The first phosphagermacyclopropane prepared *via* cycloaddition of dimethylgermylene to the C=P double bond of phosphaalkene

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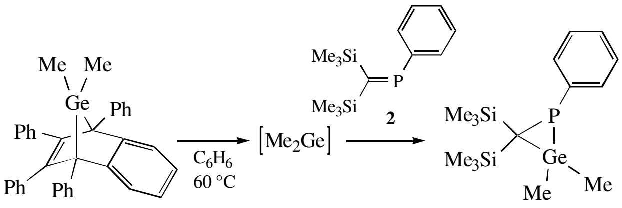
The cycloaddition reaction of phosphaalkene 2 with dimethylgermylene generated thermally *in situ* leads to the first representative of phosphagermacyclopropanes 3.

The [1+2] cycloaddition of heavy carbene analogues, silylenes and germylenes, to the C=C double bond has been successfully used for the synthesis of sila- and germacyclopropanes.[1–3] The interactions of carbene analogues with isolated carbon–heteroatom multiple bonds are studied much lesser. In particular, only two examples of the cycloaddition of silylene[4] and germylene[5] to the carbon–phosphorus triple bond resulted in the formation of phosphasila- and phosphagermacyclopropenes, respectively, are known. Reactions of carbene analogues with C=P bonds of phosphaalkenes have not been described up to now.

Here we report on the generation of the first phosphagermacyclopropane (phosphagermirane) by cycloaddition of short-lived dimethylgermylene to phosphaalkene $(Me_3Si)_2C{=}PPh$ **2**. The choice of **2** among the variety of known phosphaalkenes was prompted by the stability of **2** in an inert atmosphere at room temperature and, on the other hand, by the steric availability of the P=C double bond in **2**, since our preliminary studies have shown that phosphaalkenes with bulkier substituents were inert towards dimethylgermylene.

According to the ^{31}P NMR spectroscopy data, the reaction of Me_2Ge (thermally generated at 60 °C from 7,7-dimethyl-7-germanorbornadiene derivative **1**[6]) with phosphaalkene **2**[7] (molar ratio **1**:**2** = 1.5:1) led to the formation of a single phosphorus-containing reaction product. The reaction occurs with 100% conversion of the phosphaalkene; the overall integral intensity of the ^{31}P NMR signals remained unchanged. An excess of the Me_2Ge precursor should be used because of the polymerization of dimethylgermylene in the course of the reaction.



1 **3**

The ^{31}P NMR spectrum of the reaction product exhibits one singlet at –137.1 ppm. The position of this signal is characteristic of phosphiranes (–120 to –150 ppm).[8] The ^{1}H NMR spectrum of the product exhibits two signals of protons of two non-equivalent Me_3Si groups of the $(Me_3Si)_2C$ fragment (a singlet at –0.05 ppm and a doublet at 0.28 ppm, $^4J_{PH}$ 2.2 Hz) and two signals of protons of methyl groups of the Me_2Ge fragment (a singlet at 0.70 ppm and a doublet at 0.62 ppm, $^3J_{PH}$ 3.3 Hz) with the integral intensity ratio 3:3:1:1. The characteristic constant $^3J_{PH}$ observed for one of the signals due to the Me_2Ge group indicates the presence of a Ge–P bond in the product. The signals of phenyl protons are overlapped with those of 1,2,3,4-tetraphenylnaphthalene, which is formed upon the thermolysis of 7-germanorbornadiene **1**.

In the ^{13}C NMR spectrum of the reaction product, the signal of the quaternary carbon atom of the $(Me_3Si)_2C$ fragment is observed at 23.0 ppm (which is typical of phosphirane carbon atom signals[9]) as a doublet with the coupling constant $^1J_{PC}$ 69 Hz. We were unable to assign the signals of the carbon atoms of the Me_3Si and Me_2Ge groups since they overlap with numerous signals of the $(Me_2Ge)_n$ polymers in the region from –5 to +5 ppm.

In the ^{29}Si NMR spectrum of the reaction product, two doublets (at 0.29 and 0.93 ppm) of the non-equivalent Me_3Si groups are present. The coupling constants $^2J_{PSi}$ equal to 21.4 and 4.8 Hz, respectively, correspond to the suggested structure of **3**.

Thus, the spectroscopic data indicate that the product of the reaction of dimethylgermylene with phosphaalkene **2** has the structure of phosphagermirane **3**.[†]

Phosphagermirane **3** is a highly labile compound, which rapidly decomposes on air or upon heating. Our attempts to isolate **3** from solution were unsuccessful.

We attempted to prepare other phosphagermiranes by reactions of phosphaalkene **2** with stable germylenes and their complexes. We found that GeI_2 and $[(Me_3Si)_2N]_2Ge$ do not react with **2** at room temperature, while the interaction of **2** with $GeCl_2{\cdot}$dioxane resulted in a mixture of oxidation products of phosphaalkene **2**.

To obtain the silicon analogue of **3**, we studied the reaction of phosphaalkene **2** with dimethylsilylene generated photochemically from the silicon analogue of **1**, 7,7-dimethyl-7-silanorbornadiene **4**[10] (C_6D_6, 20 °C, **2**:**4** = 1:1). The ^{31}P NMR spectrum of reaction products exhibits a singlet at –132.4 ppm, which can be assigned to corresponding 1,1-dimethyl-2-phenyl-3,3-bis(trimethylsilyl)-2-phosphasilirane **5** by analogy with phosphagermirane **3**. Unfortunately, phosphaalkene **2** is a photolabile compound and partially photodecomposes during the reaction to give a number of products. These products exhibit signals in the ^{1}H, ^{13}C and ^{31}P NMR spectra; thus, we failed to assign unequivocally the signals belonging to phosphasilirane **5** in the ^{1}H and ^{13}C NMR spectra.

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[†] *2,2-Dimethyl-1-phenyl-3,3-bis(trimethylsilyl)-1,2-phosphagermirane* **3**. An NMR sample tube was charged with 85 mg (0.32 mmol) of phosphaalkene **2** and 258 mg (0.48 mmol) of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorbornadiene **1** in 1.0 ml of C_6D_6. The reaction mixture was heated at 60 °C in the spectrometer probehead. During the reaction the intensity of the ^{31}P NMR signal of starting phosphaalkene **2** at +376 ppm decreased down to zero and another signal at –137.1 ppm appeared simultaneously. The reaction was complete in 3 h.

^{1}H NMR (C_6D_6) δ: –0.05 (s, 9H, Me_3Si), 0.28 (d, 9H, Me_3Si, $^4J_{PH}$ 2.2 Hz), 0.62 (d, 3H, Me, $^3J_{PH}$ 3.3 Hz), 0.70 (s, 3H, Me). ^{13}C NMR (C_6D_6) δ: 23.0 [d, $C(SiMe_3)_2$, $^1J_{PC}$ 68.9 Hz]. ^{29}Si NMR (C_6D_6) δ: 0.29 (d, Me_3Si, $^2J_{PSi}$ 21.4 Hz), 0.93 (d, Me_3Si, $^2J_{PSi}$ 4.8 Hz). ^{31}P NMR (C_6D_6) δ: –137.1 (s).

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