

Syntheses and Structural Characterization of a Monomeric Tin(II) Diamide and a Novel Chlorotin(II) Amide Trimer

Yongjun Tang,[†] Ana M. Felix,[†] Lev N. Zakharov,[‡] Arnold L. Rheingold,[‡] and Richard A. Kemp^{*,†,§}

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131,
Department of Chemistry and Biochemistry, University of California, San Diego,
La Jolla, California 92093, and Advanced Materials Laboratory, Sandia National Laboratories,
Albuquerque, New Mexico 87106

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We have found that addition of a 2:1 ratio of the bulky ligand $\text{Li}[\text{N}(\text{mesityl})(\text{SiMe}_3)]$ to SnCl_2 yields $\text{Sn}[\text{N}(\text{mesityl})(\text{SiMe}_3)]_2$, which is found by X-ray crystallography to be monomeric in the solid state. Interestingly, the solid state structure of the stannylene exhibits a “minipocket” caused by the parallel arrangement of the phenyl rings. A 1:1 ratio of ligand to SnCl_2 affords the new chlorotin amide $\{\text{Sn}(\mu\text{-Cl})[\text{N}(\text{mesityl})(\text{SiMe}_3)]\}_3$, which adopts a unique trimeric structure in the solid state. The chairlike $(\text{Sn}-\text{Cl})_3$ backbone shown here has not been seen previously in Sn–halide chemistry.

Introduction

The coordination chemistry of low-valent main group metal amide compounds has been of great interest in recent years, with potential uses as varied as precursors for chemical vapor deposition to the chemical fixation of carbon dioxide.^{1–6} Of special interest to us are oxo-transfer reactions in which CO_2 undergoes metathesis reactions with other materials to form new products. Recently, this includes the elegant work of Sita on the generation of trimethylsilylisocyanates from CO_2 and Sn and Ge diamides.⁶ Via processes such as these, one can hope to discover new chemical transformations to yield valuable organics from relatively useless feedstocks. Our laboratory has recently been interested in the synthesis and characterization of novel main group amide compounds and their insertion chemistries with carbon dioxide. We here describe our initial efforts to prepare and characterize the complex $\text{Sn}[\text{N}(\text{mesityl})(\text{SiMe}_3)]_2$, **1**. During our efforts to

prepare this compound, we also discovered the first example of a trimeric μ -chlorotin(II) amide compound, $\{\text{Sn}(\mu\text{-Cl})[\text{N}(\text{mesityl})(\text{SiMe}_3)]\}_3$, **2**, which differed structurally in the solid state from a binuclear μ -chlorotin(II) amide reported earlier by Lappert.⁷

Experimental Section

General Considerations. Due to the air-sensitive nature of reactants and products, all manipulations were carried out in an Ar-filled glovebox or by using standard Schlenk techniques.⁸ Anhydrous solvents were purchased from Aldrich and stored in the glovebox over 4 Å molecular sieves. *n*-Butyllithium (2.5 M in hexanes) (**CAUTION**: alkyl lithium reagents are pyrophoric and are very reactive toward moisture and as such should be handled in an inert atmosphere), Celite filter agent, 2,4,6-trimethylaniline, trimethylsilyl chloride, and anhydrous tin(II) chloride were purchased from Aldrich and used without further purification. Benzene-*d*₆ was obtained from Aldrich and dried and stored over 4 Å molecular sieves. ¹H, ¹³C, and ¹¹⁹Sn spectra were obtained on a Bruker AMX 250 spectrometer using C₆D₆ as a solvent. UV–vis spectra were recorded on a Cary 3E UV–vis model spectrophotometer. Elemental analyses for carbon, hydrogen, and nitrogen were measured in sealed volatile sample pans using a Perkin-Elmer series II CHNS/O 2400 analyzer.

$\text{Sn}[\text{N}(\text{mesityl})(\text{SiMe}_3)]_2$ (1**).** $(\text{Me}_3\text{Si})(\text{Mesityl})\text{NH}^9$ (5.00 g, 24.1 mmol) was dissolved in 50 mL of diethyl ether and cooled to -20

* To whom correspondence should be addressed. E-mail: rakemp@unm.edu. Phone: (505) 277-0510. Fax: (505) 277-2609.

[†] University of New Mexico.

[‡] University of California, San Diego.

[§] Sandia National Laboratories.

