2\theta$  ca.  $21-22^{\circ}$ . The IR spectra of materials **9a** and **9b** did not differ much from that of the parent silica gel, showing mainly intense broad bands due to Si–O stretching vibrations (composite band centered at ca. 1080 cm<sup>-1</sup>), a broad band of associated OH groups (ca. 2800–3900 cm<sup>-1</sup>). Bands assignable to organic moieties of the organometallic modifier were only very weak, which mainly reflects the essentially very low degree of functionalization of the solid support.

According to the elemental analysis of both samples (based on the ratio of tin to carbon and tin to nitrogen, respectively) and EDS measurements for 9a, it appears likely that one or even two ligand(s) remained in the material, presumably binding the tin atom. This finding is supported by the <sup>1</sup>H and <sup>13</sup>C solid-state CP-MAS NMR spectra of the sample with higher tin content (9a), where the signals assignable to the L<sup>CN</sup> ligands were found (Supporting Information, Figures S2-S4). The solid-state <sup>117</sup>Sn NMR spectra revealed a broad signal (Figure S5) ranging from -600 to -700 ppm, which is typical for six- or seven-coordinate tin atoms. A nonsymmetric, lowfield shouldered signal was found in the solid-state <sup>29</sup>Si MAS NMR spectrum of 9a at -110.7 ppm, the shoulder being at ca. -104 ppm (Figure S6). This is consistent with a low degree of grafting but still characteristic for a highly condensed silica network with mainly Q3 and Q4 sites.<sup>19</sup> Finally, the HRTEM images showed (Figure S8) that material 9a is rather amorphous, with only partially crystallized spots containing tin atoms.

Based on literature data, several catalytic screenings, including the reaction of carbon dioxide with methanol to form dimethylcarbonate<sup>18b,20</sup> and some esterification and transesterification reactions<sup>21</sup> were conducted with **9a**. Unfortunately, no catalytic activities higher than with pure silica taken as a "blank" catalyst could be obtained.

#### 3. CONCLUSION

Our investigations into reactions of low-valent organotin compounds, TEMPO, and silicon grease, silanols, and silica presented in this paper have revealed some unexpected reactivity, for instance the spontaneous oxidation of the amino group in the  $L^{CN}$  supporting ligand by TEMPO or even air. The starting stannylene 1 was shown to undergo unprecedented protolysis with triphenylsilanol, which also served as a proton source for the released *N*,*N*-dimethylbenzylamine. No formation of free ligand was observed in the analogous reaction with activated silica, and the prepared material consisted probably of an  $(L^{CN})_2$ Sn fragment grafted to

silica. Unfortunately the prepared composite material proved to be inactive as a catalyst in all carbonations and esterifications screened.

#### 4. EXPERIMENTAL SECTION

4.1. Methods. NMR spectra were recorded in CDCl<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, toluene- $d_{81}$  and THF- $d_{8}$  solutions with a Bruker Avance 500 spectrometer (equipped with a z-gradient 5 mm probe) at frequencies of 500.13 MHz for <sup>1</sup>H, 125.73 MHz for <sup>13</sup>C, and 186.50 MHz for <sup>119</sup>Sn at 295 K. The solutions were obtained by dissolving ca. 40 mg of the analyzed compound in 0.6 mL of the appropriate deuterated solvent. Chemical shifts were calibrated to residual signals of chloroform ( $\delta$ (<sup>1</sup>H) = 7.27 ppm), benzene ( $\delta$ (<sup>1</sup>H) = 7.16 ppm,  $\delta$ (<sup>13</sup>C) = 128.4 ppm), or THF ( $\delta(^{1}H)$  = 3.57 ppm,  $\delta(^{13}C)$  = 67.4 ppm)). The  $^{119}\text{Sn}\{^1\text{H}\}$  chemical shift values are given relative to external neat tetramethylstannane ( $\delta$ (<sup>119</sup>Sn) = 0.0 ppm). <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra were measured using the inverse gated-decoupling mode. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of **6b** were measured in THF- $d_8$  on a Varian UNITY-500 spectrometer operating at 499.9 MHz for <sup>1</sup>H, at 125.7 MHz for <sup>13</sup>C, and at 99.3 MHz for <sup>29</sup>Si NMR. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the line of the solvent (THF,  $\delta$ (<sup>1</sup>H) = 1.73 ppm,  $\delta(^{13}C) = 24.58$  ppm). The <sup>29</sup>Si NMR spectra were measured with the insensitive nuclei enhanced by polarization transfer (INEPT) pulse sequence modified for the  $Si(CH_3)_2$  groups and were referenced to hexamethyldisiloxane ( $\delta = -19.79$  ppm).

