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BABEŞ-BOLYAI UNIVERSITY
Faculty of Chemistry and Chemical Engineering

Group 14 elements in multiple bonds systems.

- PhD thesis summary -

PhD Candidate:
Agota Lini (Bartók)

Scientific Advisor:
Prof. Dr. Luminiţa Silaghi-Dumitrescu

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Keywords: phosphaheteropropene; gold-, tungsten- and platinum complexes; low coordinate phosphorus compounds; multiple bonding; heterocycle; DFT; NBO analysis.

General introduction

The synthesis of heteroallenes, compounds containing one or two heavy elements from group 14 or 15, has constituted a new challenge in organometallic chemistry. The unique electronic effects are a consequence of the unusual π-bonding arrangement (the central atom of the allene is sp-hybridized and the π-bond of one double bond is orthogonal to the other). Due to this, such compounds are very interesting from both academic and applied points of view. According to this, the preparation and stabilization of new phosphaheteropropenes P=C-E (E = Si and Sn) and phosphaheteroallenes P=C=E (E = Si and Sn) is a new and important challenge.

The goals of this study were the synthesis, the physico-chemical characterization, the evaluation of the coordination capacity to transition metals, the reactivity- and the theoretical study of some new phosphaheteropropenes, which contain a heavy element of group 14 in their structure. Before this study, there was practically no work done on the theoretical investigation of phosphastannaallenic systems. We concentrated on the ways to stabilize the P=C=E (E = Si, Sn) unit and on the study of compounds deriving from the dimerization reactions occurring at the E=C bond.

Corroborating the experimental results with the theoretical study we described the stability of the studied systems and the factors which influence this stability.

Chapter I reviews the unsaturated compounds of the type E=C=E' (where E and E' are a group 14 or 15 element) described in the literature. We examined the synthesis, the physico-chemical properties (NMR and X-Ray), the theoretical study and the reactivity of group 14 elements in multiple bond systems.

The second chapter of the thesis describes the synthesis, the coordination capacity and the reactivity study of three new phosphasilapropenes Mes*P=C(Cl)-SiPh(R)Cl (R = chlorine, 9-methyl-floren-9-yl and 9-methyl-floren-9-yl). The isolation and purification of these derivatives often proved to be difficult, but NMR spectroscopy provided the means for their characterization in solution.

The third chapter reviews the investigation of unsaturated low coordinated phosphorus compounds with tin atom. After the preparation of four new phosphastannapropenes Mes*P=C(Cl)-Sn(Cl)R (R = methyl, *tert*-butyl, phenyl, 2,7-di- *tert*-butyl -fluorenyl), we describe their reaction with different strong bases (*n*BuLi, *t*BuLi, MeLi). Attempted synthesis of stable phosphastannaallenes is also described and discussed.

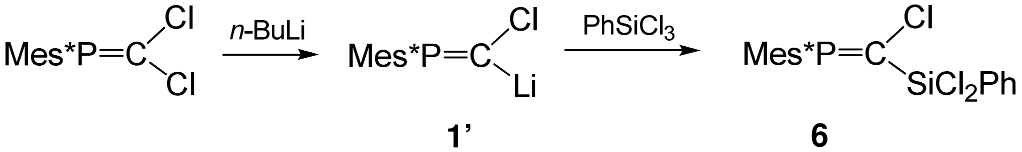
The fourth chapter consists in a theoretical analysis of phosphastannapropenes –P=C–Sn< and phosphastannaallenes –P=C=Sn<. We also study the coordination capacity of phosphastannapropenes to different transitional metals. The explanation for the chemical reactivity of the Sn–C bond in phosphastannapropenes and the Sn=C bond in phosphastannaallenes resides in the electronic structure of the derivatives and the best ways to stabilize these bonds are also indicated as a result of the theoretical study.

Chapter II.
Investigation of unsaturated low-coordinated phosphorus compounds with silicon atom

II.1. Synthesis and physico-chemical characterization of phosphasilapropene derivatives

*II.2.2.1. Synthesis of Mes*P=CCl-SiPh(Cl_2) (6)*

The silyl-substituted phosphaalkene Mes*P=C(Cl)-Si(Cl_2)Ph (**6**) was obtained by reacting the lithium derivative Mes*P=CClLi to $PhSiCl_3$ in THF at low temperature (see Scheme II.1). Derivative **6** was obtained in an almost quantitative yield, as indicated by the ^{31}P NMR spectrum.



1' **6**

Scheme II.1: Synthesis of Mes*P=CCl-$SiCl_2$Ph

Crystallization from pentane afforded single crystals of **6** suitable for X-ray diffraction. The compound crystallizes in the monoclinic system, and a solvent molecule (diethyl ether) is included in the unit cell. The molecular structure of Mes*P=C(Cl)-$SiCl_2$Ph is given in Figure II.2.

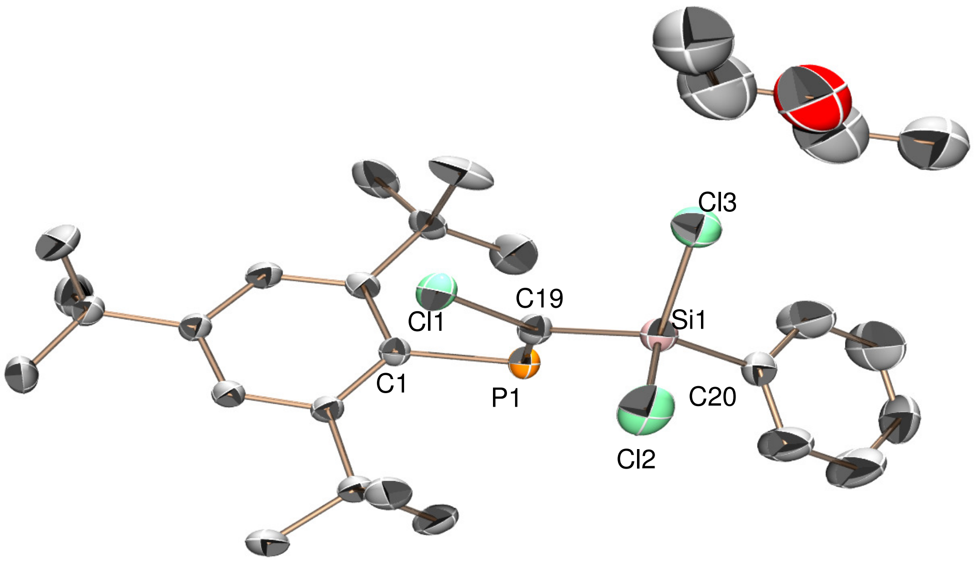
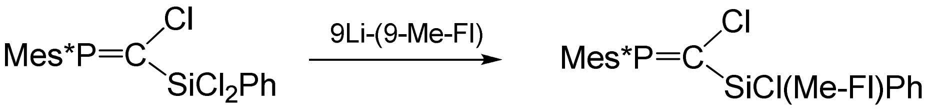


Figure II.2: Molecular structure of compound **6** in the solid state (50 % probability level for the thermal ellipsoids). Hydrogen atoms are omitted for clarity.

*II.2.2.2. Synthesis of Mes*P=CCl-SiCl(Me-Fl)Ph (7)*

In order to thermodynamically stabilize the silapropene **6**, a second R group was introduced on the silicon atom by the addition of a diluted solution of 9-Me-9Li-fluorenyl at low temperature to Mes*P=CCl-$SiCl_2$Ph (Scheme II.7). Phosphasilapropene **7** was characterized in solution through NMR spectroscopy, showing the expected resonance signals for dichlorophosphapropenes.



7.

Scheme II.2: Synthesis of Mes*P=CCl-SiCl(Me-Fl)Ph

The structure of phosphasilapropene Mes*P=CCl-SiCl(Me-Fl)Ph was confirmed in solid state by an X-ray diffraction study on monocrystal (Figure II.3). Phosphasilapropene **7** crystallizes in the monoclinic P21/C space group.

