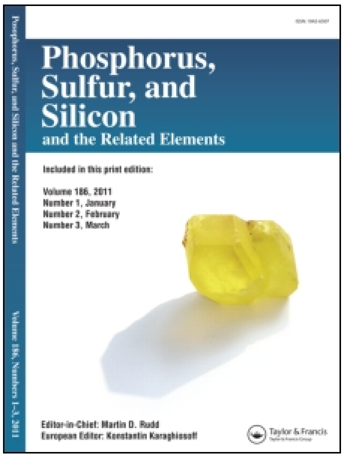

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SYNTHESIS AND REACTIVITY OF NEW GERMA- AND STANNAPHOSPHENES

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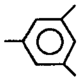
Abstract New stable compounds with a germanium (or a tin)-phosphorus double bond have been prepared respectively by a one step reaction between a lithiophosphide and a difluorogermane, or by dehydrofluorination of the corresponding fluorostannylphosphine with tert-butyllithium. Various types of cycloadditions ([2+2], [2+3] and [2+4]) have been observed with aldehydes, nitrones and α-ethylenic aldehydes and ketones.

There is now a great interest in the study of low coordinated species of group 14 (Si, Ge,Sn) and 15 (particularly P) elements. In this field, the first stable germaphosphene **1** [1] and stannaphosphene **2** [2] have been synthesized some years ago in our group :

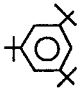
$Mes_2Ge=PAr$ $Bis_2Sn=PAr$

1 **2**

Mes :



Ar :

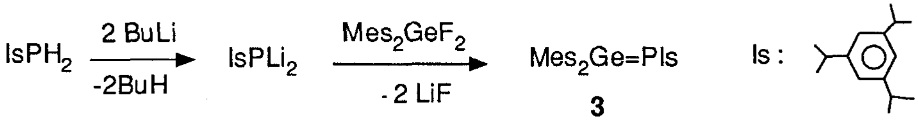


Bis : $(Me_3Si)_2CH$

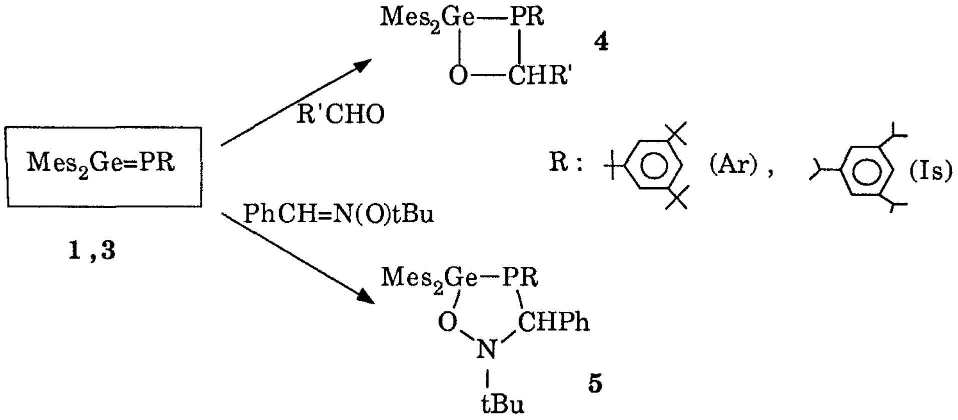
We present in this paper new stable germa- and stannaphosphenes **3** and **10** and novel aspects of their reactivity, mainly in the field of cycloadditions quite unexplored until now.

a) GERMAPHOSPHENES

The new germaphosphene **3** has been prepared by a one-step reaction between dimesityldifluorogermane and isityldilithiophosphide ; this novel route gives **3** in high yield (85 %) :



The structure of **3**[3] has been evidenced by its characteristic physico-chemical data (low field $\delta^{31}P$: +145.3 ppm...). Germaphosphenes **1** and **3** appeared very reactive in various types of heterocyclisations: for example we have observed [2+2] cycloadditions with aldehydes and [2+3] with nitrones :

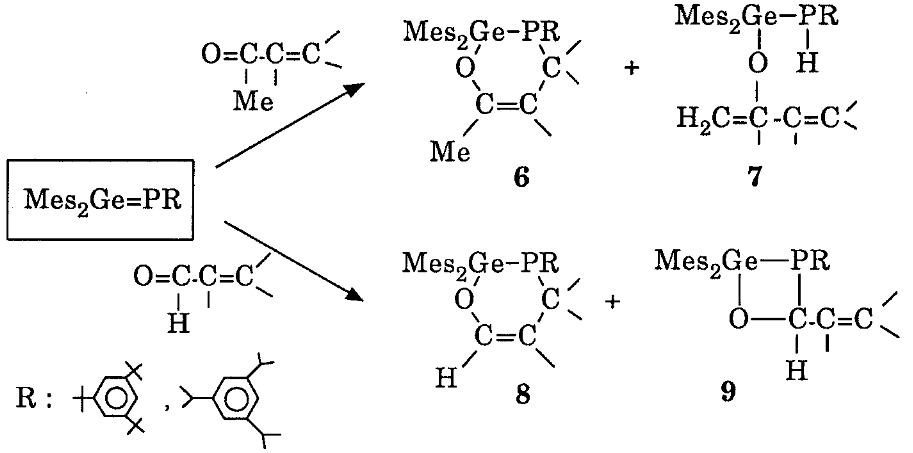


Although the Ge-P double bond is only slightly polarized, a regiospecific reaction takes place, with oxygen becoming bonded exclusively to germanium.

