



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

ONE STEP AWAY FROM PHOSPHASTANNAALLENES: EXPERIMENTAL AND *IN SILICO* INVESTIGATIONS ON PHOSPHASTANNAPROPENES

Agota LINI,^{a,b} Petronela M. PETRAR,^{a,*} Gabriela NEMES,^{a,*} Raluca SEPTELEAN,^a
Luminița SILAGHI-DUMITRESCU^a and Henri RANAIVONJATOVO^b

^a Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, 1 Kogalniceanu str.,
RO-400082, Cluj-Napoca, Roumania

^b Université de Toulouse, UPS, LHFA, 118 Route de Narbonne, F-31062 Toulouse, France, CNRS, LHFA, UMR 5069,
F-31062 Toulouse Cedex 9, France

Received February 2, 2012

New halo compounds, Mes*P=CCl-SnClBis₂ (**1**), Mes*P=C(Cl)-SnBis₂-C(=PMes*)-Sn(Cl)Bis₂ (**3**), (2*t*Bu-Fl)₂SnCl₂ (**4**), Mes*P=CCl-SnCl(2*t*Bu-Fl)₂ (**6**) potential precursors of phosphastannaallenes have been synthesized. The structure of derivatives **1**, **3**, **4** and **6** is discussed based on multinuclear NMR and mass spectrometry. The organolithium intermediates Mes*P=C(Li)-Sn(Cl)Bis₂ (**2**), SnLiCl(2*t*Bu-Fl)₂ (**5**) were evidenced by ³¹P-NMR. NBO analysis was performed on model phosphastannapropenes, in order to gain some insight on the bonding within the Sn-C=P unit.

INTRODUCTION

The lower tendency of tin relative to its group 14 analogues to form stable double bonds is mainly due to the poor orbital overlapping within the π bond. It is well known that in this group, the stabilization of a E=C bond is more difficult for the heavier elements. For example, whereas a large number of compounds containing the Si=C moiety are stable, fewer Ge=C derivatives have been obtained and only a scarce number of Sn=C compounds have been described in literature.

Starting with the synthesis of the first phosphallaene by Yoshifuji in 1984¹ and diphosphaallene simultaneously by Appel, Yoshifuji and Karsch,² the interest in analogues of allenes and propenes containing phosphorus and a heavier atom of group 14 or 15 has gradually increased. The large number of studies describing

phosphateroallenes and phosphaheteropropenes is due to the augmented reactivity of these derivatives through several reactive centers.

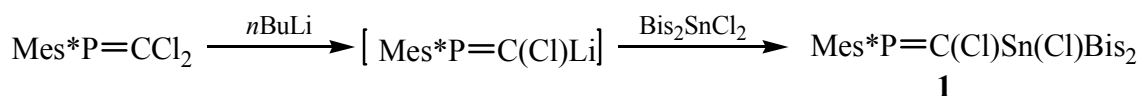
Until now, in the field of heavier group 14 elements, a series of diheteropropenic and -allenic systems have been synthesized. Most of the studies regarding these derivatives are reported in the field of phosphagermapropenes and -allenes,³ only few are focused on phosphasilapropenes and phosphasilaallenes,⁴ and a small number describe phosphastannapropenes.⁵ Until now, no phosphastannaallenes have been isolated, but the Tip₂Sn=C=CR₂ (CR₂ = fluorenylidene) stannaallene was postulated as intermediate in a reaction leading to a distannirane.⁶

The synthesis of a phosphastannaallene -P=C=Sn< thus appears to be a great challenge. For the design of the -P=C=Sn< unit, the choice of a proper synthetic pathway is as important as the

* Corresponding authors: ppetrar@chem.ubbcluj.ro or sgabi@chem.ubbcluj.ro

selection of the bulky organic groups bonded to the P and Sn atoms. A very large steric hindrance on the tin atom is essential in order to prevent the dimerization of the Sn=C double bond. Amongst the most common organic groups used for the synthesis of phosphapropenic and phosphaaellenic compounds are 2,4,6-tri-*tert*-butyl-phenyl (Mes*) 2,4,6-tri-*isopropyl*-phenyl (Tip), 2,4,6-trimethyl-phenyl (Mes), 2,7-di-*tert*-butyl-9-fluorenyl (2*t*Bu-Fl), 9-trimethylsilyl-fluoren-9-yl (Fl-SiMe₃) or bis(trimethylsilyl)methyl (Bis) as well as other bulky groups which could be easily grafted on the tin atom.

