STUDIA UBB CHEMIA, LXI, 3, Tom I, 2016 (p. 81-90)
(RECOMMENDED CITATION)

Dedicated to Professor Luminița Silaghi-Dumitrescu on the occasion of her 65th anniversary

NEW STANNEPINE DERIVATIVES. SYNTHESIS AND CHARACTERISATION

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ABSTRACT. A new diphenylstannepinic derivative has been synthesized and completely characterized in solution and in solid state (multinuclear NMR spectroscopy, HRMS, X-ray diffraction). As a result of the reaction of the diphenylstannepinic derivative with bromine, a brominated product was evidenced by NMR spectroscopy.

Keywords: *diphenylstannepine, dibromostilbene, dihalostannepine*

INTRODUCTION

The synthesis and characterization of low coordinated compounds containing heavy elements of group 14 remain in actuality [1-4] and represent a permanent interest for our research group [5-7] which is focused on the field of heterophosphapropenes [8,9] and heterophosphaallenes [10] as potential precursors in the production of materials with controlled properties. The chemistry of low coordinated silicon and germanium compounds containing a phosphaalkenyl group is well studied; however, in the case of tin, only a scarce number of phosphastannapropenes have been reported to date [9]. Furthermore, phoshastannaallenes were not reported until now, due to the difficulty in stabilizing the >Sn=C< moiety. The quest for finding the suitable geometric and steric parameters in order to stabilize these systems is a real

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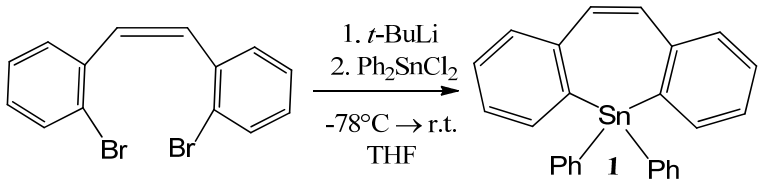
challenge in the synthesis of phospastannaallenes. To stabilize the -P=C-Sn< and -P=C=Sn< fragments, we propose a stannepine type compound based on a tin containing heterocycle, similar with other already reported species [11]. The synthesis of previous phosphastannapropenes in which the tin atom was included in a stannepine ring has been performed via a chlorination of the dimethyl stannepine [9,12]. However, the synthesis of dichlorostannepine starting from its dimethyl analogue is not very convenient; therefore we tried to find a more efficient alternative way for obtaining dihalostannepine derivatives. This paper presents the synthesis and structural characterization of a new diphenylstannepine derivative and some preliminary results regarding the bromination reaction of this compound.

RESULTS AND DISCUSSION

The synthesis of the new diphenylstannepine **1** was realized starting from 1,1'-dibromostilbene, which was allowed to react with diphenyltin dichloride, via a lithiated intermediate, according to the procedure described in literature for the dimethyl analogue [11,12]. The synthetic route to compound **1** is described in Scheme 1.



Scheme 1

Diphenylstannepine **1** was investigated in solution by multinuclear NMR spectroscopy and MS spectrometry. The ^{119}Sn NMR spectrum of compound **1** shows one signal situated at -134.48 ppm, while the dimethylstannepine analog exhibits a specific signal at –76.0 ppm, as shown in the ^{119}Sn NMR spectrum. The ^{1}H NMR spectrum highlights all the specific resonances of the protons in the chemical shift range expected for this derivative. For example, the signal of the protons situated in the CH=CH bridge appears as a singlet at the chemical shift of 6.87 ppm (see experimental part). ^{13}C NMR spectra analysis has led to an accurate attribution of all the signals, in the expected field, for all the carbons atoms. The ^{13}C NMR spectrum is shown in Figure 1.

