STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIX, 2, 2004

Dedicated to Professor Valer Fărcăşan
at his 85th anniversary

A NOVEL DISILOXANEDIOLATO - DERIVATIVE OF TIN(IV)

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ABSTRACT. Bis[µ^2-(bis(tetrahydrofuran)-lithium(tetraphenyl-disiloxane-1,5-diolato)]-dimethyltin (IV) (**1**) has been obtained from the reaction of diphenylsilanediol with butylithium and dimethyltin dichloride.

The crystal of (**1**) is monoclinic, space group P2(1)/n with the unit cell dimensions: a = 10.4609(9) Å, b = 19.9896(16) Å, c = 17.9295(15) Å, α = 90.00°, β = 105.791(2)°, γ = 90.00°. The tin atom has a slightly distorted *octahedral* environment. The silandiol ligands coordinate also two lithium atoms forming thus two planar LiO_2Sn chelate rings.

INTRODUCTION

Metallasiloxanes have known a continuously increasing interest in the last decades because of their practical applications. For instance, stannasiloxanes are precursors of inorganic polymers leading to ceramic materials or molecular sieves [1, 2], and they have found some uses in heterogeneous catalysis [3] or as single source mixed metallic oxides precursors [4]; their potential as homogeneous catalysts has also been studied [3].

RESULTS AND DISCUSSION

In an attempt to synthesize the four-member ring $Ph_2SiO_2SnMe_2$ which might easily undergo ring-opening polymerization**,** a novel stannadiphenylsiloxane was obtained using diphenylsilanediol, butylithium and dimethyltin dichloride as starting materials (Scheme 1).

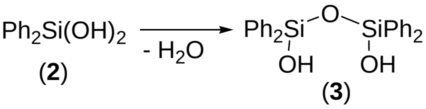
Lithiation of the diphenylsilanediol was carried out at room temperature, followed by dropwise addition of dimethyltin dichloride to the reaction mixture wherefrom compound **1** has been isolated:

$$Ph_2Si(OH)_2 \xrightarrow[\text{THF}]{\substack{\text{1) BuLi} \\ \text{2) } Me_2SnCl_2}} Ph_4Si_4O_6SnMe_2Li_2{*}4\ \text{THF}$$

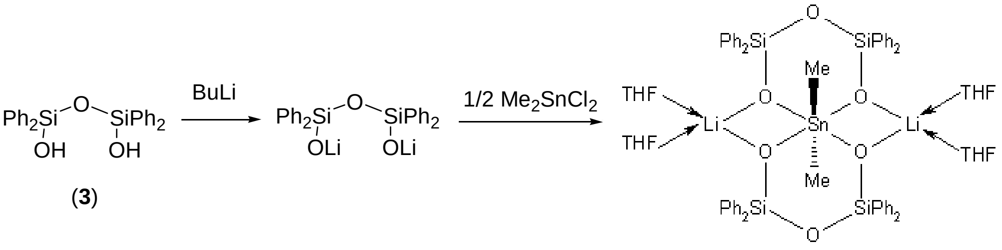
Scheme 1

The reaction mechanism resulting in the expansion of the silanediolate unit to a disiloxanediolate ligand is unknown. Similar reaction outcomes have been reported in the literature [1], but no satisfactory explanation was found for the chain expansion.

The simplest rationalization of this result consists of a condensation of silanediol (**2**) when disiloxane (**3**) is formed.

