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Dedicated to professor Gh. Marcu at his 80th anniversary

SYNTHESIS OF NEW BROMO-STANNANES: TOWARD UNSATURATED TIN DERIVATIVES

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ABSTRACT. Two novel organometallic tin derivatives, bis-dibromomethyl-bis-(2,4,6-tri*iso*propyl-phenyl)-stannane **1** and tribromomethyl--bis-(2,4,6-tri*iso*propyl-phenyl)-bromo-stannane **2** have been obtained by the reaction of Tip_2SnF_2 (Tip = 2,4,6-*tri*-*i*Pr-C_6H_2) with bromoform in the presence of *n*BuLi. The compounds were characterized through NMR spectroscopy and the solid state structure of **2** was determined by X-ray diffraction. Compound **2** is a potential precursor of novel stannaalkenes and 1,3-distannaallenes.

Keywords: stannaalkenes, stannaallenes, double bonded derivatives.

Introduction

Chemists have always shown a big interest in the similarity of carbon with other elements from the same group. The quest for analogue derivatives of alkenes, allenes and even cumulenes containing heavier group 14 elements like silicon, germanium or tin has resulted in an increasing number of publications over the last decades [1]. Alkene derivatives of the type >E=C< (E = heavy group 14 elements) are known [2] and in the last five years, heteronuclear unsaturated compounds of the type >E=E'< have been obtained [3].

Stannaalkenes seem to be more difficult to synthesize than their Si and Ge analogues, as shown by the number of such derivatives known to date: five silenes, eight germenes and only four stannenes [2a] are described in the literature. Allenic compounds >Sn=C=C< are also unknown. Only one tin derivative containing cumulated double bonds, a stannaketenimine, has been reported [4].

In this paper, we describe the synthesis and characterization of two potential precursors of stanna-alkenes and -allenes, starting from a sterricaly hindered organometallic tin derivative, Tip_2SnF_2.

For the synthesis of double bonded tin derivatives, the choice of the starting material is important, because of the protective role played by the organic groups on the tin atom in the Sn=C bond. Bulky radicals, like Tip (2,4,6-*i*Pr-C_6H_2), afford sterricaly stabilization of the very reactive tin-carbon bond. The efficiency of Tip as a protection group has already been proved [5]. Scheme 1 summarizes a possible synthetic route which might lead to stanaallenes and stannaalkenes, starting from Tip_2SnF_2:

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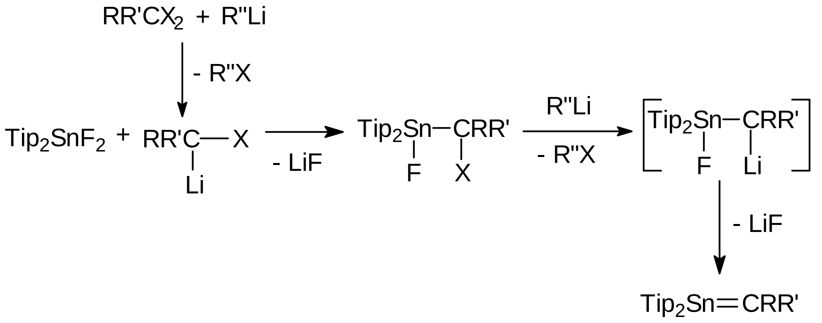
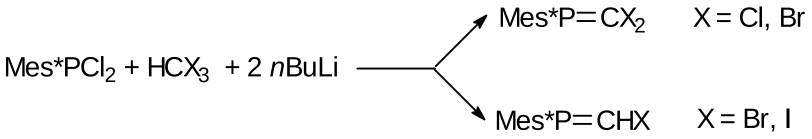


Scheme 1

The reaction of REX_2 derivatives (E = group 15 elements) with chloroform or bromoform in the presence of lithium derivatives always leads to the formation of $RE{=}CX_2$ compounds [6]. The reaction of supermesithyldichlorophosphane Mes^*PCl_2 (Mes^* = 2,4,6-*t*Bu-C_4H_2) with haloforms results in the formation of phosphaalkenes $Mes^*P{=}CX_2$, by means of a lithium carbenoid. Replacement of a halogen atom is possible in the case of bromine and iodine, as shown in Scheme 2.



