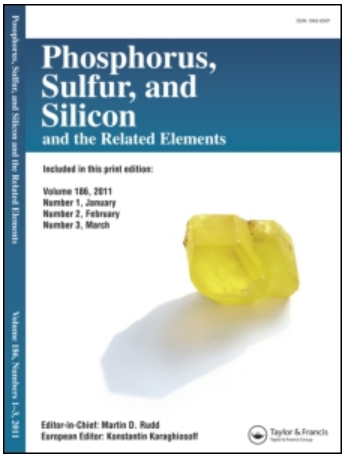

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NEW ASPECTS OF THE REACTIVITY OF THE FIRST STABLE GERMA- AND STANNAPHOSPHENES

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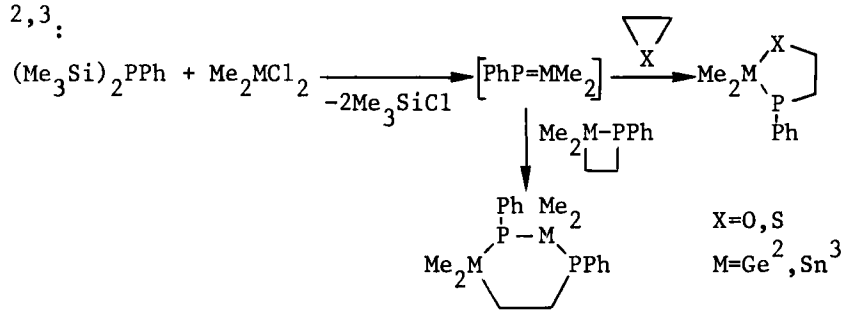
Abstract Various aspects of the reactivity of the first stable germaphosphene 1 and stannaphosphene 6 are described.

There is a particular interest at the present time in compounds of groups 14 and 15 in a low coordination state.[1] Several interesting new compounds with pπ-pπ bonds between phosphorus and heteroatoms have recently been synthesized : -P=X (X=C<,N-,P-,As-,Sb-).

Metallaphosphenes >M=P- (M=Ge,Sn) have long been speculated as reactive intermediates in dehalosilylation reactions between dichlorogermanes or stannanes and disilylphosphines, and characterized by trapping reactions on three (or four) membered heterocycles [2,3]:



GERMAPHOSPHENES

We have recently isolated the germaphosphene 1[4], the first stable compound with a germanium-phosphorus double bond, owing to very bulky substituents on germanium and phosphorus. The best route to

1 is the dehydrofluorination of the fluorogermylphosphine 2 with tert-butyllithium :

$$Mes_2Ge(F)(H)-PAr \xrightarrow[-tBuH,\ LiF]{tBuLi} Mes_2Ge=PAr$$

2 1

Mes: Ar:

The structure of 1 was confirmed by its physicochemical data ($\delta^{31}P$: +175 ppm...) and by its chemical behavior which we now report.

1 is very reactive towards protic reagents :

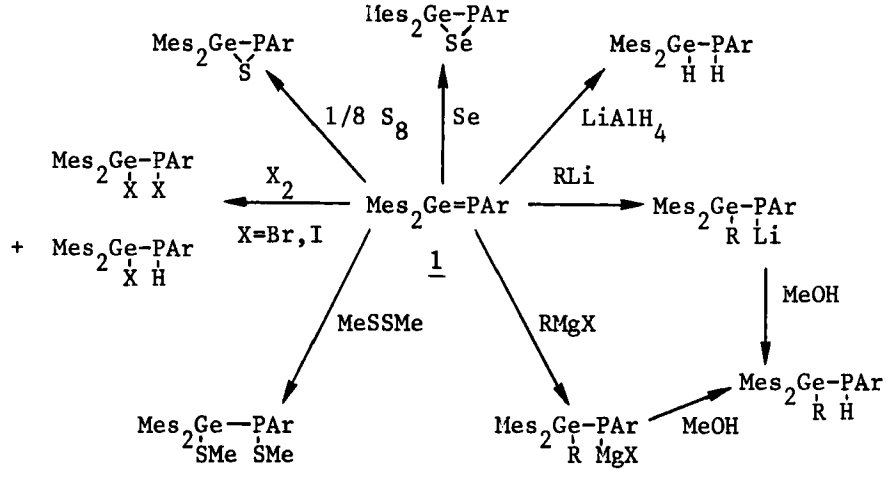
$$Mes_2Ge=PAr + AH \longrightarrow Mes_2Ge(A)(H)-PAr$$

1

(A: HO, MeO, Cl, CH_3COO, PhNH, iPrS, $Me_3P=CH$, $PhC\equiv C$)

In each case we have observed a regiospecific reaction with formation of the secondary phosphine; these results confirm the expected polarity $Ge^{\delta+}=P^{\delta-}$ of the germanium-phosphorus double bond. 1 reacts also easily with other electrophilic compounds such as halogens.

