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## In silico quest for stable phosphastannaallenes

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## ARTICLE INFO

## Article history:

Received 6 August 2012

Accepted after revision 25 October 2012

Available online 27 December 2012

## Keywords:

DFT

NBO analysis

Multiple bonding

Phosphastannaallenes

## Mots clés :

DFT

Analyse NBO

Liaison multiple

Phosphastannaallènes

## ABSTRACT

A computational study at different levels of theory was performed for the not yet synthesized phosphastannaallenes  $>Sn=C=P-$  in order to evaluate the strength of the  $Sn=C$  bond, the main postulated factor to stabilize such species, and the geometry in  $R_2Sn=C=PR$  derivatives. The influence of the substituents with various electronic effects (H, Me, Ph, F, Cl, OMe,  $SiMe_3$ ) at the Sn or P atoms of the  $Sn=C=P$  unit on the  $Sn-C$  bond order was evaluated in the quest for a substituent that would stabilize the phosphastannaallenic unit.  $P=C$  bond orders have also been calculated.

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## R É S U M É

Une étude computationnel aux différents niveaux de la théorie a été réalisée sur les phosphastannaallènes  $>Sn=C=P-$  pas encore synthétisés, afin d'évaluer la force de la liaison  $Sn=C$  (le principal facteur postulé pour stabiliser ces espèces) et la géométrie des dérivés  $R_2Sn=C=PR$ . L'influence des substituants sur les atomes Sn ou P de l'unité  $>Sn=C=P-$  avec des effets électroniques variés (H, Me, Ph, F, Cl, OMe,  $SiMe_3$ ) sur l'ordre de liaison  $Sn-C$  a été évaluée dans la quête pour un substituant qui permettrait de stabiliser l'entité phosphastannaallénique. L'ordre de liaison  $P=C$  pour chaque dérivé a également été calculé.

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## 1. Introduction

Heteroallenes<sup>1,2</sup> [1–10] and especially heterophosphaallenes  $E=C=P$  ( $E = Si$  [8],  $Ge$  [9,10]) have been the subject of intensive researches during the past 20 years. Due to their two double bonds allowing many types of additions and

cycloadditions, heteroallenes present a great interest as powerful building blocks in organometallic and heterocyclic chemistry. By contrast, tin analogues are very difficult to synthesize and no phosphastannaallenes  $>Sn=C=P-$  were obtained so far; only the stannaallene  $Tip_2Sn=C=CR_2$  ( $Tip = 2,4,6$ -triisopropylphenyl,  $CR_2 = fluorenylidene$ ) was

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<sup>1</sup> The first heteroallenes to be synthesized were the phosphoallenes  $-P=C=X$  ( $X=C, N, P, As, O, S$ ) [1acde] followed by some metallaallenes  $>Si=C=C<$  [1,2] and  $>Ge=C=C<$  [1,4]. Such derivatives have been successfully obtained as stable compounds using bulky substituents, which prevent their dimerization and thus kinetically stabilize them.

<sup>2</sup> When  $E_{15}$  is a nitrogen atom, SiCN derivatives generally behave as silylenes  $>Si$  and isocyanides  $C=N-$  due to their intermediary structure between azasilaallenes  $>Si=C=N-$  and silylene-isocyanide complexes  $>Si-C=N-$  [5] at the exception of the compound prepared by Kira [6]. The same phenomenon has been reported for the tin derivative analogue  $SnCN$  [7]. By contrast, when  $E_{15}$  is a phosphorus atom, the  $Si=C$  and  $Ge=C$  bonds in  $>E_{14}=C=P-$  ( $E_{14} = Si, Ge$ ) are not cleaved and these compounds behave as heteroallenic derivatives; transient phosphasilaallene  $>Si=C=P-$  [8] and phosphagermaallene  $>Ge=C=P-$  [9] have been characterized by low temperature NMR and trapping reactions.

postulated as intermediate in a reaction leading to a distannirane [11] and the stanna ketenimine  $R_2Sn=C=NR'$  is more considered as stannylene–isocyanide complexes  $>Sn-C=N-$  [7].

