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NEW HALO COMPOUNDS OF SILICON AND TIN, POTENTIAL PRECURSORS OF >E=C=P- HETEROALLENIC SYSTEMS

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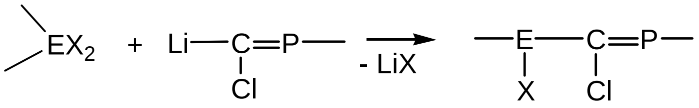
ABSTRACT. New halo compounds of Si and Sn potential precursors of doubly-bonded derivatives of type >E=C=P- (E = 14 main group elements) have been synthesized. Compounds **1**-**3** (bearing a 2,4,6-tri-*tert*-butylphenyl group bound to phosphorus and one 2,4,6-tri-methylphenyl radical bonded to Si) are stabilized by the large steric hindrance which prevents the approach of monomers to form dimers or oligomers.

Introduction

The chemistry of the –P=C< phosphaalkenes has been intensively studied since the synthesis of the first such compound [1] in 1965. Its stabilization was then achieved by resonance effects; however, it was found that bulky organic groups, such as 2,4,6-tri-tert-butylphenyl (Mes*), 2,4,6-*tri*-*iso*-propylphenyl (Tip), 2,4,6-*tri*-metylphenyl (Mes), *tert*-butyl (t-Bu), etc offer a supplementary stabilization through their sterically protective effect .

The general available synthetic route to make a bond of an E 14 group element to the C=P moiety is shown in Scheme 1:



Scheme 1

Due to the pronounced π–electron accepting effect, phosphaalkenes containing low coordinated phosphorus atoms have been investigated in various catalytic processes (polymerization of ethylene, hydroformylation reactions, direct conversion of allylic alcohols) [2-5] and proved also to be useful synthons in organoelement chemistry [6].

Several metal complexes of phosphaalkenes in different coordination modes have been already synthesized and have been recently reviewed [6, 7].

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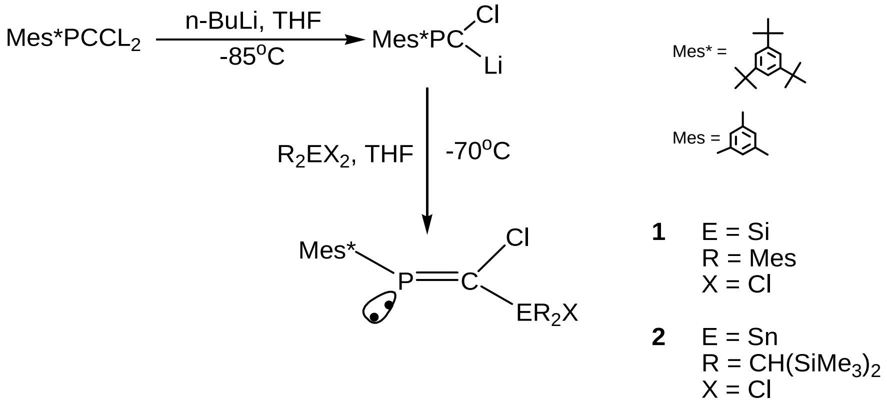
Silylated and stannylated phosphaalkenes are described in the literature [8-12]. The presence of group 14 elements in the phosphaalkene molecule could induce interesting electronic effects that would allow the fine tuning of the metal centre properties of the complexes. Their use as building block of new polymeric materials could also lead to interesting outcomes.

We report herein the synthesis and characterization of three novel phosphaalkenes substituted with group 14 organometallic groups starting from the sterically hindered Mes*$PCCl_2$.

Results and Discussion

The treatment of the dihalogenated phosphaalkene Mes*$PCCl_2$ with one equivalent of n-BuLi at -85℃ leads to the formation of Mes*PC(Cl)Li, which can be used as a nucleophilic agent in the synthesis of silylated and stannylated compounds.

Thus, compounds **1** and **2** were obtained following the route shown in Scheme 2.



Scheme 2

Although these compounds were not completely purified, they were characterized through multinuclear NMR spectroscopy, and relevant data are given in Table **1**. The phosphorus and carbon chemical shifts of **1** are in the expected region for a P=C system [13,15].

In case of compound **2** the presence of a diastereotopic carbon atom ($Me_3Si\underline{C}H$) leads to two different signals in ^1H-NMR for the methyl groups.

