Small Neutral P_n Molecules

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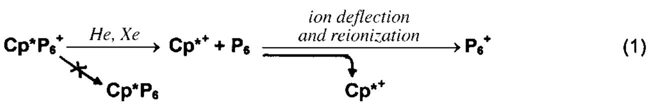
Among the stable and well-studied element modifications of phosphorus are, besides the „parent structure" of white, tetrahedral P_4, the modifications resulting from thermolysis, namely, black phosphorus (double layers of chairlike P_6 rings), violet or Hittorf's phosphorus (P_2-P_8-P_2-P_9 repeating units that form tubes of five-membered rings, which, in a simplified way, can be described as being arranged crosswise like wood piles),[1] and red phosphorus, whose controversial structure was only recently predicted by theory by Häser et al.[2] (P_{10}-P_2 repeating units) and structurally confirmed in $(CuI)_3P_{12}$ by Pfitzner et al.[3] as helical P_{10}-P_2 strands embedded in a matrix of CuI layers.

There have been numerous attempts to experimentally characterize the small molecules P_3, P_4, P_5, and P_6 as neutral species. In this respect, the research groups of Schwarz (Berlin) and Jutzi (Bielefeld) have now achieved a major breakthrough[4] with the detection of neutral P_6 in the gas phase by neutralization–reionization (NR) mass spectrometry.[5]

Starting from the structurally characterized P_6 benzvalene derivative $Cp^*_2P_6$[6] ($Cp^* = \sigma$-bound C_5Me_5), whose EI mass spectrum shows $Cp^*P_6^+$ and Cp^{*+} as the major fragments along with the molecular ion, P_6^+ and P_n^+ ($n = 1-5$) are detected in the following order of intensity $P_4^+ \gg P_3^+ > P_2^+ \approx P_6^+ \gg P_5^+ \approx P^+$ [Eq. (1)] by means of the neutral fragment reionization method (N_fR), a variation of the NR method.



(1)

Extensive theoretical investigations[7] have established the following order for the stability of the five P_6 isomers (Figure 1):[7a] (a) > (b) > (c) > (d) ≫ (e). On the basis of this finding along with the P_6 benzvalene framework of $Cp^*_2P_6$ the authors propose a benzvalene structure ((a) in Figure 1) for the neutral P_6 molecule detected in the gas phase.

As a general rule, neutral and charged P_n molecules are more stable the fewer double bonds the molecule contains

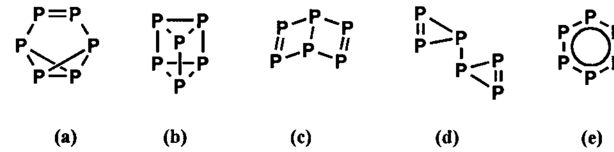
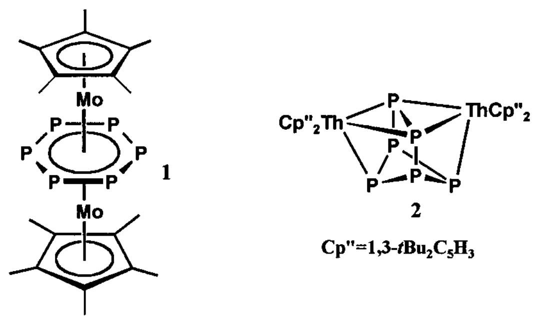


Figure 1. The P_6 isomers isoelectronic to the five $(CH)_6$ valence isomers (isolobal relationship: P $\leftrightarrow$ CH) of benzene. P_6 benzvalene (a), P_6 prismane (b), P_6 Dewar benzene (c), P_6 bicyclopropenyl (d), and P_6 benzene (e).

and the larger the value of n is. The slightly higher stability of P_6 benzvalene over P_6 prismane (Figure 1) can be explained when additional strain and resonance energies are taken into consideration.[7b]

To characterize unstable molecules, one can either turn to matrix techniques or to coordinative stabilization; it is also possible in certain cases to achieve kinetic stabilization by using sterically demanding substituents. Pertinent examples from the organometallic chemistry of phosphorus are the compounds **1** and **2**, whose P_6 ligand in the molybdenum triple-decker sandwich complex **1** contains the all-phosphorus analogue of benzene as the middle deck,[8a,b] whereas the dinuclear thorium complex **2** contains an open-edge P_6 benzvalene unit.[8c]



Neutral P_5 has so far not been detected. Of the structures calculated (Figure 2), the P_4 butterfly framework (f) (cf. P_6

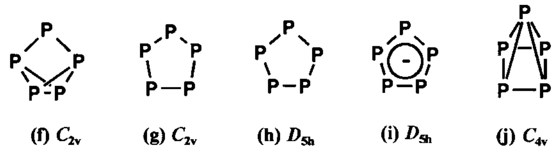


Figure 2. Calculated geometries (f), (g), (h), and (j) of neutral P_5 as well as planar, aromatic *cyclo*-P_5^- (i).