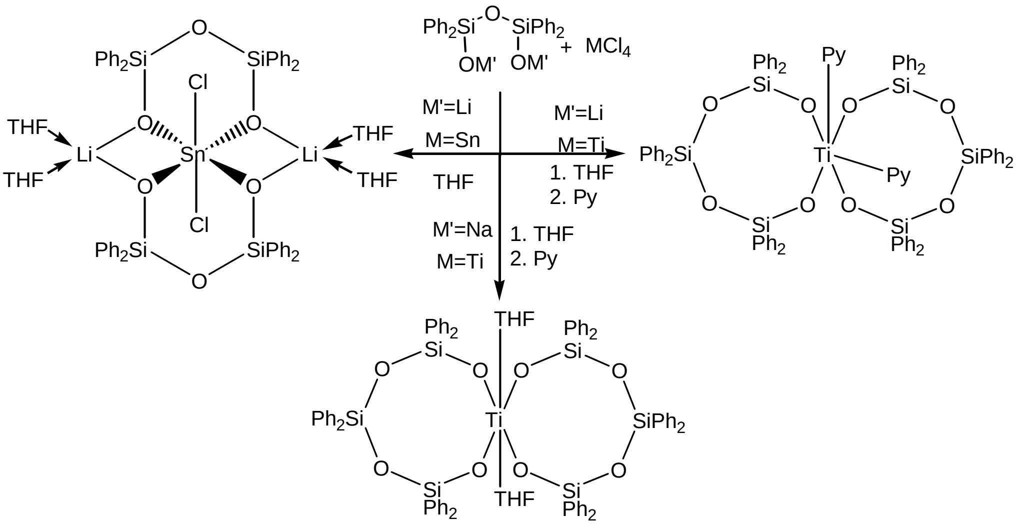


Subsequent lithiation of (**3**) followed by addition of Me_2SnCl_2 leads to bis[μ^2-(bis(tetrahydrofuran)-lithium(tetraphenyldisiloxane-1,5-diolato)]-dimethyltin (IV) (**1**)



(1)

An analogous product was reported in the case of reaction of the dilithium salt of tetraphenyldisiloxane-1, 5-diol with MCl_4 [2], (M = Sn, Zr, Hf) but an expansion of the siloxane unit to eight-membered rings occurs in the case of titanium tetrachloride [3] (Scheme 2).



Scheme 2

It can be said that the target metal to which the siloxanediolate ligand is transferred plays an important role in the outcome of the reaction.

Thus, the chain expansion does not necessarily occur during the lithiation step since tin has been known to favor the cleavage of Si-O bonds and rearrangement of the disiloxane ligand into a trisiloxanediolate unit [4].

It is yet difficult to say whether the nature of the alkali metal or that of the target metal is the determining factor in the chain expansion in the case of siloxane or silandiolate units transfer.

CRYSTAL AND MOLECULAR STRUCTURE OF 1

Transparent, acicular crystals of **1** were crystallized from THF and characterized through single-crystal X-ray diffraction.

The unit cell of **1** is shown in Figure 1, and, the data collection, crystal data and refinement data are summarized in Table 1.

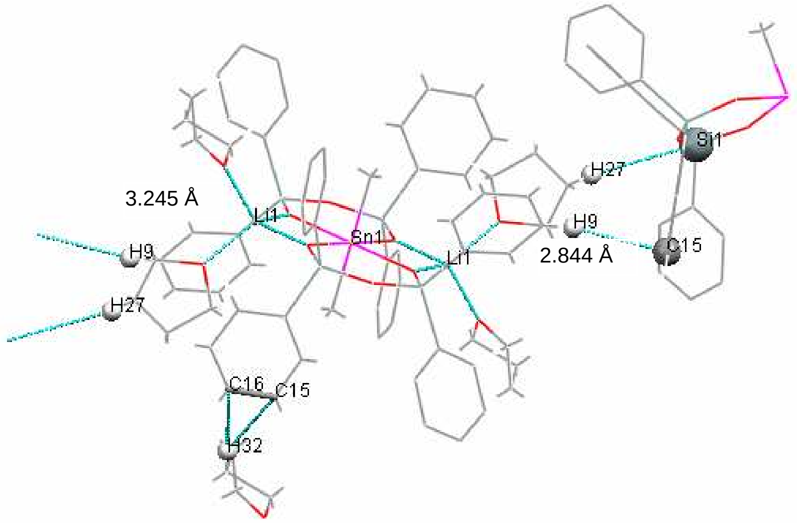


Figure 1. View along the *a* axis of a unit cell of **1**

The unit cell of the stannadisiloxane contains six molecules of **1**, four of them having the tin atom positioned in the center of the *a* axis, while the other two lie in the middle of the *bc* plan and are oriented in opposite direction. Thus, infinite, parallel sheets are formed through H(phenyl)···C(phenyl) (2.844 *Å*) and H(THF)···Si (3.245 *Å*) interactions.