Herein, we describe the synthesis and characterization of new phosphastannapropenes, precursors of low-coordinated tin species.



Scheme 1

Surprisingly, derivative **1** was obtained as a mixture of *E/Z* isomers, in a relative ratio of 4:1. The *E* isomer showed a doublet at 43.6 ppm ($^2J_{\text{PSn}} = 363.7$ Hz) in the ^{119}Sn -NMR spectrum and a singlet in the ^{31}P spectrum at 305.5 ppm. The *Z* isomer gives signals at 306.1 ppm in the ^{31}P -NMR spectrum and 12.1 ppm (d, $^2J_{\text{PSn}} = 374.9$ Hz) in ^{119}Sn NMR respectively. The structure of the two isomers was confirmed by mass spectrometry, where all preponderant peaks were assigned to Mes*P=C(Cl)Sn(Cl)Bis₂. The *E* isomer should be formed in higher ratio, because of the selective formation of the *E*-lithiated derivative of Mes*P=CCl₂.

Compound **1** has also been characterized through ^{29}Si -NMR spectroscopy and the spectrum exhibits a doublet at -5.65 ppm with a silicon-phosphorus coupling constant of 58 Hz for the

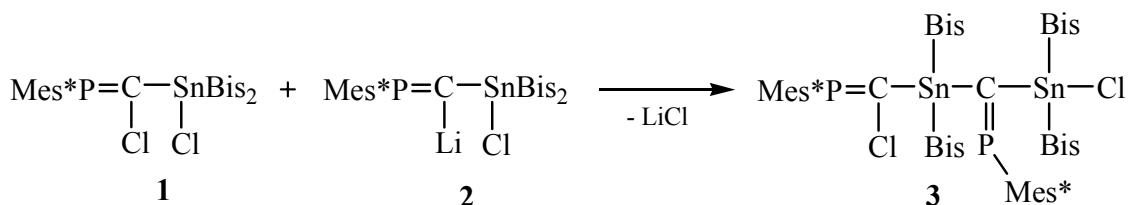
RESULTS AND DISCUSSION

This work presents the synthesis and characterization of new phosphastannapropenes, precursors for new compounds containing the P=C=Sn fragment. For the stabilization of the C=Sn double bond, bulky organic groups such as bis(trimethylsilyl)methyl (Bis) and 2,7-di-*tert*-butyl-9-fluorenyl (2*t*Bu-Fl) have been employed. The Mes* group was used for the stabilization of the P=C unit.

The synthesis of phosphastannapropene Mes*P=C(Cl)-Sn(Cl)Bis₂ **1** was performed starting from Mes*P=CCl₂ and Bis₂SnCl₂,⁷ as depicted in Scheme 1:

major compound. The two Me₃Si groups of a (Me₃Si)₂CH unit are diastereotopic and display two singlets in ^1H -NMR.

The reaction of **1** with *t*BuLi was monitored by ^{31}P -NMR spectroscopy. The presence at 409.8 ppm of a phosphorus signal was assigned to the formation of the lithium derivative Mes*P=C(Li)-Sn(Cl)Bis₂ **2**. After a few hours, the signal at 409.8 ppm disappeared and the postulated lithiate **2** led to a derivative (about 30% ratio) that showed two doublets in the ^{31}P -NMR spectra at 327.1 ppm and 451.4 ppm ($^4J_{\text{PP}} = 33.6$ Hz). Based on these considerations, we propose that rather than undergoing intramolecular elimination of LiCl, the lithium halide was eliminated intermolecularly as the result of a condensation between **1** and derivative **2**, according to Scheme 2.

