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A THEORETICAL APPROACH ON THE STRUCTURE AND REACTIVITY OF MODEL PHOSPHASTANNAPROPENES

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ABSTRACT. The stability of phosphastannapropenes and their coordination ability towards transition metal centers was estimated by DFT calculations. The influence of several substituents on the stabilization of the model compounds Mes*P(ML_n)=CCl-SnClRR', Mes*P(η^2-ML_n)=CCl-SnClRR' (R = H, R'; R' = H, Me, Mes, Ph, Fl, Mes*; ML_n = $W(CO)_6$, $PdCl_2Me$, $PtCl_2Me$ has been studied.

Keywords: *phosphastannapropenes; palladium-, tungsten- and platinum complexes; low coordinate phosphorus compounds; multiple bonding; DFT.*

INTRODUCTION

The synthesis of heteroallenescontaining one or two heavy elements from group 14 or 15 is a challenge in Organometallic chemistry. The electronic properties and the reactivity of structures like E_{15}=C=E_{14} or E_{15}=C=E_{15} are significantly different than those of allenes, as a consequence of the involvement of the heavy atom in the π-bonding [1]. It was already shown that derivatives like heteroallenes (>C=C=$E_{14/15}$) and phosphheteroallenes (-P=C=$E_{14/15}$) are very interesting from both fundamental and applied points of view [2,3,4]. Literature data show that the stability of heteroallenes is highly dependent on the type of substituents on the heavier atoms [5,6].

Due to the high reactivity of phosphastannapropenes and phospha-stannaallenes towards a wide range of chemical species, an insight in their electronic structure and properties using computational chemistry offers a good starting point for the synthetic chemist [1,3,7]. One of the first systematic computational studies in the field of heavier group 14 analogues of allenes was reported by Apeloig [8]. Recently, a theoretically study performed on

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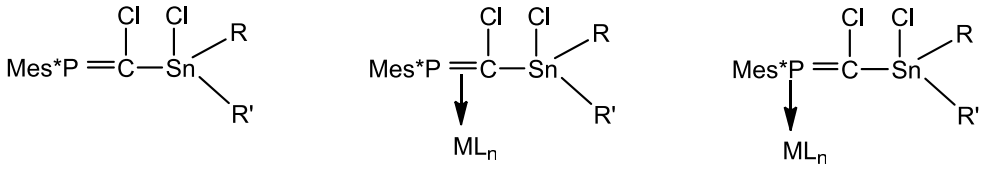
the not yet synthesized phosphastannaallenes >Sn=C=P– [9] showed that the BP86/LANL2DZ [10,11] level of theory is appropriate in the description of such unsaturated systems. Although there are theoretical studies on several substituted phosphastannaallenes [12], there are no studies yet on their precursors, stannyl-phosphapropenes.

The choice of the appropriate stannyl-substituted phosphaalkenes precursor is crucial for the synthesis of a stable phosphastannaallene. As shown by the experimental attempts to obtain stable phosphastannaallenes, one of the most useful substituents on the phosphorus atom is the 2,4,6-tri-*tert*-butylphenyl group (Mes*) (excellent in terms of steric protection of the P=C bond and readily available). Therefore the model compounds subjected in the present study are Mes*P=CCl-SnClRR' (where R = H, R'; R' = H, Me, Mes, Ph, Fl, Mes*). Coordination compounds of phosphastannapropenes were also investigated as the electronic effects induced by the transition metals could also make the phosphastannapropenes more prone to vicinal halogen elimination and maybe afford more stability to the phosphaallenic unit thus obtained [13].

RESULTS AND DISCUSSION

Bearing in mind our goals in the research of the phosphastannapropenes' coordination capacity to transition metals through computational [9], as well as experimental methods [14], we have studied several model compounds (Mes*P(ML_n)=CCl-SnClRR', Mes*P(η^2-ML_n)=CCl-SnClRR'), using $W(CO)_6$, $PdCl_2Me$ and $PtCl_2Me$ as the metal-containing fragment (see Scheme 1), by alternating the substituent only on the tin atom and modifying the coordination possibilities.



