

New substituents for the stabilization of low-coordinate germanium species: use in access to diazogermylenes.

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Streszczenie

The reactions of the P-bis(trimethylsilyl)amino-N-(trimethylsilyl)iminophosphine with various dialkoxydichlorogermanes (alkoxy: OR = OMe, OEt and Oi-Pr) at 0 °C led to the stable dichlorogermylene-complexes $[(RO)_2P(NSiMe_3)(N(SiMe_3)_2)]GeCl_2$ [R = Me (**1**), Et (**2**) and R = *i*-Pr (**3**)]. The solid-state structure of (**2**) has been determined by X-ray crystallography. A mechanism for the formation of these compounds is proposed, based on the transient species observed in the case of the isopropoxy derivatives. At room temperature in benzene solution, compounds (**1**) and (**2**) eliminate chlorotrimethylsilane without side reactions leading to the corresponding 2,4-diaza-3-phosphagermatidines $[(RO)_2P(NSiMe_3)_2]GeCl$ (**4**) and (**5**), respectively. At the opposite, complex (**3**) showed a modulated behavior: at room temperature, (**3**) still slowly eliminates mainly chlorotrimethylsilane with the formation of $[(i-PrO)_2P(NSiMe_3)_2]GeCl$ (**6**). Structure of this chlorinated germanium(II) compound which can also be seen as a germyl anion has been evidenced by an X-ray analysis. But at higher temperature (40–50 °C) (**3**) mainly decomposes with elimination of isopropylchloride leading to the formation of $[(i-PrO)(Me_3SiO)P(NSiMe_3)_2]GeCl$ (**7**) as a mixture of Z- and E-isomers. The mechanism of this reaction is discussed. The Z-isomer of (**7**) was successfully isolated after a selective crystallization, and investigated by an X-ray analysis. The interconversion mechanism of the two diastereoisomers is also discussed. Reaction of compound (**5**) with the lithio derivative of the trimethylsilyldiazomethane leads to the diazogermylene (**8**), a potential precursor of germa-alkyne.

Słowa kluczowe

Chlorinated germanium(II), Donor ligands, Mechanism, Diazogermylene

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