Experimental Evidence for the Existence of Neutral P_6: A New Allotrope of Phosphorus**

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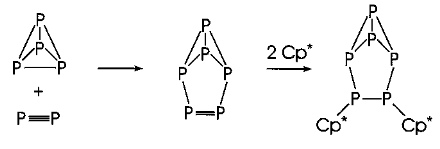
Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Despite the cross-relationship to carbon and the neighboring position of sulfur, experimental evidence for the existence of molecular allotropes of phosphorus P_n with n larger than 4 is scarce. In contrast, numerous computational studies on small phosphorus clusters such as hexaphosphabenzene and cubic P_8 have been performed since the 1980s.[1, 2] More recent theoretical studies of phosphorus clusters[3] also included ionic species such as cyclic P_5^-,[4] anionic P_n^- clusters with $n = 1-9$,[5] $P_{(2n+1)}^+$ cations with $n = 3-5$[6] as well as multiply charged phosphorus species, for example cyclic P_7^{3-}.[7] Far fewer experimental facts are known about phosphorus clusters larger than P_4. Positively charged P_n^+ with n up to 89 and P_n^- anions ($n \leq 49$) have been produced by laser ablation of red phosphorus.[8] Admixture of other elements to phosphorus in the laser-ablation process also affords the formation of heteronuclear clusters X_mP_n (X = B, C, Al, Si, Co, Ni).[8, 9] Further, a PtP_6^+ cation has recently been generated in the successive dehydrogenation of phosphane by bare platinum ions.[10]

The most salient experimental information about the energetics of phosphorus clusters is so far provided by the photoelectron detachment spectra of P_n^- anions ($n = 1-9$);[5] for the P_6^- species of interest here, a vertical electron binding energy of 2.22 ± 0.05 eV was determined.

While knowledge about molecular allotropes of phosphorus larger than P_4 is limited, a huge variety of polyphosphane derivatives is known, and the research conducted by Baudler and co-workers[11] is representative in this respect.[12] Here we report the use of such a polyphosphane derivative to probe the existence of the neutral P_6 molecule in the gas phase by means of neutralization–reionization (NR)[13] mass spectrometry.

The synthesis of the tricyclic polyphosphane **1** was described in 1989.[14] Compound **1** contains a P_6 unit having a benzvalene skeleton with two η^1-coordinated pentamethylcyclopentadienyl (Cp*) ligands. Conceptually, structure **1** can be viewed as arising from a formal [2+2] cycloaddition of a P_2 unit to a P_4 tetrahedron followed by saturation of the remaining P–P double bond in the hexaphosphabenzvalene with two Cp* ligands (Scheme 1). Conversely, **1** might serve as a precursor for the generation of P_6 due to the leaving-group character of the Cp* moiety,[15] provided that P_6 is (at least kinetically) stable with respect to the dissociation into P_4 and P_2; the atomization energies calculated by Jones and Hohl predict the dissociation $P_6 \rightarrow P_4 + P_2$ to be endothermic by about 1 eV.[3a]



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Scheme 1. Hypothetical cycloaddition of P_2 and P_4 to hexaphosphabenzvalene and its stabilization by two Cp* ligands resulting in **1**.

Electron ionization (EI) of gaseous **1** affords a molecular ion along with $Cp^*P_6^+$ and Cp^{*+} as major fragments.[14] Not surprisingly, loss of one Cp* unit to afford $Cp^*P_6^+$ prevails in the unimolecular dissociation of the metastable radical cation $\mathbf{1}^{+\bullet}$.[16] In the present context, the $Cp^*P_6^+$ cation is of particular interest. Unimolecular dissociation of the metastable ion $Cp^*P_6^+$ affords $Cp^*P_2^+$ and Cp^{*+} fragments in a ratio of about 10:1 (Figure 1 a), corresponding to formal losses of P_4 and P_6, respectively. The latter dissociation gains in importance upon collisional activation (CA) of $Cp^*P_6^+$ (Figure 1 b) in that the $Cp^*P_2^+$:Cp^{*+} ratio decreases to 1.5:1. Abundant