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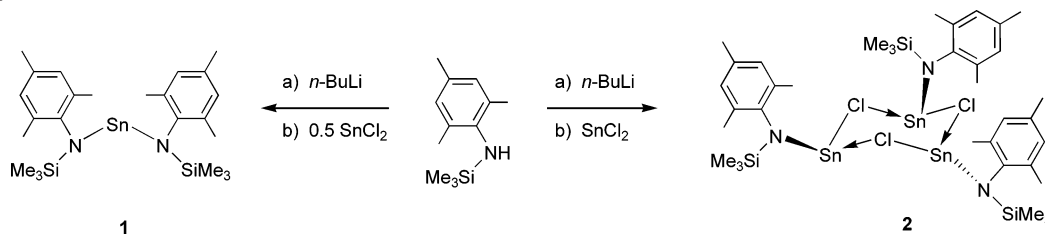
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Scheme 1. Synthetic Routes to **1** and **2**

°C. *n*-Butyllithium (9.64 mL, 24.1 mmol, 2.5 M in hexane) was slowly added to the diethyl ether solution. The solution was allowed to warm to room temperature and stir for 5 h. This solution was then added dropwise to a stirred suspension of 2.29 g (12.05 mmol) of anhydrous SnCl₂ in 20 mL of diethyl ether. After stirring for 12 h, the volatiles were then removed in vacuo, and the crude product was taken up in hexane and filtered through Celite held on a glass frit. After concentrating the filtrate, 4.99 g of pure **1** was obtained in 78% yield as orange-red crystals after storage at −20 °C for several days. ¹H NMR (250 MHz, *d*₆-benzene): δ 0.53(s), 2.37(s), 2.53(s), 6.82(s). ¹³C NMR (250 MHz, *d*₆-benzene): δ 4.95, 20.86, 21.56, 128.64, 130.53, 131.88, 147.13. ¹¹⁹Sn (93.275 MHz, Me₄-Sn): δ 473. Anal. Calcd for C₂₄H₄₀N₂Si₂Sn (531.45): C, 54.24; H, 7.59; N, 5.27%. Found: C, 53.62; H, 7.45; N, 5.12%.

{Sn(μ-Cl)[N(mesityl)(SiMe₃)]₃ (**2**). (Me₃Si)(mesityl)NH⁹ (5.0 g, 24.1 mmol) was dissolved in 50 mL of diethyl ether and cooled to −20 °C. *n*-Butyllithium (9.64 mL, 24.1 mmol, 2.5 M in hexane) was slowly added to the diethyl ether solution. The solution was allowed to warm to RT and stir for 5 h. The resulting solution was then added to a stirred suspension of 4.57 g (24.1 mmol) of anhydrous SnCl₂ in 75 mL of diethyl ether cooled to 0 °C. After gradual warming to room temperature and stirring for 12 h, the volatiles were then removed in vacuo, and the crude product was taken up in a toluene/hexane mixture (1:5) and filtered through Celite held on a glass frit. After concentrating the filtrate in vacuo, 6.08 g of pure **2** was obtained in 70% yield as yellow crystals after storage at −20 °C for 2 days. ¹H NMR (250 MHz, *d*₆-benzene): δ 0.26(s), 2.11(s), 2.30(s), 6.79(s). ¹³C NMR (250 MHz, *d*₆-benzene): δ 4.00, 20.75, 21.37, 129.55, 132.63, 136.61, 143.24. ¹¹⁹Sn (93.275 MHz, Me₄-Sn): δ 67. Anal. Calcd for C₃₆H₆₀Cl₃N₃-Si₃Sn₃ (1081.56): C, 39.98; H, 5.59; N, 3.88%. Found: C, 39.59; H, 5.57; N, 3.88%.

X-ray Crystallography. X-ray quality crystals of **1** and **2** were grown from either hexane or a mixture of toluene and hexane. X-ray diffraction intensities were collected using λ(Mo Kα) = 0.71073 Å radiation on Bruker P4/CCD (**1**) and a Smart Apex CCD (**2**) diffractometers at 223 and 100 K, respectively. Crystallographic data and details of the X-ray studies are given in Table 1. As all of the compounds are extremely air-sensitive, the crystals were always handled under inert atmosphere. They were covered with oil and immediately transferred to the N₂ stream of the diffractometer prior to data collection. SADABS absorption corrections were applied in both cases (*T*_{min}/*T*_{max} = 0.729 (**1**), and 0.862 (**2**)). Non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were found from the difference F-maps and refined with isotropic thermal parameters. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).¹⁰