The first systematic computational study in the field of heavier group 14 analogues of allene was reported by Apeloig [12]. Ab initio and DFT methods have been used to determine the geometry of heteroallenes of the types  $E=C=C$  and  $C=E=C$  ( $E =$  group 14 element). In both cases, the deviations of the skeleton from linearity increase from Si to Pb. The singlet-triplet energy separation was estimated for XCPSi [13] and CPSiX [14] systems by ab initio and DFT calculations as a function of electronegativity of the X atom ( $X = F, Cl, Br, I$ ). The stability of 1,3-diphospha-2-silaallenes  $-P=Si=P-$  relatively to possible isomers was also investigated through theoretical calculations [15].

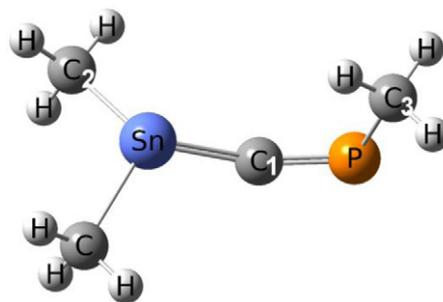
The first computational study in the field of phosphagermaallenes refers to the calculations of the relative energies of the dimers of the parent  $H_2Ge=C=PH$  by restricted HF methods [9]: a small energy difference separates the head-to-head and head-to-tail forms for each pair of dimers. The geometries of all possible isomers of the model compound  $H_2Ge=C=PH$  were optimized at the B3LYP/6-31G(d,p) level of theory in order to determine the most stable isomers and the main geometrical parameters (Ge=C, P=C bond lengths and GeCP bond angle) [16]. The most stable isomer is, as expected, the phosphalkyne  $H_3Ge-C\equiv P$ , which is lower in energy by 130.21 kJ/mol than the corresponding allene  $H_2Ge=C=PH$ . A recent computational study at DFT level explains the [3 + 2] cycloaddition of  $H_2E=C=PH$  with  $HC\equiv CH$  ( $E = Si, Ge, Sn$ ) by the presence of a heavier group 14 element [17].

Computational data are available for  $>Si=C=P-$  and  $>Ge=C=P-$  derivatives, but so far, no extended theoretical studies have been reported in the case of 1-phospha-3-stannaallenes  $>Sn=C=P-$ . As there are no examples in the literature of such compounds and in order to determine the right substituents to be successful in their synthesis and stabilization, we undertook a theoretical study to provide an insight on their structure and properties, especially in the case of the tin-carbon double bond within the phosphaaallenic unit. We have thus investigated and herein report the results on a series of phosphastannaallenes with the general formula  $RR'Sn=C=PR$  ( $R = H, Me, Ph, R'$ ;  $R' = F, Cl, OMe, SiMe_3$ ).

## 2. Results and discussion

### 2.1. Methods and basis sets

Several computational methods have been employed in this study. Both the BP86 and the B3LYP functionals were tested. Moreover, two different basis sets were considered



Scheme 1.

for the tin atom, the Gaussian 09 [18] built-in LANL2Z [19] and the CRENBL [20] 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  $Me_2Sn=C=PMe$ . However, all the model compounds presented in this study have also been optimized at the MP2/CRENBL/6-311+G(d,p) level. All calculations were carried out using the Gaussian 09 program.

Table 1 presents selected geometrical parameters obtained with each method in the case of the 1-phospha-3-stannaallene fully substituted with methyl groups (Scheme 1, color codes for atoms are also given).

The data for  $Me_2Sn=C=PMe$  summarizes well the trends obtained for all the other derivatives. The calculated values for the Sn-C distances are close to those obtained experimentally in stannenes  $>Sn=C<$ : around 2 Å for the Sn=C double bond [21] and between 2.10 and 2.20 Å for the Sn-C single bond [22]. The B3LYP/LANL2DZ method seems to slightly underestimate the length of the Sn=C double bond for the models with  $R=Me$ , but in the case of other substituents ( $R = H, Ph$ ) the same trend is not observed. The larger basis sets give smaller values for the Sn-C-P bond angle. The geometrical parameters obtained are also in agreement with experimental data for C=P bonds [23] and there is a good correlation with the values obtained with all the methods studied. We will discuss further only the optimized structures using B3LYP/6-311+G(d,p)/CRENBL (which are almost identical to those obtained at the BP86 level). All the presented structures were identified as local minimas through frequency calculations.