Elemental analyses were determined with an EA 1108 automatic analyzer (FISONS Instruments). Tin loading in **9a** and **9b** was determined with an ICP-OES spectrometer (IRIS Intrepid Duo; Thermo Fisher Scientific) equipped with a Burgener nebulizer (conditions: plasma power 1150 W, sample uptake 1.0 mL min<sup>-1</sup>, axial plasma observation). The samples (20 mg) were mineralized in a poly(propene) vial by a consecutive addition of 36% HCl, 30% hydrogen peroxide, and 48% HF (0.50 mL each; in this order) and standing at room temperature for 1 h. The mineralized samples were diluted with redistilled water and directly used for the measurement. The calibration was performed over a range of 0–20 ppm using a commercial 1000 ppm Sn standard solution (Analytika, Prague), and the results are the average of three independent measurements. The content of C and N was determined by conventional combustion analysis.

FTIR spectra were recorded for neat samples using a Nicolet 7600 (Thermo Fisher Scientific) spectrometer (range 500–4000 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup>). Powder X-ray diffraction patterns were recoded with a PANalytical X'Pert Pro diffractometer (Cu K $\alpha$  radiation, PIXcel detector, 2 $\theta$  range: 10–80°, 2 $\theta$  step: 0.1°, integration time: 10 s per step).

A sample of **9a** was studied by HRTEM (high-resolution transmission electron microscopy) measurements on a JEOL JEM 3010 microscope operated at 300 kV (LaB6 cathode, 1.7 Å point resolution) with an EDX (energy dispersive X-ray INCA Oxford) detector. Samples were ground in an agate mortar, the powder was dispersed in ethanol, and the suspension was treated in an ultrasound bath for 10 min. A drop of a very dilute suspension was placed on a carbon-coated Cu grid and allowed to dry by evaporation at ambient temperature.

The solid-state <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer in a doubleresonance 4 mm probe head. Direct-polarization MAS NMR experiments with a high-power dipolar decoupling and sufficiently long recycle delays were preformed to obtain quantitative NMR spectra.

The solid-state <sup>117</sup>Sn NMR spectra were acquired at 89.12 MHz, using a Bruker Avance 250 NMR spectrometer in a double-resonance 4 mm probe head. Typically, a contact time of 2 ms, a relaxation delay of 2, and 30 000 scans were used for <sup>117</sup>Sn CP-MAS measurements. The <sup>119</sup>Sn chemical shifts were referenced indirectly to tetracyclohexyltin ( $\delta = -97.4$  ppm with respect to tetramethyltin). The <sup>119</sup>Sn NMR chemical shift was read as the center of gravity of the signal. Standard

 $\rm ZrO_2$  rotors (7 mm) were used at spinning rates between 7000 and 9000 Hz.

 $^{29}\text{Si}$  MAS NMR spectra were recorded with a relaxation delay of 5 and 2000 scans, while CP-MAS spectra were recorded with contact times varying from 2 to 8 ms and 2000 scans. The Hartmann–Hahn condition for  $^{1}\text{H}-^{29}\text{Si}$  cross-polarization was set on kaolinite.  $^{22}$ 

X-ray diffraction data (Tables S1 and S2; see Supporting Information file) were obtained at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream low-temperature device using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), a graphite monochromator, and the  $\phi$  and  $\chi$  scan mode. Data reductions were performed with DENZO-SMN.<sup>23</sup> The absorption was corrected by integration methods.<sup>24</sup> The structures were solved by direct methods (SIR92)<sup>25</sup> and refined by full matrix least-squares based on  $F^2$  (SHELXL97).<sup>26</sup> Hydrogen atoms could mostly be localized on the difference Fourier maps. However, to ensure uniformity of the treatment of the crystal data, they were recalculated into idealized positions (riding model) and assigned temperature factors set to a multiple of that of their pivotal atom. Some atoms in the structures of **6b** and 7 were disordered, but these disorders were treated with the standard restraint and constraint procedures as incorporated in the SHELXL97<sup>26</sup> program.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. 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 or www: http://www.ccdc.cam.ac.uk). CCDC deposition numbers 921175–921180.