Table 1. Crystallographic Data and Parameters for Complexes **1** and **2**

	1	2
empirical formula	C ₂₄ H ₄₀ N ₂ Si ₂ Sn	C ₃₆ H ₆₀ Cl ₃ N ₃ Si ₃ Sn ₃
fw	531.45	1081.56
<i>T</i> , K	213	100
cryst size (mm ³)	0.40 × 0.35 × 0.20	0.30 × 0.27 × 0.23
cryst syst	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.4745(9)	17.3324(11)
<i>b</i> , Å	14.5719(12)	13.6799(9)
<i>c</i> , Å	17.1003(13)	19.6416(12)
α, deg	100.2770(10)	90
β, deg	95.159(2)	90.5220(10)
γ, deg	90.1720(10)	90
<i>V</i> , Å ³	2801.5(14)	4656.9(5)
<i>Z</i>	4	4
calcd density, g/cm ³	1.260	1.543
μ(Mo Kα), mm ^{−1}	1.009	1.873
indep reflns	12 594 [<i>R</i> _{int} = 0.0260]	10 568 [<i>R</i> _{int} = 0.0228]
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0580, 0.1250	0.0305, 0.0614
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0458, 0.1166	0.0252, 0.0592
GOF on <i>F</i> ²	1.021	1.047

Results and Discussion

We have recently been investigating the reactions of main group amides or diamides with CO₂. In particular, we are interested in examining ligands attached to Sn that might prove useful to generate carbamates or isocyanates after the reaction with CO₂. Sita has shown previously that silyl-containing Sn(II) diamides react with CO₂, albeit somewhat slowly, to liberate isocyanates.⁶ We were interested in determining whether different silyl-containing ligands attached to Sn might accelerate this insertion reaction. During the process of synthesizing a number of these modified ligands, we prepared Sn(II) complexes using the −N(mesityl)(SiMe₃) ligand. While the 2:1 ligand/Sn(II) ratio gave us the expected stannylene, the 1:1 ligand/Sn(II) afforded a new chlorotin amide species which adopts a unique trimeric structure in the solid state. The chairlike (Sn–Cl)₃ backbone reported here has not been seen previously in Sn–halide chemistry.

The ligand precursor Li[N(mesityl)(SiMe₃)]⁹ was generated in situ by the reaction of (Me₃Si)(mesityl)NH with *n*-BuLi, followed by the treatment with 0.5 equiv of SnCl₂ to yield **1** (Scheme 1). The ¹H NMR spectrum of **1** in *d*₆-benzene consisted of four single resonances, indicating retention of the basic ligand structure. The −SiMe₃ resonance is seen at δ 0.53 ppm, the two distinct methyl resonances from the mesityl group are at δ 2.37 (2,6-positions) and 2.53 ppm (4-position), and the two protons on the mesityl ring are found at δ 6.82 ppm. The ¹³C NMR spectrum of **1** was consistent with the ¹H NMR data. The −SiMe₃ resonance is found at δ 4.95 ppm, the two different methyl peaks from

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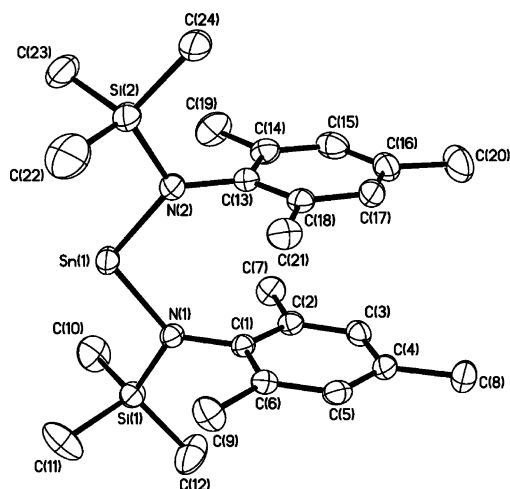


Figure 1. Thermal ellipsoid plot for one of the two independent molecules of **1** shown at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) for the two independent molecules: Sn(1)–N(2) 2.060(3) (2.057(3)), Sn(1)–N(1) 2.058(3) (2.057(3)), Si(1)–N(1) 1.743(3) (1.742(3)), Si(2)–N(2) 1.740(3) (1.744(3)); N(1)–Sn(1)–N(2) 105.8(1) (105.6(1)), Sn(1)–N(1)–Si(1) 114.9(1) (114.9(1)), Sn(1)–N(1)–C(1) 126.1(2) (125.7(2)), Si(1)–N(1)–C(1) 118.6(2) (118.5(2)), Sn(1)–N(2)–Si(2) 114.8(1) (115.6(1)), Sn(1)–N(2)–C(13) 125.2(2) (126.0(2)), Si(2)–N(2)–C(13) 119.1(2) (117.8(2)).