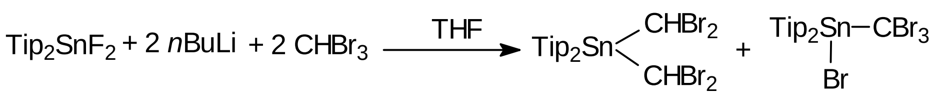
Scheme 2

Similar behavior was recorded for Mes^*AsF_2 [7].

It was therefore interesting to explore the reactivity of halostannanes towards bromoform, in the hope of obtaining the corresponding stanaalkenes $RR'Sn{=}CBr_2$. However, the behavior of dihalosubstituted group 14 derivatives in such reactions is quite different from that of similar group 15 compounds. Thus, when Tip_2SnF_2 was reacted with one equivalent of $CHBr_3$ followed by 2 equivalents of *n*BuLi, several unidentified products were obtained with a very poor yield. In order to improve the yield of the formation of the lithium carbenoids $CLiHBr_2$ and $CLiBr_3$, the reaction of the dihalostannane with two equivalents of bromoform was attempted.

Results and discussion

The reaction of Tip_2SnF_2 with two equivalents of $CHBr_2$ and *n*BuLi was performed at -90°C, in THF and leads to the formation of two main compounds **1** and **2** in a 4:1 ratio (Scheme 3).



1 **2**

Scheme 3

As reported in the literature [6], both $CLiHBr_2$ and $CLiBr_3$ may be formed by the reaction of lithium derivatives with bromoform. The action of the $CLiHBr_2$ carbenoid on Tip_2SnF_2 leads to compound **1**, while $Tip_2Sn(F)CBr_3$ is formed with $CLiBr_3$. A fluorine-bromine exchange is supposed to take place between $Tip_2Sn(F)CBr_3$ and the LiBr formed *in situ*, leading to compound **2**.

Compounds **1** and **2** have been characterized by multinuclear NMR spectroscopy. The relevant NMR data for **1** are given in Table 1.

Table 1

NMR data for $Tip_2Sn(CHBr)_2$

^{1}**H NMR**	^{119}**Sn NMR**	^{13}**C NMR**
1.50 ppm (d, $^{3}J_{HH}$ = 6.4 Hz, 24H, $C\underline{H}_3$, orto-*i*Pr) 1.18 ppm (d, $^{3}J_{HH}$ = 6.4 Hz, 12H, $C\underline{H}_3$, para- *i*Pr) 2.58 (m, $^{3}J_{HH}$ = 6.4Hz, 4H, C$\underline{H}$, orto-*i*Pr) 2.82 (m, $^{3}J_{HH}$ = 6.4 Hz, 2H, C$\underline{H}$, para-*i*Pr) 5.80 (s, 2H, $C\underline{H}Br_2$) 6.96 (s, 4H, meta-C$\underline{H}$ Tip).	-134.2 ppm ($^{2}J_{SnBr}$ = 11.8 Hz)	23.9 ppm ($\underline{C}H_3$, orto-*i*Pr) 24.7 ppm ($\underline{C}H_3$, para-*i*Pr) 32.5 ppm ($\underline{C}$H, orto-*i*Pr) 34.3 ppm ($\underline{C}$H, para-*i*Pr) 40.1 ppm ($\underline{C}HBr_2$) 122.6 (meta-$\underline{C}$H Tip), 150.9 and 151.6 ppm (orto and para-C Tip).

The ^{119}Sn NMR spectrum of compound **1** shows the multiplet resulted from the coupling with the four bromine atoms (Figure 1). Such signals are usually broad and the coupling constant is not observed; to our best knowledge, it is the first time that coupling of tin with such an important number of bromine atoms resulted in an observed hyperfine splitting of the signal and not just in its widening.