**4.2.** Synthesis. 4.2.1. Materials. All solvents and starting materials such as  $SnCl_2$ , *n*-BuLi, Ph<sub>3</sub>SiOH, and dimethylbenzylamine were purchased from Sigma-Aldrich and were used without further purification.  $(L^{CN})_2Sn$  (1) and  $(L^{CN})_2Sn(OSiPh_3)_2$  (5) were synthesized according to the literature.<sup>7,10</sup> Dow Corning high-vacuum silicon grease was used in the syntheses. Solvents were distilled from K/Na alloy and stored over a potassium mirror under an argon atmosphere or dried and degassed using a commercial drying column apparatus (Innovative Technology Inc., USA). 4.2.2. Preparation of cyclo-[( $L^{CN})_2SnOSn(L^{CN})_2OSiMe_2O$ ] (6a).

4.2.2. Preparation of  $cyclo-[(L^{CN})_2SnOSn(L^{CN})_2OSiMe_2O]$  (6a). (L<sup>CN</sup>)<sub>2</sub>Sn (1) (1.01 g, 2.61 mmol) was dissolved in toluene (50 mL), and TEMPO (0.421 g, 2.69 mmol) was added in five portions. The resulting solution was stirred overnight. Subsequently, in a first experiment, 0.234 g (ca. 3 mmol calculated to a monomeric unit) of silicon grease was added and the solution was stirred for one day. Afterward, the reaction mixture was evaporated to dryness and the solid residue was washed with 20 mL of hexane and extracted with 30 mL of diethyl ether to give, after crystallization at -30 °C, 6a as colorless crystals (0.643 g, 56%).

In another experiment, freshly prepared  $Me_2Si(OH)_2^{27}$  (0.120 g, 1.31 mmol) was added in toluene (15 mL), and the mixture stirred overnight and then heated under a Dean–Stark apparatus for 3 h. The resultant solution was concentrated to ca. 5 mL and crystallized at -30 °C to give **6a** (0.530 g, 46%).

Alternatively, compound **6a** was obtained from the reaction of **1** (2.197 g, 5.68 mmol) with metallic lithium (40 mg, 5.68 mmol), 12crown-4 (1.0 g, 5.68 mmol), and silicon grease (0.21 g, 2.84 mmol) in diethyl ether (30 mL). These starting materials were stirred for 3 weeks. The obtained suspension was filtered through Celite and extracted with THF (50 mL). The combined organic solution was concentrated to ca. 6 mL and crystallized at -30 °C to afford **6a** (1.374 g, 55%).

Analytical data for **6a**. Mp: 204–207 °C. <sup>1</sup>H NMR (THF- $d_8$ , 295 K, ppm): 7.86 (broad, 2H, H(6')), 7.80 (d, 2H, H(6)); 7.30 (m, 12H, H(3, 4, 5)), 3.47 (broad, 8H, CH<sub>2</sub>N); 2.03 (s, 24H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>119</sup>Sn<sup>{1</sup>H} NMR (THF- $d_8$ , 295 K, ppm): –292, (toluene- $d_8$ ): –288.2, <sup>3</sup>J(<sup>119</sup>Sn–<sup>117</sup>Sn) = 458 Hz. Anal. Found: C, 51.9; H, 6.3; N, 6.4. Calcd for C<sub>38</sub>H<sub>54</sub>N<sub>4</sub>O<sub>3</sub>SiSn<sub>2</sub> (880.35): C, 51.85; H, 6.18; N, 6.36.

