

Introduction

It is long known that the reaction of sodium-potassium phosphanide $\text{Na}_3\text{P}/\text{K}_3\text{P}$ with chlorosilanes ClSiR_3 proceeds to the heptaphosphanes $\text{P}_7(\text{SiR}_3)_3$ ^[1]. Here we report on the reactions of two silylheptaphosphanes, $\text{P}_7(\text{SiMe}_3)_3$ and $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$.

Synthesis and Reactions

$\text{P}_7(\text{SiMe}_3)_3$

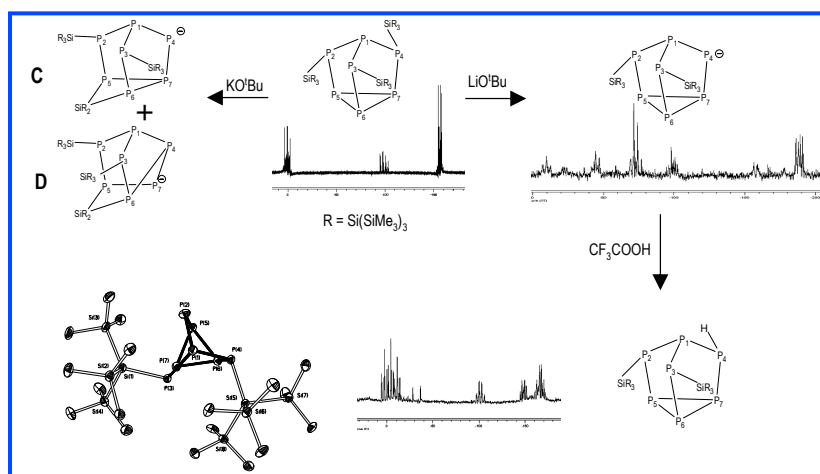
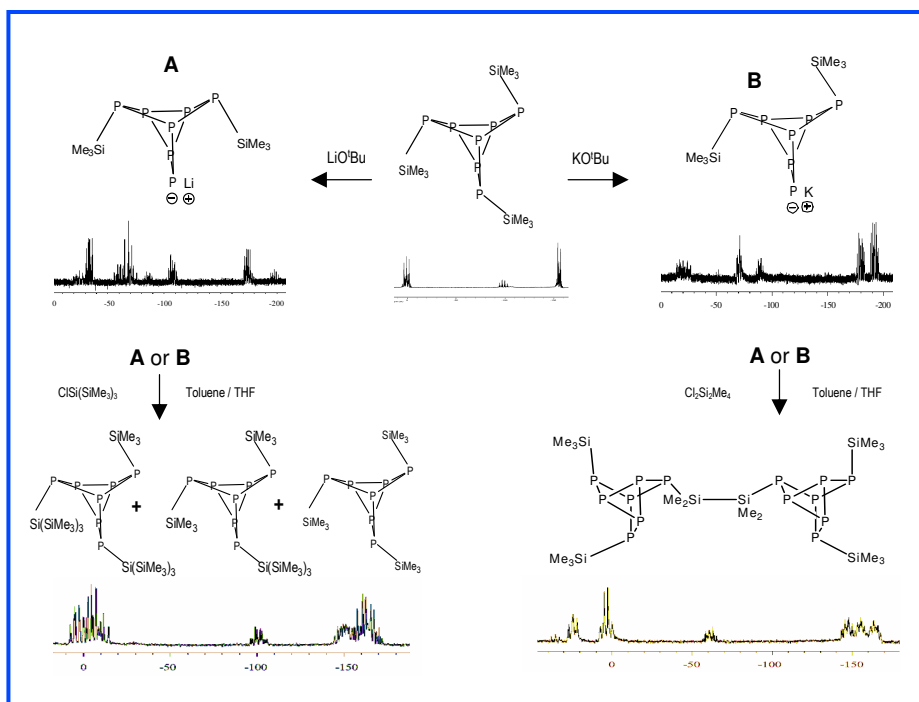
By reaction of $\text{P}_7(\text{SiMe}_3)_3$ with one equivalent of KO^tBu or LiO^tBu , different isomers of the monoanion $[\text{R}_2\text{P}_7]^-$ (**A** or **B**) can be prepared. Contrary to the results of G.Fritz^[2], we found that both salts of $[(\text{SiMe}_3)_3\text{P}_7]^-$ are thermally stable for days.

The use of one equivalent of NaO^tBu led to a mixture of symmetric and asymmetric monoanions **A** and **B**.

From these monoanions, we were able to synthesize $(\text{SiMe}_3)_2\text{P}_7\text{Si}_2\text{Me}_4\text{P}_7(\text{SiMe}_3)_2$. The reaction of **A** or **B** with $\text{Si}(\text{SiMe}_3)_3\text{Cl}$ led to a mixture of at least three compounds $\text{P}_7(\text{SiMe}_3)_3$, $(\text{SiMe}_3)_2\text{P}_7\text{Si}(\text{SiMe}_3)_3$, $(\text{SiMe}_3)\text{P}_7\text{Si}(\text{SiMe}_3)_3$.

The reactions with MgBr_2 , HgCl_2 , $\text{MgBr}_2\text{Et}_2\text{O}$, $\text{BrCH}_2\text{CH}_2\text{Br}$, DMF , $^t\text{BuOH}$, Ph_2SnCl_2 gave different results: either a degradation of the P_7 -cage or a reformation of the starting product $\text{P}_7(\text{SiMe}_3)_3$.

We also discovered a new direct route for the preparation of the well known hexadecaphospanide $[\text{P}_{16}]^{2-}$ using an excess of KO^tBu (1:2)^[3].



$\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$

Due to the bulkiness of the substituent, $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$ reacted with KO^tBu or LiO^tBu in a way very different from $\text{P}_7(\text{SiMe}_3)_3$.

With one equivalent of KO^tBu , 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^tBu produced the asymmetric monoanion $\text{Li}^+[\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_2]^-$ which further reacted with CF_3COOH to give $[\text{Si}(\text{SiMe}_3)_3]_2\text{P}_7\text{H}$. Here we report on the first crystal structure of a cage $\text{P}_7\text{R}_2\text{H}$.

Conclusion and Outlook

We showed that we can prepare preferentially **A** or **B** using KO^tBu or LiO^tBu . 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 heptaphosphanide ions $[\text{P}_7\text{R}]^{2-}$. Further work in this field is in progress.

Acknowledgement

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References

- [1] Schmidbauer H; Bauer A. *Phosphorus, Sulfur, and Silicon*, **1995**, *102*, 217-219
- [2] Fritz G.; Uhlmann R. Z. *Anorg. Allg. Chem.*, **1978**, *440*, 168-170.
- [3] Milyukov V.A.; Kataev A.V.; Sinyashin O.G.; Hey-Howkins E. *Russian Chemical Bulletin*, **2006**, *55*, 1295-1296.