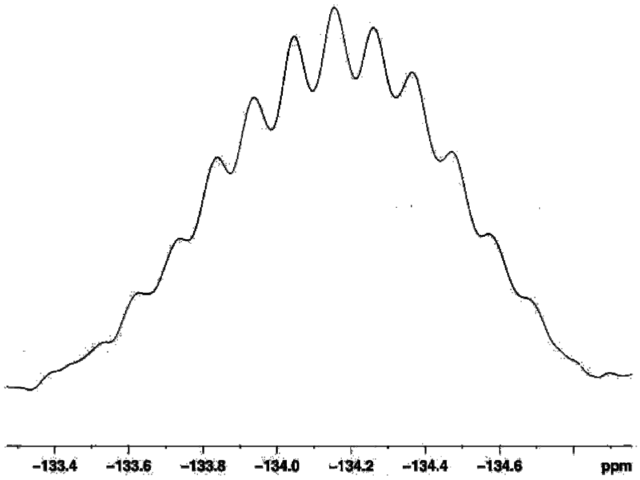


Figure 1. ^{119}Sn NMR signal for $Tip_2Sn(CHBr_2)_2$

The ^{1}H-NMR chemical shifts for compound **2** are within the expected range; the position of all signals is given in the Experimental section. Two different signals were recorded for the two methyl groups in the *o-iso*propyl groups (1.050 ppm, 1.080 ppm respectively). This indicates that the free rotation around the Sn-C bond is significantly hindered, no doubt due to the presence of the sterricaly challenging groups on the tin atom.

Compound **2,** $Tip_2Sn(Br)CBr_3$, was characterized in solid state through X-ray diffraction on single crystal. An ORTEP rendering of the molecular structure is shown in Figure 2. Some geometrical data are also given in Table 2. The presence of the heavy bromine atoms makes the refinement of the structure more difficult. Two equivalent positions atom are possible for the CBr_3 groups, as well as for the Br1 atom, with respect to an axis containing the central tin and acting as a two-fold symmetry axis for the Tip groups. The Sn-Br distance (2.714 Ǻ) is remarkably larger than those found in similar compounds (2.50 - 2.60 Ǻ) [8, 9]. As expected, the geometry about the tin atom is distorted tetrahedral, with wider angles with atoms belonging to the CBr_3 group.

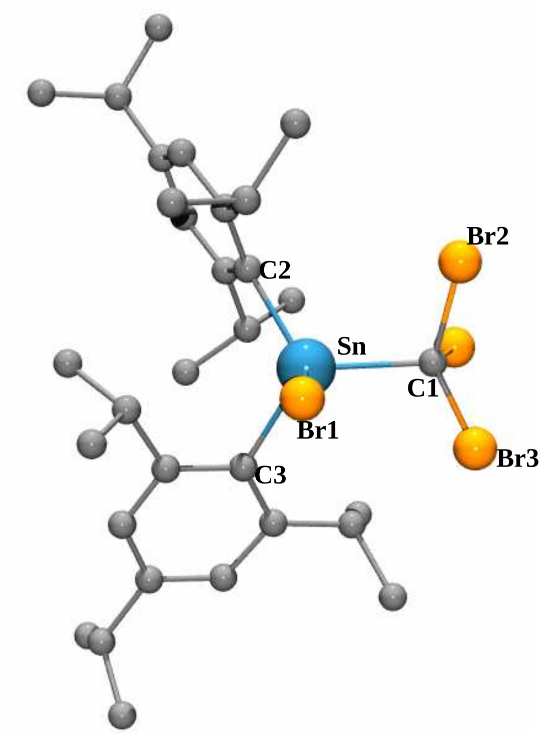


Figure 2. Molecular structure of $Tip_2Sn(Br)CBr_3$ (hydrogen atoms were omitted for clarity)

