Derivatization of Silylated Heptaphosphanes

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Introduction

It is long known that the reaction of sodium-potassium phosphane Na₅P/K₅P with chlorosilanes ClSiR₃ proceeds to the heptaphosphoranes P₃(SiMe₃)₉[1]. Here we report on the reactions of two silylheptaphosphoranes, P₃(SiMe₂)₃ and P₃(Si(SiMe₃)₂)₃.

Synthesis and Reactions

P₃(SiMe₃)₃

By reaction of P₃(SiMe₃)₃ with one equivalent of KO'Bu or LiO'Bu, different isomers of the monoanion [K(P₃(SiMe₃)₃)]⁻ or [Li(P₃(SiMe₃)₃)]⁻ can be prepared. Contrary to the results of Fritz[2], we found that both salts of [(SiMe₃)₂P]⁻ are thermally stable for days.

The use of one equivalent of NaO'Bu led to a mixture of symmetric and asymmetric monoanions A and B.

From these monoanions, we were able to synthesize (SiMe₃)₃P·SiMe₂P(SiMe₃)₃. The reaction of A or B with Si(SiMe₃)₃Cl led to a mixture of at least three compounds P₃(SiMe₃)₃, (SiMe₃)₃P·Si(SiMe₃)₃, (SiMe₃)₂P(Si(SiMe₃)₂)₃.

The reactions with MgBr₂, HgCl₂, MgBr₂·Et₂O, B(CH₃)₃·CH₂Br, DMF, tBuOH, Ph₂SnCl₂ gave different results: either a degradation of the P₃-cage or a reformation of the starting product P₃(SiMe₃)₃.

We also discovered a new direct route for the preparation of the well known hexadecaphosphane [P₁₈]²⁺ using an excess of KO'Bu (1:2)[3].

P₃(Si(SiMe₃)₂)₃

Due to the bulkiness of the substituent, P₃(Si(SiMe₃)₂)₃ reacted with KO'Bu or LiO'Bu in a way very different from P₃(SiMe₃)₃.

With one equivalent of KO'Bu, a SiSi-bond instead of a SiP-bond was cleaved. A rearrangement occurred quickly and led to the compounds C and D.

The reaction with one equivalent of LiO'Bu produced the asymmetric monoanion Li⁺[P₃(Si(SiMe₃)₂)₃]⁻ which further reacted with CF₃COOH to give [Si(SiMe₃)₂]P₃H. Here we report on the first crystal structure of a cage P₃P₃H.

Conclusion and Outlook

We showed that we can prepare preferentially A or B using KO'Bu or LiO'Bu. Is this also possible with other silylsubstituents?

We were able to link two cages starting from A and B. We plan to synthesize polymers starting from the heptaphosphane ions [P₃P₃]²⁺. Further work in this field is in progress.

Acknowledgement

Austrian Science Foundation (FWF) – Project P19167

References