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Dedicated to the memory of
Professor Candin Liteanu on his 100th anniversary

SYNTHESIS OF NOVEL FUNCTIONALIZED DIBENZOSTANNEPINE DERIVATIVES

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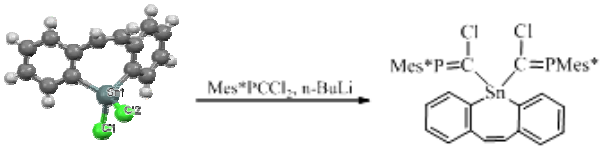
Two novel stannepinic derivatives have been synthesized starting from dimethyl-stannepine. Their structure has been investigated by both experimental (multinuclear NMR spectroscopy, MS, X-ray diffraction) and theoretical methods. The compound bearing two phosphaalkenyl moieties on the tin atom is the first phosphastannapropene with the tin atom contained in a ring reported to date.



INTRODUCTION

A poorly exploited class of organotin derivatives is represented by stannepinic compounds, seven-atom rings with C-C double bonds. While the synthesis and characterization of diorgano-stannepine compounds has been previously reported,[1] no dihalo-derivative of this type has been obtained so far.

In the quest for new unsaturated (propenic and allenic structures) heteroatomic compounds,[2] the use of the common organic groups (trisopropyl, mesityl, etc) for the stabilization of the P=C-Sn moiety has been assessed, proving that the stabilization induced by the steric effect alone is not sufficient for the preparation of phosphastanna-propenes or -allenes. Thus, the design of new phosphastannapropenes (some of them appropriate as precursors of phosphastannaallenes) must take into consideration a combined steric and electronic effect of the substituting organic groups on the tin atom. With this in mind, the synthesis of a new organic dicholorostannane and its functionalization with phosphaalkenyl groups was carried out. Both derivatives have the tin atom included in a stannepine-type ring and have never been reported in the literature.

RESULTS AND DISCUSSION

The preparation of the new dichlorostannane **2** has been achieved in several steps, starting from dibromostilbene. The dimethylstannepine **1** was obtained according a slightly modified literature procedure,[3] by a cyclisation reaction of the dibromo derivative with dimethyltin dichloride, in the presence of butyl lithium (Scheme 1).

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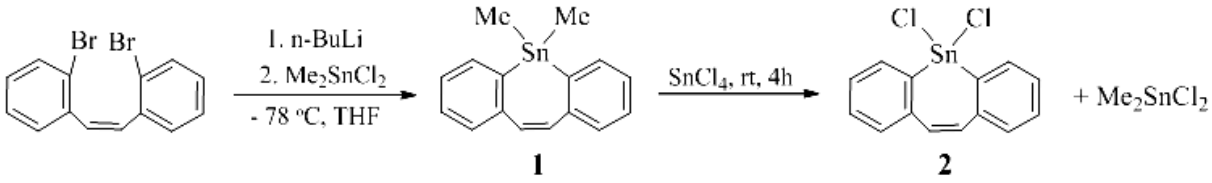
A subsequent solvent-free, redistribution reaction afforded the novel derivative **2** (Scheme 1). The reaction was carried out at 20°C, in the presence of a high excess of tin tetrachloride. The process was monitored by ^{119}Sn NMR spectroscopy. The complete transformation to the dichlorostannepine **2** (giving rise to a signal at -12.49 ppm in ^{119} Sn-NMR) was evidenced after a few hours. The new compound was separated from the reaction mixture and recrystallized from hexane as colorless crystals.

Compound **2** was found to be extremely stable towards air and water and was completely characterized in solution by multinuclear NMR. Its structure in solid structure was also confirmed by single crystal X-ray diffraction. Fig. 1a shows the molecular structure of the new dichlorostannepine **2**.

The tin atom presents an almost ideal tetrahedral geometry. The planes including the two aromatic rings are intersecting at an angle of 62˚. The crystalline structure contains chains formed along the *b* axis by secondary interactions between the Cl1 atom of each molecule and the H4 atom of another, in which the orientation of two subsequent molecules is alternating (see Fig. 1b). The chains are stacked, creating a channeled structure (Fig. 1c).

DFT calculations at the B3LYP[4] level using LANL2DZ[5] were performed using the solid state structure of **2** as an input geometry. The NBO analysis shows that charge transfers occur from bonding orbitals situated on the two Sn-C bonds (see Fig. 2a) to antibonding σ* orbitals on C=C double bonds from the aromatic rings (Fig. 2b, c), suggesting delocalization of the tin electrons on the entire cyclic structure. All calculations were carried out with the Gaussian09 program package.[6]

The novel dichloro-stannepine **2** was used as a precursor in the synthesis of the first phosphastannapropene containing two phosphaalkenyl groups substituted at a tin atom contained in a cyclic structure, derivative **5** (Scheme 2). Treatment of derivative **2** with supermesityl phosphaetenyllithium Mes*P=CClLi (**4**, Mes* = 2, 4, 6-tritertbutylphenyl) at low temperature in THF leads to the formation of the novel phosphastannapropene **5**.