the mesityl group are at δ 20.86 (4-position) and 21.56 ppm (2,6-positions), and the four aromatic carbons are found at δ 128.64 (3,5-positions), 130.54 (4-position), 131.88 (2,6-positions), and 147.13 ppm (1-position). The single resonance at 473 ppm in the ^{119}Sn NMR spectrum of **1** indicated that a monomeric structure was likely. This value was similar to the value of 501 ppm obtained by Sita for $\text{Sn}[\text{N}(\text{SiMe}_2\text{Ph})_2]_2$, a monomer whose existence was established by X-ray diffraction.¹¹ Since the nuclearity of **1** could not be determined with certainty via NMR, it was necessary to determine this by single-crystal X-ray diffraction analysis.

Crystals of **1** suitable for X-ray structural analysis were grown from a hexane solution by cooling to -20°C for several days. There are two symmetrically independent molecules in the crystal of **1**. As can be seen in Figure 1, the overall structure is monomeric, similar to the structure of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ reported previously by Lappert.¹² The Sn atom in **1** resides at the bottom of a pocket formed by the two phenyl rings of the mesityl groups which are essentially parallel to each other (in both independent molecules the two rings are approximately 1.5° removed from coplanarity). The distance between the two parallel phenyl ring centers is approximately 3.60 Å. While the rings are not absolutely concentric, they do provide a pocket that should be accessible by other atoms and molecules. Interestingly, in the solid state **1** adopts a planar zigzag conformation in the Si(1)–N(1)–Sn–N(2)–Si(2) backbone. Furthermore, due to the pseudo- C_2 axis that is present in this conformation, the two-aryl groups are essentially identical. It is also interesting to note that the structure of **1**, with parallel aromatic rings, is quite different from the solid state structure of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.

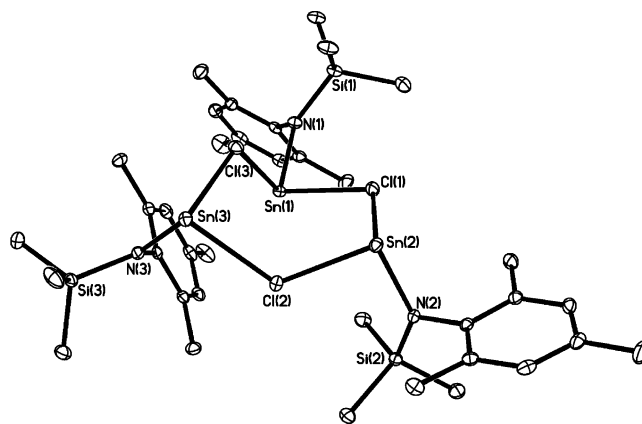


Figure 2. Thermal ellipsoid plot of **2** shown at the 30% probability level. Selected bond lengths (Å) and bond angles (deg): Sn(1)–N(1) 2.0890(19), Sn(1)–Cl(1) 2.6844(6), Sn(1)–Cl(3) 2.6868(6), Sn(2)–N(2) 2.0703(18), Sn(2)–Cl(2) 2.5789(6), Sn(2)–Cl(1) 2.6201(6), Sn(3)–N(3) 2.0864(19), Si(1)–N(1) 1.744(2), Si(2)–N(2) 1.746(2), Si(3)–N(3) 1.744(2); N(1)–Sn(1)–Cl(1) 92.56(5), N(1)–Sn(1)–Cl(3) 96.20(5), Cl(1)–Sn(1)–Cl(3) 84.99(2), N(2)–Sn(2)–Cl(1) 98.35(5), N(2)–Sn(2)–Cl(2) 92.83(5), Cl(1)–Sn(2)–Cl(2) 91.33(2), N(3)–Sn(3)–Cl(2) 93.27(5), N(3)–Sn(3)–Cl(3) 96.43(5), Cl(2)–Sn(3)–Cl(3) 83.32(2), Sn(1)–Cl(1)–Sn(2) 114.16(2), Sn(2)–Cl(2)–Sn(3) 116.96(2), Sn(1)–Cl(3)–Sn(3) 113.99(2).

isopropylphenyl)]₂, a significantly more sterically crowded analogue prepared previously by Sita, a molecule in which the rings are twisted away from each other.¹¹