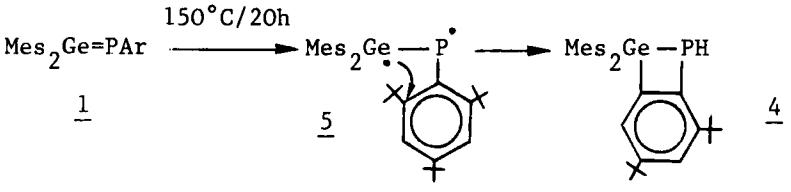
Nucleophilic additions are observed with lithio compounds, Grignard reagents and hydrides. 1 reacts probably in a radicalar process with dimethyldisulfide and gives cycloaddition reactions with sulfur and selenium. All these reactions are summarized in the following table :



Generally only the germanium-phosphorus double bond reacts and the single bond remains unaffected; the only exception is the reaction of 1 with carbon tetrachloride leading quantitatively to a compound with a phosphorus-carbon double bond, the phospha-alkene 3:

$$\underset{1}{Mes_2Ge{=}PAr} + CCl_4 \longrightarrow \underset{3}{ArP{=}CCl_2} + Mes_2GeCl_2$$

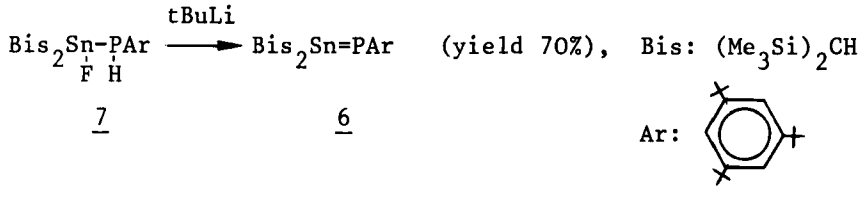
Thermolysis of 1 affords the first stable 2-germaphosphetane 4 which has been characterized by X-ray :



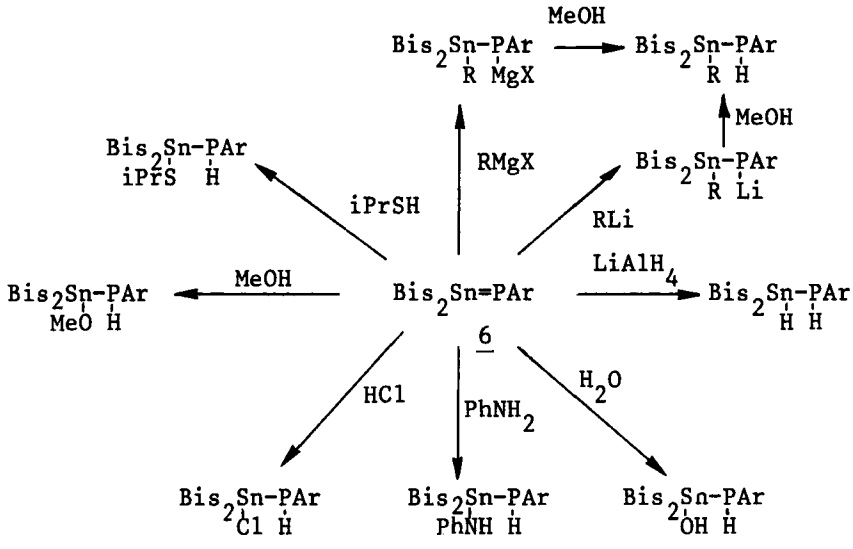
Formation of 4 involves a radicalar aromatic substitution by the intermediate 5.

STANNAPHOSPHENES

The first stable stannaphosphene 6[5] has been prepared by dehydrofluorination of fluorostannylphosphine 7 by tert-butyllithium :



The highly air-sensitive 6 has not yet been isolated in pure form but unambiguously characterized by its physicochemical data (low field $\delta^{31}P$ and $\delta^{119}Sn$, respectively + 204.7 and + 658.3 ppm, and large coupling constant $^1J(^{31}P\text{-}^{119}Sn)$: 2295 Hz and $^1J(^{31}P\text{-}^{117}Sn)$: 2191 Hz) and by its chemical reactivity; 6 is very reactive towards compounds with active hydrogens, lithio derivatives, Grignard reagents, hydrides, as summarized in the following scheme :



The heating of 6 at 65°C for 1h leads to the stannylene 8 and to the diphosphene 9 :

$$\underset{6}{Bis_2Sn{=}PAr} \xrightarrow{\Delta} \underset{8}{Bis_2Sn} + 1/2\ \underset{9}{ArP{=}PAr}$$

This reaction is one of the most important difference in the germaphosphene 1 and stannaphosphene 6 chemical behavior.

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