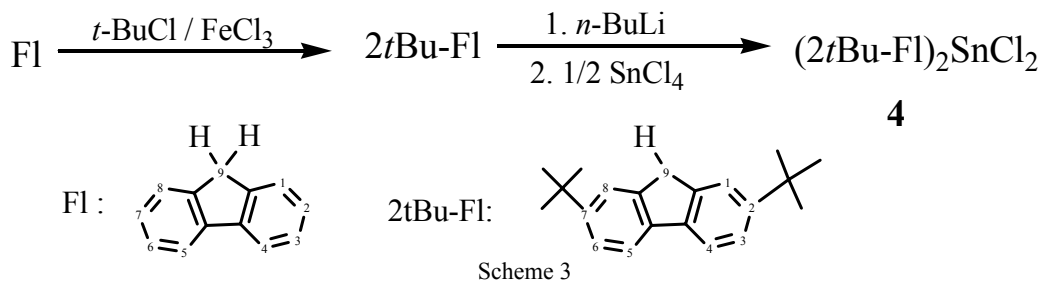


Scheme 2

The proposed structure of **3** would account for the value of 451.4 ppm for the phosphorus atom in the P=C unit bonded to two tin atoms.

In order to avoid such condensation reactions, a slight increase in the sterical hindrance at the tin atom is necessary and we envisaged the synthesis

of phosphastannapropene Mes*P=C(Cl)-SnCl(2*t*Bu-Fl)₂ **6**. The new dichlorostannane (2*t*Bu-Fl)₂SnCl₂ **4**, a precursor in the synthesis of **6**, was prepared following the series of reactions showed in Scheme 3. Compound **4** was crystallized from pentane as white, air- and moisture-stable crystals.



The dichlorostannane **4** was completely characterized in solution by multinuclear NMR spectroscopy and mass spectrometry. The ^1H -NMR spectra shows a signal at 4.37 ppm, specific for the proton placed in the 9-fluorenyl position (Scheme 3), with a coupling constant with the Sn atom of $^2J_{\text{SnH}} = 84.6$ Hz.

Compound **6** was subsequently obtained by the reaction of the lithium derivative **5** with $(2t\text{Bu-Fl})_2\text{SnCl}_2$ (Scheme 4). This reaction was followed through ^{31}P and ^{119}Sn -NMR spectroscopy. The ^{31}P NMR signal corresponding to the supermesityldichlorophosphaalkene ($\text{Mes}^*\text{P}=\text{CCl}_2$) disappeared, giving raise to two other signals, one

at 307.21 ppm ($^2J_{\text{PSn}} = 190.09$ Hz) which corresponds to compound **6** and the second at 250 ppm ($^2J_{\text{PH}} = 46.17$ Hz) specific for $\text{Mes}^*\text{P}=\text{CHCl}$. The ^{31}P -NMR signal attributed to phosphastannapropene **6** has a chemical shift in the specific range for this type of compounds. For example, $\text{Mes}^*\text{P}=\text{CCl}-\text{SiClPhTip}$ with two chlorine atoms in the near vicinity of the group 15 element – which afford about the same electronic environment as for **6** – gives a resonance signal at 319.7 ppm.⁸ In the ^{119}Sn NMR spectrum, the specific signal of the tin atom in compound **6** is observed at 95 ppm ($^2J_{\text{PSn}} = 200$ Hz) (Scheme 4).