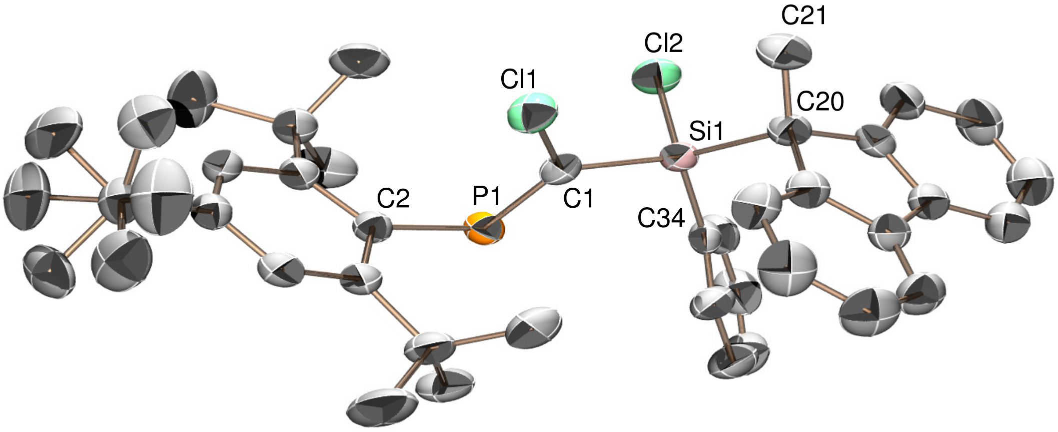
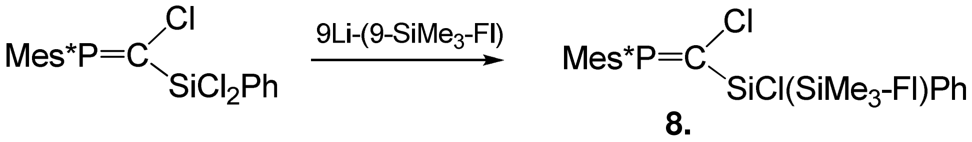


Figure II.3: Molecular structure of compound **7** in solid state (50 % probability level for the thermal ellipsoids). Hydrogen atoms are omitted for clarity.

*II.2.2.3. Synthesis of Mes*P=CCl-SiCl(SiMe$_3$-Fl)Ph (8)*

For the synthesis of a stable phosphasilaallene in monomer state we planned to use the bulkier Mes*P=CCl-SiCl(SiMe$_3$-Fl)Ph (**8**). The preparation of phosphasilapropene (**8**) (Scheme II.3) is similar to the one used in the synthesis of the Mes*P=CCl-SiCl(Me-Fl)Ph (**7**) described above. After the addition of 9Li-9SiMe$_3$-Fl to the starting compound at low temperature, the formation of Mes*P=CCl-SiCl(SiMe$_3$-Fl)Ph was evidenced by ^{31}P-NMR (with a chemical shift at 321.5 ppm).



Scheme II.3: Synthesis of Mes*P=CCl-SiCl(9-SiMe$_3$Fl)Ph

Single crystals of **8** were obtained by recrystallization from pentane (crystal system: triclinic, P1) and the molecular structure was determined in solide state by single crystal X-ray diffraction (Figure II.5).

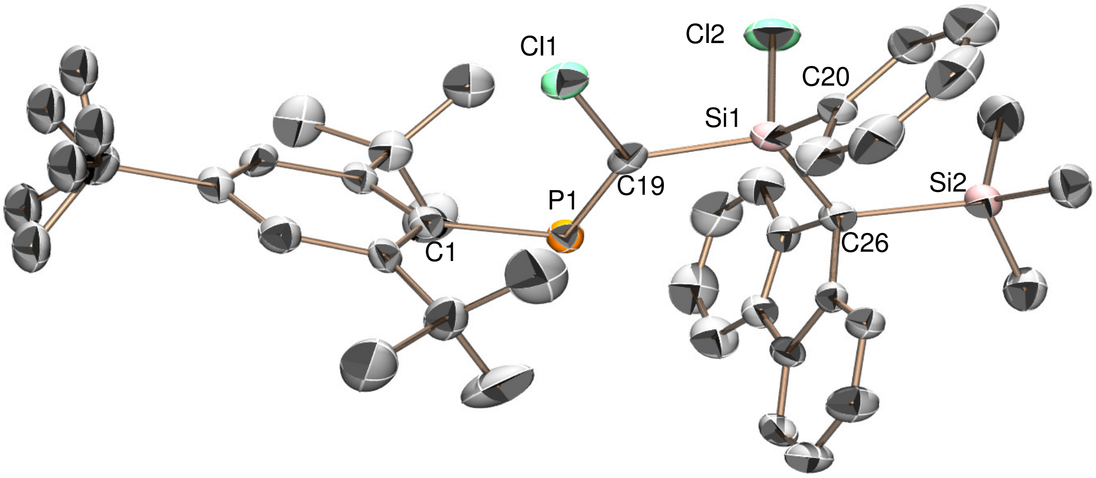


Figure II.5: Molecular structure of compound **8** in solid state (50 % probability level for the thermal ellipsoids). Hydrogen atoms are omitted for clarity.

II. 3. Evaluation of the coordination capacity of phosphasilapropenes to transitional metals

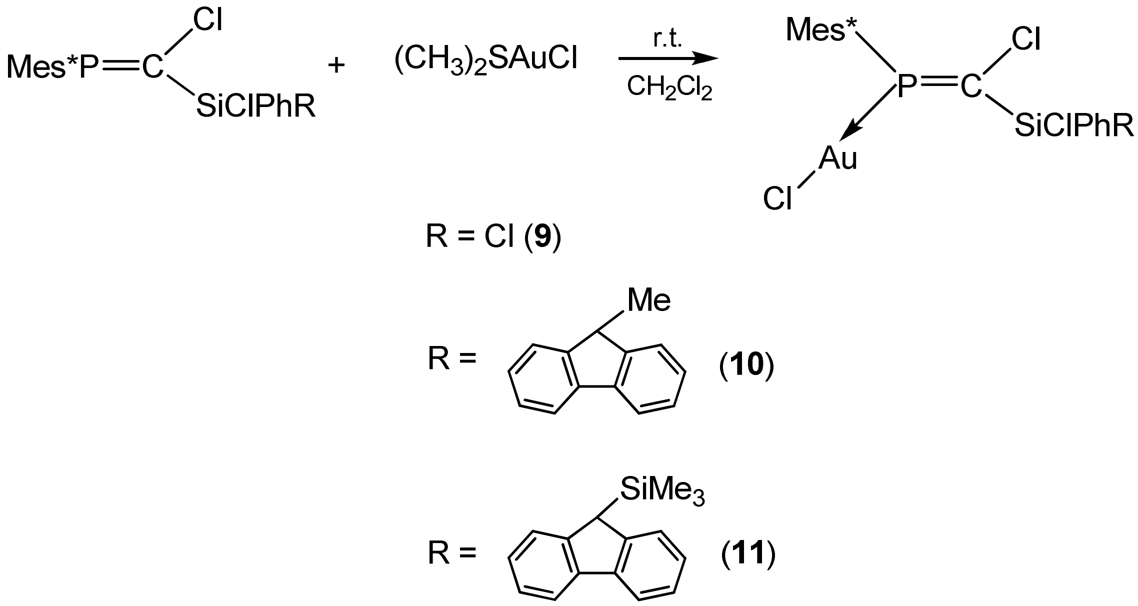
The presence of several reactive centers in the molecules of phosphasilapropenes, such as the phosphorus atom, the P=C double bonds and the chlorine atoms, recommends them as excellent molecular building blocks in organometallic and coordinative chemistry. The introduction of certain groups with different electronic effects like MLn organometalic fragment in the molecule represents an alternative means to stabilize heteroatomic systems with multiple unsaturations.

A reactivity study of phosphasilapropenes towards gold, platinum and tungsten derivatives has been conducted in order to determine their use as ligands for transition metal complexes. In this regard, the coordination possibilities of phosphasilapropenes **6** to platinum atoms, tungsten atoms and **6** - **8** to gold atoms were investigated.

In the literature a similar compound can be found, namely the gold complex of *N*-(trimethylsilyl)imino-bridged-bis-(phosphaalkenes).

II.3.1. Synthesis of gold complexes

Reaction of derivatives **6** - **8** with $Au(SMe_2)Cl$ leads to the formation of new coordination products **9**, **10** and **11** respectively (Scheme II.9). Compounds **9-10** were characterized in solution by multinuclear NMR spectroscopy and MS spectrometry. In order to obtain the desired complexes, we added at room temperature to the corresponding phosphasilapropene the 1 molar equivalent, commercially available chloro(dimethylsulfide)gold(I) using dichloromethane as solvent. According to the molecular structure of phosphasilapropene **12**, the resulted reaction mixture contains only the *E* isomer.



Scheme II.9: General synthetic method for phosphasilapropene-based gold complexes

During recrystallization from commercial pentane, coordinative compound **9** hydrolyzed with the formation of siloxane **12**, for which the solid state structure was determined by single crystal X-ray diffraction (Figure II.8).