4.2.3. Preparation of  $cyclo-[(L^{CN})(L^{CN}=O)SnOSiMe_2OSiMe_2O]$ (**6b**). A solution of TEMPO (0.032 g, 0.21 mmol) in toluene (20 mL) was added dropwise to a solution of stannylene 1 (0.08 g, 0.21 mmol) in the same solvent (50 mL). The resulting solution was stirred overnight prior to another portion of TEMPO (0.032 g, 0.21 mmol) together with silicon grease (50 mg) being added, and the solution was stirred for another three weeks. The reaction mixture was filtered and evaporated to dryness. The solid residue was washed with hexane (20 mL) and extracted into THF (30 mL). Subsequent crystallization of the THF extract at -30 °C gave 6b as a colorless crystalline solid (0.113 g, 69%). Mp: 118–123 °C. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 295 K, ppm): the N-oxide group containing ligand: 7.93 (d, 1H, H(6)); 7.15 (dd, 1H, H(5)), 7.10 (dd, 1H, H(4)); 6.91 (d, 1H, H(3)); 3.74 and 3.33 (d, 2  $\times$  1H, CH<sub>2</sub>N); 2.16 (broad, 6H, NMe); the amine group containing ligand: 8.21 (d, 1H, H(6)); 7.40 (dd, 1H, H(5)), 7.27 (dd, 1H, H(4)); 7.18 (d, 1H, H(3)); 5.40 and 4.24 (d,  $2 \times 1$ H, CH<sub>2</sub>N); 3.28 and 2.89 (broad,  $2 \times 3H$ , NMe); -0.01 and -0.43 ppm (s,  $2 \times 3$  H, Si(1)Me<sub>2</sub>); -0.12 and -0.38 (s,  $2 \times 3$  H, Si(2)Me<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ , 295 K, ppm): the amine group containing ligand: 140.7 (C<sub>1</sub>), 149.6 (C<sub>2</sub>), 125.8 (C<sub>3</sub>), 127.1 (C<sub>4</sub>), 126.4 (C<sub>5</sub>), 135.5  $(C_6)$ , 64.5 (NCH<sub>2</sub>), 45.8 (N(CH<sub>3</sub>)<sub>2</sub>); the N-oxide group containing ligand: 137.3 (C1), 154.6 (C2), 130.0 (C3), 127.8 (C4), 127.9 (C5), 136.5 (C<sub>6</sub>), 70.2 (NCH<sub>2</sub>), 59.4 and 56.0 (N(CH<sub>3</sub>)<sub>2</sub>); 2.0-1.8 (m, 4 C n.r., Si(1)Me<sub>2</sub> and Si(2)Me<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (THF- $d_8$ , 295 K, ppm): -14.3 and -14.5 (Si(1) and Si(2)). <sup>119</sup>Sn{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 295 K, ppm): -456. Anal, Found: C, 46.7; H, 6.6; N, 5.0. Calcd for C<sub>22</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>Sn (567.41): C, 46.57; H, 6.40; N, 4.94.

4.2.4. Preparation of  $[(L^{CN})(L^{CN}=O)Sn(OSiPh_3)Cl]$  (7).  $(L^{CN})_2Sn-(OSiPh_3)_2$  (5) (1.0 g, 0.11 mmol) was dissolved in chloroform (50 mL), and the solution was exposed to air for one week. The resulting slurry was filtrated, and the solid was crystallized from chloroform to give white crystals of 7 (0.274 g, 36%). Mp: 269–270 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 295 K, ppm): the N-oxide group containing ligand: 8.13 (broad, 1H, H(6)); 6.85 (broad, 1H, H(3)); 3.71 and 3.23 (d, 2 × 1H, CH<sub>2</sub>N); 1.75 (broad, 6H, NMe); the amine group containing ligand: 8.01 (broad, 1H, H(6)); 6.83 (broad, 1H, H(3)); 5.32 and 3.99 (d, 2 × 1H, CH<sub>2</sub>N); 2.04 and 1.24 (broad, 2 × 3H, NMe); 7.10 (m, 4H, H(4, 5)); 7.62 (d, 2H, SiPh\_3) and 7.50 (d, 2H, SiPh\_3) and 7.41 (d, 2H, SiPh\_3) and 7.36 (m, 9H, SiPh\_3). <sup>119</sup>Sn{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 295 K, ppm): -304. Anal. Found: C, 60.7; H, 5.6; N, 4.0. Calcd for C<sub>36</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub>SiSnCl (713.95): C, 60.57; H, 5.51; N, 3.92.