With benzaldehyde only one diastereoisomer is obtained with phenyl and the substituent on phosphorus in a trans disposition as proved by the examination of the $^{2}J_{PCH}$ coupling constant. The cycloadducts display unexpected low field $\delta^{31}P$ (+ 45.6 (R: Is) and + 82.5 ppm(R: Ar)) ; the reasons of these surprising chemical shifts could be a substantial folding of the four-membered ring along the Ge-C axis giving rise to an interaction between phosphorus and oxygen lone pairs.

On the contrary with nitrones two diastereoisomers of **5** are obtained; their configuration has been determined as previously by a comparison between the $^{2}J_{PCH}$ coupling constant and the corresponding Karplus type curve.

α-Ethylenic aldehydes give with **1** and **3** six-membered ring **8** (major compound) and four-membered ring **9** derivatives. With α-ethylenic ketones, six-membered ring compounds **6** are still predominant, but, in some cases, products **7** are also formed. The ratio of compounds **6**, **7**, **8**, **9** is very dependant on the size of substituents on phosphorus and on carbonyl compound :

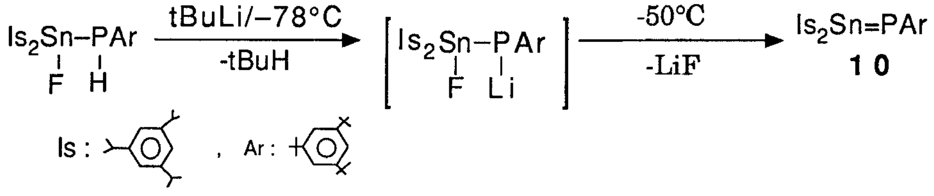


All these heterocycles have been characterized by NMR (^1H, ^{13}C, ^{31}P) , IR, mass spectroscopy and in one case (**1** + crotonaldehyde) by X-ray.

When phosphorus is substituted by the very bulky 2,4,6-tri-tert-butylphenyl group, the rapid inversion of phosphorus occurs at room temperature in some six-membered ring compounds. The factors which have the most important influence on this low barrier (ΔG^*: 13.2 to 13.7 kcal/mole) seem to be the very important steric hindrance and the presence of the rather electropositive germanium bonded to phosphorus.

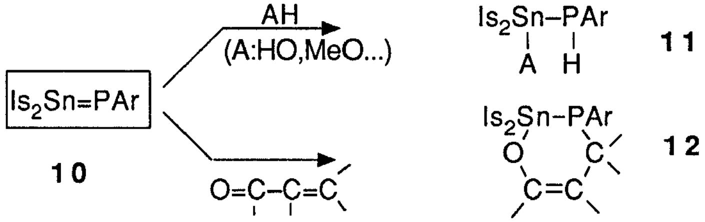
b) STANNAPHOSPHENES

A new stable stannaphosphene **10**[4] has been prepared in high yield by dehydrofluorination of the corresponding fluorostannylphosphine by tert-butyllithium :



10 presents a very good thermal stability : red solutions of **10** in Et_2O are recovered unchanged after heating at 80°C for some hours contrary to stannaphosphene **2** which disproportionates at 65°C to give stannylene and phosphinidene[2]. This result proves once more, the stabilizing effect of aryl groups in relation to alkyl groups on doubly-bonded derivatives of phosphorus germanium and tin.

10 has been characterized by the expected low field chemical shift in ^{31}P and ^{119}Sn NMR (respectively + 173.4 and + 499,7 ppm) with a large tin-phosphorus coupling constant ($^{1}J_{^{119}Sn\text{-}P}$: 2208 Hz, $^{1}J_{^{117}Sn\text{-}P}$: 2110 Hz); the $\delta^{31}P$ of **10** is dependent of the temperature (+ 170.7 ppm at + 25°C, +155 ppm at - 89°C) and presents some thermochromism. The presence of the tin-phosphorus double bond in **10** has also been evidenced by its chemical reactivity particularly with protic reagents (formation of **11**), but also in cycloaddition reactions; for example **10** gives nearly quantitative [2+4] cycloadditions with various α-ethylenic aldehydes and ketones (acrolein, crotonaldehyde, methacrolein, methyl vinyl ketone, methyl isopropenyl ketone) to give the corresponding 6-membered ring compounds **12** ($\delta^{31}P$ + 2 to - 20 ppm).



All these reactions are regiospecific with oxygen always bonded to tin. The study of other aspects of the reactivity of **1**,**3** and **10** are now in progress.

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