1 **2**

Scheme 1

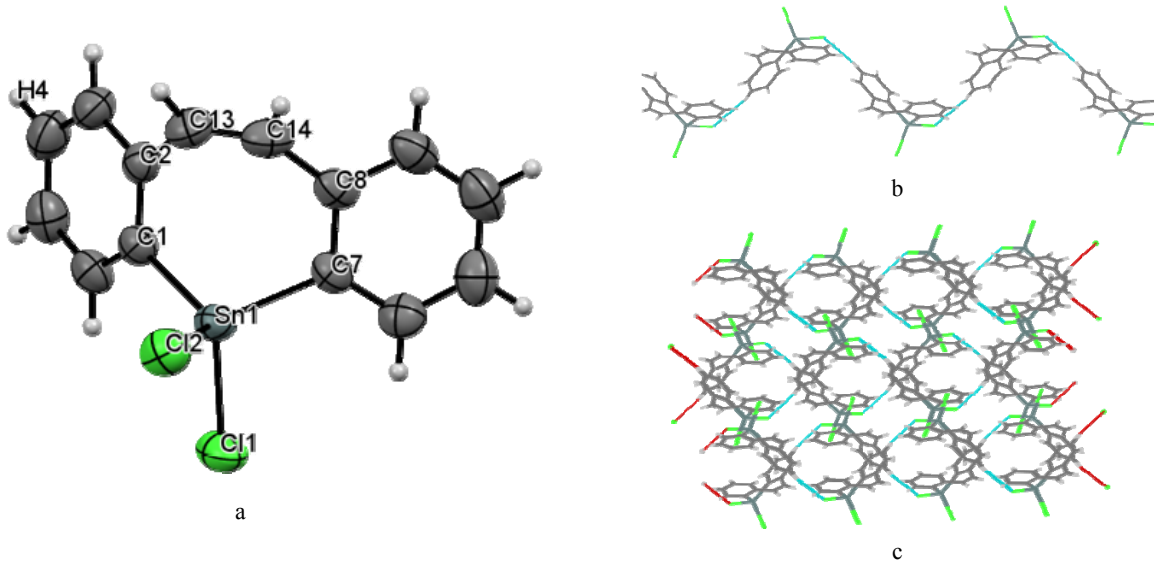
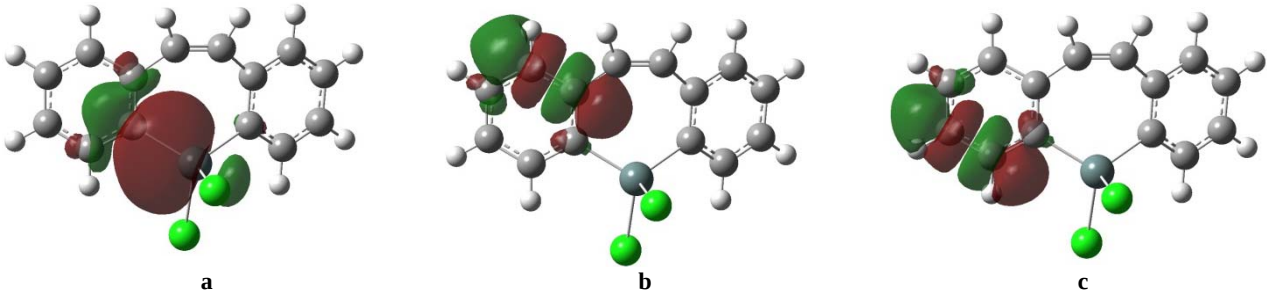
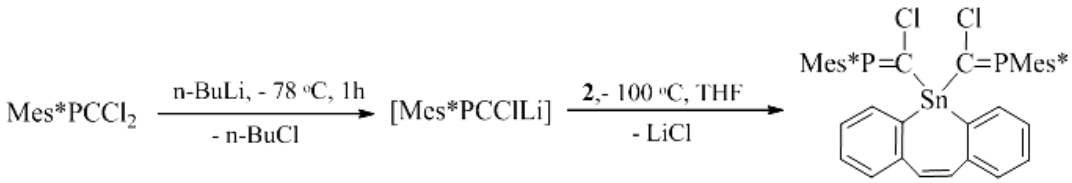


Fig. 1 – a) Molecular structure of derivative **2**; b) chains formed through Cl···H interactions; c) packing of **2** in solid state. Selected geometrical parameters: Sn1-Cl1 2.328 Å, Sn1-C1 2.110 Å, C13-C14 1.342 Å, Cl1-Sn-C1 109.9˚, Cl2-Sn-C7 112.65˚, Cl1···H4 2.936 Å.



a **b** **c**

Fig. 2 – NBO orbitals involved in second order interactions in derivative **2**: a) bonding orbital on the Sn1-C1 bond; b, c) antibonding orbitals on C-C double bonds from the benzenic ring containing the C1 atom.



