

Gerüstumlagerungen bei einem Yliddiylphosphan-Tetrameren

Skeletal Rearrangements of an Ylidediylphosphane Tetramer

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Condensation of the bis(trimethylsilyl)ylide $\text{Ph}_3\text{PC}(\text{SiMe}_3)_2$ with PX_3 ($\text{X} = \text{Cl}, \text{Br}$) yields the ionic tetramers **4a,b** of ylidediyl-halophosphanes. Their cations $(\text{Ph}_3\text{PC})_4\text{P}_4\text{X}_3^+$ possess a tetraphosphabicyclo[2.2.2]octane (or tetraphospha-barrelane) skeleton ($[\text{AC}]_3\text{BD}$ spin system in ^{31}P NMR spectra). Reaction of **4a** with AlCl_3 or GaCl_3 converts the singly charged cation into the tetracation $(\text{Ph}_3\text{PC})_4\text{P}_4^{4+}$ having a cubane structure ($[\text{AB}]_4$ spin system in the ^{31}P NMR spectrum). SbCl_5 oxidizes **4a** to give the dication $(\text{Ph}_3\text{PC})_4\text{P}_4\text{Cl}_4^{2+}$ (counter ion: SbCl_5^{2-}) with the barrelane skeleton either preserved (**7**) or rearranged into a tetraphospha-bicyclo[3.3.0]-octane structure **8**. In the latter case the dication contains a central diphosphanedionium bridge. Replacement of a chloro-substituent in **4a** by an amino group also gives rise to a further dissociation and a concomitant rearrangement. The resulting dications $(\text{Ph}_3\text{PC})_4\text{P}_4\text{NR}_2\text{Cl}^{2+}$ possess a tetraphospha-bicyclo-[3.2.1]octane structure (with eight nonequivalent phosphorus atoms).

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