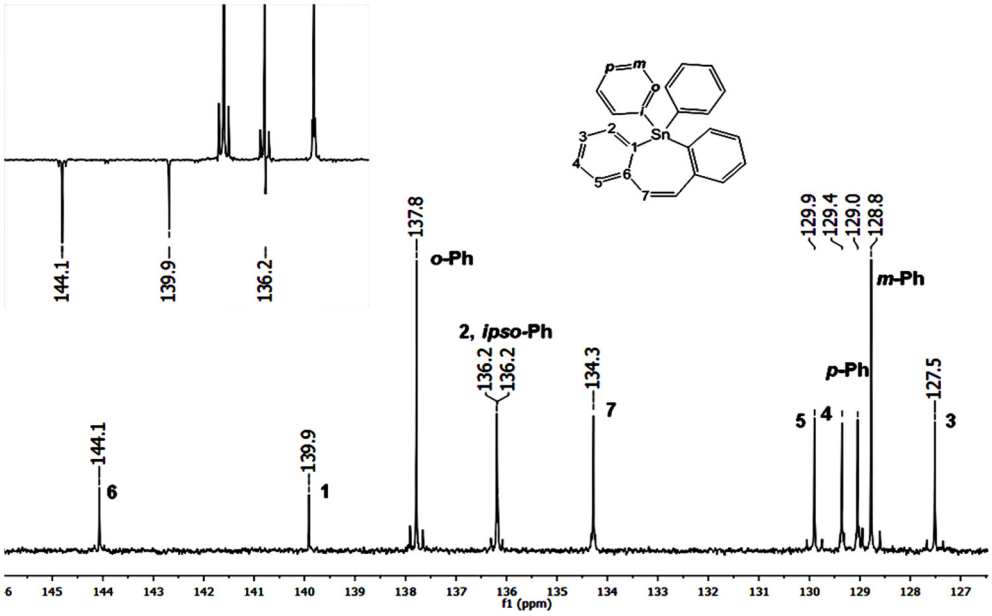


Figure 1. ^{13}C NMR spectrum for the diphenylstannepine **1**.

The assignment of all NMR signals was challenging, since all the resonances appear in a tight area of chemical shifts. Actually, the correct assignment of all signals (in carbon and proton NMR spectrum) was possible using various 2D-NMR experiments (COSY, HSQC, HMBC,) at two working frequencies (400.13 and 600.13 MHz for ^{1}H and 100.61 MHz for ^{13}C, respectively). Two of the most relevant bidimensional NMR spectra (HSQC and HMBC) used for the assignment of the carbon and hydrogen atoms are presented in Figure 2.

From the HSQC experiments (Figure 2a), the assignment of carbon atoms, such as the CH=CH bridge was possible; for this fragment a strong correlation can be seen between the corresponding hydrogen and carbon atoms, respectively the peaks at 6.86 ppm (^{1}H) and 134.3 ppm (^{13}C) in Figure 2. In the HMBC spectra, the same hydrogen atom (namely the protons of the CH=CH fragment situated at 6.86 ppm and highlighted in red on Figure 2) exhibits strong correlations with three other carbon atoms from the stannepinic ring. The identification of all signals from the hydrogen and carbon atoms from compound **1** was possible by corroboration of all the NMR analysis results.