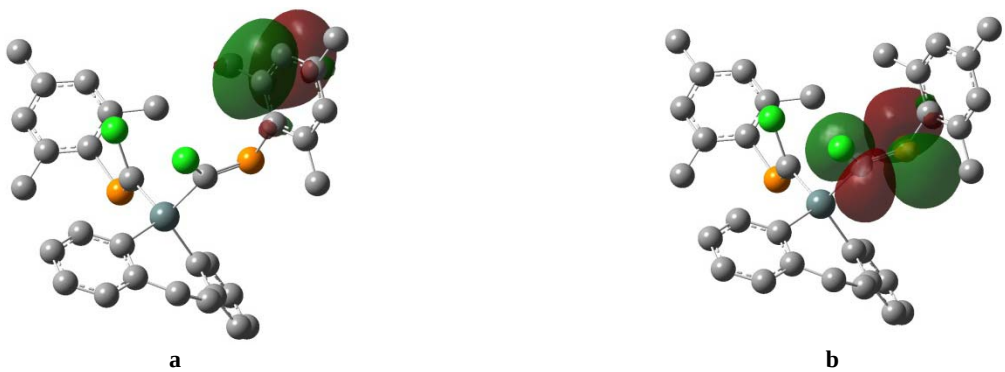
3 **4** **5**

Scheme 2

The new compound was characterized in solution through multinuclear NMR. The ^{119}Sn NMR spectrum shows a triplet at -162.11 ppm, with a Sn-P coupling constant of 338 Hz. The signal corresponding to the phosphorus atoms in the ^{31}P NMR spectrum (298 ppm) is in agreement with the expected value for such derivatives.[7] For instance, the chemical shift of the phosphorus atom in the germaphosphapropene Mes*P=C(Cl)-GeCl(t-Bu)$_2$ is 293.5 ppm.[8] The same reaction product is evidenced noticed even when a molar ratio of derivatives **2** and **4** of 1:1 is employed, which in theory could result in the formation of a 4-atom ring containing two tin atoms and bridging two Mes*P=C moieties. However, in analog digerma-cyclobutanes, the resonance in the ^{31}P NMR can be observed at 367 ppm. This proves that the reaction of **2** with phosphaalkenyllithium leads to the proposed structure of **5**. Additional data from ^{13}C and ^{1}H NMR spectroscopy and mass spectrometry also confirms the formation of the stannepine **5**.

DFT calculations were performed on a model compound of derivative **5**, with Mes (2,4,6-trimethylphenyl) groups in the place of the bulkier Mes* ones. The structure was optimized, leading to a configuration of the dibenzostannepinic rings very close to that observed for compound **2** through experimental methods. The LUMO of the novel phosphastannapropene is a π orbital with pronounced antibonding character situated on the P=C bonds (Fig. 3a).

Similar observations were made from the NBO analysis as in the case of derivative **2**.



a **b**

Fig. 3 – Calculated HOMO (a) and LUMO (b) for the model compound of derivative **5**.

EXPERIMENTAL

All the reactions have been carried out under inert conditions (argon) using Schlenk techniques. THF was freshly distilled over Na/benzophenone.

NMR experiments were performed on BrukerAvance 400 MHz and BrukerAvance 600 MHz spectrometers in $CDCl_3$ at the following frequencies: 400.13 and 600.13 MHz (reference TMS) for ^1H; 100.58 and 150.90 MHz (reference TMS) for ^{13}C; 149.09 MHz (reference $SnMe_4$) for ^{119}Sn. Mass spectra were recorded on Shimadzu QP-2010 PLUS GC-MS Spectrometer.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1025586. Data were collected at room temperature on a Bruker-SMART APEX with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods [9] and all non-hydrogen atoms were refined anisotropically.[10]

Synthesis of (Z)-5,5-dichloro-5H-dibenzo[b,f]stannepine **(2)**

Tin tetrachloride (5 mL, 11.13 g, 42.64 mmol) was added, under vigorous stirring, over compound **1** (dimethyl stannepine) (2 g, 6.19 mmol). A cooling bath at 20°C was used to keep the reaction under control. After the addition of $SnCl_4$, the cooling bath was removed and the reaction mixture was allowed to stir for 4h. The excess tin tetrachloride was removed under reduced pressure and the remaining solid was dissolved in toluene (10 mL). Water (20 mL) was added to the mixture and the organic layer was separated. The aqueous layer was washed with chloroform (3x50 mL) and the combined organics were washed with HCl (0.5 M, 20 mL) and water (50 mL). The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. Crystallization from hexane afforded **2** as colorless crystals (8.84 mmol, 1.6 g, yield 70%).