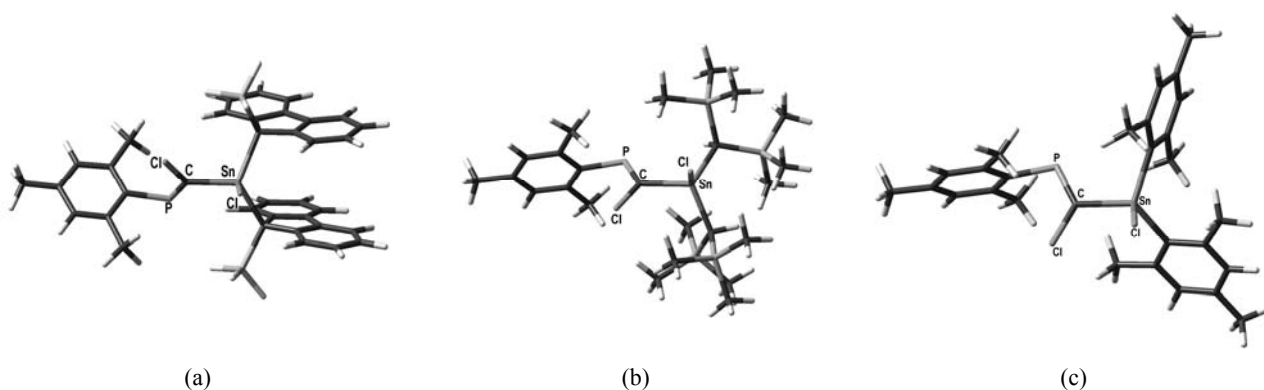
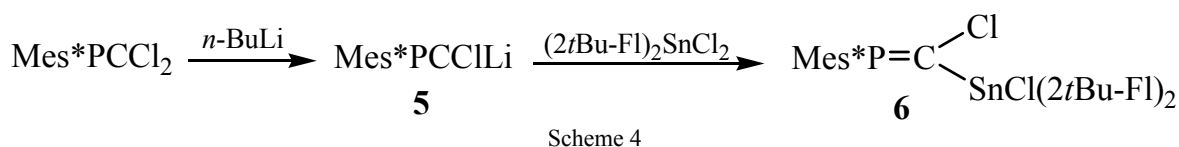


Fig. 1 – B3LYP optimized structures for model compounds of phosphastannapropenes $\text{MesP}=\text{C}(\text{Cl})-\text{Sn}(\text{Cl})\text{R}_2$. (a) R = 9-sylil-9-fluorenyl ($\text{H}_3\text{Si-Fl}$) Sn-C: 2.176 Å, Sn-Cl: 2.379 Å, C-P: 1.683 Å, Sn-C-P: 122.0°, Cl-Sn-C: 101.1°; (b) R = bis(trimethylsilyl)methyl (Bis): Sn-C: 2.182 Å, Sn-Cl: 2.401 Å, C-P: 1.683 Å, Sn-C-P: 121.7°, Cl-Sn-C: 100.9°; (c) R = 2,4,6-trimethyl-phenyl (Mes): Sn-C: 2.166 Å, Sn-Cl: 2.390 Å, C-P: 1.685 Å, Sn-C-P: 118.5°, Cl-Sn-C: 100.2°.

A preliminary theoretical investigation was performed on model phosphastannapropenic derivatives of the type $\text{MesP}=\text{C}(\text{Cl})-\text{Sn}(\text{Cl})\text{R}_2$, using bulky groups as substituents on the tin atom. The calculations were performed at the B3LYP⁹/6-311+G(d,p) level of the theory, using the LAND2TZ basis set for the tin atom. The optimized geometries for three model compounds (R = bis(trimethylsilyl)methyl (Bis), 9-sylil-9-

fluorenyl($\text{H}_3\text{Si-Fl}$), and 2,4,6-trimethyl-phenyl (Mes)) are given in Fig. 1, together with selected geometrical parameters. The values for the Sn-C bond lengths are in fair agreement with experimental data.¹⁰ The geometry around the tin atom is distorted tetrahedral, while the carbon atom of the P=C unit displays a trigonal planar geometry. The calculations showed that even on the model compounds, the steric hindrance at the

tin atom is very important in all the cases. Thus, while the Sn-C bond is kinetically protected, it could be just the presence of such bulky groups on the tin atom which prevents the formation of the lithium derivative of the phosphastannapropene and the subsequent elimination of the lithium salt, leading to the desired phosphastannaallene.

The Mulliken analysis shows that the tin atom has a significant positive charge in all four cases considered, while the carbon atom of the C=P double bond bears a negative charge (Table 1). The calculated Wiberg bond order for the Sn-C bond is low for all the model compounds considered, around 0.53, while the P-C bond order is close to 1.8.