The molecular structure of **1** is shown in Figure 2 and some selected bond lengths and angles are given in Table 2.

Table 1.

Crystal data and refinement data for **1**

Empirical formula	C66 H78 Li2 O10 Si4 Sn
Formula weight	1276.21
Temperature	297(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Unit cell dimension	a=10.4609(9)Å, α =90.00° b =19.9896(16)Å, β =105.791(2)° c =17.9295(15)Å, γ =90.00° Volume 3607.7(5) Å^3
Space group	P2(1)/n
Z	2
Density (calculated)	1.175Mg/m^3
Absorption coefficient	0.471mm^{-1}
F(000)	1332
Crystal size	0.39 mm block-colorless
θ range for data collection	1.56 to 26.37°
Reflections collected	7366
Independent reflections	6230 (R_{int} = 0.0000)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11/378
Goodness-of-fit on F^2	1.222
Final R indices	[I>2σ(I)] R1 =0.0630, wR2 = 0.1971
R indices (all data)	R1 =0.0743, wR2 =0.2047

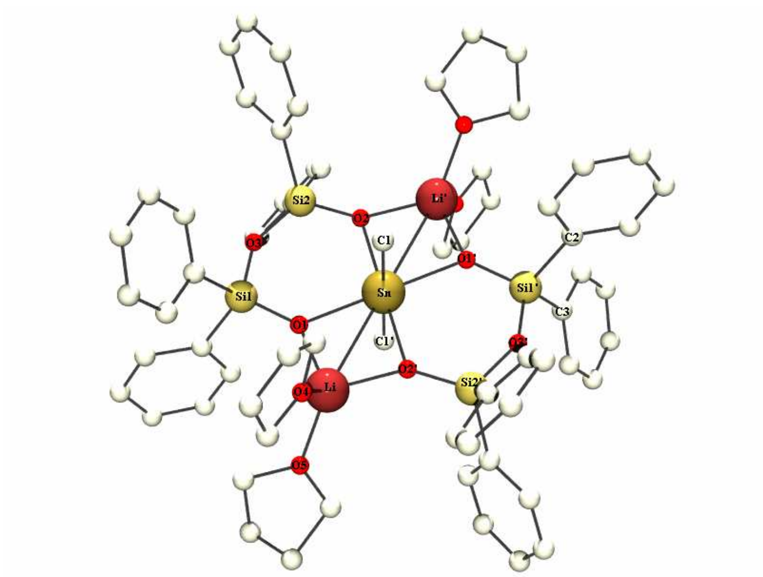


Figure 2. Molecular structure of **1**

Table 2.

Selected geometrical data for **1**

Bond	Length (Å)	Angle	Value (°)
Sn-C1	2.116(4)	C1-Sn-C1’	180.000(1)
Sn-O1	2.181(3)	O1’-Sn-O1	180.000(1)
Sn-O2	2.191(3)	O1-Sn-O2	80.47(10)
Si1-O1	1.597(3)	Sn-O1-Si1	126.34(16)
Si1-O3	1.597(3)	Sn-O2-Si2	126.01(17)
Si2-O2	1.597(3)	O3-Si1-O1	110.88(16)
Si2-O3	1.597(3)	Si1-O3-Si2	146.0(2)
Si1-C2	1.883(5)	O3-Si2-O2	110.91(16)
Si1-C3	1.866(5)	C3-Si1-C1	109.4(2)
O1-Li	1.934(8)	C1-Si1-O3	106.7(2)
O2-Li	1.946(8)	C3-Si1-O1	112.1(2)
		O1-Li-O2	93.4(3)
		Li-O2-Sn	93.36(3)
Dihedral	**Value (°)**	**Atoms**	**Distance (Å)**
O1-Si1-O3-Si2	-7.5(4)	Li-Sn	2.999(7)
O1’-Si1’-O3’-Si2’	7.5(4)	Li-O4	1.982(9)
O2-Si2-O3-Si1	3.1(5)	Li-O5	1.965(9)
Sn-O1-Si1-O3	4.5(3)	Li-O1	1.934(8)
Sn-O2-Si2-O3	3.7(3)	Li-O2	1.934(8)
O1-Li-O2-Sn	-1.9(3)		