### 2.2. Geometry and bond orders of $RR'Sn=C=PR$ and $R_2Sn=C=PR'$ derivatives

It is well known that the  $-P=C<$  double bond is generally fairly stable with various groups on P and C atoms; thus, it is reasonable to presume that the instability

Table 1  
Selected geometrical parameters for the  $Me_2Sn=C=PMe$  derivative.

Method	Sn=C1 (pm)	Sn=C2 (pm)	C1=P (pm)	P-C3 (pm)	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

**Table 2**  
Selective data for  $RR'Sn=C=PR$  and  $R_2Sn=C=PR'$ , calculated at the B3LYP level.

Molecule	$\Delta E$ (kJ/mol)	Sn=C (pm)	C=P (pm)	Sn-C-P ( $^\circ$ )	W BO Sn=C	W BO C=P
H <sub>2</sub> Sn=C=PH	–	2.06	1.64	162.7	1.37	2.09
Me <sub>2</sub> Sn=C=PMe	–	2.06	1.64	159.5	1.28	2.04
Ph <sub>2</sub> Sn=C=PPh	–	2.04	1.63	161.0	1.26	1.99
HFSn=C=PH	0.00	2.12	1.64	153.9	1.17	2.13
H <sub>2</sub> Sn=C=F	7.26	2.01	1.62	161.0	1.34	1.99
MeFSn=C=PMe	0.00	2.10	1.63	150.6	1.14	2.09
Me <sub>2</sub> Sn=C=PF	6.46	2.01	1.62	155.6	1.20	2.02
PhFSn=C=PPh	0.00	2.09	1.64	151.5	1.13	2.04
Ph <sub>2</sub> Sn=C=PF	8.83	2.02	1.62	149.4	1.16	2.03
HClSn=C=PH	0.00	2.10	1.64	155.2	1.20	2.12
H <sub>2</sub> Sn=C=PCl	14.05	2.01	1.61	164.4	1.29	2.06
MeClSn=C=PMe	0.00	2.09	1.63	152.0	1.17	2.08
Me <sub>2</sub> Sn=C=PCl	12.67	2.02	1.61	160.9	1.15	2.09
PhClSn=C=PPh	0.00	2.08	1.64	153.0	1.16	2.03
Ph <sub>2</sub> Sn=C=PCl	14.82	2.02	1.61	157.8	1.10	2.11
H(OMe)Sn=C=PH	0.00	2.11	1.64	151.8	1.20	2.11
H <sub>2</sub> Sn=C=POMe	1.04	2.01	1.63	157.7	1.38	1.93
Me(OMe)Sn=C=PMe	0.16	2.09	1.64	148.7	1.16	2.08
Me <sub>2</sub> Sn=C=POMe	0.00	2.02	1.63	151.4	1.24	1.95
Ph(OMe)Sn=C=PPh	0.00	2.08	1.64	151.4	1.14	2.02
Ph <sub>2</sub> Sn=C=POMe*	4.52	2.02	1.63	146.3	1.21	1.96
H(SiMe <sub>3</sub> )Sn=C=PH	1.34	2.06	1.65	151.1	1.37	2.06
H <sub>2</sub> Sn=C=PSiMe <sub>3</sub>	0.00	2.13	1.62	163.2	1.18	2.21
Me(SiMe <sub>3</sub> )Sn=C=PMe	2.09	2.05	1.64	166.9	1.33	2.03
Me <sub>2</sub> Sn=C=PSiMe <sub>3</sub>	0.00	2.12	1.63	161.2	1.14	2.17
Ph(SiMe <sub>3</sub> )Sn=C=PPh	0.00	2.04	1.64	170.1	1.31	1.97
Ph <sub>2</sub> Sn=C=PSiMe <sub>3</sub>	2.08	2.13	1.63	159.9	1.11	2.19

of phosphastannaallenes should be mostly due to the weakness of the Sn=C double bond; so we particularly studied the influence on the tin–carbon bond order of the substituents at both the tin and phosphorus atoms; however, we also calculated the P=C bond order; they have been calculated through an NBO analysis [24] which can also give us an intuitive look at the nature of the bonds and the electronic factors weakening them. The isomers of  $R_2R'PCSn$  (R = H, Me or Ph; R' = F, Cl, OMe, SiMe<sub>3</sub>) derivatives containing the Sn=C=P unit were investigated, by varying the nature and the position of the R' substituent on Sn or P.