In the case of the substitution with the bis(trimethylsilyl)methyl group, the bonding model

given by the NBO analysis gives an sp hybridization for the valence shell orbitals of the tin atom, with two virtual orbitals corresponding to the p pure orbitals (Fig. 2a and 3a). The bonding between the C=P unit is seen as a donor-acceptor bond, the donor being the carbon atom, with the two electrons localized in an sp^2 orbital (Fig. 2b). The NBO analysis shows a second order perturbation energy with a value of 137.26 kcal for the $C(sp^2) \rightarrow Sn(p)$ electron donation. The high value is also reflected by the important contribution of the carbon NB orbital to the tin one. A similar situation is found for the Sn-Cl bond, where a $Cl(p) \rightarrow Sn(p)$ interaction is evidenced in the NBO analysis (see Fig. 3 for the shape of the orbitals involved).

Table 1

Selected NBO and Mulliken analysis data

R	WBO			Mulliken Charges		
	Sn-C	C-P	Sn-Cl	Sn	C	P
Bis	0.53	1.76	0.62	1.65	-0.68	-0.90
H ₃ Si-FI	0.54	1.75	0.65	1.69	-0.94	-1.03
Mes	0.55	1.76	0.64	1.47	-1.43	-0.47

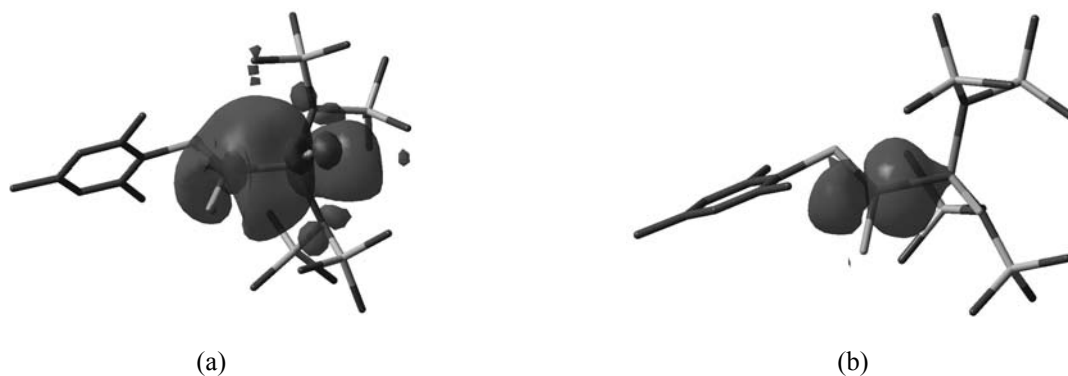


Fig. 2 – Vacant p orbital on the tin atom (a) and occupied sp^2 orbital on the carbon atom (b), involved in the $C(sp^2) \rightarrow Sn(p)$ charge transfer and formation of the Sn-C bond in $MesP=C(Cl)-Sn(Cl)Bis_2$.



Fig. 3 – Vacant p orbital on the tin atom (a) and lone pair on the chlorine atom (b), involved in the $Cl(p) \rightarrow Sn(p)$ electron donation and formation of the Sn-Cl bond in $MesP=C(Cl)-Sn(Cl)Bis_2$.

This correlates well with low bond orders for both the Sn-C and the Sn-Cl bonds, seen as donor-acceptor bonds, rather than covalent ones. The same model applies for the other systems investigated. For the substitution with 2,4,6-trimethyl-phenyl groups at the tin atom, slightly larger values for the second order perturbation energy are reflected by a small increase in the calculated bond orders.

EXPERIMENTAL

All manipulations were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line techniques. Solvents were purified with the MBRAUN SBS-500 purification system. NMR spectra were recorded with a Bruker Avance 300 spectrometer: ^1H (300.13 MHz), ^{13}C (74.48 MHz), ^{31}P (121.50 MHz), ^{119}Sn (111.92 MHz) and ^{29}Si (59.62 MHz) at 298 K in CDCl_3 . Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{\text{H}\}$) or with an external reference (H_3PO_4 for ^{31}P and SnMe_4 for ^{119}Sn). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV.