4.2.5. Preparation of  $[Sn(OSiPh_3)_2].C_6H_5CH_2NMe_2$  (**8***a*). Triphenylsilanol (0.714 g, 2.58 mmol) in diethyl ether (20 mL) was added dropwise to 1 (1.0 g, 2.58 mmol) dissolved in the same solvent (20 mL). The resulting solution was stirred overnight and crystallized at -30 °C to afford **8a** as a colorless, crystalline solid (1.393 g, 67%). Mp: 218–220 °C. <sup>1</sup>H NMR ( $C_6D_6$ , 295 K, ppm): 7.84 (m, 4H, H(2, 3)); 7.07 (dd, 1H, H(4)), 7.33 (d, 12H, SiPh\_3); 7.18 (m, 18H, SiPh\_3); 3.25 (s, 2H, CH\_2N); 2.06 (s, 6H, NMe\_2). <sup>119</sup>Sn{<sup>1</sup>H} NMR ( $C_6D_6$ , 295 K, ppm): -157. Anal. Found: C, 67.3; H, 5.4; N, 1.8. Calcd for  $C_{45}H_{43}NO_2Si_2Sn$  (804.71): C, 67.17; H, 5.39; N, 1.74.

4.2.6. Preparation of  $[C_6H_5CH_2N(H)Me_2]^+[Sn(OSiPh_3)_3]^-$  (**8b**). A solution of triphenylsilanol (1.428 g, 5.17 mmol) in diethyl ether (50 mL) was added dropwise to a solution of 1 (1.0 g, 2.583 mmol) in the same solvent (50 mL). The resulting mixture was stirred and then evaporated to dryness. The solid residue was washed with hexane (30 mL) and extracted with diethyl ether (30 mL). Subsequent crystallization at -30 °C gave **8b** as a colorless solid (2.008 g, 73%). Mp: 150–152 °C. <sup>1</sup>H NMR ( $C_6D_{6^2}$  295 K, ppm): 7.87 (broad, 20H); 7.18 (broad, 29H), 6.97 (broad, 1H, H(4)); 3.28 (broad, 2H, CH<sub>2</sub>N); 1.89 (broad, 6H, NMe<sub>2</sub>).<sup>119</sup>Sn{<sup>1</sup>H} NMR ( $C_6D_6$ , 295 K, ppm): -341. Anal. Found: C, 71.2; H, 5.6; N, 1.3. Calcd for  $C_{63}H_{59}NO_2Si_3Sn$  (1065.13): C, 71.04; H, 5.58; N, 1.32.

4.2.7. Preparation of Materials **9a** and **9b**. Twenty grams of conventional chromatography-grade silica gel (70–230 mesh), which was calcinated at 500 °C for 12 h and cooled in a desiccator prior to use, was suspended in dry toluene (100 mL). A solution of **1** in dry toluene (22 mL of 0.09 M solution) was introduced, and the resulting suspension was stirred at room temperature for 4 days. Subsequently, the solid was filtered off and extracted with dichloromethane in a Soxhlet extractor for 24 h. The solid residue was dried in air, first at room temperature and then at 100 °C, to give material **9a**. Material **9b** was prepared in exactly the same way, using only a half-volume of the stannylene solution (11 mL).

Analytical data for material **9a**. Analysis: C 2.36, N 0.21, Sn 1.18%. Powder X-ray diffraction:  $2\theta = 21-22^{\circ}$  (very broad). IR (neat): 3476 (w), ca. 2800–3700 (br m), 1867 (w), 1626 (w), ca. 1465 (vw), 1080 + shoulder at ca. 1190 (vs), 811 (m) cm<sup>-1</sup>. For <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>117</sup>Sn NMR in the solid state see Supporting Information Figures S2–S6.

Analytical data for material **9b**. Analysis: C 1.64, N 0.11, Sn 0.57%. Powder X-ray diffraction:  $2\theta = 21-22^{\circ}$  (very broad). IR (neat): 3476 (w), ca. 2800-3700 (br m), ca. 1975 (w, shoulder), 1868 (w), 1628 (w), 1475 (w), 1460 (w), 1080 + shoulder at ca. 1190 (vs), 980 (m), 807 (m) cm<sup>-1</sup>.

### ASSOCIATED CONTENT

#### **Supporting Information**

Solid-state NMR spectra and further details of the structure determination of all compounds, including atomic coordinates, anisotropic displacement parameters, and geometric data, are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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#### DEDICATION

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