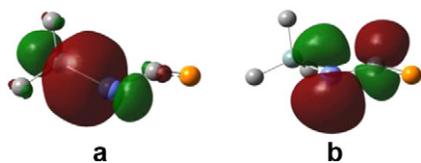
Table 2 presents selected geometrical parameters and calculated Wiberg bond orders [25] for the considered phosphastannaallenes. The computed data for  $R_3PCSn$  model compounds are also given for comparison.

As predicted by other computational studies on similar derivatives (like  $>Ge=C=P$ – [16] and  $-As=C=P$ – [26]), the Sn–C–P bond angle is strongly deviated from the ideal linearity of allenic units, even for the model compound  $H_2Sn=C=PH$ ; thus, the steric effect is not a factor to explain

this. The NBO analysis shows that this deviation is correlated with the Sn=C bond order. The most significant second order interaction involves the  $\lambda^3\sigma^2P$  lone pair as a donor and the antibonding  $\sigma^*$  orbital on the Sn–C bond, which is present for all the derivatives discussed (Fig. 1).

A scan of the Sn–C–P bond angle was performed, with a step of  $10^\circ$ , in the range  $130^\circ$ – $180^\circ$  and the value of the stabilization energy afforded by the  $LP_P-\sigma^*_{Sn-C}$  interaction was examined. It is obvious (Table 3) that the higher the value of the Sn–C–P bond angle, the stronger the interaction and thus the higher tin–carbon bond order becomes. Assuming that the instability of the phosphastannaallene 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 phosphastannaallenic moiety.

From Table 2, we can conclude that the isomer substituted by an electron-withdrawing group at the phosphorus atom is less stable than that with the same



**Fig. 1.** NB orbitals involved in second order perturbation interactions for  $H_2Sn=C=PH$ : (a) lone pair electrons on P; (b) antibonding non-Lewis orbital on the Sn–C bond.

**Table 3**  
Correlation between the Sn–C–P bond angle and Sn–C parameters.

Sn–C–P ( $^\circ$ )	W BO Sn=C	W BO C=P	Sn=C (pm)	C=P (pm)	$E(2)^a$ (kJ/mol)
130	1.34	2.04	216	167	60.71
140	1.35	2.06	209	166	74.61
150	1.36	2.07	208	165	89.01
160	1.37	2.09	206	164	102.24
162 <sup>b</sup>	1.37	2.09	206	164	105.47
170	1.38	2.09	205	164	112.88
178	1.39	2.09	204	163	117.19

<sup>a</sup>  $E(2)$  is the stabilization afforded by the interaction  $LP_P \rightarrow \sigma^*_{Sn-C}$  (kJ/mol).

<sup>b</sup> Calculated global minimum.

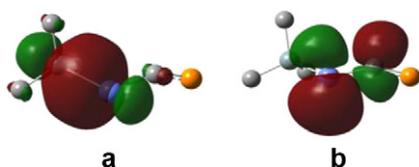


Fig. 2. (a) NBO situated along the Si–Sn bond and (b) antibonding  $\pi^*$  orbital on the Sn–C bond (hydrogen atoms were omitted for clarity).

group on the tin atom (for  $R' = \text{OMe}$  the difference in energy is insignificant) while the Sn=C bond order tends to go higher. In the case of the substitution with  $\text{SiMe}_3$ , the position of the group does not influence much the relative stability of the two isomers. However, the calculated Wiberg bond order for the Sn=C bond is always higher for the  $\text{R}(\text{SiMe}_3)\text{Sn}=\text{C}=\text{PR}$  than for the  $\text{R}_2\text{Sn}=\text{C}=\text{PSiMe}_3$  one. We can also note that the P=C bond order is always around 2 and generally higher. The main interaction evidenced by NBO analysis contributing to the higher Sn–C bond order is a charge transfer from the bonding orbital situated along the Si–Sn bond to the antibonding orbital  $\pi^*$  on the Sn–C bond (Fig. 2). The structure depicted by the natural bond orbital analysis is very close to an allenic Lewis structure  $\text{H}(\text{Me}_3\text{Si})\text{Sn}=\text{C}=\text{PH}$ , with the tin valence orbitals participating in double bonding through a  $sp^2$  hybridized and an almost pure  $p$  orbital. It should be therefore interesting to envisage a silyl-substituted phosphastannaallene as an experimental target.