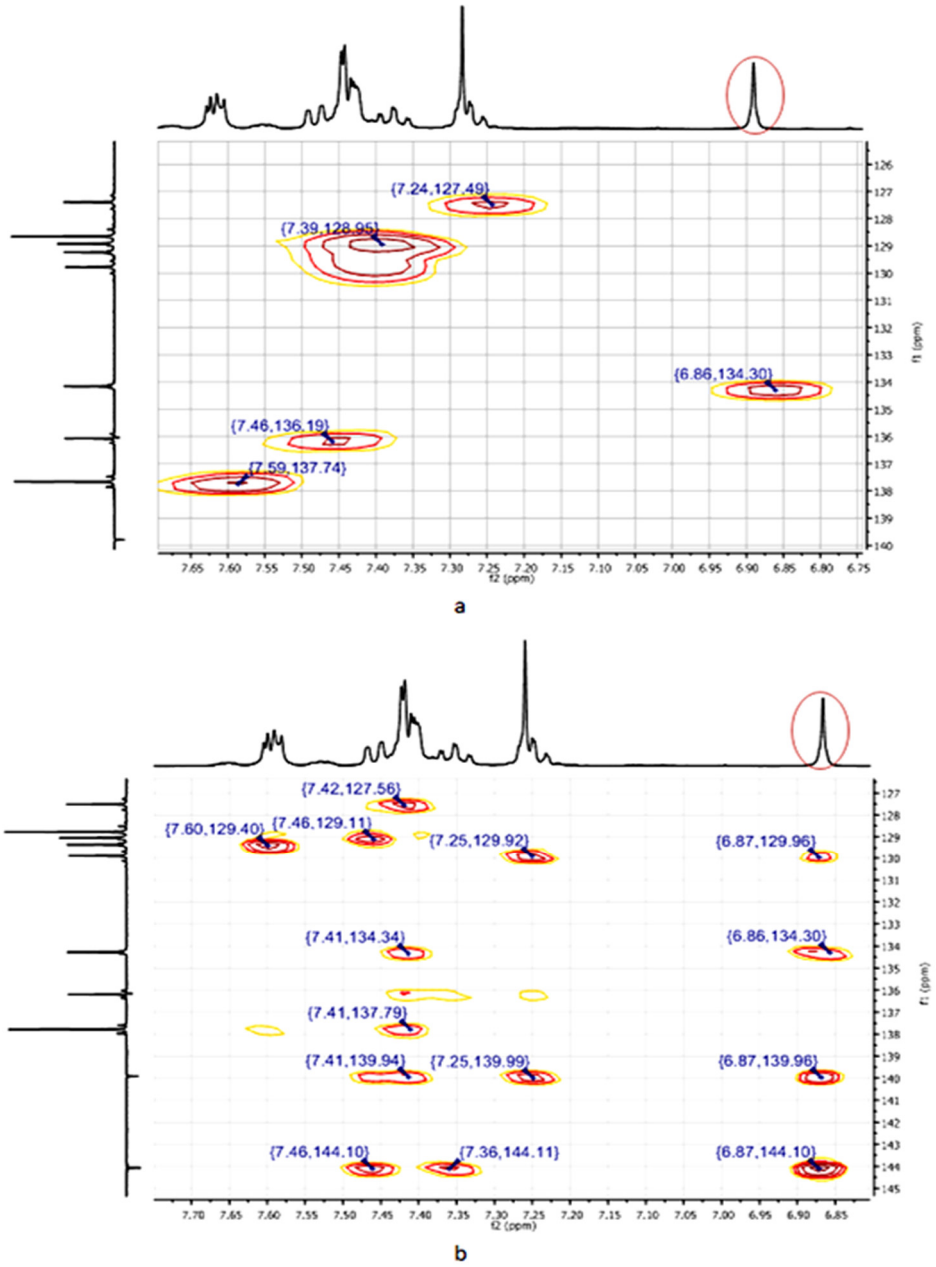


Figure 2. Details of the HSQC (a) and HMBC (b) NMR spectra of the diphenylstannepine **1**.

The molecular structure of compound **1** was determined in solid state by single crystal X-Ray diffraction. The compound crystallizes in a triclinic system in the P1 space group with 2 molecules per unit cell. The crystal and refinement data are summarized in Table 1, (see experimental part). The tin atom has a tetrahedral environment, with the C(13)–Sn(1)–C(21) angle of 100.98(1)° and the C(1)–Sn(1)–C(7) angle of 108.59(1)° respectively (Figure 3). The value of the dihedral angle between the two planes, each containing an aromatic stannepinic phenyl ring is 66.15° in **1**, slightly more open than in the dichlorostannepine analogue (62.06°) [12].

The main geometrical parameters of **1** (bond lengths and bond angles) are shown in Table 2. Comparing the geometrical parameters of diphenylstannepine **1** with the dichloro analogue it is noticed that the $Sn–C_{(stannepine)}$ bond length has similar values (2.12 Å in **1** and 2.11 Å in dichlorostannepine) while the $C_{(stannepine)}–Sn–C_{(stannepine)}$ angle ranges from 100.98° in **1** to 108.55° in the dichlorostannepine [12].