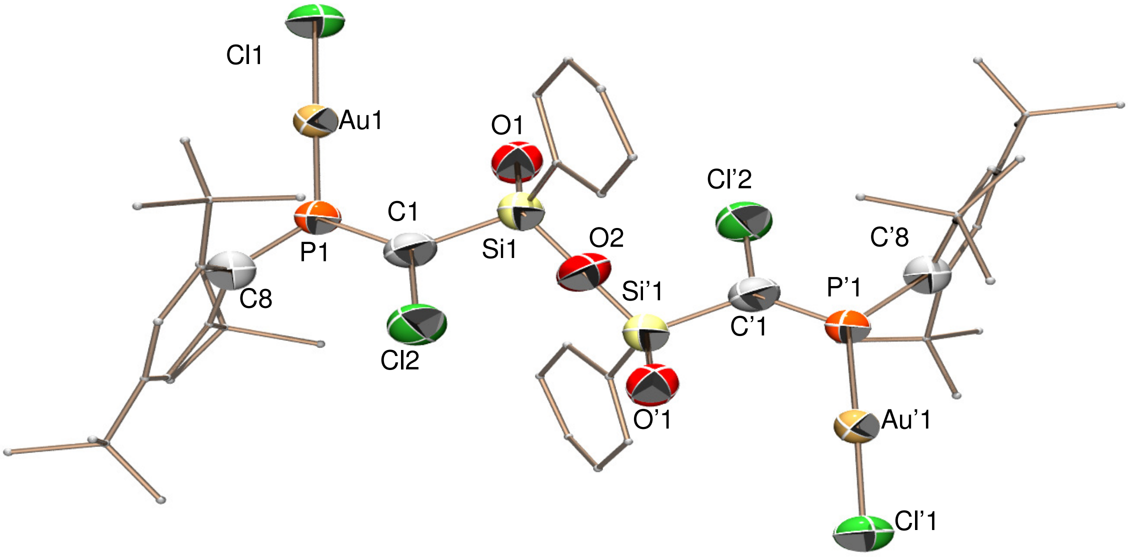
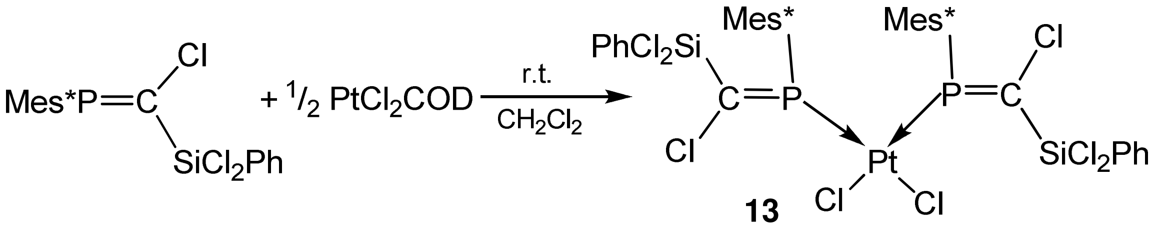


Figure II.8: Molecular structure of **12**. Atoms are drawn as 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

II. 3.2. Synthesis of platinum and tungsten complexes

Other transitional metals used for the complexation of phosphasilapropene **6** were the platinum ($PtCl_2COD$) and tungsten ($W(CO)_6$). To achieve this goal, in the first step we prepared the $PtCl_2COD$ using the methods described in the literature.

The reaction between Mes*P=C(Cl)-$SiCl_2$ and $PtCl_2COD$ fragment is shown in Scheme II.10. Compound **13** was prepared starting from MesP=C(Cl)-$SiCl_2Ph$ and ½ molar equivalent dichloro(cycloocta-1,5-diene)platinum(II) ($PtCl_2COD$), in toluene after the 7 hours of reflux.



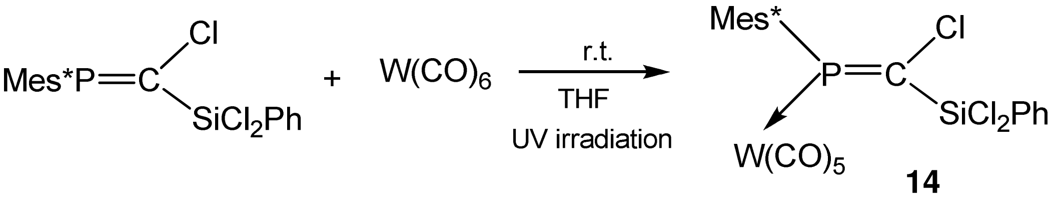
13

Scheme II.10: Synthesis of platinum complex

So far, this compound was characterized through ^{31}P-NMR spectroscopy and the analysis of the spectrum shows that propene **6** has coordinated to the organometallic $PtCl_2$

fragment through the phosphor atom, due to the small shielding of the phosphorus atom induced by the metallic fragment.

In order to synthesize the complex **14**, in the first stage the UV irradiation of the commercially available mono tungsten derivative ($W(CO_6)$) takes place for 1.5 hours in tetrahydrofurane. The one molar equivalent of **6** was dissolved in the same solvent and added to the irradiated $W(CO)_5$ at room temperature (Scheme II.11).



Scheme II.11: Synthesis of tungsten complex

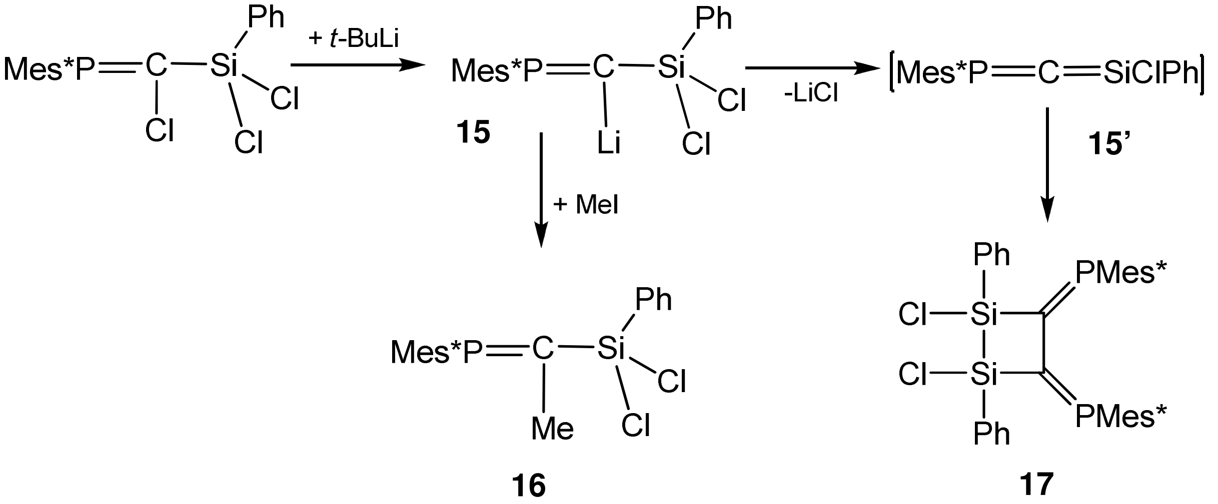
The entire characterization of platinum and tungsten complexes is not complete, because the separation of the compounds failed.

II.4. Reactivity study of phosphasilapropenes with strong bases

One of the aims of the current study was to find the appropriate methods for the synthesis and characterization of stable phosphasilaallene derivatives. According to the procedure used in the case of phosphagermaallenes we have realized a study of the influence of strong bases on phosphasilapropenes **6-8**.

II.4.1. Reaction of Mes*P=C(Cl)-$SiCl_2Ph$ (6) with *t*BuLi

In order to synthesize a stable heteroallene we added *t*BuLi to the Mes*P=C(Cl)-$SiCl_2Ph$ (**6**), forming the lithiated Mes*P=C(Li)-$SiCl_2Ph$ (**15**). Formation of the lithiated compound was revealed in ^{31}P-NMR spectrum. The characteristic signal of the lithiated phosphasilapropene **15** appeared at 394.70 ppm. Then the elimination of lithium salt took place, but the expected phosphasilaallene **15'** was not stable enough to be evidenced by physicochemical methods.