Compound **1** is a bicyclic stannasiloxane with hexacoordinated tin atom. The slight distortion from octahedral geometry around the tin is due to the strain in the lithiostannoxane rings. The stannadisiloxane rings are almost planar, coplanar with each other and additionally two four-member rings containing lithium are formed. The methyl groups are in *trans* orientation, with a C-Sn-C angle of 180°. The Sn-O, Si-O and Si-C bond lengths are in the range of values observed for other cyclic stannasiloxanes [5, 6, 7]. A feature of this specific type of cyclostannasiloxanes seems to be a large Si-O-Si angle. Thus, for the dichloro-substituted tin analogue this angle is 141.3(8)°, with about 10° larger than the values obtained for related lithium-bridged cyclometallasiloxanes [5]. In **1,** this angle is even larger (around 146°). The Si-O-Si angle value is often regarded as a measure of the strain in siloxanic rings [7].

^{1}H-NMR CHARACTERISTICS

The ^{1}H-NMR spectrum of (**1**) (recorded in $CDCl_3$) shows that the six hydrogen atoms coming from the two methyl groups give a singlet at 0.5 ppm, which proves their equivalency (at least at the temperature of measurement). This in turn, suggests that the octahedral environment of Sn is retained in solution.

Lockhart and Manders established an empirical relation (eq. 1) between $^2J_{Sn\text{-}H}$ and the C-Sn-C angle and applied it successfully to several compounds [8]:

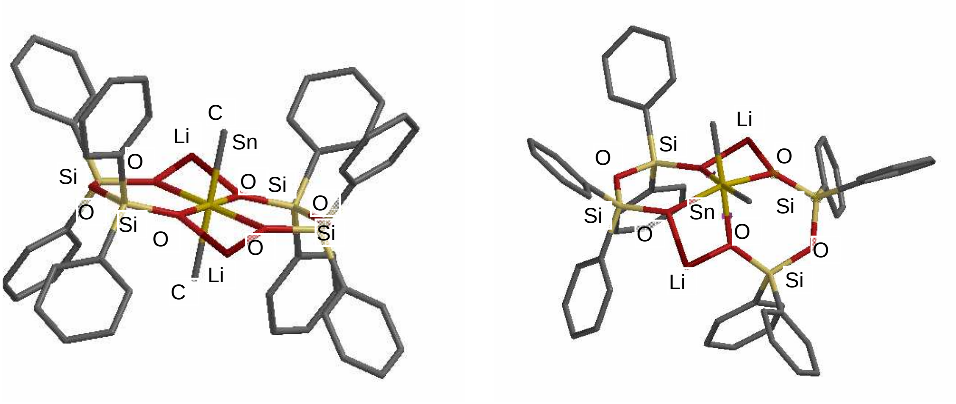
$$\theta = 0.0161\left|{}^2J\right|^2 - 1.32\left|{}^2J\right| + 133.4 \qquad \text{eq. 1}$$

In the case of hexacoordinated dimethyltin derivatives, with the methyl groups in a *trans* orientation the values of $^2J_{Sn\text{-}H}$ are greater than 83 Hz, which correlates with an C-Sn-C angles larger than 135°.

A coupling constant smaller than 80 Hz indicates a *cis* geometry, which is however rare for this kind of compounds. Nevertheless, the relation has been applied with good results to some *cis* isomers of hexacoordinated tin derivatives as well [8]. In our case, $^2J_{Sn\text{-}H}$ from the spectrum of **1** is 70.6 Hz leading to a θ angle of 120.45°, in accordance with a very deformed *cis* geometry.

THEORETICAL CHARACTERIZATION OF (1) THROUGH SEMIEMPIRICAL CALCULATIONS

Calculations at the PM3 semiempirical level [9] were performed using the Spartan'02 program [10] in order to estimate the relative stability of *cis* and *trans* isomers of **1**. Their optimized molecular structures and heats of formation are given in Figure 3**.**



a, ΔH_f^o= -384.11 kcal/mol **b,** ΔH_f^o = -384.22 kcal/mol

Figure 3. Calculated structures and heats of formation of simplified models (THF ommited) of the *trans* (**a**) and *cis* (**b**) isomers of stannasiloxane **1** (hydrogen atoms have been omitted for clarity)

The difference between the heats of formation of the two isomers is insignificant, so we can assume that the formation of the *trans* isomer in the solid state is kinetically controlled, rather than being thermodynamically dictated.