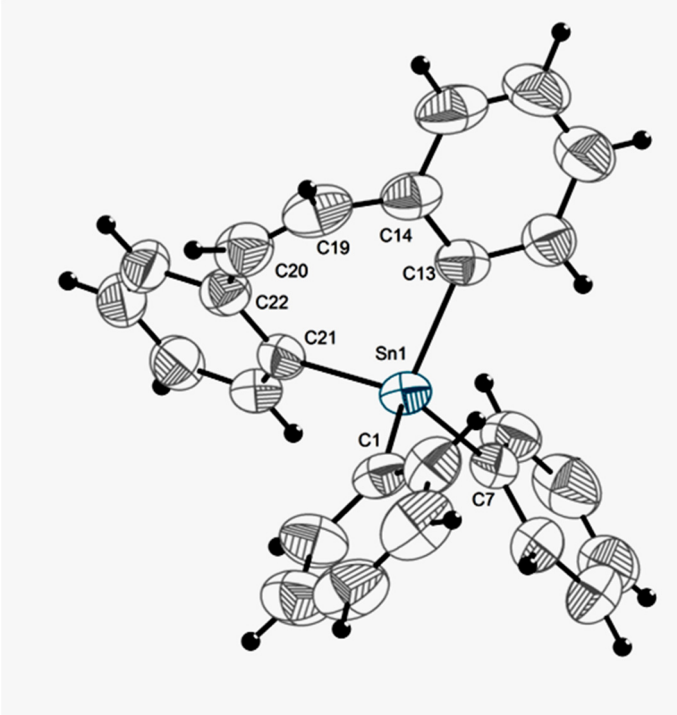


Figure 3. Molecular structure of diphenylstannepine **1** in solid state.
The atoms are drawn with 50% probability ellipsoids

Table 2. Relevant interatomic distances (Å) and angles (°) for compound **1**.

Distances (Å)		**Angles (°)**	
Sn(1) - C(1)	2.1385(3)	C(1) - Sn(1) - C(7)	108.59(1)
Sn(1) - C(7)	2.1319(3)	C(1) - Sn(1) - C(13)	115.45(1)
Sn(1) - C(13)	2.1259(3)	C(1) - Sn(1) - C(21)	111.37(1)
Sn(1) - C(21)	2.1232(3)	C(7) - Sn(1) - C(13)	108.59(1)
C(13) - C(14)	1.3910(2)	C(7) - Sn(1) - C(21)	111.74(1)
C(14) - C(19)	1.4750(2)	C(13) - Sn(1) - C(21)	100.98(1)
C(19) - C(20)	1.3395(2)		
C(20) - C(22)	1.4770(2)		
C(21) - C(22)	1.3921(2)		

An association between two molecules of **1** was revealed in the crystal packing, formed through C–H ··· π contacts as shown in Figure 4. The C-H··· π distance (2.78 Å) and corresponding C–H ··· π α plane angle (29°) are appropriate for such intermolecular interaction and in agreement with the literature data (2.60 - 2.86 Å for sp^2-C–H··· π distance and the α angle <30°). [13, 14, 15]