The main problem encountered in the synthesis of heavy phosphaaallenes of the type  $>\text{E}=\text{C}=\text{P}$  ( $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$ ) is the increased reactivity exhibited at the level of the  $\text{E}=\text{C}$  bond once the unsaturated compound is formed. The “head-to-head” or “head-to-tail” dimers have been evidenced for both  $\text{E} = \text{Si}$  and  $\text{Ge}$  [10,11]. In most of the model compounds discussed above, both the HOMO and the LUMO are situated along the Sn=C bond (Fig. 3), which would favor the formation of the cyclic compounds, even in the absence of other reactive species. Only in  $\text{Ph}_2\text{Sn}=\text{C}=\text{PPh}$  and three other considered phosphastannaallenes bearing phenyl groups, the frontier orbitals are not situated on this bond, but along the P=C or P–X bond.

Mulliken charges for the atoms in the allenic unit are given in Table 4 for derivatives with  $\text{R} = \text{H}$ . Similar values are calculated for the other model compounds. As expected, the polarity of the Sn–C bond varies, depending on the nature of the substituent on the tin atom.

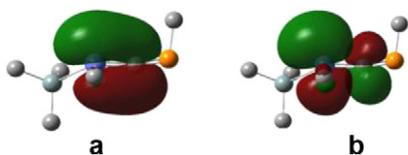


Fig. 3. Calculated HOMO (a) and LUMO (b) for  $\text{Me}(\text{Me}_3\text{Si})\text{Sn}=\text{C}=\text{PMe}$  (hydrogen atoms were omitted for clarity).

Table 4

Mulliken charges for  $\text{H}_2\text{R}'\text{SnCP}$  derivatives.

Molecule	Mulliken atomic charges		
	Sn	C	P
$\text{H}_2\text{Sn}=\text{C}=\text{PH}$	0.62	−0.34	0.05
$\text{HFSn}=\text{C}=\text{PH}$	0.84	−0.32	0.09
$\text{H}_2\text{Sn}=\text{C}=\text{PF}$	0.76	−0.50	0.24
$\text{HClSn}=\text{C}=\text{PH}$	0.71	−0.31	0.08
$\text{H}_2\text{Sn}=\text{C}=\text{PCl}$	0.76	−0.29	0.00
$\text{H}(\text{MeO})\text{Sn}=\text{C}=\text{PH}$	0.81	−0.36	0.06
$\text{H}_2\text{Sn}=\text{C}=\text{POMe}$	0.71	−0.53	0.23
$\text{H}(\text{Me}_3\text{Si})\text{Sn}=\text{C}=\text{PH}$	0.48	−0.36	0.00
$\text{H}_2\text{Sn}=\text{C}=\text{PSiMe}_3$	0.47	−0.12	−0.20

### 2.3. Geometry and bond orders of $\text{R}'_2\text{Sn}=\text{C}=\text{PR}$ and $\text{RR}'\text{Sn}=\text{C}=\text{PR}'$ derivatives

Phosphastannaallenes bearing two  $\text{R}'$  groups have also been investigated. Two types of isomers,  $\text{R}'_2\text{Sn}=\text{C}=\text{PR}$  and  $\text{RR}'\text{Sn}=\text{C}=\text{PR}'$  have been considered and compared. The results are summarized in Table 5.

