

## Poster Presentation

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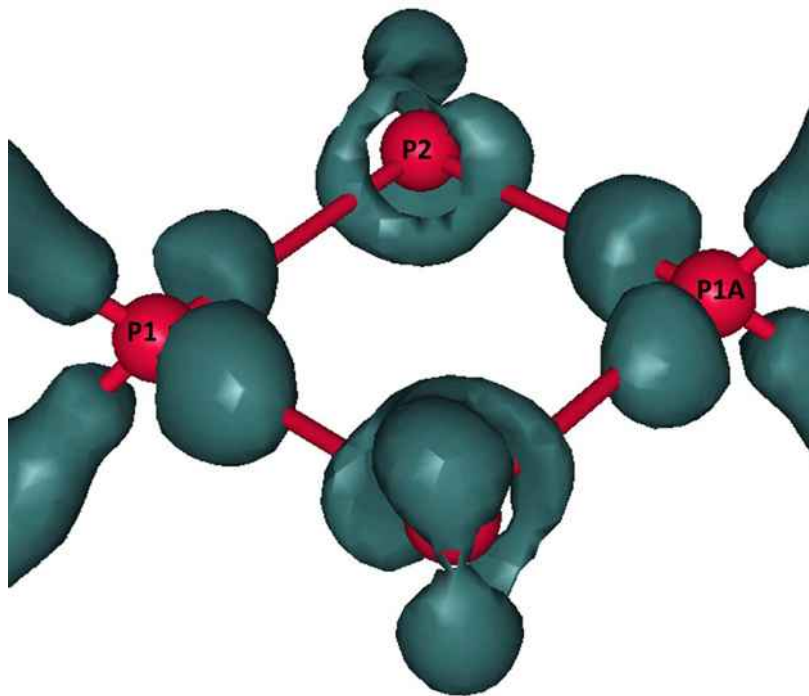
### Charge density study of the first mixed-valent tetraphosphete

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The first  $\lambda^3, \lambda^5$ -tetraphosphete contains a  $4\pi$ -electron four-membered ring as the central structural unit of a dispirocyclic system and can thus be classified as an analogue to diphosphetes and cyclodiphosphazenes. According to its crystal structure the central  $P_4$  unit exhibits not only P–P bonds which are of equal length (P1–P2 2,139(1) Å, P1–P2A 2,142(1) Å), but also rhombic distortion (P1–P2–P1A 79,4(1)°, P2–P1–P2A 100,6(1)°).[1] Therefore its electronic structure cannot be described as 'Phosphacyclobutadiene' but either as a bis(ylide) or as a system with delocalized double bonds. After various quantum chemical calculations and an extensive examination of its reaction and coordination behavior failed to answer this question, we addressed the problem via a detailed analysis of its charge density distribution. The experimental charge density based on high resolution X-ray diffraction data collected at low temperature is determined by multipole least squares refinement using the program package XD2006.[2] In a first step, the static deformation density exhibits charge density which is located mainly outside of the  $P_4$  ring plane at the  $\lambda^3$ -phosphorus atoms but simultaneously redistributed into the P–P bond area. In addition to that, a study of its topological properties and an inspection of the Laplacian of the electron density according to Bader's 'Quantum Theory of Atoms in Molecules' (QTAIM)[3] further highlight the bonding features. They reveal polar Si–N, Si–C and P–N bonds with a decreasing amount of electrostatic contribution as well as four valence shell charge concentrations (thus  $sp^3$  hybridization) at each of the phosphorus atoms. Finally supported by theoretical calculations, the results illustrate the unique bonding situation in the  $P_4$  unit combining a high ylidic character with unusual not exclusively sigma-like P–P bonds.

[1] W. Frank, V. Petry, E. Gerwalin et al, *Angew. Chem. Int. Ed.* 1996, 35, 1512., [2] (a) N. K. Hansen, P. Coppens, *Acta Crystallogr.* 1978, A34, 909. (b) A. Volkov, P. Macchi, L. J. Farrugia et al., *XD2006*, 2006., [3] R. W. F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1990.



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