

## Introduction

The synthesis and X-Ray structure of  $P_7(\text{SiMe}_3)_3$  was first reported by G.Fritz<sup>[1]</sup>, who also prepared the heptaphosphanide anion  $[P_7(\text{SiMe}_3)_2]^-$  by reaction with  $t\text{BuLi}$

Or  $\text{LiP}(\text{SiMe}_3)_2$ . He observed the quick decomposition of the anion<sup>[2]</sup>. We have investigated whether more stable monoanions of this type can be prepared?

## Synthesis, Reactions and NMR calculations

Because of the reactive P-Si bond in  $P_7(\text{SiMe}_3)_3$  it can be used for further reactions. For instance, it may serve as a precursor for  $P_7\text{H}_3$ <sup>[3]</sup>.  $P_7(\text{SiMe}_3)_3$  can exist in two isomeric forms **A** and **B**. Only the formation of **A** is observed.

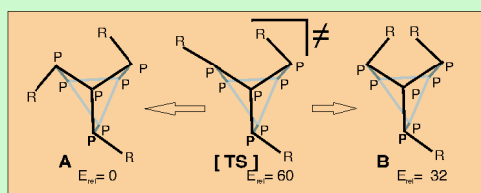


Fig. 1: Relative energies (kJ/mol B3LYP/6-31+G\*) of  $P_7(\text{SiMe}_3)_3$  geometries

For geometry optimization the B3LYP/6-31+G(d) method has been used as implemented in GAUSSIAN package of programs<sup>[4]</sup>. In the population analysis the Mulliken method<sup>[5]</sup> was applied:

The  $C_3$  symmetric isomer **A** of  $P_7(\text{SiMe}_3)_3$  is 32 kJ/mol more stable at B3LYP/6-31+G\* than the asymmetric structure **B** with two substituents pointing towards each other. According to earlier calculations the inversion barrier is 60 kJ/mol high.

We have investigated the reaction of  $P_7(\text{SiMe}_3)_3$  with  $\text{KO}^i\text{Bu}$  and  $\text{LiO}^i\text{Bu}$  which led to different isomers of  $[P_7(\text{SiMe}_3)_2]^-$ , **D** and **E** (see Fig. 2). We can prepare predominantly monoanion **D** from **A** using  $\text{KO}^i\text{Bu}$  in presence of 18-crown-6 in toluene and monoanion **E** using  $\text{LiO}^i\text{Bu}$  in THF.

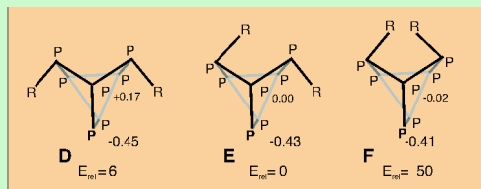


Fig. 2: Relative energies (kJ/mol B3LYP/6-31+G\*) of the isomers of  $[P_7(\text{SiMe}_3)_2]^-$  anion.

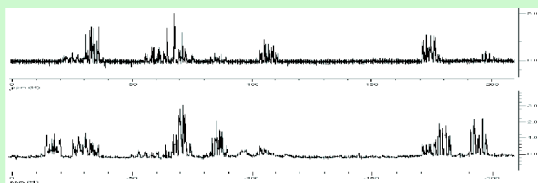


Fig. 3:  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of monoanions  $[P_7(\text{SiMe}_3)_2]^-$  **D** (top) and **E** (bottom).

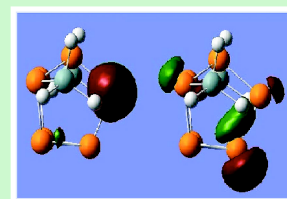
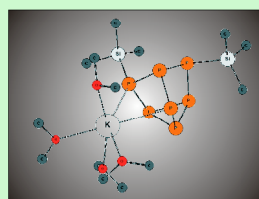


Fig. 4: Framework geometry of  $D\text{-K}(\text{OMe})_4$  and HOMO (left) and HOMO-1 (right) of **E**.

The HOMO of **E** (Figure 4; B3LYP/6/31+G\*) has  $\pi$  character and explains why the counterion in optimised **E** -  $\text{M}(\text{OMe})_3$  geometries is not in the mirror plane but bent towards the bulky  $\text{SiMe}_3$  groups.

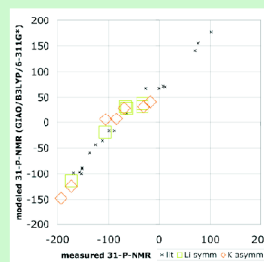


Fig. 5: Measured vs. calculated (B3LYP/6-311G\*/B3LYP/6-31+G\*)  $^{31}\text{P}$ NMR chemical shifts (theoretical reference is  $\text{PH}_3$  with shift=-240 ppm and magn. Shielding = 556.2 ppm). Squared Correlation Coefficient,  $cc$ , is 0,989 for the  $P_7\text{Me}_3$  and  $P_7\text{R}_3$  with  $\text{R}=\text{Me}$  [6],  $\text{SiMe}_3$  [7] (crosses) and  $CC=0,920$  for the 14 data points of the  $P_7(\text{SiMe}_3)_2\text{M}(\text{Me}_2\text{O})_3$  complexes with  $\text{M}=\text{Li}$  and  $\text{K}$ .

The calculated chemical shifts (Figure 5) of phosphorus in the  $P_7\text{R}_3$  molecules and  $P_7\text{R}_2^-$  anions are systematically calculated at about 70 ppm too low field with the B3LYP/6-311G\*/B3LYP/6-31G\* method. Nevertheless, agreement between the measured and modeled shifts is well enough to confirm the expected semi-symmetric structure for the Li salt and the semi- $C_3$  conformation for the corresponding potassium salt.

We have also investigated the reaction of  $\text{Si}_2\text{Me}_4\text{Cl}_2$  with monoanion **E**. In the resulting molecule, two cages are linked by a disilane unit as depicted in Fig. 6.

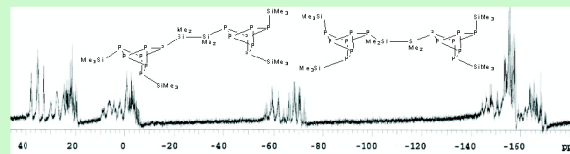


Fig. 6: Stereoisomers of  $(\text{SiMe}_3)_2\text{P}_7\text{Si}_2\text{Me}_4\text{P}_7(\text{SiMe}_3)_2$  - left RRR/RRR, right SSS/RRR.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the stereoisomers of  $(\text{SiMe}_3)_2\text{P}_7\text{Si}_2\text{Me}_4\text{P}_7(\text{SiMe}_3)_2$ .

## Conclusions and Outlook

In contrary of the results of Fritz we observe that the anion  $[P_7(\text{SiMe}_3)_2]^-$  does not decompose quickly. Other stable or moderately stable compounds are expected starting from structure **D**. Further work in this field of synthesis is in progress.

## Acknowledgement

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## References

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