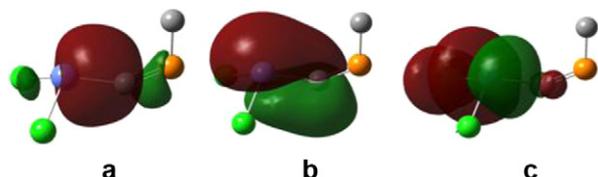
It can be noticed that by placing two electron-withdrawing groups on the tin atom, the bond order drastically drops. For  $\text{R}' = \text{Cl}$  and  $\text{OMe}$ , the reason is a charge transfer from bonding orbitals along the Sn–C bond (both of  $\sigma$  and  $\pi$  symmetry) towards non-Lewis vacant orbitals situated on the Sn–Cl or Sn–O bond of  $\sigma$  symmetry (see Fig. 4 for an example in the case of  $\text{Cl}_2\text{Sn}=\text{C}=\text{PH}$ ). For the  $\text{RR}'\text{Sn}=\text{C}=\text{PR}'$  isomers, only one such interaction can exist, as the other electron-withdrawing group is placed on the phosphorus atom, and thus the bond order for Sn–C is higher than in the case of  $\text{R}'_2\text{Sn}=\text{C}=\text{PR}$  derivatives. Such interactions do not occur in the case of substitution with trimethylsilyl.

In the case of  $\text{F}_2\text{Sn}=\text{C}=\text{PR}$  derivatives, the NBO analysis suggests a structure with a high charge on the tin atom (NPA gives a value of 1.91) and a lone pair on the carbon atom, while the Sn–F bond is depicted as a donation from  $\text{F}^-$  lone pairs to tin. This is not the case for the  $\text{RFSn}=\text{C}=\text{PF}$  derivatives, where the allenic structure has a more important contribution to the correct description of bonding within the Sn–C–P unit.

From this study, it appears that the trimethylsilyl substituent proves to be the best choice for the stabilization of a phosphastannaallene, as the Wiberg bond order of the Sn=C bond is the highest calculated for all considered compounds. Moreover, substitution of the phosphorus atom by a phenyl group appears also to be efficient. It can be noticed that the value of the Sn–C–P bond angle also tends to an ideal value of  $180^\circ$ . A similar interaction to that mentioned for the silyl-monosubstituted derivatives  $\text{R}(\text{Me}_3\text{Si})\text{Sn}=\text{C}=\text{PR}$  also occurs. As for the  $\text{R}_2\text{R}'\text{SnCP}$  derivatives, the frontier orbitals of the considered model compounds are situated on the Sn–C bond, with HOMO displaying a bonding character and the LUMO an antibonding one, with a larger contribution from tin orbitals than the ones from the carbon atom. This is the case even for every phosphastannaallene with  $\text{R}' = \text{SiMe}_3$ ; so in order to check the potential of the TMS groups for