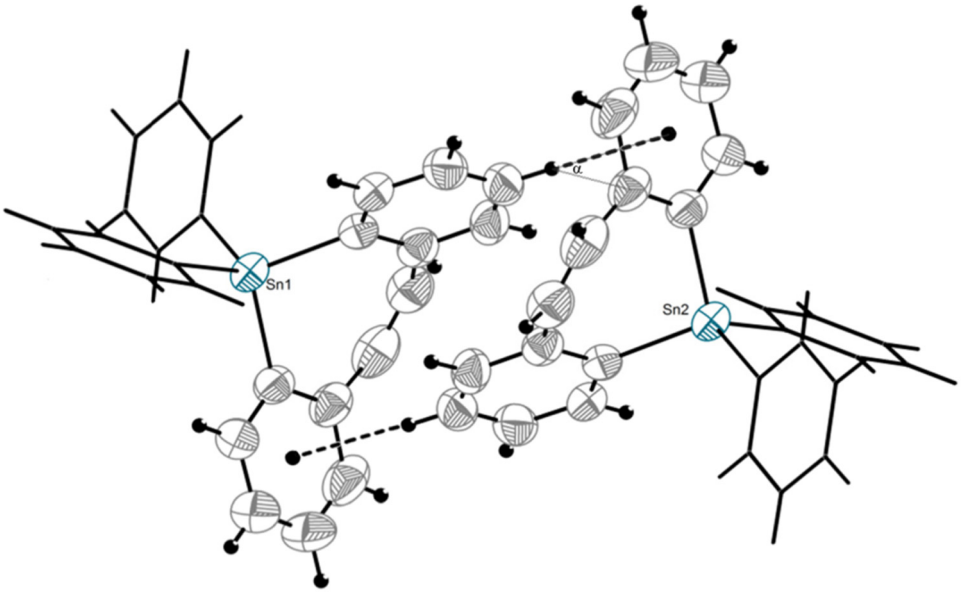


Figure 4. Association in the crystal packing of diphenylstannepine **1**.

Concerning the reactivity of diphenylstannepine **1,** a reaction with bromine in the presence of iron (as a catalyst) [16] was performed. This reaction led to a mixture of compounds, among them a brominated derivative was identified by NMR spectroscopy. ^{119}Sn NMR spectra showed a resonance at -53.26 ppm, at a value of the chemical shift expected for such compounds (when compared to -12.49 for the dichlorinated analogue [12]).

CONCLUSIONS

Two novel stannepine derivatives were evidenced. Diphenylstannepine derivative **1** was completely characterized in solution, by multinuclear NMR spectroscopy experiments, and in the solid state, by a single-crystal X-ray diffraction study. A new brominated stannepine product was evidenced by a preliminary NMR study. The complete characterization of this compound is still in progress since its separation from the reaction mixture could not be achieved yet.

EXPERIMENTAL SECTION

All manipulations were performed under a dry and oxygen free atmosphere (argon) using standard Schlenk techniques. THF was freshly distilled upon Na/benzophenone. 2-bromobenzyl bromide, Ph_3P and 2-bromobenzylaldehide were purchased from Alfa Aesar, *t*-BuOK, *t*-BuLi, Ph_2SnCl_2 from SIGMA-ALDRICH and used as supplied. *Z*-2,2'-dibromostilbene was prepared according to the literature procedure [17].

NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 MHz spectrometer at the following frequencies: 400.13 (reference TMS) for ^{1}H; 100.61 MHz (reference TMS) for ^{13}C; 149.21 MHz (reference $SnMe_4$) for ^{119}Sn and Bruker Avance 600 MHz spectrometer at the following frequencies: 600.13 (reference TMS) for ^{1}H; 125.61 MHz (reference TMS) for ^{13}C. The general notation of the hydrogen and carbon atoms used for assignment of the NMR resonances of compound **1** is shown in Figure 1.

Crystallographic data for the structural analysis were collected at room temperature on a Bruker-SMART APEX instrument by using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å). The crystals were attached with paraton/N oil to cryoloops and the data were collected at room temperature (294 K) (Table 1). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the

software package SHELX-97 was used [18].The drawings were created with the Diamond program [19]. The Crystallographic data for the structural determinations have been deposited in the Cambridge Crystallographic Data Base (CCDC 1465305).

Table 1. Crystal Data and Structure Refinement for **1**.

