The First Stable Monomeric Triaminostannane of Composition $[(Me_3Si)_3CSn(NHtBu)_3]$ Containing Three Substituted NH Groups

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Dedicated to Professor G. Ourisson for his outstanding contributions to chemistry

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Triaminostannanes of secondary amines have been known since 1977 and are widely used in tin organic chemistry. However, the corresponding nitrogen substituted stannanes of primary amines are not cited in the literature. Herein we report on the ammonolysis reaction of $[(Me_3Si)_3CSnCl_3]$ with $tBuNH_2$ in the presence of a strong base and the X-ray structural analysis of $[(Me_3Si)_3CSn(NHtBu)_3]$, the first monomeric triaminostannane containing protons at the nitrogen atoms.

Introduction

Hydrolysis as well as ammonolysis of mono-organotrihalides of the heavier group 14 elements has been a topic of interest for a long time. In the case of silicon there are many compounds of composition $RSi(OH)_3$ and $RSi(NH_2)_3$ (R = organic substituent) known, which can be used as precursors for generating molecular building blocks of heterosilicates or zeolite-like materials. These systems containing silicon, nitrogen and various metal atoms are often much more stable than the oxygen-based ceramics.[1]

Although hydroxy-substituted compounds of the congener tin are widely used in organic synthesis,[2] there is only one example known of a structurally characterized mono-organotin acid, the trimeric $[TsiSn(OH)O]_3$ [Tsi = $C(SiMe_3)_3$].[3] A monomeric trihydroxystannane has not been reported so far.

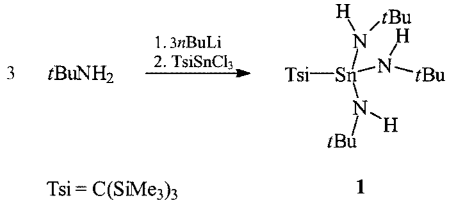
The corresponding isoelectronic nitrogen compounds of tin $[RSn(NH_2)(NH)]_3$ and $RSn(NH_2)_3$ are not reported in the literature, whereas tin compounds of composition $RSn(NR'_2)_3$ have been known since 1977 and are widely used as precursors in organometallic reactions.[4] Moreover, tin compounds of primary amines such as $RSn(NHR')_3$ are also unknown.

Finally a computer-based literature search showed that there are no known tin-nitrogen compounds with four-coordinate tin atoms, containing substituted NH groups. This fact indicates the instability of those compounds against condensation reactions.

The successful recently published hydrolysis reaction of $TsiSnCl_3$, which yields the trimeric mono-organotin acid chloride $[TsiSn(Cl)O]_3$,[3] showed that the so-called trisyl ligand[5] is able to stabilise unusual tin organic compounds.

Results and Discussion

Previously we tried ammonolysis reactions under mild conditions with liquid ammonia, but we were not able to isolate any products except the starting material $TsiSnCl_3$. However, the reaction of $TsiSnCl_3$ with an excess of $tBuNH_2$ in toluene containing three equivalents of nBuLi yields the first monomeric, triaminostannane $[TsiSn(NHtBu)_3]$ (**1**), with four-coordinate tin bound to primary amine groups. Compound **1** is stable against condensation reactions (Scheme 1).



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Scheme 1

We were able to confirm the tetrahedral coordination site of the tin atom in compound **1** by characteristic resonances in the ^{119}Sn NMR spectrum (δ = −94.7 ppm). There are similar ^{119}Sn NMR resonances reported in the literature.[6] Crystallisation of the crude product from n-pentane resulted in single crystals of **1**, which could be characterized