Scheme II.12: Attempted synthesis of Mes*P=C=SiPhCl

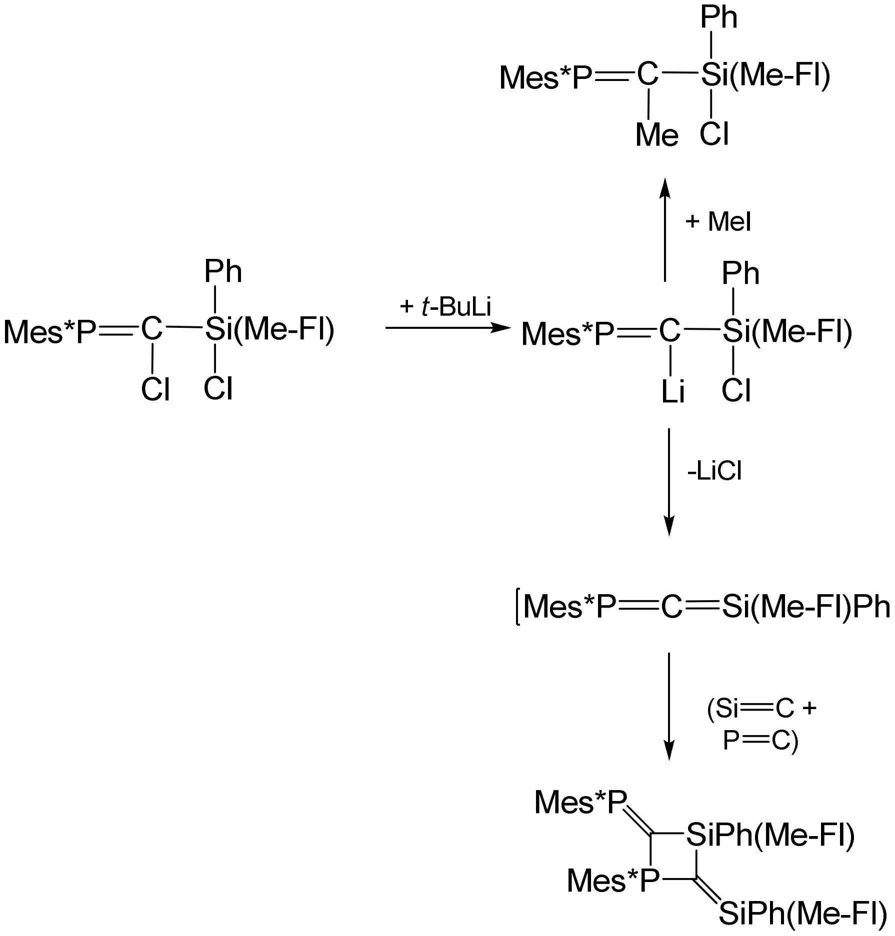
We also studied the reaction between the lithiated Mes*P=C(Li)-$SiCl_2Ph$ (**15**) and the commercially available iodomethane. As the result of the reaction, we have obtained the methilated dichlorophosphasilapropene **16**.

Highlighting the methilated dichlorophosphasilapropene **16** gives the certainty that the synthesis of lithiated derivative **15** took place according to the illustrated method in Scheme II.12.

II.4.2. Reaction of Mes*P=C(Cl)-SiClPh(Me-Fl) (7) with *t*BuLi

The second attempt to prepare a stable silaallene was realized starting from Mes*P=CCl-SiClPh(Me-Fl) (7) and *t*BuLi. A low temperature ^{31}P NMR study was performed on the reaction mixture. Between -30 and 0 degrees only the presence of a singlet at 409.12 ppm could be noticed, which corresponds to the formation of the lithiated derivative Mes*P=CLi-SiClPh(Me-Fl). With the increase of the temperature, the signal characteristic to the lithiated derivative disappeared and two (doublet) signals appeared instead: one of them positioned at 289.6 ppm, while the other at 60.6 ppm (J_{PP} = 30.1 Hz). This chemical shift corresponds to the formation of the head-to-tail dimer from Scheme II.13. The appearance of this dimer certifies the existence of the intermediate phosphasilaallene **18'**.

To be convinced that the addition of *t*BuLi was successful, we added one molar equivalent methyl iodide at - 78 °C to the Mes*P=C(Li)-SiClPh(Me-Fl) (**18**). The synthesized methilated **19** was completely characterized in solution by multinuclear NMR spectroscopy and mass spectometry.



19

18

18’

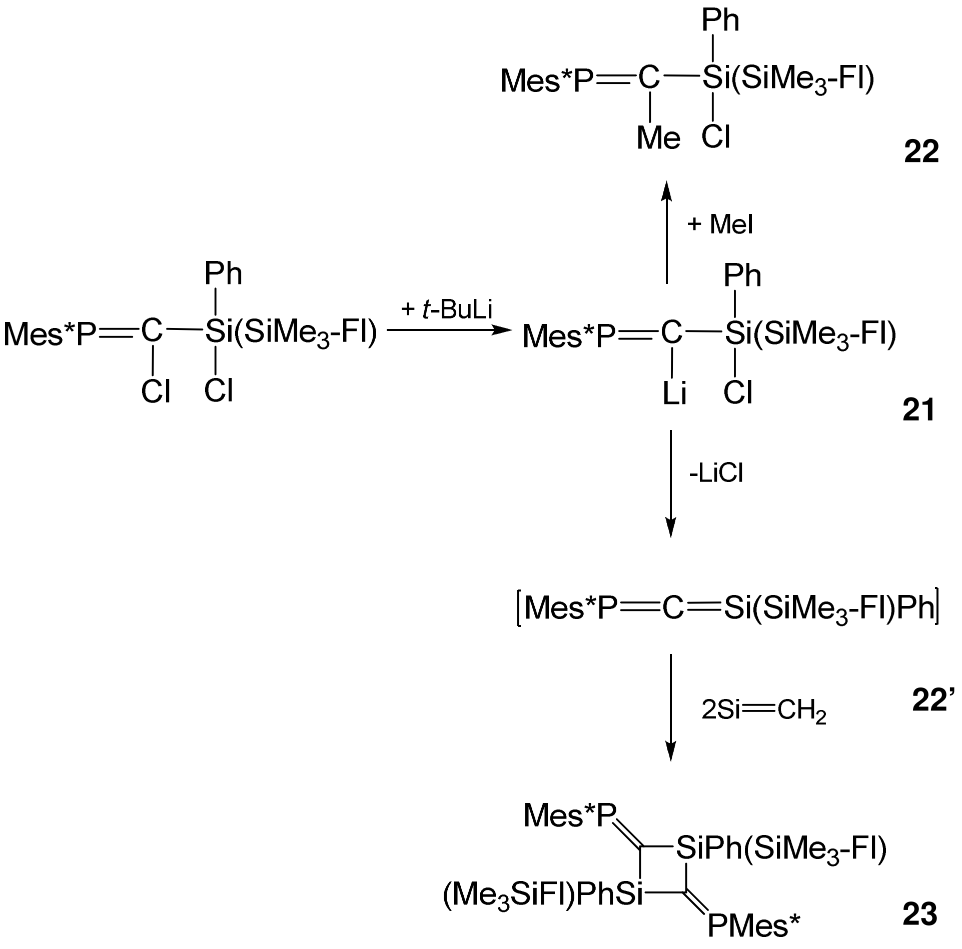
20

Scheme II.13: Attempted synthesis of Mes*P=C=SiPh(Me-Fl)

II.4.3. Reaction of Mes*P=C(Cl)-SiClPh($SiMe_3$-Fl) (8) with *t*BuLi

During the attempt to obtain a stable Mes*P=C=SiPh($SiMe_3$-Fl), the propene **8** undergoes a lithiation reaction with *t*-butyllithium (Scheme II.14). The reaction was monitored with ^{31}P NMR spectroscopy. It could be noticed that the lithiated derivative obtained in this case was stable until 0 °C (400.3 ppm). The formation of a new compound was observed in the reaction mixture at room temperature, giving a singlet signal in the ^{31}P NMR positioned at 435.9 ppm, which corresponds to the formation of a head-to-tail dimer in which the P=C bonds remain outside of the cycle **23**. The appearance of this dimer does neither confirm nor exclude the transition through the intermediary allene state.

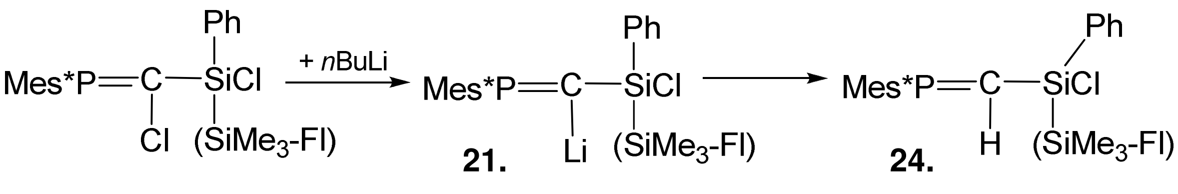
The methilated phosphasilapropene **22** was also prepared by the addition of MeI after the formation of the lithiated compound **21**.