The geometrical data for the *trans* isomer agree fairly well with experimental data obtained through single-crystal X-ray diffraction. A deviation from planarity in the case of the four rings (for instance the dihedral O1-Si1-O3-Si2 has a calculated value of 12.5°) could be explained by the lack of the packing forces, which appear in crystalline state.

There are no significant differences between the two isomers at the PM3 level, as far as bond lengths are concerned. The geometry around the silicon atoms is in both cases a distorted tetrahedron and that around the tin- a distorted octahedron. The distortion is as expected greater for the *cis* isomer and it is correlated with an increased ring-strain in the stannasiloxanic cycles. A measure of this tension is the Si1-O3-Si2 angle, which takes a value of around 132° for six-member siloxanic rings and of about 165° in the strain-free polydiphenylsilanediolate chain. Based on these grounds, the tension within the stannasiloxanic cycles is greater in the case of the *cis* isomer for which the calculated value of the Si1-O3-Si2 angle is around 127° for both rings. The *trans* isomer exhibits less ring-strain, but the calculated angle is still far from the experimental-determined value of 145.95°, which is indicative of a very low-tensioned ring.

CONCLUSIONS

The X-ray diffraction analysis indicates the formation of the isomer with the *trans* geometry of bis[μ2-(bis(tetrahydrofuran)litihium (tetraphenyldisiloxane-1,5-diolato)]dimetil-tin(IV) **1**. This structure does not seem to be retained in solution: the C(methyl$_1$)-Sn- C(methyl$_2$) has a value of 120.45, calculated from ^{1}H-NMR $^2J_{Sn-H}$, which could imply a rearrangement of the stannasiloxane. This comes as no surprise, given the kinetic labilety of the Sn-O bond in organometallic derivatives. A computational study at the PM3 level of the theory indicates that the two geometric isomers have very similar heats of formation in gaseous phase. The formation of the *trans* isomer seems thus to be kinetically controlled.

EXPERIMENTAL DETAILS

All the reactions were carried out in a standard vacuum line (Schlenck Line) under inert atmosphere at room temperature. The solvent used in the synthesis was freshly distilled.

The NMR spectrum was recorded on a Varian Gemini 300 MHz apparatus in $CDCl_3$ and using TMS as internal standard. The melting point was determined on a Leitz microscope heating stage 250.

The crystal data were collected at room temperature (293 K) on a Brucker AHX diffractometer and Graphite monochromated MoK α radiation (λ=0.71073 Å).

Refinement was carried out using the SHELXL-97 program [11] and the structure as solved by direct method and refined by the full matrix least square method. Probably that some disorder in the crystal prevent a better wR2 (0.1971) value.

Molecular orbital calculation were performed with the Spartan 02 package [10].

Preparation of bis[μ^2-(bis(tetrahydrofuran)lithium(tetraphenyldisiloxane-1,5-diolato)] dimethyltin (IV).

2 g of diphenylsilanediol were dissolved in 10 ml THF and 11.69 ml BuLi 1.6 M were added dropwise, while continuously stirring. The mixture was stirred for another half an hour and then one equivalent of Me_2SnCl_2 was added dropwise to the reaction mixture. The white precipitate was filtrated of, and on cooling the THF solution below 0°C, acicular, transparent crystals of **1** were obtained (mp: 132°C).

^{1}H RMN (CDCl3) δ(ppm): 0.5 (s, Me)**,** 1.8 (t, THF), 3.7 (t, THF), 6.7 - 7.0 (m, Ph).

ACKNOWLEDGEMENTS

The financial support from Romanian National University Research Council (CNCSIS Grant A 195/2003) is gratefully acknowledged. We thank dr. Varga Richard for the technical assistance in determining the X-ray structure.

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