Table 2

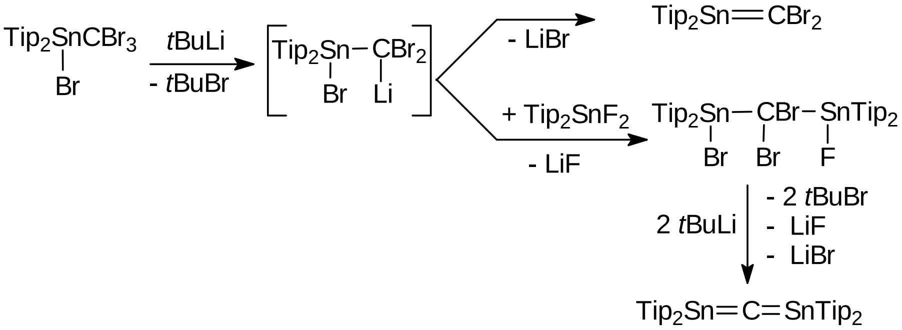
Geometrical data for $Tip_2Sn(Br)CBr_3$

Bond lengths (Å)		**Bond angles (°)**	
Sn-C1	2.227	Br1-Sn-C1	94.19
Sn-C2	2.156	C2-Sn-C3	110.81
Sn-Br1	2.714	C1-Sn-C3	122.70
C1-Br2	1.932	Br2-C1-Sn	104.52
C1-Br3	1.940	Br1-C1-Br2	114.98

Conclusions and perspectives

Two novel organometallic tin derivatives have been obtained. Their structure in solution was elucidated by NMR spectroscopy. The solid-state structure of $Tip_2Sn(Br)CBr_3$ was also determined.

Even though the reaction of Tip_2SnF_2 with bromoform did not lead to the expected stannaalkene, it afforded a potential precursor of double bonded derivatives of tin. Scheme 4 shows the possible use of $Tip_2Sn(Br)CBr_3$ in the synthesis of stannaalkenes and 1,3-distannaallenes.



Scheme 4

The distaannallene $Tip_2Sn=C=SnTip_2$ would be the first compound of this type obtained to date. The proposed synthetic routes are currently under experimental investigation.

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Experimental procedure

All manipulations were carried out under N_2 or Ar using standard Schlenk techniques with solvents freshly distilled from sodium benzophenone. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 250. NMR Spectra were recorded on a Bruckner Varian 200 MHz for ^1H and ^{31}P and 300 MHz for ^{13}C and ^{119}Sn nucleus. $CDCl_3$ was used as a solvent.

Crystal Data for **2** were collected at room temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with MoKα radiation (λ =

0.71073 Å). The structure was solved by direct methods (SHELXS-97) [10] and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 [11].

Synthesis of bis-dibromomethyl-bis-(2,4,6-triisopropyl-phenyl)-stannane **1** *and tribromomethyl--bis-(2,4,6-triisopropyl-phenyl)-bromo-stannane* **2:**

A mixture of 2 g (0.0035 mols) Tip_2SnF_2 and 1.77 g $CHBr_3$ (0.007 mols) in 70 ml THF was cooled at -90℃ and 4.5 ml *n*BuLi 1.6 M (0.0072 mols) were added dropwise. The reaction mixture was stirred for half an hour at -90℃ and then it was allowed to warm up at room temperature. The solvent was removed under vacuum and replaced with 20 ml pentane. Lithium salts were removed by filtration and the filtrate was stored at -25℃. After 24 hours, compound **1** was isolated by filtration as a white powder with a 45% yield. The remaining solution was further concentrated under vacuum and stored at -25℃. Transparent crystals of **2** were isolated after a few hours with a 11% yield.

1: NMR data are given in Table 1;

MS (Z/e): 697 (M-$CHBr_2$), m.p. = 177℃

2: ^{1}H-NMR: 1.050 ppm (d, $^3J_{HH}$=6.2 Hz, 6H, C$\underline{H}_3$, orto-*i*Pr); 1.080 ppm (d, $^3J_{HH}$=5.8 Hz, 6H, C$\underline{H}_3$, orto-*i*Pr); 1.194 ppm (d, $^3J_{HH}$=7 Hz, 6H, C$\underline{H}_3$, para-*i*Pr); 2.567 ppm (m, 1H, C$\underline{H}$, para-*i*Pr); 3.35 ppm (m, 2H, C$\underline{H}$, orto-*i*Pr), 7.080 ppm (s, 4H, meta-C$\underline{H}$ Tip).

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