Synthesis of *E*-{[Bis(bis-trimethylsilylmethyl)chlorostanny]-chloro-methylene}-(2,4,6-tri-*tert*-butyl-phenyl)phosphane **1**

To a solution of 2.12 g $\text{Mes}^*\text{P}=\text{CCl}_2$ (5.9 mmol) in 30 ml of THF, 3.3 ml of *n*BuLi 1.6 M were added at -90°C . The reaction mixture was stirred for an hour at -85°C and then added dropwise to a solution of 3 g of $\text{Bis}_2\text{SnCl}_2$ (5.9 mmol) in 30 ml of THF, cooled at -70°C . The solution was allowed to warm up at room temperature and the solvent was removed under vacuum and replaced with pentane. LiCl was removed by filtration. Several attempts to obtain a crystalline product failed but by eliminating the pentane, a white solid mixture was obtained from which compound **1** was identified by ^{31}P -NMR ($\eta = 50\%$ from ^{31}P -NMR).

^{31}P -NMR: 305.49 ppm (s, $^2J_{\text{PSn}} = 365.66$ Hz), ^{119}Sn -NMR: 43.60 ppm (d, $^2J_{\text{PSn}} = 363.74$ Hz), ^1H -NMR: 0.24 ppm (s, 3H, Me_3Si); 0.27 ppm (s, 3H, Me_3Si); 1.33 ppm (s, 9H, *p*-*t*Bu); 1.49 ppm (s, 18H, *o*-*t*Bu), 7.40 ppm (s, 2H, arom H), ^{13}C NMR: 4.45 ppm (Me_3Si), 31.56 ppm (*p*- $\text{CMe}_3\text{-Mes}^*$), 33.36, 33.44 ppm (*o*- $\text{CMe}_3\text{-Mes}^*$), 35.11 ppm (*p*- $\text{CMe}_3\text{-Mes}^*$), 38.15 ppm (*o*- $\text{CMe}_3\text{-Mes}^*$), 121.80 ppm (*m*-CH- Mes^*), 135.1 ppm (d, $^1J_{\text{PC}} = 71.61$ Hz, ipso- Mes^*), 150.62 ppm (*p*-C- Mes^*), ^{29}Si -NMR: 5.65 ppm ($^3J_{\text{PSi}} = 58$ Hz) 153.86 ppm (*o*-C- Mes^*), 174.25 ppm (d, $^2J_{\text{PC}} = 102.85$ Hz).

Action of *t*BuLi on {[Bis(bis-trimethylsilylmethyl)chlorostanny]-chloro-methylene}-(2,4,6-tri-*tert*-butyl-phenyl)phosphane

A solution of 3.77 g of **1** (4.7 mmol) in 50 ml THF was cooled down to -80°C and then 3.4 ml *t*BuLi 1.5M in hexane (10 % excess) were added dropwise. The reaction mixture was allowed to warm up slowly to room temperature and the THF was removed under vacuum and replaced with pentane. The lithium salts were removed by filtration. Attempts to separate the derivative **3** failed, but the compound was identified

through ^{31}P and ^{119}Sn -NMR. The lithium derivative **2** was also identified in ^{31}P -NMR (409.8 ppm, $^2J_{\text{PSn}} = 982$ Hz).

^{31}P -NMR: 327.12 ppm (d, $^4J_{\text{PP}} = 33.56$ Hz, $^2J_{\text{PSn}} = 365.05$ Hz); 451.35 ppm (d, $^4J_{\text{PP}} = 33.56$ Hz, $^2J_{\text{PSn}} = 415.05$ Hz), ^{119}Sn NMR: 176.7 ppm (d, $^2J_{\text{PSn}} = 415.1$ Hz); 43.9 ppm (d, $^2J_{\text{PSn}} = 365.1$ Hz).