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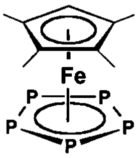
benzvalene, (a) in Figure 1) bridged by one P atom represents the most stable P_5 structure, followed by (g) (slightly distorted planar P_5 ring) and the almost energetically equivalent structures of the undistorted P_5 ring (h) and of the square-pyramidal P_5 (j).[7a]

If for P_5 one goes from the 25 valence electron (VE) radical to the 26 VE anion ((i) in Figure 2) by introduction of a negative charge, then, as shown by Baudler et al.,[9a] the all-phosphorus analogue of the cyclopentadienide ion (*cyclo*-$P_5^- \triangleq$ *cyclo* $C_5H_5^-$) can be prepared in solution in the form of the MP_5 salts (M = Li, Na) and characterized; *cyclo*-P_5^- is almost as aromatic as the $C_5H_5^-$ analogue.[10] As for the P_6 benzene (see complex **1**), the 6π-electron system of *cyclo*-P_5^- can also be coordinatively stabilized in the form of the unusually stable (cf. the isoelectronic ferrocene, $[Cp_2Fe]$) sandwich complex **3**[9b,a].



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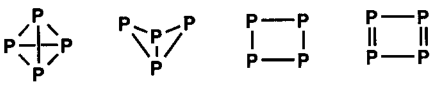
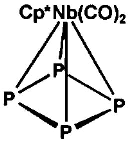
Of the calculated structures for neutral P_4[7a], as expected the P_4 tetrahedron ((k) in Figure 3) of white phosphorus is by far the most stable form. It is followed by the P_4 butterfly (roof-type) form (l) and then by the P_4 rectangle (m). A P_4 zigzag chain comprising two weakly bound P_2 units is a particularly unstable form.



(k) T_d (l) D_{2d} (m) D_{2h} (n)

Figure 3. Calculated geomtries (k)–(m) of neutral P_4 as well as planar tetraphosphacyclobutadiene (n).

All P_4 structure alternatives shown in Figure 3 can be coordinatively stabilized in the form of complexes with 17-VE L_nM fragments (2 × terminal for (l)), 16-VE L_nM fragments (μ-bridging for (l), and terminal for (k)) and 14-VE L_nM fragments (type (n) as tetraphosphacyclobutadiene complex **4**).[11]



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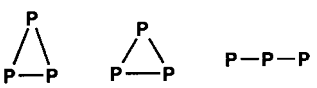
For the neutral 15-VE P_3 radicals theoretical studies[7a] report the isosceles P_3 triangle ((o) in Figure 4) to be slightly more stable than the equilateral triangle (p), and the linear arrangement (q) is significantly more unstable.



(o) C_{2v} (p) D_{3h} (q) $D_{\infty h}$

Figure 4. Calculated geometries (o)–(q) of the neutral P_3 radical.

The equilateral P_3 triangle (p) can be stabilized both in triple-decker complexes $[L_nM(P_3)ML_n]^{n+}$ as well as in triphosphametallatetrahedranes $[L_nMP_3]$ with one 15-VE L_nM fragment.[12] Bent P_3 ligands are found in polynuclear complexes.[11]

If white phosphorus P_4 is heated to 1000–1500 °C, one finds exclusively the equilibrium $P_4 \rightleftarrows 2P_2$ and no indication of other P_n species.[13] P_2, :P≡P:, a well-characterized molecule both theoretically[7] and in the gas phase, displays diverse ligand properties similar to those of acetylene HC≡CH to which it is the isoelectronic and isolobal.[11]

The extension of the use of neutralization-reionization mass spectrometry for the detection of new neutral P_n allotropes will be dependent primarily on the availablity of suitable P_n starting materials bearing easily removable substituents or ligands—a new challenge for preparative phosphorus chemistry. A worthwhile goal besides P_5[9a,b] (provided that suitable precursors can be found) would be P_8 cuneane, which according to calculations [7, 14] is the most stable P_8 isomer. As an almost ubiquitous P_8 building block it is a structural motif of Hittorf's phosphorus, is discussed for the clusters P_{25}^+, P_{33}^+, P_{41}^+, and P_{49}^+, whose P_n^+ frameworks possibly consist of nP_8 cuneane building blocks ($n = 3-6$) each with an additional P cap,[14] and could be complex-chemically stabilized as a P_8 cuneane with two open-edges.[15] If one goes from the small to the larger neutral P_n molecules, then P_{20}, the all-phosphorus analogue of the Paquette's $(CH)_{20}$ dodecahedron (a platonic solid with 12 pentagons, 20 vertices, and 30 edges) represents a modification of phosphorus, the search for which should not be a search for utopia, particularly since theory predicts that P_{20} lies energetically only slightly above the value for $5 \times P_4$ units.[16, 7d]

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