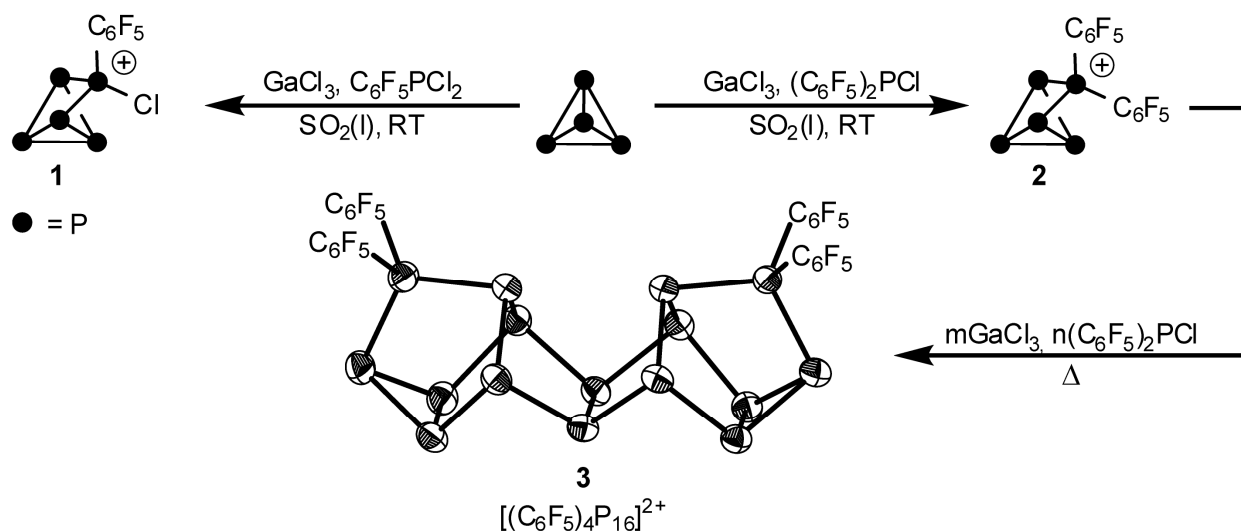


Cationic Phosphorus Clusters – Preparation of $[(C_6F_5)_xP_5Cl_{2-x}]^+$ ($x=1-2$) and $[P_{16}(C_6F_5)_4]^{2+}$

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Several transition metal complexes are suitable for the activation of P_4 .^[1] In contrast, activation and functionalisation of white phosphorus by reactive main group element species is a rather unexplored, but a rapidly developing field.^[2,3] Our group recently reported on a molten medium approach^[3a,4] to cationic phosphorus clusters such as $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$ and $[Ph_6P_7]^{3+}$ by consecutive insertion of the phosphonium cation $[Ph_2P]^+$ into the P–P-Bonds of P_4 .^[3a] This methodology was extended by using electron deficient pentafluorophenyl substituted monochloro- and dichlorophosphanes as phosphonium sources. The phosphorus rich clusters $[(C_6F_5)_2P_5]^+$ (**1**) and $[(C_6F_5)P_5Cl]^+$ (**2**) can be prepared in high yields from a melt reaction or reactions in liquid SO_2 as a solvent. Furthermore, **2** undergoes a subsequent transformation to the dicationic cluster $[P_{16}(C_6F_5)_4]^{2+}$ (**3**) by the reaction with $(C_6F_5)_2PCl$ at elevated temperatures. The core of the dicationic cluster **3** represents a structural analogue of the anionic P_{16}^{2-} and neutral R_2P_{16} .^[5]



The syntheses and characterizations of cations **1** – **3** are discussed in this poster.

References:

- [1] M. Peruzzini, L. Gonsalvi, A. Romerosa, *Chem. Soc. Rev.* **2005**, *34*, 1038; [2] J. M. Lynam, *Angew. Int. Ed.* **2008**, *47*, 831; [3] a) J. J. Weigand, M. H. Holthausen, *Angew. Chem. Int. Ed.* **2009**, *48*, 295; b) M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, *131*, 14210; [4] J. J. Weigand, N. Burford, A. Decken, *Eur. J. Inorg. Chem.* **2008**, 4343; [5] M. Baudler, *Angew. Chem. Int. Ed.* **1982**, *21*, 492.