Scheme II.14: Attempted synthesis of Mes*P=C=SiPh($SiMe_3$-Fl)

II.4.4. Reaction of Mes*P=C(Cl)-SiClPh($SiMe_3$-Fl) (8) with *n*BuLi

Due to the failure of making prominent allenes by the addition of *t*BuLi in monomer state, we have made another attempt to obtain a stable heteroallene by the addition of another type of organolithium. The addition of the base takes place amongst the same reaction conditions as in the case of *t*-BuLi, but the formation of the phosphasilaallene could not be observed, the resulted mixture contained only the hydrolyzed phosphasilapropene **24** (see Scheme II.15).



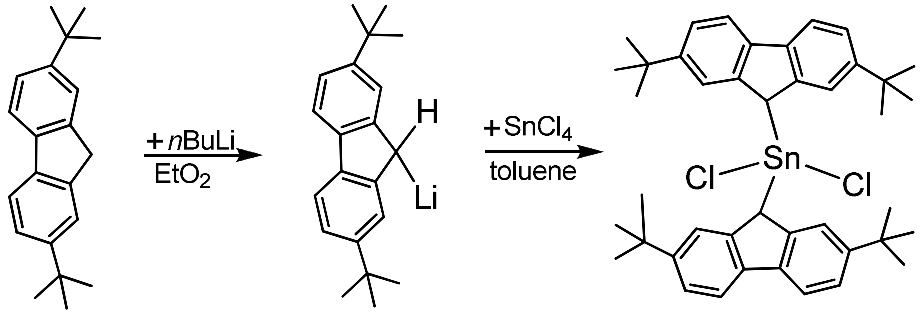
Scheme II.15: Attempted synthesis of Mes*P=C(H)-Si(Cl)Ph($SiMe_3$-Fl)

Chapter III.
Investigation of unsaturated low coordinated phosphorus compounds with tin atom

III.2. Synthesis and physico-chemical characterization of phosphastannapropenes

III.2.1. Synthesis of new dichlorostannane (1)

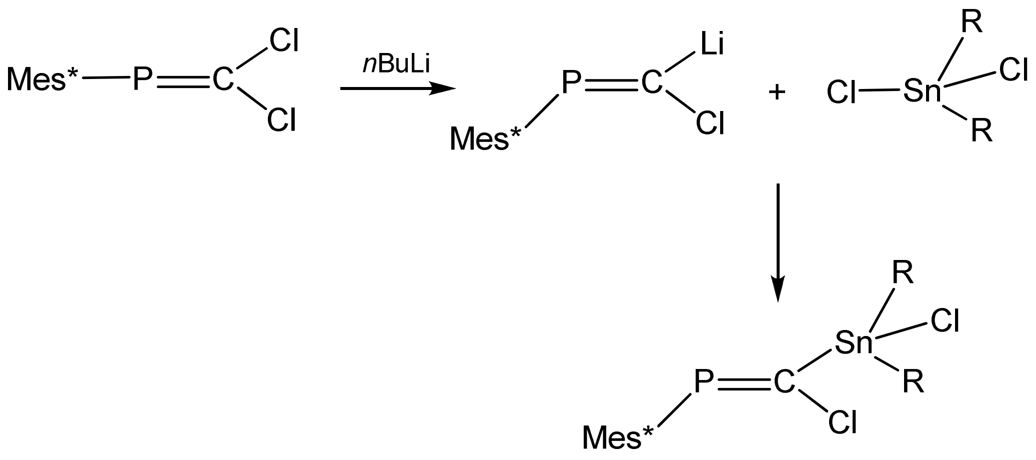
The other precursor used in the synthesis of Mes*P=C(Cl)-SnCl(tBu$_2$-Fl) (**5**) was the (tBu$_2$-Fl)$_2$SnCl$_2$ (**1**). To obtain this precursor, the lithiated dichlorostannane (**1**) was first prepared by the addition of *n*-BuLi to fluorene, at -78 ^{o}C in diethyl ether. The solvent was then removed, and toluene was used in the step involving the addition of SnCl$_4$ (Scheme III.1). The bulky structure of the obtained dichlorostannane **1** can be an advantage in the elimination of the lithium salt from the corresponding phosphastannapropene (**5**).



Scheme III.1: Synthesis of (tBu$_2$-Fl)$_2$SnCl$_2$ (**1**)

III.2.2. Synthesis of phosphastannapropenes

Herein, we describe the synthesis and characterization of new phosphastannapropenes, precursors of low-coordinated tin species containing the P=C=Sn fragment. The general synthetic method for the preparation of phosphastannapropenes **2**-**4** is given in Scheme III.2.



Scheme III.2: General synthetic method for the preparation of phosphastannapropenes **2**-**4**

*III.2.2.1. Synthesis of Mes*P=C(Cl)-SnClMe$_2$ (2)*

The synthesis of the substituted phosphastannaalkene Mes*P=C(Cl)-SnMe$_2$(Cl) (**2**) was performed starting from Mes*P=CCl$_2$ and the commercially available dimethyltin dichloride, as depicted in Scheme III.2. After separation through fractionate recrystallization from pentane, the purified phosphastannapropene **2** was characterized by multinuclear NMR spectroscopy and mass spectrometry.

*III.2.2.2. Synthesis of Mes*P=C(Cl)-SnClBu$_2$ (3)*

Another new phosphaalkene, Mes*P=C(Cl)-SnBu$_2$(Cl) **3**, was prepared in the same conditions, but slightly increasing the sterical hindrance at the tin atom. The commercially available dichlorostannane Bu$_2$SnCl$_2$ was reacted to the lithium derivative of Mes*P=CCl$_2$ (see Scheme III.2). As in the case of derivative **2**, the reaction was carried out at low temperature (-78 ^{o}C) in tetrahydrofuran and due to the selective formation of the *E*-lithiated derivative of Mes*P=CCl$_2$, the *E* isomer of Mes*P=C(Cl)-Sn(tBu)$_2$Cl **3** was obtained. The tin compound **3** was completely characterized in solution by multinuclear NMR spectroscopy.

*III.2.2.3. Synthesis of Mes*P=C(Cl)-SnClPh$_2$ (4)*

The synthesis of Mes*P=C(Cl)-Sn(Cl)Ph$_2$ **4** was carried out in a similar way as the one of phosphastannapropenes **2** and **3**. The lithium derivative of the Mes*P=CClLi was added to a solution of Ph$_2$SnCl$_2$ in tetrahydrofurane at -78 °C (see Scheme III.2).

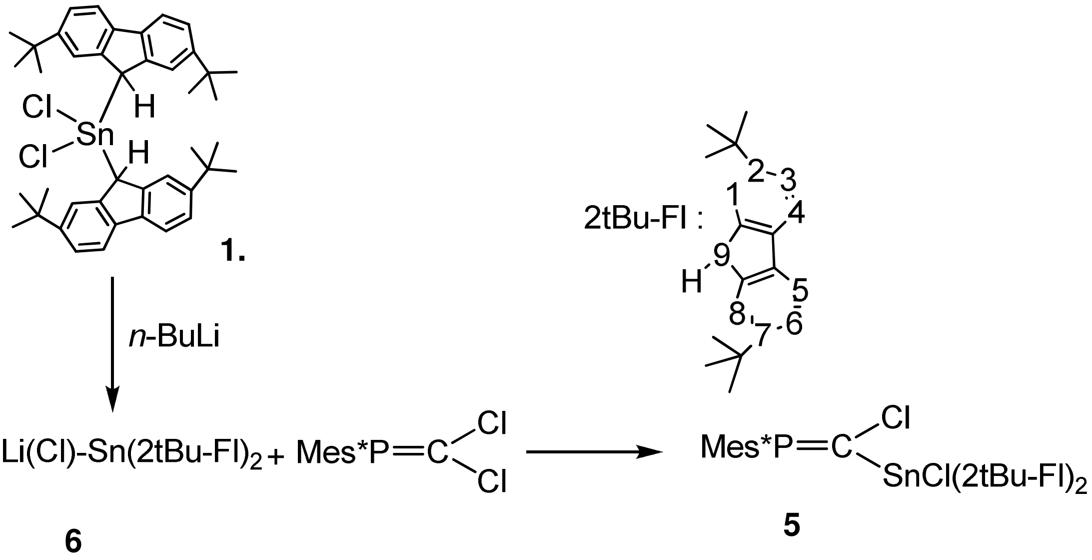
Table II.2: Relevant NMR data for phosphastannapropenes **2** - **4**.