ML_n = $W(CO)_6$, $PdCl_2Me$, $PtCl_2Me$ R = H, R'; R' = H, Me, Mes, Ph, Fl, Mes*

Scheme 1

Selected computed geometrical parameters for the 1,3-phosphastannapropenes are given in Table 1, together with results from the Mulliken and NBO analysis.

Table 1. Calculated geometrical parameters, bond orders and charges for phosphastannapropenes Mes*P=C(Cl)-Sn(Cl)RR'

R	R'	C-Sn (Å)	P=C-Sn (°)	WBO C=P	WBO Sn-C	Müll.ch. C	Müll.ch. Sn
H	H	2,14	125,60	1,77	0,66	-0,74	0,65
H	Me	2,14	120,38	1,75	0,64	-0,72	0,84
H	Mes	2,15	118,79	1,75	0,62	-0,71	0,72
H	Ph	2,14	119,76	1,75	0,64	-0,72	0,79
H	Fl	2,15	120,67	1,75	0,62	-0,74	0,88
H	Mes*	2,17	119,35	1,76	0,60	-0,74	0,65
Me	Me	2,15	120,95	1,76	0,6	-0,74	1,09
Mes	Mes	2,17	123,88	1,77	0,55	-0,79	0,97
Ph	Ph	2,15	121,19	1,75	0,60	-0,77	1,06
Fl	Fl	2,11	121,54	1,75	0,64	-0,80	0,93
Mes*	Mes*	2,24	125,33	1,76	0,53	-0,82	0,90

The calculated Sn-C bond distances lie between 2.137 (R = R' = H) and 2.240 (R = R' = Mes*). This is in agreement with experimental determinations in solid state for the single tin-carbon bond, lying between 2.11 and 2.24 Å [15]. The P-C double bond is shown not to be influenced significantly by the nature of the R and R' substituents. The calculated values are close to those previously reported in the literature from X-ray data [16]. The P-C-Sn angles vary between 118.79° and 125.6° in good agreement with the results reported for similar systems (phosphagermapropenes [17] and phosphasilapropenes [18]). The Mulliken atomic charge on the tin atom varies between 0.65 and 1.09. The lowest value was found when R = R' = H and R = H, R' = Mes*. The highest positive value is found in the case of R = R' = Me or Ph. In the case of the hydrogen containing derivatives, charge transfer occurs from a σ(Sn-H) bonding orbital to the antibonding σ^*(Sn-C_c) orbital, leading to an average Sn-C bond order of 0.62 (C_c denotes the central carbon atom). In the phosphastannapropenes whithout at least one Sn-H bond the donation from the σ (Sn-$C_{R,R'}$) bonding orbital to the antibonding σ^*(Sn-C_c) orbital ($C_{R,R'}$ denotes the *ipso* carbon atom of the R and R' substituents) was observed. In these cases the average Sn-C bond order is around 0.60. No donor-acceptor interactions involving the Sn-C_c bond could be identified in the compounds with R = R' = Mes, Fl and Mes*, therefore the average Sn-C bond order is lower than in the previous two cases (i.e. 0.54).