Compound **2** **(**the E isomer) show a doublet at 43.6 ppm ($^3J_{P\text{-}Sn}$=363.74 Hz) in the ^{119}Sn-NMR spectra and a singlet in the ^{31}P spectra [13,14].

A byproduct in the synthesis of **2** was the Z geometrical isomer, which gives signals at 306.07 ppm in ^{31}P NMR spectra and 12.06 ppm (d, $^3J_{P\text{-}Sn}$=374.93

Hz) in ^{119}Sn NMR respectively. The relative proportion of the E/Z stereoisomers as shown by ^{31}P-NMR is 4/1.

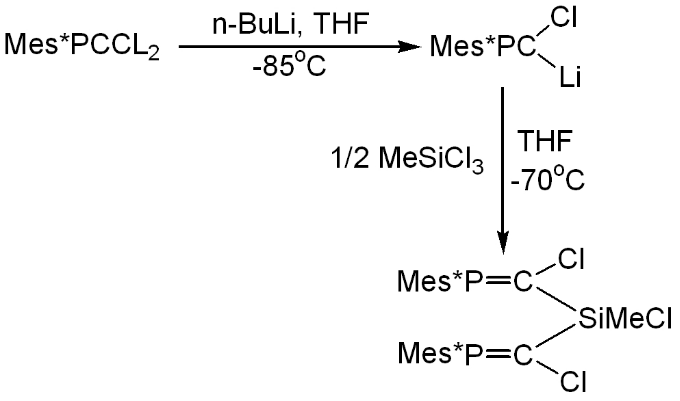
Compound **2** has also been characterized through ^{29}Si-NMR spectroscopy and gives a doublet at -5.65 ppm with a silicon-phosphorus coupling constant of 58 Hz.

Table 1.

Relevant NMR data for compounds**1** and **2**

Compound	**^{1}H NMR**	**^{31}P NMR**	**^{13}C NMR**
1	1.34 ppm (d, $^5J_{HP}$ = 0.33 Hz, 18H, *o*-t) 1.44 ppm (s, 9H, *p*-tBu) 2.25 ppm (s, 12 H, *o*-Me) 2.41 ppm (s, 6H, *p*-Me) 7.41 ppm (s, 2H, H_{arom})	323.8 ppm ($^2J_{PSi}$ =58 Hz)	173 ppm (dd, C=P)
2	0.24 ppm (s, 9H, Me_3Si) 0.27 ppm (s, 9H, Me_3Si) 1.33 ppm (s, 9H, *p*-tBu) 1.49 ppm (s, 18H, *o*-tBu) 7.40 ppm (s, 2H, H_{arom})	305.490 ppm ($^2J_{PSn}$ = 365.66 Hz)	4.40 ppm (wide signal, $\underline{C}H_3Si$) 174.25 ppm (d, $^2J_{PC}$ =102,85 Hz) 14.42 ppm (s, $\underline{C}$HSn) 135.09 ppm (d, $^2J_{CP}$ = 71.61 Hz, ipso C Mes*)

The reaction of $MeSiCl_3$ with two equivalents of Mes*PC(Cl)Li (Scheme 3) lead to the formation of the sterically hindered silylated phosphaalkene **3**:



3

Scheme 3

NMR data for **3** are given in Table 2.

Table 2.

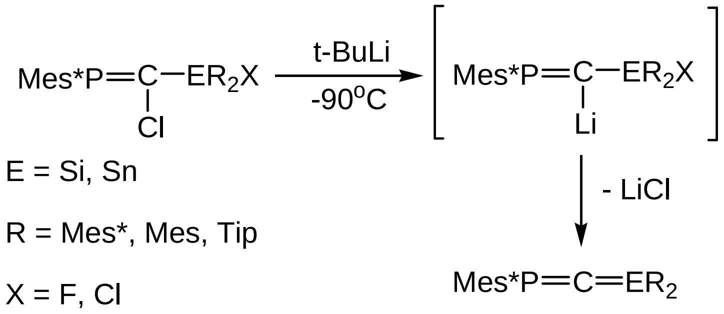
NMR chemical shift and coupling constants for **3**.