^{119}Sn NMR, 149.21 MHz ($CDCl_3$): -12.49 ppm

^1H NMR, 400.13 MHz ($CDCl_3$): 6.98 ppm, 2H, s, $^4J_{H-Sn}$= 5.5 Hz, bridge CH=CH; 7.43-7.54, 6H, m; 7.77, d, J_{H-H}=7.1 Hz, $^4J_{SN-H}$=75.0 Hz.

^{13}C NMR, 100.61 MHz ($CDCl_3$): 128.80 ppm, J_{C-Sn}= 72.1 Hz, 130.88 ppm, J_{C-Sn}= 82.2 Hz, 131.57 ppm, J_{C-Sn}= 15.5 Hz, 133.96 ppm, J_{C-Sn}= 17.3 Hz, 134.13 ppm, J_{C-Sn}= 34.28 Hz, 139.95 ppm, 142.16 ppm, J_{C-Sn}= 62.7 Hz.

MS: *m/z* (%) 368 (5) [M^+]; 333 (4) [M^+-Cl]; 178 (100) [stilbene]

Synthesis of ((5H-dibenzo[b,f]stannepine-5,5-diyl)bis(chloromethanylylidene))bis(supermesitylphosphine) **(5)**

A solution of 1.6 M *n*BuLi in hexanes (3.83 ml, 2.87 mmol) was added dropwise over a solution of Mes*$PCCl_2$ (1g, 2.79 mmol) in THF (100ml) at -80 °C. The reaction mixture was held for an additional hour at -80 °C after which it was transferred dropwise, via a cannula, over a solution of **2** (1.03 g, 2.79 mmol) in 100 ml THF at -100 °C. The reaction mixture was allowed to slowly warm to room temperature under stirring. After removal of volatile compounds under reduced pressure and addition of pentane as solvent, the lithium salt was removed by filtration. Recrystallization yielded **5** as a white powder (yield 65%).

^{31}P NMR, 121.91 MHz ($CDCl_3$): 298.50 ppm, s, $^2J_{P-Sn}$ = 338.0Hz

^{119}Sn NMR, 149.21 MHz (CDCl3): -162.11 ppm, t, $^2J_{P-Sn}$ = 338.0 Hz.

^1H NMR, 400.13 MHz ($CDCl_3$):1.34 ppm, 18H, s, p-tert-butyl; 1.53 ppm, 36 H, s, o-tert-butyl; 6.88 ppm, 2H, s, bridge CH=CH; 7.28-7.42, 12H, m; 7.75, d, J_{H-H}= 7.4Hz, 2H

^{13}C NMR, 150.90 MHz ($CDCl_3$): 31.49 ppm, *p*-C($\underline{C}H_3)_3$; 33.14 ppm, *o*-C($\underline{C}H_3)_3$; 35.21ppm, *p*-$\underline{C}(CH_3)_3$; 37.97 ppm, *o*-$\underline{C}(CH_3)_3$; 121.97 ppm, *m*-C Arom Mes*; 127.57 ppm, J_{C-Sn}= 53.5 Hz ; 129.57 ppm, J_{C-Sn}= 10.9 Hz; 130.10 ppm; 134.30 ppm, J_{C-Sn}= 12.7 Hz; 136.25 ppm, J_{C-Sn}= 32.9 Hz, 143.57 ppm, J_{C-Sn}= 35.7 Hz (C atoms in the dibenzostannapine rings); 140.14 ppm, t, $^2J_{C-P}$= 4.7 Hz, $\underline{C}$-Sn-C=P; 150.73 ppm, *p*-C arom Mes*; 153.45 ppm, *o*-C arom Mes*; 167.65 ppm, dd, $^1J_{C-P}$= 85.0 Hz, $^3J_{C-P}$= 5.7 Hz, Sn-$\underline{C}$=P.

MS: *m/z* (%) 699 (1) [M+-Mes*P]; 611 (2) [M+-Mes*P-t-Bu]; 423 (2) [M+-Mes*P-Mes*]; 178 (10) [stilbene].

CONCLUSIONS

Two novel tin derivatives in which the tin atom is contained in a stannepine ring, bearing two chlorine atoms, or two Mes*PC(Cl) moieties were obtained. The derivatives were characterized through NMR spectroscopy and the solid state of **2** was determined through X-ray diffraction. Theoretical calculations suggest a large delocalization of the electrons of tin in the dibenzostannepinic rings for both compounds. The derivatives are stable in the presence of air and moisture, which further improves their potential use as building blocks in the chemistry of organometallic tin compounds. Studies on the use of derivative **5** as a ligand in transition metal compounds are in progress.

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