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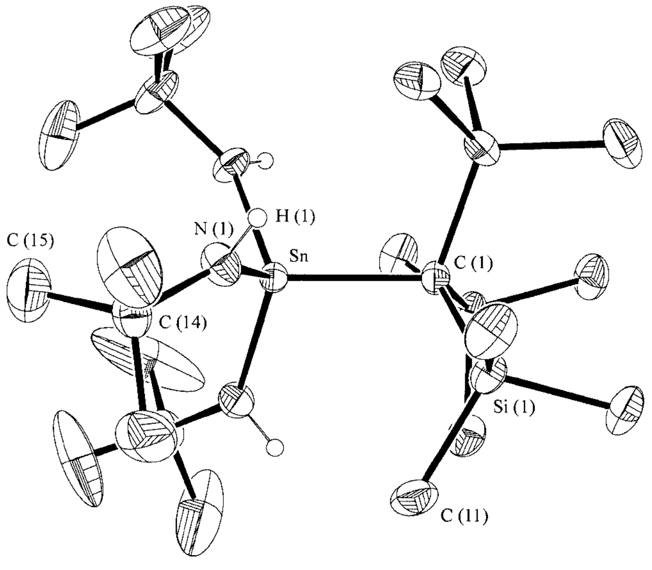

Figure 1. Molecular structure of **1** [ORTEP drawing[8] thermal ellipsoids (30% probability)]; the methyl groups are omitted for clarity; selected bond lengths [Å] and angles [°]: Sn(1)−N(1) 2.028(4), Sn(1)−C(1) 2.212(4), N(1)−C(14) 1.466(6), C(1)−Si(1) 1.895(5); N(1)−Sn(1)−C(1) 107.4(16), Sn(1)−C(1)−Si(1) 109.5(2), N(1)−Sn(1)−N(2) 110.2(17), C(1)− Si(1)−C(11) 113.4(2), Si(1)−C(1)−Si (2) 110.4(2), C(14)−N (1)−Sn (1) 135.0(3), C(15)−C (14)−N (1) 110.8(5)

for the first time by single-crystal X-ray structural analysis (Figure 1).[7]

Compound **1** exhibits a very high symmetrical arrangement and is built up by two staggered tetrahedral centers of carbon and tin. The angles between the C, N and Sn atoms range from 135.0 to 137.9° whereas the others are close to 108° (103.8−113.9°). This finding demonstrates distinctly the high symmetry of **1**. The tin-nitrogen bond lengths range from 2.017 to 2.028 Å and are similar to those in known tin-nitrogen systems of the type [RSn(NR′R′′)$_3$].[9] The Sn(1)−C(1) bond length amounts to 2.212 Å and could be compared with that in [TsiSn(OH)O]$_3$.[3] The N−C bond lengths range from 1.466 to 1.510 Å. They are similar to those in *tert*-butyl-substituted organometallic nitrogen compounds.[10]

Interactions between two molecules of **1** through hydrogen bonding were not observed. This crystallographic observation could be additionally supported by the determination of the molecular mass of **1** in liquid toluene, which is close to the calculated value for **1**. The mass spectrum shows a characteristic signal at *m/z* = 567. Furthermore the ^{1}H NMR investigation exhibits one resonance for the three nitrogen-bonded, chemically identical *tert*-butyl groups. The NH resonance was assigned as a singlet at δ = 0.5 ppm, whereas in the IR spectrum the NH stretching frequency was observed at 3371 cm^{-1}.

Conclusion

The herein presented synthesis and single-crystal X-ray analysis of the monomeric, four-coordinate triaminostannane [TsiSn(NH*t*Bu)$_3$] (**1**) is the first example of a tetrahedral tin-nitrogen system with N-bonded protons. Now we are looking forward to a multitude of new reactions with this compound. Presently we are studying the chemistry of **1** using this compound as a precursor for preparing zeolite-like materials, but based on nitrogen and tin instead of silicon and oxygen.

Experimental Section

General Remarks: Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under dry nitrogen, using standard Schlenk techniques. NMR spectra were recorded using a Bruker Avance 200, Bruker MSL 400 or a Bruker Avance 500 spectrometer and referenced to the resonances of the residual protons in deuterated benzene. ^{1}H NMR: internal standard C_6D_6, external standard TMS. ^{13}C NMR: internal standard C_6D_6, external standard TMS. ^{29}Si NMR: internal standard C_6D_6, external standard TMS. ^{119}Sn NMR: internal standard C_6D_6, external standard $SnMe_4$. Infrared spectra were recorded on a BIO-RAD Digilab FTS 7 spectrometer as solution in *n*-pentane. The starting material $TsiSnCl_3$ was prepared as described in the literature.[3]