Compound	**^{1}H NMR**	**^{31}P NMR**	**^{13}C NMR**
3	0.88 ppm (s, 3H, Me) 1.33 ppm (s, 9H, *p*-tBu) 1.44 ppm (s, 18H, *o*-tBu) 7.41 ppm (s, 2H, Harom)	313.57 ppm ($^{2}J_{PSi}$ = 44.63 Hz)	162.90 ppm (dd, $^{2}J_{CP}$ = 75.46 Hz, $^{3}J_{CP}$ = 5,5 Hz) 134.37 ppm (d, $^{2}J_{CP}$ = 64.14 ppm, ipso C Mes*)

The ^{29}Si NMR spectrum shows a triplet at -1.61 ppm, with a $^{2}J_{SiP}$ coupling constant of 47.7 ppm, which is close to that observed in the ^{31}P NMR spectrum.

In the analogues halosilylphosphaalkenes Mes*PC(Cl)SiPhTipX (X = Cl, F) the silicon atom appears more shielded (-6.8 ppm and -10 ppm respectively), but the $^{2}J_{PSi}$ coupling constant is comparable (54 Hz in both cases).

The reactivity of these new compounds is under current study. Their potential application in the synthesis of new, stable heteroallenes of >E=C=P- type is also currently investigated. An approach to the obtaining of such unsaturated derivatives would be the reaction of **1**-**3** with t-BuLi, followed by intramolecular elimination of LiCl (Scheme 4):



Scheme 4

Conclusions

Three new compounds containing –P=C(Cl)-E(Cl)< (E = Si, Sn) skeleton stabilized by bulky substituents at phosphorus and E have been synthesized.

The use of these dihaloderivatives for the synthesis of heteroallenes containing low coordinated phosphorus atoms is under current investigation.

Experimental

All manipulations were carried out using Schlenk techniques under inert atmosphere. Solvents were dried and freshly distilled from sodium/benzophenone.

NMR Spectra were recorded in $CDCl_3$ on a Bruker AC 200 instrument at 200.1, 50.1, 81.01 MHz (for ^{1}H, ^{13}C and ^{31}P respectively) and an AC 300 instrument at 100.6 MHz for ^{13}C, ^{29}Si and ^{119}Sn.

$MeSiCl_3$ and MesH were available commercially (Aldrich). 1.6 M solution of n-BuLi and t-BuLi (Aldrich) in hexane were used throughout. Mes*$PCCl_2$ has been prepared according to the literature procedure [16].

Synthesis of {Chloro-[chloro-bis-(2,4,6-trimethyl-phenyl)-silanyl]-methylene}-(2,4,6-tri-tert-butyl-phenyl)-phosphane (1):

To a solution of 1 g Mes*$PCCl_2$ (2.7 mmols) in 20 mL THF 1.9 mL of n-BuLi 1.6M were added at -90℃. The reaction mixture was stirred for an hour at -85℃ and than added dropwise to a solution of 0.98 g Mes_2SiCl_2 (2.7 mmols) in 30 mL THF, cooled at -70℃. 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. MS(m/z): 624 (M+), 609 (M^+-Me), 491 (M^+-Mes-Me), 379 (M^+-Mes*), 119 (Mes)

Synthesis of {[Bis-(bis-trimethylsilanyl-methyl)-chloro-stranyl]-chloro-methylene}-(2,4,6-tri-tert-butyl-phenyl)-phosphane (2):

To a solution of 2.12 g Mes*$PCCl_2$ (5.9 mmols) in 30 mL THF 3.3 mL of n-BuLi 1.6M were added at -90℃. The reaction mixture was stirred for an hour at -85℃ and than added dropwise to a solution of 3 g of Bis_2SnCl_2 (5.9 mmols) in 30 mL THF, cooled at -70℃. 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 **2** was identified through the NMR data. MS(m/z): 796 (M), 681 (M-2 t-Bu+1); 637 (M-Bis); 602 (M-Bis-Cl)

Synthesis of Bis[1-chloro-2-(1,3,5-*tri-tert*-butyl-phenyl)phosphaalkene] methylchlorosilane (3):

To a solution of 2 g Mes*$PCCl_2$ (5.4 mmols) in 30 mL THF 3.8 mL of n-BuLi 1.6M were added at -90℃. The reaction mixture was stirred for an hour at -85℃ and than added dropwise to a solution of 0.40 g Me_3SiCl (2.7 mmols) in 15 ml THF, cooled at -70℃. 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. Attempts to obtain crystalline product failed. By removing the pentane a light-yellow solid mixture was obtained from which compound **3** was identified through NMR data.

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