Empirical formula	$C_{26}H_{20}Sn$	Absorption coefficient (mm^{-1})	1.230
Formula weight	451.11	F(000)	452
Temperature (K)	294(2)	Crystal size, mm	0.330 x 0.280 x 0.260
Wavelength (Å)	0.71073	θ range for data collection (°)	1.835 to 25.000
Crystal system	Triclinic	Reflections collected	9058
Space group	*P -1*	Independent reflections	3517 [R(int) = 0.0461]
Unit cell dimensions		Refinement method	Full-matrix least-squares on F^2
a (Å)	9.3401(13)	Data/restraints/parameters	3517 / 0 / 244
b (Å)	10.3276(15)	Goodness-of-fit on F^2	0.981
c (Å)	11.3543(16)	Final R indices [I>2σ(I)]	R1 = 0.0405, wR2 = 0.0830
α (°)	80.999(2)		
β (°)	80.119(2)	R indices (all data)	R1 = 0.0561, wR2 = 0.0909
γ (°)	77.272(2)		
Volume ($Å^3$)	1044.4(3)	Largest diff. peak and hole, eA^{-3}	0.684 and -0.327
Z	2	Calculated density (g/cm^3)	1.434

***Synthesis of (Z)-5,5-diphenyl-5H-dibenzo[b,f]stannepine* (1)**

A solution of *t*-BuLi (9.18 ml, 15.6 mmol, 1.7 M in pentane, 10% excess) was added dropwise to (*Z*)-2,2'-dibromostilbene (2.4 g, 7.1 mmol) dissolved in 170 ml THF at -78°C. After 2h at this temperature, a solution of diphenyltin dichloride (2.54 g, 7.4 mmol) in 20 ml THF was added dropwise and the reaction mixture was allowed to warm up to room temperature overnight. The resulting solution was quenched with 100 ml of a water:diethylether mixture (1:1). After separation of the phases, the aqueous layer was washed with diethyl ether (2 x 25 ml) and the combined organic layers were washed with brine and dried over Na_2SO_4. All volatile compounds were removed under reduced pressure. Recrystallization from diethyl ether yielded **1** as colorless crystals (1.5 g, 47%).

^{1}H NMR, 400.13 MHz ($CDCl_3$) ppm: 6.87 (2H, s, *CH=CH bridge*), 7.22-7.27 (2H, m, *H-3*), 7.35 (2H, dt, $^3J_{H-H}$ =7.3, $^4J_{H-H}$ = 1.4 Hz *H-para-Ph*), 7.42-7.44 (8H, m, *H-4,5, H-meta-Ph*), 7.46 (2H, $^3J_{H-H}$ = 7.3, $^4J_{H-H}$ = 1.0 Hz, dd, *H-2*), 7.59 (4H, *m*, $^3J_{H-Sn}$ = 50.0 Hz, *H-orto-Ph*).

^{13}C NMR, 100.61 MHz ($CDCl_3$) ppm: 127.5 (*C-3,* $^3J_{C-Sn}$ = 49.1 Hz), 128.8 ($^3J_{C-Sn}$ = 51.5 Hz, *C-meta-Ph*), 129.0 ($^4J_{C-Sn}$ = 9.8 Hz, *C-4*), 129.3 ($^4J_{C-Sn}$ = 11.3 Hz, *C-para-Ph*), 129.9 ($^3J_{C-Sn}$ = 45.7 Hz, *C-5*), 134.3 ($^3J_{C-Sn}$ = 12.0 Hz, *C*H=*C*H), 136.1 ($^1J_{C-Sn}$ = 526.6 and 551.2 Hz, *ipso-C Ph*), 136.2 ($^2J_{C-Sn}$ = 34.1 Hz, *C-2*), 137.8 ($^2J_{C-Sn}$ = 37.9 Hz, *C-orto-Ph*), 139.9 ($^1J_{C-Sn}$ = 499.1 and 477.8 Hz, *C-1*), 144.1 ($^2J_{C-Sn}$ = 28.5 Hz, *C-6*).
^{119}Sn NMR, 149.21 MHz ($CDCl_3$), ppm: -134.48

HRMS [APCI] (m/z): 453.0691 [M^{+1}](calcd. for $C_{26}H_{21}Sn$ = 453.0665); 375.0215 [M^{+1} – Phenyl] (calcd. for $C_{20}H_{15}Sn$ = 375.0196).

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