Compound **2** was prepared in 70% yield in a manner similar to that of **1**; however, in this case 1 equiv of SnCl_2 was used. Yellow crystals of **2** were obtained by recrystallization from a toluene/hexane solution at -20°C . This compound is air-sensitive in solution, yet is relatively stable to air in solid state. The ^1H NMR spectrum in d_6 -benzene again consisted of four peaks, which are shifted slightly to higher chemical field when compared with the corresponding peaks in compound **1**. The $-\text{SiMe}_3$ resonance for **2** is seen at δ 0.26 ppm, the two distinct methyl resonances from the mesityl group are at δ 2.11 (4-position) and 2.30 ppm (2,6-positions), and the two protons on the mesityl ring are found at δ 6.79 ppm. In the ^{13}C NMR spectra, the $-\text{SiMe}_3$ resonance is found at δ 4.00 ppm, the two different methyl peaks from the mesityl group are at δ 20.75 (4-position) and 21.37 ppm (2,6-positions), and the four aromatic carbons are found at δ 129.55 (3,5-positions), 132.63 (4-position), 136.61 (2,6-positions), and 143.24 ppm (1-position). Again, both ^1H NMR and ^{13}C NMR data indicate retention of the basic ligand structure. The ^{119}Sn NMR spectrum of **2**, however, was a single peak at 67 ppm, at significantly higher field than found in **1**. This value is at even higher field than the ^{119}Sn shifts of 181 and 193 ppm seen earlier by Lappert with the binuclear μ -chlorotin(II) amides.⁷ This indicated to us that the structure of **2** may well be different from that seen in the solid state with the dimeric species. To examine the exact structure, we studied the structure of **2** using single-crystal X-ray diffraction analysis (Table 1).

As is shown in Figure 2, the crystal structure indicates that the molecule adopts a chairlike configuration in the solid state. Two of the $-\text{N}(\text{mesityl})(\text{SiMe}_3)$ groups lie on one side of the six membered ring (up), while the third group is located on the opposite side of the ring (down). This can be

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ascribed to the sterically crowded nature of the ligands in **2** as well as the presence of the stereochemically active lone pairs on the Sn atoms. The tin–chlorine bonds range from 2.5789(6) to 2.6868 (6) Å in length. These values fall within the range observed for the sterically stabilized dimeric *trans*-{Sn(μ -Cl)[N(SiMe₃)₂]}₂ (Sn–Cl 2.5998(1) Å and Sn–Cl' 2.741(1) Å) and *cis*-{Sn(μ -Cl)[NCMe₂(CH₂)₃CMe₂]}₂ (Sn–Cl 2.704(1) Å and Sn–Cl' 2.786(1) Å).⁷ As such, they are not particularly informative with respect to the nature of any steric interactions. Further, the tin–chlorine–tin angles (Sn(2)–Cl(1)–Sn(1) 114.16(2)°, Sn(2)–Cl(2)–Sn(3) 116.96(2)°, and Sn(3)–Cl(3)–Sn(1) 113.99(2)°) are much larger than those in *trans*-{Sn(μ -Cl){N(SiMe₃)₂}}₂ and *cis*-{Sn(μ -Cl)[NCMe₂(CH₂)₃CMe₂]}₂ (Sn–Cl–Sn' 98.67(4)°, and Sn–Cl–Sn' 100.91(4)°).⁷ While the exact reason is not known for the existence of this new trimeric chairlike structure for **2**, there may be clues in the structure of a related lead compound, {Pb[C(SiMe₃)₃]Cl}₃, in which the six-membered ring adopts a distorted boat form rather than a chair form.¹³ In this molecule, the –[C(SiMe₃)₃] groups are so sterically crowded that the boat configuration allows them to get as far apart as possible. It is clear that in our case the

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steric requirements for mesityl are much less than for the –[C(SiMe₃)₃] group.

Summarizing, we have examined the reaction of the bulky ligand –N[(mesityl)(SiMe₃)] with both 2:1 and 1:1 molar ratios of SnCl₂. These reactions produce a monomeric stannylene and a structurally unique trimeric tin amide. We have synthesized and characterized the first example of a trimeric μ -Cl tin(II) amide, {[Sn(μ -Cl)[N(mesityl)(SiMe₃)]}₃, **2**, whose crystal structure indicates that the molecule adopts a chairlike conformation in the solid state. The structure of the monomeric tin amide Sn[N(mesityl)(SiMe₃)]₂, **1**, reveals it to be a highly symmetric molecule with the phenyl groups virtually parallel to each other. Insertion reactions of carbon dioxide into these tin(II) complexes are currently in progress in our laboratory.

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Supporting Information Available: X-ray crystal data in CIF format for **1** and **2**. UV–vis spectra of **1**, **2**, and the free ligand HN[(mesityl)(SiMe₃)]₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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