R	^{31}P-NMR		^{119}Sn-NMR		^{13}C-NMR	
	δ(ppm)	J_{PSn} (Hz)	δ(ppm)	J_{PSn} (Hz)	δ*(ppm)	J_{PC} (Hz)
Me	295.0	410.6	69.8	410.6	171.6	88.3
Bu	294.1	339.0	53.1	339.0	172.5	89.0
Ph	301.8	400.6	-87.4	400.6	168.7	89.4
tBu$_2$-Fl	307.2	190.1	-95.0	190.1		

III.2.2.4. Synthesis of Mes*P=C(Cl)-SnCl(tBu$_2$-Fl)$_2$ (5)

In order to increase the sterical hindrance on the tin atom we envisaged the synthesis of phosphastannapropene Mes*P=CCl-SnCl(tBu-Fl)$_2$ (**5**).

Compound **5** was obtained by the reaction of Mes*P=CCl$_2$ with the lithium derivative **6** of SnCl$_2$(tBu$_2$-Fl)$_2$ (**1**) (Scheme III.3). This reaction was followed through ^{31}P and ^{119}Sn NMR spectroscopy.



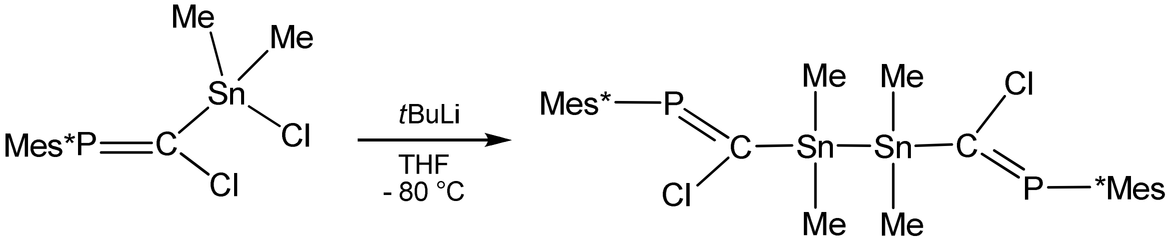
Scheme III.3: Synthesis of Mes*P=C(Cl)-SnCl(tBu$_2$-Fl)$_2$ **5**

III.3. Reactivity study of phosphastannapropene 2 with strong bases

The obtained and characterized stable phosphastannapropenes **2**-**5** are possible precursors in the synthesis of the corresponding phosphastannaallenes. Therefore, a couple of preliminary studies were performed regarding the reaction of strong bases on **2**-**5** derivatives.

III.3.1. Reaction of Mes*P=C(Cl)-Sn(Cl)Me$_2$ 2 with *t*BuLi and MeLi

During the attempt to obtain a stable phosphastannaallene, the 1,3-phosphastannapropene **2** was reacted to *tert*-butyllithium (Scheme III.4). The reaction took place at low temperature, following the same method as in the case of phosphasilapropenes. Probably due to the increased reactivity, highlighting the formation of the corresponding lithiated derivative failed.



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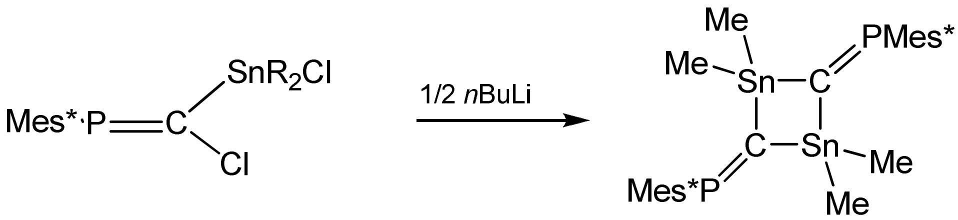
Scheme III.4: Synthesis of Mes*P=C(Cl)-Sn(Me$_2$)-Sn(Me$_2$)-C(Cl) **7**

The same compound was obtained when the reaction was carried out with methyl-lithium instead of *tert*-butyl-lithium.

III.3.2. Reaction of Mes*P=C(Cl)-SnMe$_2$Cl 2 with *n*BuLi

In an attempt to synthesize and structurally characterize a novel phosphastannaallene substituted by two Me groups on the tin atom and a supermesityl group on the phosphorus atom, a 1,3-distanna-cyclobutane with exocyclic P=C double bonds was obtained. The structure of the synthesized derivative **8** was characterized in solution.



2 **8**

Scheme III.7: Synthesis of heterocycle **8**.

IV.3. Theoretical study of model 1,3-phosphastannaallenes

Several computational methods have been tested in order to compare the results obtained and to select the best suited method in the theoretical characterization of phosphastannaallenes. Apeloig already showed that DFT methods describe better than *ab initio* ones the geometry of metallallenes, so both the BP86 and the B3LYP functionals were tested within this study. Also, two different basis sets were considered for the tin atom, the Gaussian built-in LANLDZ and the CRENBL effective potential, both accounting for relativistic effects. High-correlated methods should also be included, although they prove to be time-consuming in the case of vibrational analysis in systems larger than $Me_2Sn=C=PMe$.

We have investigated a series of phosphastannaallenes of the type RR'Sn=C=PR derivatives (R=H, Me, Ph, R', R'= F, Cl, OMe, $SiMe_3$). Table 1 presents selected geometrical parameters obtained with each method in the case of the 1-stanna-3-phosphaallene fully substituted with methyl groups (Figure IV.3).

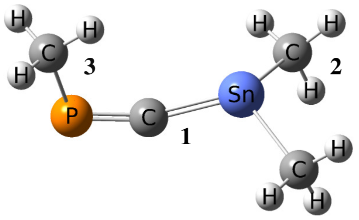


Figure IV.3: The studied model compound.

Table IV.5: Selected geometrical parameters for the $Me_2Sn=C=PMe$ derivative

Method	Sn=C1 (Å)	Sn=C2 (Å)	C1=P (Å)	P-C3 (Å)	Sn-C2-P (°)	C2-Sn-C1 (°)	C1-P-C3 (°)
BP86/LANL2DZ	2.00	2.17	1.69	1.96	165.4	115.5	106.4
B3LYP/LANL2DZ	1.97	2.15	1.68	1.94	167.2	117.7	106.2
B3LYP/CRENBL/ 6-311+G(d,p)	2.05	2.21	1.64	1.89	159.5	115.4	108.7
MP2/CRENBL/ 6-311+G(d,p)	2.01	2.16	1.65	1.87	160.5	116.7	105.1

The data for $Me_2Sn=C=PMe$ summarizes well the trends obtained for all the other derivatives (Table IV.5). In the case of B3LYP/6-311+G(d,p)/CRENBL (which are almost identical to those obtained at the BP86 level), the geometrical parameters obtained are in agreement with experimental data. We will discuss further only the optimized structures using B3LYP/6-311+G(d,p)/CRENBL.

A scan of the Sn-C-P angle was performed, with a step of 10 degrees, and starting from a value of 130°. The value of the stabilization energy afforded by the above mentioned interaction was followed. It is evident that with the increased linearization of the angle, the interaction becomes stronger, thus contributing to a higher bond order of the Sn-C bond. Assuming then that the instability of the stannaphosphaallene is mainly due to the lability of this bond, it would be useful to identify a substituent that would allow a linear structure for the phosphaallenic moiety.

Table IV.7: Correlation between the Sn-C-P angle and Sn-C parameters

Sn-C-P (°)	**WBO Sn=C**	**WBO C=P**	**Sn=C (Å)**	**C=P (Å)**	**E(2) * kcal/mol**
130	1.34	2.04	2.105	1.671	14.5
140	1.35	2.06	2.09	1.658	17.82
150	1.36	2.07	2.076	1.648	21.26
160	1.37	2.09	2.063	1.641	24.42
162	1.37	2.09	2.06	1.639	25.19
170	1.38	2.09	2.05	1.636	26.96
178	1.39	2.09	2.036	1.633	27.99

An experimentalist should also be interested in the fact that the isomer substituted by electron-withdrawing groups at the phosphorus atom is less stable than when the same group is on the tin atom. In the case of the substitution with $SiMe_3$, the position of the group does not influence much the relative stability of the two isomers.

