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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. Several interesting new compounds with $p\pi-p\pi$ 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 $\underline{1}^4$, the first stable compound with a germanium-phosphorus double bond, owing to very bulky substituents on germanium and phosphorus. The best route to

 $\underline{1}$ is the dehydrofluorination of the fluorogermylphosphine $\underline{2}$ with tert-butyllithium :

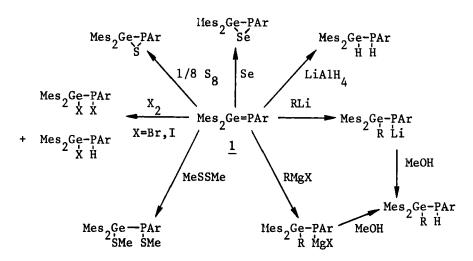
The structure of $\underline{1}$ was confirmed by its physicochemical data ($\delta^{31}P$: +175 ppm...) and by its chemical behavior which we now report.

1 is very reactive towards protic reagents:

Mes₂Ge=PAr + AH
$$\longrightarrow$$
 Mes₂Ge-PAr (A: H0, MeO, C1, CH₃COO, PhNH, iPrS, Me₃P=CH, PhC=C)

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

Nucleophilic additions are observed with lithio compounds, Grignard reagents and hydrides. $\underline{1}$ 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 $\underline{1}$ with carbon tetrachloride leading quantitatively to a compound with a phosphorus-carbon double bond, the phospha-alkene 3:

$$\frac{\text{Mes}_2\text{Ge=PAr} + \text{CC1}_4}{\frac{1}{2}} + \frac{\text{ArP=CC1}_2}{\frac{3}{2}} + \frac{\text{Mes}_2\text{GeC1}_2}{\frac{3}{2}}$$

Thermolysis of $\underline{1}$ affords the first stable 2-germaphosphetane 4 which has been characterized by X-ray :

Mes₂Ge=PAr
$$\xrightarrow{150^{\circ}\text{C}/20\text{h}}$$
 Mes₂Ge $\xrightarrow{\text{P}}$ Mes₂Ge $\xrightarrow{\text{PH}}$ $\xrightarrow{\underline{4}}$

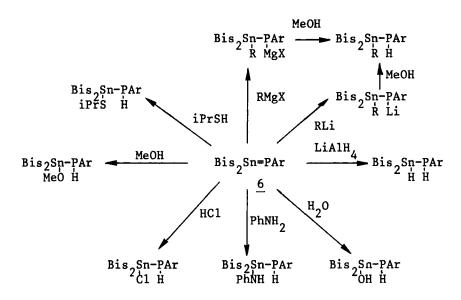
Formation of $\frac{4}{2}$ involves a radicalar aromatic substitution by the intermediate 5.

STANNAPHOSPHENES

The first stable stannaphosphene $\underline{6}^5$ has been prepared by dehydrofluorination of fluorostannylphosphine 7 by tert-butyllithium:

Bis₂Sn-PAr
$$\rightarrow$$
 Bis₂Sn=PAr (yield 70%), Bis: (Me₃Si)₂CH \rightarrow Ar: \rightarrow

The highly air-sensitive $\underline{6}$ 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 ${}^{1}J({}^{31}P^{-119}Sn)$: 2295 Hz and ${}^{1}J({}^{31}P^{-117}Sn)$: 2191 Hz) and by its chemical reactivity; $\underline{6}$ is very reactive towards compounds with active hydrogens, lithio derivatives, Grignard reagents, hydrides, as summarized in the following scheme:



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

$$Bis_2Sn=PAr \xrightarrow{\Delta} Bis_2Sn + 1/2 ArP=PAr$$

$$\frac{6}{2} \frac{8}{2} \frac{9}{2}$$

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

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