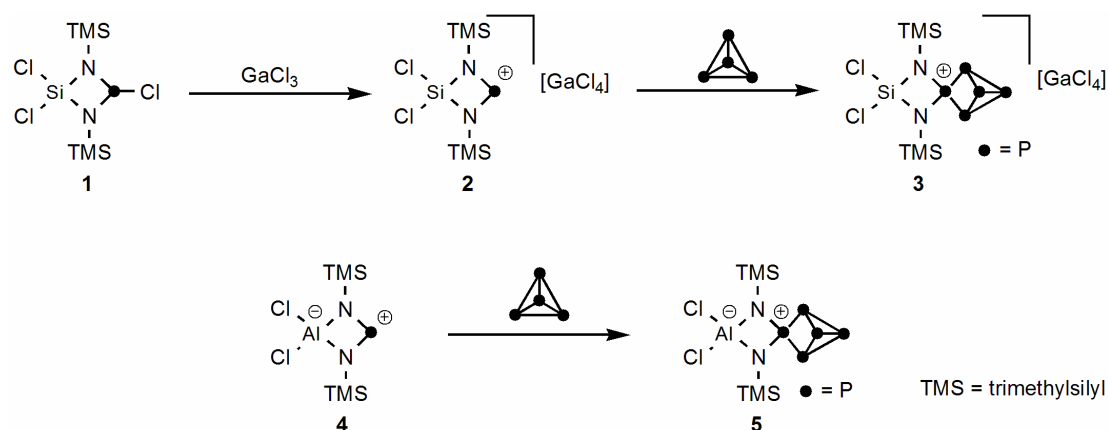


Zwitterionic and Cationic P₅-Clusters from Four-membered Phosphorus–Nitrogen–Metal Heterocycles

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Many transition metal complexes containing a broad variety of P_n ligands resulting from P₄ activation have been discovered. In comparison, the functionalization of P₄ with main group fragments represents a new and rapidly developing field.^[1] We recently reported a solvent-free methodology^[2] for the functionalization of the P₄ tetrahedron to form the new cationic phosphorus-rich cluster systems [Ph₂P₅]⁺, [Ph₄P₆]²⁺ and [Ph₆P₇]³⁺ by consecutive insertion of [Ph₂P]⁺ into the P–P bonds of the P₄ tetrahedron.^[3] Furthermore we were able to utilize the disguised bifunctional Lewis acid [DippNP]₂²⁺, obtained from *cyclo*-1,3-diphospha-2,4-diazane [DippNP(Cl)₂], for the stepwise insertion in the P₄ tetrahedron to form the novel clusters [P₄(DippNP)₂Cl]⁺ and [(P₄)₂(DippNP)₂]²⁺.^[4]



In this contribution, we present the reactions of 1,3-diaza-2-phospha-4-silacyclobutane **1** and 1,3-diaza-2-phosponia-4-aluminatacyclobutane **4**, which are easily prepared from bis[(trimethylsilyl)amino](trimethylsilylimino)phosphane.^[5] In case of **1** addition of GaCl₃ leads to the formation of the phosphonium ion **2**, which undergoes an insertion reaction with the P₄ tetrahedron to form the cationic cluster **3**. Compound **4** describes a zwitterionic phosphonium ion, which also reacts in a P–P bond insertion reaction with P₄ to form the novel zwitterionic cluster **5**.^[6]

References:

- [1] J. M. Lynam, *Angew. Chem.* **2008**, *120*, 843; *Angew. Chem. Int. Ed.* **2008**, *47*, 831. [2] J. J. Weigand, N. Burford, A. Decken, *Eur. J. Inorg. Chem.* **2008**, 4343. [3] J. J. Weigand, M. H. Holthausen, *Angew. Chem.* **2009**, *121*, 301; *Angew. Chem. Int. Ed.* **2009**, *48*, 295. [4] M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, *131*, 14210. [5] E. Niecke, R. Kröher, *Angew. Chem.* **1976**, *88*, 758. [6] M. H. Holthausen, C. Richter, A. Hepp; J. J. Weigand, *Chem. Commun.* **2010**, in press.