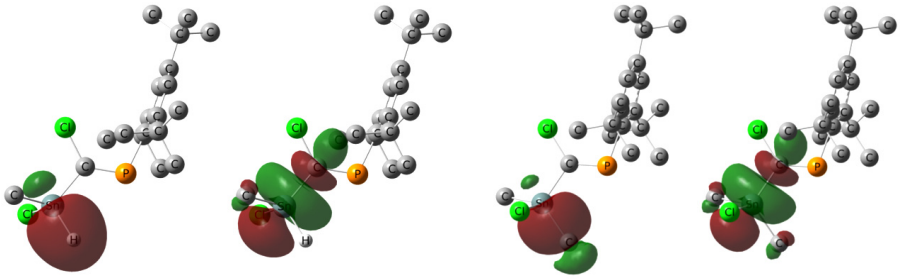
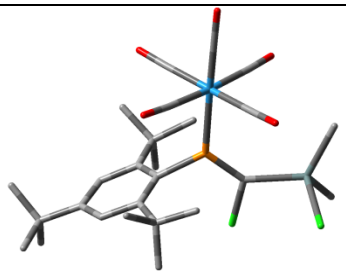
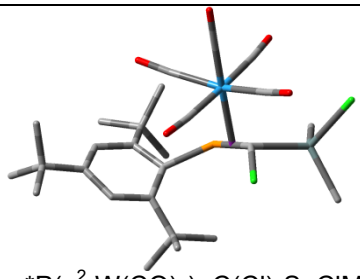
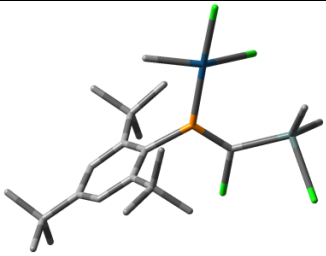
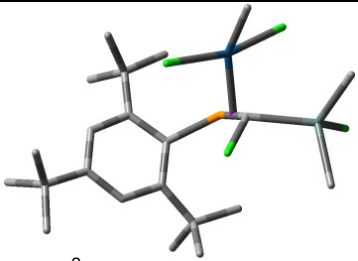


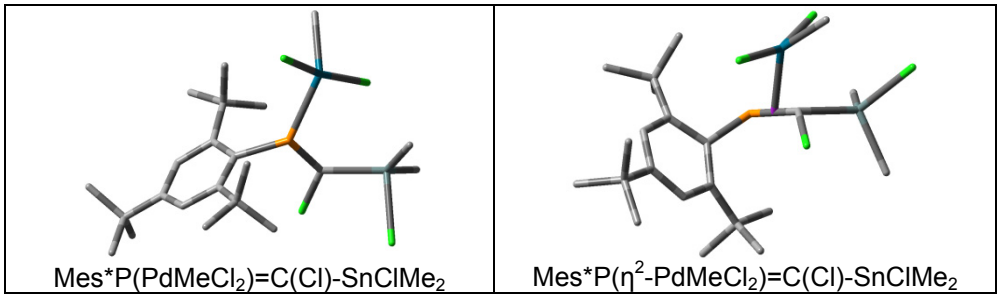
Figure 2. Natural bond orbitals involved in second order perturbation interactions: σ (Sn-H) → σ*(Sn-C_c) for Mes*P=CCl-SnClHMe and σ (Sn- $C_{R,R'}$) → σ*(Sn-C_c) interactions for Mes*P=CCl-$SnClMe_2$

The coordination of phosphastannapropenes to different transitional metals through the phosphorus atom or the P=C double bond was evaluated using model compounds. The optimized geometries obtained are presented in Table 2.

A comparison of the coordination through the phosphorus atom or the double bond can be inferred on the basis of the data in Tables 2 and 3. The highest positive Mulliken atomic charge value on the tin atom is found when R = R' = Me or Ph (varying between 0.65 and 1.09). We chose the methyl group to compare the specified coordinated phosphastanna-propenes.

Table 2. Optimized Mes*P(ML_n)=CCl-$SnClMe_2$ and Mes*P(η^2-ML_n)=CCl-$SnClMe_2$ geometries

 Mes*P($W(CO)_6$)=C(Cl)-$SnClMe_2$	 Mes*P(η^2-$W(CO)_6$)=C(Cl)-$SnClMe_2$
 Mes*P($PtMeCl_2$)=C(Cl)-$SnClMe_2$	 Mes*P(η^2-$PtMeCl_2$)=C(Cl)-$SnClMe_2$



Mes*P(PdMeCl$_2$)=C(Cl)-SnClMe$_2$ | Mes*P(η^2-PdMeCl$_2$)=C(Cl)-SnClMe$_2$

The energy difference between the phosphorus coordinated and the double bond coordinated metal compounds is 7.35 kcal/mol for the platinum derivatives and as high as 15.76 kcal/mol in the case of the tungsten complexes (Table 3). The same preference was noticed for all platinum and tungsten complexes. If we compare the two types of coordination to the PdMeCl$_2$ fragment, the energetically favoured situation is found to be the one where the metal is coordinated by the phosphorus-carbon double bond (Table 3). This behaviour is the same for all palladium derivatives.