Synthesis of [Bis(2,7-di-*tert*-butyl-fluoren-9-yl)]dichlorostannane (2*t*Bu-FI) $_2\text{SnCl}_2$ **4**

A solution of *n*BuLi 1.6 M in hexane (4.66 ml, 7.4 mmol) was added dropwise, at -90°C , to a solution of 2,7-di-*tert*-butyl-9-fluorene (2 g, 7.2 mmol) in diethyl ether (30 mL). The resulting brown solution was stirred at -35°C for 2 hours and the solvents replaced by 30 mL toluene. The tin tetrachloride SnCl_4 (0.94 g, 3.6 mmol) was then added to the toluene solution of 2,7-di-*tert*-butyl-fluorenyl lithium cooled at -90°C . The reaction mixture was allowed to slowly warm up to room temperature while stirring. Solvents and volatile products were removed in vacuo and the residue was dissolved in pentane (20 mL). Lithium salts were filtered out; yellow crystals were obtained after 12 hours at -20°C (1.2 g, $\eta = 45\%$, mp = 202°C).

^1H -NMR: 1.15 ppm (s, 18, *t*-Bu); 4.37 ppm (t, $^3J_{\text{SnH}} = 84.6$, 1H, C^9); 7.08 ppm (s, 2H, C^1 and C^8); 7.23 ppm (dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H, C^3 and C^6); 7.60 ppm (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H, C^4 and C^5), ^{13}C -NMR: 31.71 ppm (*t*Bu); 34.93 ppm (*t*Bu); 45.34 ppm (C^9); 119.83 ppm (C^1 and C^8); 121.24 ppm (C^4 and C^5), 123.44 ppm (C^3 and C^6); 137.59 ppm (C^{12} and C^{13}); 142.97 ppm (C^{10} and C^{11}); 149.59 ppm (C^2 and C^7), ^{119}Sn -NMR: -11.78 ppm, EI-MS *m/z* (%): 57 (*t*-Bu, 22.2), 189 ($\text{M}^+ - 2\text{Cl}$, 7.5); 277 (FI*, 100); 554 (2FI*, 14.8); 673 ($\text{M}^+ - 2\text{Cl}$, 1); 709 ($\text{M}^+ - \text{Cl}$, 7.5); 774 (M^+ , 1).

Synthesis of {[Bis(2,7-di-*tert*-butyl-9-fluorenyl)chlorostanny]-chloro-methylene}-(2,4,6-tri-*tert*-butyl-phenyl)phosphane $\text{Mes}^*\text{P}=\text{CCl-SnClFI}^*_2$ **6**

To a solution of 1.25 g $\text{Mes}^*\text{P}=\text{CCl}_2$ (3.5 mmol) in 30 ml of THF, 2.29 ml of *n*BuLi 1.6 M in hexane (3.6 mmol) were added at -90°C . The reaction mixture was stirred for 2 hours at -80°C . Then the lithium derivative $\text{Mes}^*\text{P}=\text{CClLi}$ was cannulated slowly on a solution of 2.6 g of (2*t*Bu-FI) $_2\text{SnCl}_2$ **4** (3.5 mmol) in 30 ml THF, cooled at -70°C . The reaction mixture was allowed to warm up to room temperature and the solvent was removed under vacuum and replaced with pentane. LiCl was removed by filtration.

^{31}P -NMR: 307.21 ppm ($^2J_{\text{PSn}} = 200$ Hz), ^{119}Sn - NMR: 95 ppm (d, $^2J_{\text{PSn}} = 200$ Hz).

CONCLUSIONS

The new phosphastannapropenes **1** and **6** containing the P=C-Sn fragment were highlighted. The ability of these compounds to lead to phosphastannaallenic P=C=Sn systems is under investigation. The bond order of the tin-carbon bond in phosphastannapropenes is calculated to be low, around 0.5. The NBO analysis shows that the Sn-C bond has a donor-acceptor character.

Acknowledgements: We thank the Roumanian Ministry of Education and Research (PCCE-140/2008 project) for financial support of this work. A. Lini thanks also POSDRU

(contract 88/1.5/S/60185 – *Investing in people!* “Innovative Doctoral Studies in a Knowledge Based Society” Babeş-Bolyai University, Cluj-Napoca, project co-financed by the Sectoral Operational Program for Human Resources Development 2007-2013.