[Tris(trimethylsilyl)methyl]tri(*tert*-butylamino)stannane (1): At 0 °C *t*BuNH$_2$ (2.26 mL, 21.5 mmol) was dissolved in toluene (30 mL) and a solution of *n*BuLi in hexane (2 M, 2.60 mL, 6.45 mmol) was slowly added. The mixture was stirred for 0.5 h at this temperature to complete the lithiation reaction. A solution of $TsiSnCl_3$ (0.98 g, 2.15 mmol) in toluene (30 mL) was added to the resulting fine suspension of LiNH*t*Bu. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was stirred for an additional 48 h. While warming the solution, the mixture was intensively yellow colored and a gel-like consistence resulted. After the reaction was completed a colorless liquid was obtained. Finally all volatile components were removed in vacuo and the residue was dissolved in *n*-pentane. The insoluble components were removed by filtration and the resulting colorless solution was concentrated under reduced pressure. The concentrated solution was stored for 2 days at −26 °C and **1** crystallised as a colorless solid (1.16 g, 2.04 mmol, 95%). M.p. 132−136 °C. ^{1}H NMR (C_6D_6, 300 K, 500 MHz): δ = 0.42 [s, 27 H, $(H_3C)_3Si$], 0.50 (br., 3 H, N*H*), 1.42 [s, 27 H, $(H_3C)C$]. ^{13}C NMR (C_6D_6, 300 K, 125 MHz): δ = 6.27 [s, $(H_3C)_3Si$], 11.34 [s, $\{(H_3C)_3Si\}_3C$], 35.68 [s, $(H_3C)_3C$], 53.94 [s, $(H_3C)_3C$]. ^{29}Si NMR (C_6D_6, 300 K, 99 MHz): δ = −1.66 [s, $(H_3C)_3Si$]. ^{119}Sn NMR (C_6D_6, 300 K, 186 MHz): δ = −94.7. $C_{22}H_{57}N_3Si_3Sn$ (566.65): calcd. C 46.6, H 10.1, N 7.4; found C 46.8, H 10.0, N 7.6. IR (*n*-pentane) ṽ = 468 w cm^{-1}, 615 w, 660 w, 676 w, 718 w, 800 w, 852 vs, 970 s, 1024 w, 1096 w, 1190 s, 1257 s, 1358 vs, 3371 w. MS (70 eV): *m/z* (%) = 567 (3) [M$^+$], 494 (10) [M$^+$ − TMS], 479 (8) [M$^+$ − TMS − Me], 422 (100) [M$^+$ − TMS − Me − *t*Bu].

Crystal Data for 1: A colorless crystal of compound **1** was mounted onto a STOE Siemens Huber Diffractometer System equipped with a four-circle goniometer and a graphite monochromator. Data collection was performed at 200 K using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least-squares on F^2 with SHELX-97.[11a] The hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters.[11b] Monomeric, space group $P2_1/n$, a = 9.6292(15), b = 32.260(3), c = 11.006(3) Å, α = 90, β = 113, γ = 90°, V =

3150.0(1) Å^3. $Z = 4$, $\rho_{\text{calcd.}} = 1.194$ Mg·m^{-3}, $T = 200(2)$ K, 7770 measured, 5485 crystallographic independent reflections, $\theta_{\max} = 25.03°$, numeric absorption correction ($\mu = 0.937$ mm^{-1}), $wR = 0.0481$, $wR2 = 0.1355$ (all data). The figures were drawn with ORTEP-3 for Windows.[8]

Table 1. Crystallographic data for **1**

Empirical formula	$C_{22}H_{57}N_3Si_3Sn$
Molecular mass [gmol^{-1}]	566.65
Temperature [K]	200 (2)
Wavelength λ [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	9.6292 (15)
b [Å]	32.260 (3)
c [Å]	11.006 (3)
α [°]	90
β [°]	113
γ [°]	90
Volume [Å^3]	3150.0 (1)
Z	4
D_c [gcm^{-3}]	1.194
μ [mm^{-1}]	0.937
F(000)	1208
θ range [°]	3.59−25.03
Unique refl. with [$I > 2\sigma(I)$]	5485
GooF	1.073
Final $R1$, $wR2$	0.0444, 0.1306
Residual density (max/min) [e·Å^{-3}]	1.073/− 0.976

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