Table 3. Calculated energies and geometrical parameters for Mes*P(ML$_n$)=CCl-SnClMe$_2$, Mes*P(η^2-ML$_n$)=CCl-SnClMe$_2$

Coordination mode	PtMeCl$_2$		PdMeCl$_2$		W(CO)$_6$	
	P atom	P=C db	P atom	P=C db	P atom	P=C db
ΔE (kcal)	0	7.35	8.49	0	0	15.76
C=P (Å)	1.73	1.89	1.76	1.86	1.73	1.85
C-Sn (Å)	2.18	2.23	2.19	2.23	2.16	2.20
P=C-Sn (°)	126.5	118.10	124.03	114.01	134.74	108.36
WBO C=P	1.67	1.11	1.59	1.20	1.68	1.25
WBO C-Sn	0.52	0.46	0.51	0.48	0.57	0.51
M←L (Å)	2.36	2.28*	2.50	2.14*	2.61	2.18*
Mülliken charge C	-0.73	-0.97	-0.64	-0.87	-0.71	-0.93
Mülliken charge Sn	1.05	1.13	1.10	1.13	1.06	1.11

**the distance between the metal and the middle of the P=C bond is given*

These results indicate that the preferred coordination mode is influenced by the nature of the transition metal atom and that the substituents on tin have little or no effect. It should be noted, however, that coordination through the phosphorus atom favors a *syn* arrangement of the two chlorine atoms, which in turn would facilitate their elimination through a lithium derivative leading to a C=Sn bond.

The P=C-Sn angles (Table 3, Table 4) obtained by the DFT method are in the range with the values reported in the literature for coordination compounds containing the P=C-Si unit or P=C-Ge unit (124.83° and 119.22° [19], respectively) with a phosphorus-metal bond.

Table 4. Calculated geometrical parameters for Mes*P(W(CO)$_6$)=C-SnClRR'

R	R'	C-Sn (Å)	P=C-Sn (°)	WBO C=P	WBO C-Sn	M←L (Å)	Müll. ch. C	Müll. ch.Sn
H	H	2,14	129,70	1,64	0,65	2,60	-0,68	0,62
H	Me	2,15	131,12	1,67	0,61	2,65	-0,68	0,84
H	Mes	2,19	112,85	1,23	0,54	2,88	-0,90	0,78
H	Ph	2,15	132,16	1,68	0,60	2,65	-0,70	0,80
H	Fl	2,17	133,14	1,68	0,58	2,65	-0,69	0,85
H	Mes*	2,17	128,43	1,67	0,57	2,62	-0,73	0,66
Me	Me	2,16	134,74	1,68	0,57	2,61	-0,71	1,06
Mes	Mes	2,22	132,89	1,69	0,52	2,66	-0,79	0,96
Ph	Ph	2,15	130,35	1,68	0,56	2,62	-0,77	1,04
Fl	Fl	2,17	132,62	1,67	0,53	2,61	-0,77	1,12
Mes*	Mes*	2,29	136,06	1,70	0,48	2,70	-0,79	0,88

CONCLUSIONS

A computational study of the influence of substituents on the tin atom on the stabilization of P=C-Sn species as precursors for phosphastannaallenes was reported. Tin-carbon bond orders are shown to be increased by the presence of methyl or phenyl groups on the tin atom. The coordination ability of model phosphastannapropenes to tungsten-, platinum- and palladium-organometallic fragments has also been investigated. The data indicates that, as in the case of silyl-phosphaallkenes, coordination through the phosphorus atom is preferred by platinum and tungsten. Coordination *via* phosphorus-carbon double bond is preffered by palladium.

METHODS AND BASIS SETS

Calculations were carried out using the Gaussian 09 [12] program, at the BP86/LANL2DZ[10,11] level of theory. All structures were optimized and a vibrational analysis was performed to confirm that the obtained geometries are a global minimum.

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