The main problem encountered in the synthesis of heavy phosphaallenes of the type E=C=P (E=Si, Ge, Sn) is the increased reactivity exhibited at the level of the E=C bond once the insaturated compound is formed. The “head-to-head” or “head-to-tail” dimers have been evidenced for both E=Si and Ge. In most of the model compounds discussed above, both the HOMO and the LUMO are situated along the Sn=C bond (see Figure IV.6), which would favor the formation of the cyclic compounds, even in the absence of other reactive species.

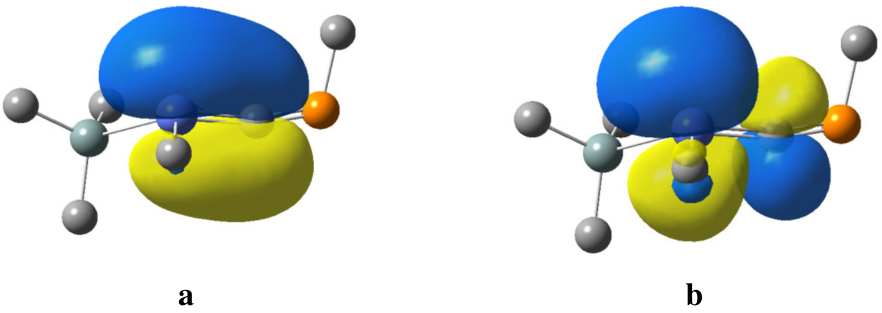


Figure IV.6: Calculated HOMO (a) and LUMO (b) for Me(Me_3Si)Sn=C=PMe (hydrogen atoms were omitted for clarity)

The polarity of the Sn-C bond varies, as expected with the nature of the substituent on the tin atom. Mulliken charges for the atoms in the allenic unit are given in Table IV.8.

Table IV.8: Mulliken charges for H_2R'SNCP derivatives

Molecule	**Mulliken atomic charges**		
	Sn	**C**	**P**
H_2Sn=C=PH	0.62	-0.34	0.05
HFSn=C=PH	0.84	-0.32	0.09
H_2Sn=C=PF	0.76	-0.5	0.24
HClSn=C=PH	0.71	-0.31	0.08
H_2Sn=C=PCl	0.76	-0.29	0
H(MeO)Sn=C=PH	0.81	-0.36	0.06
H_2Sn=C=POMe	0.71	-0.53	0.23
H(Me_3Si)Sn=C=PH	0.48	-0.36	0
H_2Sn=C=PSiMe$_3$	0.47	-0.12	-0.2

Stannaphosphaallenes bearing two R' groups have also been investigated. Two types of isomers, R'$_2$Sn=C=PR and RR'Sn=C=PR' have been considered and compared. The results are summarized in Table IV.9.

Table IV.9: Selected data for R'$_2$Sn=C=PR and RR'Sn=C=PR', calculated at the B3LYP level

Molecule	**ΔE (kcal)**	**Sn=C (Å)**	**C=P (Å)**	**Sn-C-P (°)**	**WB O Sn=C**	**WB O C=P**
F_2Sn=C=PH	0	2.225	1.642	145.42	0.93	2.22

HFSn=C=PF	10.06	2.023	1.63	138.49	1.19	1.99
F_2Sn=C=PMe	0	2.194	1.63	143.59	0.94	2.21
MeFSn=C=PF	6.36	2.029	1.629	135.99	1.13	2.01
F_2Sn=C=PPh	0	2.178	1.63	146.53	0.94	2.17
PhFSn=C=PF	7.81	2.033	1.629	133.22	1.1	2.02
Cl_2Sn=C=PH	0	2.185	1.64	148.69	0.99	2.19
HClSn=C=PCl	16.64	2.031	1.622	150.21	1.19	2.05
Cl_2Sn=C=PMe	0	2.164	1.63	146.81	1	2.17
MeClSn=C=PCl	13.26	2.035	1.62	148.72	1.12	2.07
Cl_2Sn=C=PPh	0	2.15	1.63	149.36	1.01	2.13
PhClSn=C=PCl	14.93	2.036	1.619	146	1.1	2.08
(MeO)$_2$Sn=C=PH	0	2.169	1.649	142.34	1.03	2.15
H(MeO)Sn=C=POMe	2.23	2.036	1.637	131.16	1.18	1.96
(MeO)$_2$Sn=C=PMe	0	2.154	1.64	139.53	1.02	2.13
Me(MeO)Sn=C=POMe	0.77	2.047	1.637	126.08	1.11	1.99
(MeO)$_2$Sn=C=PPh	0	2.136	1.639	144.09	1.03	2.09
Ph(MeO)Sn=C=POMe	6.08	2.031	1.652	126.97	1.24	1.9
(SiMe$_3$)$_2$Sn=C=PH	2.79	2.043	1.643	175.92	1.39	2.04
H(SiMe$_3$)Sn=C=PSiMe$_3$	0	2.115	1.633	154.95	1.22	2.12
(SiMe$_3$)$_2$Sn=C=PMe	2.09	2.043	1.636	174.1	1.39	2.01
Me(SiMe$_3$)Sn=C=PSiMe$_3$	0	2.107	1.637	153.74	1.21	2.1
(SiMe$_3$)$_2$Sn=C=PPh	0	2.028	1.637	178.25	1.4	1.95
Ph(SiMe$_3$)Sn=C=PSiMe$_3$	0.9	2.11	1.636	153.72	1.19	2.11

It can be noticed that by placing two electron-withdrawing groups on the tin atom, the bond order drastically drops. For R'=Cl and OMe, the reason is charge transfer from bonding orbitals along the Sn-C bond (both of σ and π symmetry) towards non-Lewis vacant orbitals situated on the Sn-Cl or Sn-O bond of σ symmetry. See Figure IV.7 for an example in the case of Cl_2Sn=C=PH.

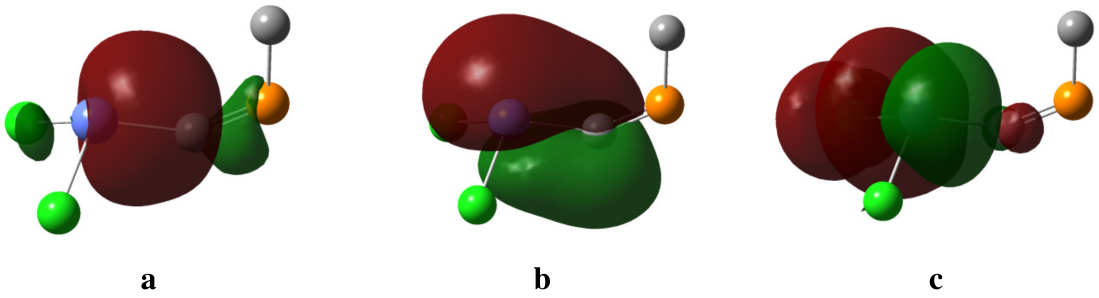


Figure IV.7: NB orbitals involved in electron-transfer interactions leading to a decrease in the Sn=C bond order for $Cl_2Sn=C=PMe$: (a,b) occupied bonding orbitals situated on the Sn-C bond; (c) vacant orbital with antibonding character on the Sn-Cl bond

The trimethylsilyl substituent proves to be the best choice for the stabilization of a stannaphosphaallene, as the Wiberg bond order of the Sn=C bond is the highest calculated for all considered compounds. It can be noticed that the value of the Sn-C-P also tends to an ideal value of 180°.