**Table 5**  
Selective data for  $R_2Sn=C=PR$  and  $RR'Sn=C=PR'$ , calculated at the B3LYP level.

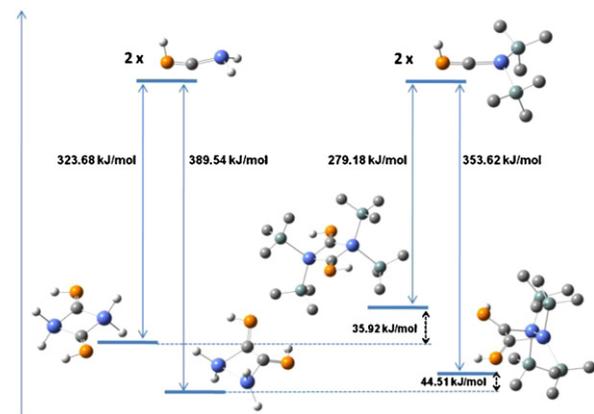
Molecule	$\Delta E$ (kJ/mol)	Sn=C (Å)	C=P (Å)	Sn-C-P (°)	W BO Sn=C	W BO C=P
$F_2Sn=C=PH$	0.00	2.23	1.64	145.4	0.93	2.22
$HFSn=C=PF$	10.06	2.02	1.63	138.5	1.19	1.99
$F_2Sn=C=PMe$	0.00	2.19	1.63	143.6	0.94	2.21
$MeFSn=C=PF$	6.36	2.03	1.63	136.0	1.13	2.01
$F_2Sn=C=PPh$	0.00	2.18	1.63	146.5	0.94	2.17
$PhFSn=C=PF$	7.81	2.03	1.63	133.2	1.10	2.02
$Cl_2Sn=C=PH$	0.00	2.19	1.64	148.7	0.99	2.19
$HClSn=C=PCl$	16.64	2.03	1.62	150.2	1.19	2.05
$Cl_2Sn=C=PMe$	0.00	2.16	1.63	146.8	1.00	2.17
$MeClSn=C=PCl$	13.26	2.04	1.62	148.7	1.12	2.07
$Cl_2Sn=C=PPh$	0.00	2.15	1.63	149.4	1.01	2.13
$PhClSn=C=PCl$	14.93	2.04	1.62	146.0	1.10	2.08
$(MeO)_2Sn=C=PH$	0.00	2.17	1.65	142.3	1.03	2.15
$H(MeO)Sn=C=POMe$	2.23	2.04	1.64	131.2	1.18	1.96
$(MeO)_2Sn=C=PMe$	0.00	2.15	1.64	139.5	1.02	2.13
$Me(MeO)Sn=C=POMe$	0.77	2.05	1.64	126.1	1.11	1.99
$(MeO)_2Sn=C=PPh$	0.00	2.14	1.64	144.1	1.03	2.09
$Ph(MeO)Sn=C=POMe$	6.08	2.03	1.65	127.0	1.24	1.90
$(SiMe_3)_2Sn=C=PH$	2.79	2.04	1.64	176.0	1.39	2.04
$H(SiMe_3)Sn=C=PSiMe_3$	0.00	2.12	1.63	155.0	1.22	2.12
$(SiMe_3)_2Sn=C=PMe$	2.09	2.04	1.64	174.1	1.39	2.01
$Me(SiMe_3)Sn=C=PSiMe_3$	0.00	2.11	1.64	153.7	1.21	2.10
$(SiMe_3)_2Sn=C=PPh$	0.00	2.03	1.64	178.3	1.40	1.95
$Ph(SiMe_3)Sn=C=PSiMe_3$	0.90	2.11	1.64	153.7	1.19	2.11



**Fig. 4.** 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.

stabilizing the allenic unit, a preliminary evaluation of the dimerization tendency of such species was performed.

The energies of “head-to-head” and “head-to-tail” dimers of  $(Me_3Si)_2Sn=C=PH$  by the Sn=C double bond were calculated at the B3LYP level. The dimerization



**Fig. 5.** “Head-to-head” and “head-to-tail” dimerization energies for  $H_2Sn=C=PH$  and  $(Me_3Si)_2Sn=C=PH$ .

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 on Fig. 5.

As expected, both forms of dimerization are thermodynamically likely to occur for the two derivatives considered, with the formation of the “head-to-head” dimer being more energetically favored. However, the computational data show that the presence of the bulkier silyl groups on the tin atom disfavors the additions at the Sn=C double bond, the stabilization afforded by the dimeric structures compared with the monomeric units being smaller by 33–42 kJ/mol in the case of  $(Me_3Si)_2Sn=C=PH$  than for  $H_2Sn=C=PH$ .

### 3. Conclusions

The bond order of the Sn-C bond in phosphastannaallenes depends on the nature of the substituents on both the tin and the phosphorus atoms. Electron-withdrawing groups on the tin atom induce orbital interactions that generally decrease the bond order whereas  $Me_3Si$  groups increase it. The frontier molecular orbitals of such derivatives are usually situated on the Sn-C bond. P=C bond orders are in all cases high, close to or greater than 2, regardless of the substituents.

We propose that a stable phosphastannaallene can be in theory obtained by substituting the tin atom with silyl groups, and further on, that it should have a linear Sn-C-P unit, very close to that of the allenic carbon analogues. This kind of substituent would also afford steric hindrance around the Sn=C bond preventing the dimerization. A further amount of stabilization could be due to the presence of a phenyl (or of a bulkier substituted aromatic group) on the phosphorus atom.

## Acknowledgments

This work is supported by UEFISCDI (Contract no. PCCE-129/2008). A.B. thanks POSDRU for financial support (Contract no. 88/1.5/S/60185).

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