REFERENCES

1. M. Yoshifuji, K. Toyota, K. Shibayama and N. Inamoto, *Tetrahedron Lett.*, **1984**, 25, 1809-1812.
2. a) M. Yoshifuji, K. Toyota and N. Inamoto, *J. Chem. Soc. Chem. Commun.*, **1984**, 689-690; b) H. H. Karsch, F. H. Kohler and H.-U. Reisacher, *Tetrahedron Lett.*, **1984**, 25, 3687-3690; c) R. Appel, P. Folling, B. Josten, M. Siray, V. Winkhaus and F. Knoch, *Angew. Chem. Int. Ed. Engl.*, **1984**, 23, 619-620.
3. D. Ghereg, E. Andre, H. Gornitzka, J. Escudie, F. Ouhaine, N. Saffon, K. Miqueu and J. M. Sotiropoulos, *Chem. Eur. J.*, **2011**, 45, 12763-12772; b) D. Ghereg, H. Gornitzka and J. Escudie, *Eur. J. Inorg. Chem.*, **2011**, 2, 281-288; c) D. Ghereg, H. Gornitzka, J. Escudie and S. Ladeira, *Inorg. Chem.*, **2010**, 49, 10497-10505; d) J. Escudie and G. Nemes, *Comptes Rendus Chimie*, **2010**, 13, 954-963; e) G. Dumitru, E. Andre, J. M. Sotiropoulos, K. Miqueu, H. Gornitzka and J. Escudie, *Angew. Chem. Int. Ed. Engl.*, **2010**, 49, 8704-8707; f) H. Ramdane, H. Ranaivonjatovo, J. Escudie, S. Mathieu and N. Knouzi, *Organometallics*, **1996**, 15, 3070-3075; g) P. Durand and J.-C. Barthelat, *Theor. Chim. Acta.*, **1975**, 38, 283-302; h) P. M. Petrar, G. Nemes, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, H. Gornitzka and J. Escudie, *Chem. Commun.*, **2007**, 4149-4151; i) Y. El Harouch, H. Gornitzka, H. Ranaivonjatovo and J. Escudie, *J. Organomet. Chem.*, **2002**, 202, 643-644.
4. a) L. Rigon, H. Ranaivonjatovo, J. Escudie, A. Dubourg and J.-P. Declercq, *Chem. Eur. J.*, **1999**, 5, 774-781; b) G. Cretiu Nemes, H. Ranaivonjatovo, J. Escudie, I. Silaghi-Dumitrescu, L. Silaghi-Dumitrescu and H. Gornitzka, *Eur. J. Inorg. Chem.*, **2005**, 6, 1109-1113; c) J. Escudie, H. Ranaivonjatovo, M. Bouslikhane, Y. A. El Harouch, L. Baiget and G. Cretiu Nemes, *Russ. Chem. Bull., Int. Ed.*, **2004**, 53, 1020-1033.
5. P. M. Petrar, G. Nemes, I. Silaghi-Dumitrescu and L. Silaghi-Dumitrescu, *Studia Univ. Babeş-Bolyai, Chemia*, **2006**, 51, 77-82.
6. L. Baiget, H. Ranaivonjatovo, J. Escudie and H. Gornitzka, *J. Am. Chem. Soc.*, **2004**, 126, 11792-11793.
7. N. Wiberg and G. Wagner, *Chem. Ber.*, **1986**, 119, 1455-1466.
8. L. Rigon, H. Ranaivonjatovo, J. Escudie, A. Dubourg and J. P. Declercq, *Chem. Eur. J.*, **1999**, 5, 774-781.
9. a) A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648-5652; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785-789; c) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, **1980**, 58, 1200-1211; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M.J. Frisch, *J. Phys. Chem.*, **1994**, 98, 11623-11810.
10. a) V. D. Romanenko, A. O. Gudima, A. N. Chernega and G. Bertrand, *Inorg. Chem.*, **1992**, 31, 3493-3494; b) C. Jones and A. F. Richards, *J. Chem. Soc., Dalton Trans.*, **2000**, 3233-3234.