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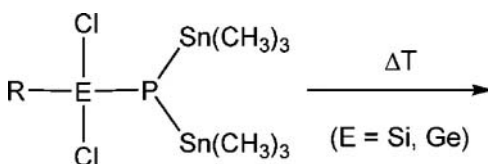
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TOWARDS HETERONUCLEAR TRIPLE BONDS INVOLVING SILICON OR GERMANIUM

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GRAPHICAL ABSTRACT



Abstract The thermal stability of stannylated phosphanosilanes/germanes has been explored, where chlorostannane elimination should yield multiply bonded systems. Although destannylation occurs, the resulting products are hydrophosphanes and polymeric materials.

Keywords Germanium; multiple bonds; NMR; phosphorus; silicon; tin

INTRODUCTION

Recently, the groups of Wiberg,¹ Sekiguchi,² and Tokitoh³ have demonstrated independently that stable compounds containing a silicon–silicon triple bond can be stabilized by a combination of steric and electronic effects. Other stable triply bonded silicon species are, however, unknown to date despite several attempts. We ourselves prepared precursors **1a,b**, which upon chlorostannane elimination should be prone to generate SiP and GeP multiply bonded systems.^{4,5} Moreover we explored the possibility to approach -Si≡C- units via conjugate addition to suitably functionalized alkynylsilanes,^{6,7} which in the course of the reaction lead to the generation of the first heterosubstituted 1-silaallenes.^{6,7} In this article, we describe recent efforts to encompass the destannylation of **1**.

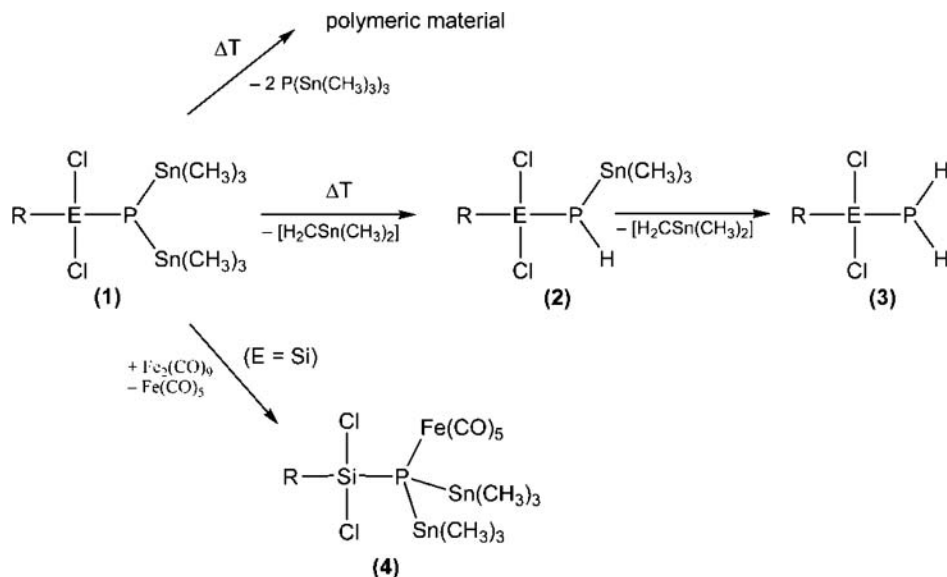
RESULTS AND DISCUSSION

The thermal elimination behavior of phosphanostannanes **1a,b** has been explored.⁴ Heating of the neat compounds to 200°C under inert conditions does not lead to the envisioned chlorostannane elimination but to destannylated hydrophosphanes **2** and **3** or

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Scheme 1 Elimination and complexation reactions of **1a,b(I-III)** [E = Ge (a), E = Si (b); R = Cp* (I), Mes (II), Tip(III)].

polymeric materials (Scheme 1). The complexation of the phosphorus center with an $\text{Fe}(\text{CO})_5$ fragment leading to **4** has also been explored successfully.⁸

CONCLUSIONS

The thermal treatment of stannylphosphano halo-silanes and germanes leads to destannylation under preservation of the halogen silicon/germanium bonds. The P-Sn bond seems to be the most reactive site of these molecules.

EXPERIMENTAL

Heating of neat **1** to 200°C under inert conditions leads to polymeric materials and compounds **2** and **3**. Relevant NMR data of **1-4** from Ref.⁸ are listed in Table 1.

Table 1 Selected NMR parameters of **1-4**

E =	R =	Entry	$\delta(^{31}\text{P})$ [ppm]	$^1\text{J}(\text{P}-^{117}\text{Sn})$ [Hz]	$^1\text{J}(\text{P}-^{119}\text{Sn})$ [Hz]	$^1\text{J}(\text{P-Si})$ [Hz]	$^1\text{J}(\text{P-H})$ [Hz]
Ge	Cp*	1a	-242.4	718	752	—	—
Si	Cp*	1bI	-272.1	669	721	116	—
Si	Mes	1bII	-242.5	681	713	99	—
Si	Tip	1bIII	-235.0	693	725	101	—
Si	Cp*	2bI	-261.1	538	563	96	176
Si	Mes	2bII	-210.0	593	621	83	179
Si	Tip	2bIII	-206.0	—	617	—	181
Ge	Cp*	3a	-224.8	—	—	—	183
Si	Cp*	3bI	-228.7	—	—	41	187
Si	Mes	3bII	-189.2	—	—	45	193
Si	Tip	3bIII	-183.0	—	—	43	191
Si	Cp*	4bI	-196.8	—	304	—	—
Si	Mes	4bII	-195.7	—	330	—	—

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