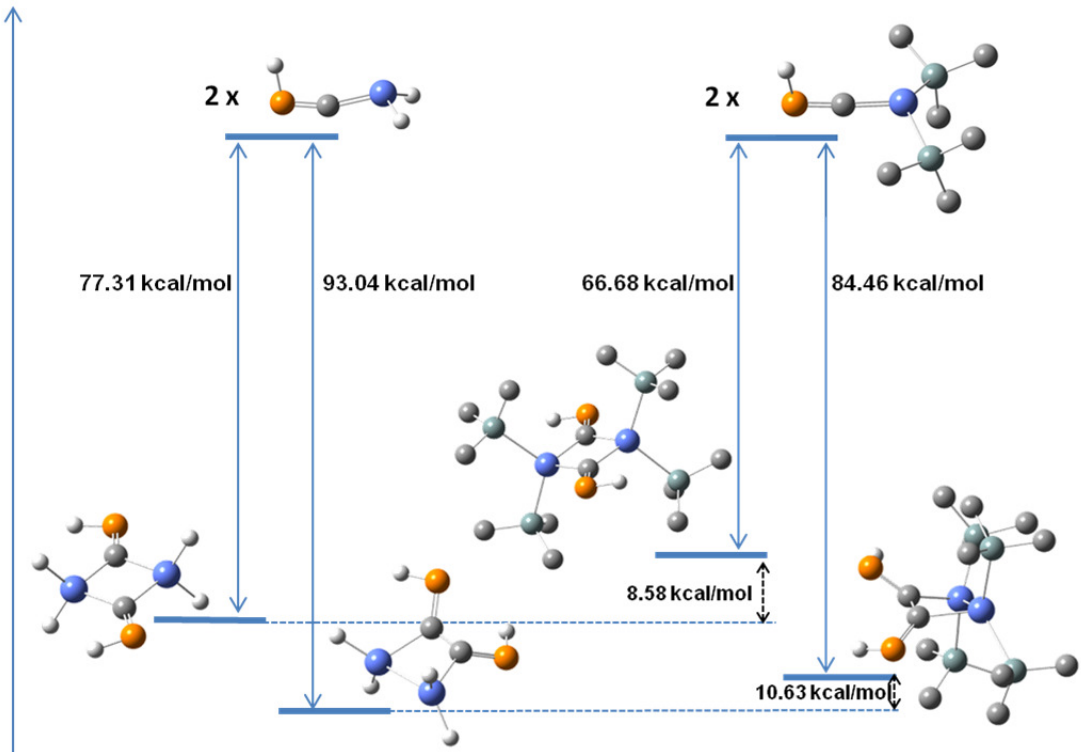


Figure IV.9: “Head-to-head” and “head-to-tail” dimerisation energies for $H_2Sn=C=PH$ and $(Me_3Si)_2Sn=C=PH$

The energies of ‘head-to-head’ and ‘head-to-tail’ dimers of $(Me_3Si)_2Sn{=}C{=}PH$ were calculated and the dimerisation energy was estimated by the formula $E=E_{dimer}-2*E_{monomer}$. For comparison, the same procedure was applied to the $H_2Sn{=}C{=}PH$ derivative. The results are given in Figure IV.9.

General conclusions

This study presents the synthesis, reactivity and theoretical investigations of new species of group 14 elements containing double bonds. The original results focus on the synthesis of novel unsaturated derivatives containing the -P=C-E< unit (E = Si, Sn).

Stable phosphasilaalkenes of the type Mes*P=C(Cl)-Si(Cl)R_2, potential precursors of phosphasillaallenes, are the target of the study described in the second chapter of the thesis. Starting from synthetic routes already described in the literature, but varying the nature of the substituents on the heavier atom, *three new silyl-substituted phosphaalkenes have been obtained and fully characterized*. The elucidation of their structure brings new insight on the possibilities of synthesizing stable phosphasilaallenes. The reactivity of these species was also investigated. Their reaction with different strong bases was performed in order to find the path to new phosphasilaaallenes. In the same time, we evaluated their coordination ability to transition metals which led to six novel transition metal complexes, in which the phosphaalkenes P atom acts as a lone pair donor. During these studies, *nineteen novel derivatives containing the P=C-Si unit have been synthesized.*

The synthesis of the phosphaalkenyl-tin analogues was also carried out. Four new phosphastannapropenes Mes*P=C(Cl)-Sn(R_2) (R = Me , *t*Bu, Ph, di-*tert*-butyl-fluorenyl) were prepared and characterized displaying an unexpected stability. The action of strong bases (*t*BuLi, MeLi) on the less crowded Mes*P=C(Cl)-SnMe_2 leads to a novel heterocycle, a 1,3-distanna-cyclobutane with exocyclic C=P bonds. On the contrary, reaction with *n*BuLi promotes the formation of a Sn-Sn bond within a novel derivative, the structure of which has been proposed based on NMR data. A total of *eight compounds have been prepared and characterized for the first time, six of which contain the P=C-Sn unit.*

Theoretical studies have also been carried out in order to increase the experimental knowledge obtained and are described in chapter four. They focus on tin derivatives and include an analysis of the role that substituents on both phosphorus and tin play in the stabilization of P=C=Sn species. Thus, the bond order of the Sn=C bond can be increased by using groups with electron-donor effects, like silyl or trimethylsilyl. Our results suggest that Mes*P=C=Sn($SiMe_3$)$_2$ would be a stable phosphastannaallene. The coordination ability of model phosphastannaalkenes to various transition metal organometallic fragments has also been investigated. The data indicates that, as in the case of phosphasilaallkenes, coordination through the phosphorus atom is preferred.

This work provides a useful insight in the chemistry of organometallic derivatives of group 14 elements and their ability to lead to unsaturated compounds with cumulated double bonds.

Scientific papers

1. Agota Bartok, Raluca Septelean, Petronela Petrar, Gabriela Nemes, Luminita Silaghi-Dumitrescu, Henri Ranaivonjatovo, Sonia Mallet-Ladeira, Nathalie Saffon, Catherine Hemmert, Heinz Gornitzka, **New Silyl-Substituted Phosphaalkenes Mes*P=C(Cl)-Si(Cl)Phr, Promising Building Blocks In Silicon and Phosphorus Chemistry**, *J. Organomet. Chem.*, **2012**, *10.1016/j.jorganchem.2012.10.017*

2. Petronela Petrar, Agota Bartok, Gabriela Nemes, Luminita Silaghi-Dumitrescu, Jean Escudié , **In Silico Quest for Stable Phosphastannaallenes**, *Comptes Rendus Chimie*, **2012**, *DOI: 10.1016/j.crci.2012.10.013.*

3. Agota Lini, Petronela Petrar, Gabriela Nemes, Raluca Septelean, Luminita Silaghi-Dumitrescu and Henri Ranaivonjatovo, **One Step Away From Phosphastannaallenes: Experimental and *In Silico* Investigations On Phosphastannapropenes**, *Rev. Roum. Chim.* **2012,** *vol.omagial I. Haiduc*, *in press.*

4. Petronela Petrar, Raluca Septelean, Agota Bartok, Noemi Deak, Gabriela Nemes, Ioan Silaghi-Dumitrescu, **Novel Phosphagermapropenes, Precursors for Heteroallenes Stabilized Through Intramolecular Coordination**, *Studia Chemia*, **2012,** 57(2), 119-127.

5. Cristina Bischin, Camelia Tusan, Agota Bartok, Ionel Haiduc, Radu Silaghi-Dumitrescu, **A Battery of Tests for Evaluation the Effect of Experimental Drugs on Oxidative and Nitrosative Stress Pathways Involving Metallocenters,** *Studia Chemia*, **2012**, sent for publication.

Oral communications

1. Raluca Şeptelean, Agota Bartok, Petronela Petrar, Luminiţa Silaghi-Dumitrescu, Gabriela Nemeş, **New Phosphasilapropenes- Synthesis and Coordination Ability**, *XXXII-a Conferinţă Naţională de Chimie,* Căciulata, 03-05 October 2012.

Poster communications

1. Agota Bartok, Raluca Septelean, Petronela Petrar, Gabriela Nemes, Luminita Silaghi-Dumitrescu, **Synthesis And Characterization Of New Phoshasilapropenes,** *4th EuCheMS Chemistry Congress,* Praha, 26-30 August 2012.

2. Noémi Deak, Petronela Petrar, Agota Bartók, Gabriela Nemeş, **Synthesis and Characterization of New Phosphastannapropenes**, *XXXII-a Conferință Națională de Chimie,* Căciulata, 03-05 October 2012.

3. Agota Lini, Raluca Septelean, Gabriela Nemes, Luminita Silaghi-Dumitrescu, Henri Ranaivonjatovo, **Group 14 elements in multiple bonds systems**, *11th International Symposium on "Metal Elements in Environment, Medicine and Biology", MEEMB 2011*; Cluj-Napoca, 05 December 2011.

4. Agota Lini, Noemi Deak, Raluca Septelean, Gabriela Nemes, Luminita Silaghi-Dumitrescu, Henri Ranaivonjatovo; **New Ruthenium Coordinative Compound Using Dichlorophosphasilapropene as Ligand** ; *"Molecular Modeling in Chemistry and Biochemistry",* Cluj-Napoca, 09-10 December 2011.

5. Agota Lini, Petronela M. Petrar, Gabriela Nemes, Luminita Silaghi-Dumitrescu, Jean Escudié, **The first step in obtaining stable 1,3-phosphastannaallenes: choosing substituents through theoretical calculations,** *"Molecular Modeling in Chemistry and Biochemistry",* Cluj-Napoca, 28 May 2010.