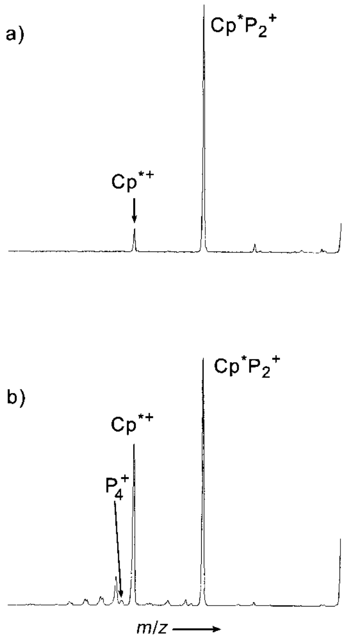

Figure 1. a) Metastable ion and b) collisional activation mass spectra (collision gas: helium) of B(1)/E(1)-mass-selected $Cp^*P_6^+$ generated by dissociative electron ionization of **1**. Note the characteristic series of hydrocarbon fragments $C_mH_n^+$ at lower masses due to consecutive decay of ionized Cp*.

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signals corresponding to P_n^+ cations are not observed in either the CA or the EI spectra. This finding is in accordance with the assumption that the ionization energies (IEs) of phosphorus clusters are larger than that of the Cp* radical. For example, even for the unsubstituted cyclopentadienyl radical, IE(Cp) = 8.4 eV is well below IE(P_4) = 9.1 eV[19] and equals the computed IE(P_6) = 8.4 eV of the benzvalene structure;[7b] complete methylation is safely assumed to further reduce the IE of the cyclopentadienyl unit. Formation of Cp^{*+} as a product of the unimolecular dissociation of $Cp^*P_6^+$ suggests the interesting perspective that an intact P_6 molecule is lost as a neutral species. However, sequential evaporation of P_4 and P_2 according to 1) $Cp^*P_6^+ \rightarrow Cp^*P_2^+ + P_4$ and 2) $Cp^*P_2^+ \rightarrow Cp^{*+} + P_2$ cannot be ruled out, and loss of neutral P_2 indeed constitutes a major process in the dissociation of $Cp^*P_2^+$.

The possible formation of neutral P_6 can only be monitored if a technique is used which samples the neutral species liberated upon dissociation of $Cp^*P_6^+$. The "ideal" experiment for this task is collision-induced dissociative ionization (CIDI),[20] in which the neutral species formed upon dissociation of metastable ions are selectively ionized. Unfortunately, however, the CIDI method is not very sensitive, and no useful CIDI spectra were obtained for metastable $Cp^*P_6^+$. Instead, we examined $Cp^*P_6^+$ by means of neutralization–reionization (NR) mass spectrometry,[13] in which two electron transfer events occur sequentially: First the ion of interest is neutralized in a high-energy collision with a suitable target gas, and the remaining ions are deflected, then the pure beam of neutral molecules is reionized in a second collision event, and the ions formed are mass-analyzed and detected; here, reionization to cations is applied.[13]

The NR spectra of $Cp^*P_6^+$ are unexpectedly dominated by P_n^+ fragments ($n = 1-6$); hydrocarbon fragments due to the cyclopentadienyl ligand are almost absent (Figure 2). This result implies that only minor amounts of neutral C_mH_n fragments are formed in the experiments. To achieve further insight, two different collision gases were used for neutralization, xenon (Figure 2a) and helium (Figure 2b). Xenon (IE = 12.1 eV) is known to serve as a versatile collision gas for the neutralization of cations.[13] In the present case, neutralization of $Cp^*P_6^+$ would result in formation of neutral $Cp^*P_6^{\bullet}$ radical; whether or not this neutral is long-lived, it should inevitably give rise to $C_mH_n^+$ fragments upon reionization (c.f. the predominance of $C_mH_n^+$ over P_n^+ signals in Figure 1b). This is not observed experimentally (Figure 2a), and thus it appears as if neutralization does not take place to a major extent. According to arguments outlined by Wesdemiotis and co-workers,[21] the use of helium in the first collision almost prevents neutralization because, even in a high-energy collision event, IE(He) = 24.5 eV is much too large to allow for efficient electron transfer from He to the cation under study. Instead, the high-energy collision with helium prompts dissociation of the cation, whose neutral fragments are reionized in the second step. Consequently, the resulting reionization spectrum contains information about the neutral fragments; Wesdemiotis and co-workers coined this variant of NR as neutral fragment reionization (N_fR). The clean P_n^+ pattern ($n = 1-6$) observed in Figure 2b fully supports this conjecture. Accordingly, neutralization of $Cp^*P_6^+$ seems to be particularly unfavorable, and instead dissociation of the cation predominates. The distinctive P_6^+ signals in Figures 2a and 2b can thus be associated with the reionization of intact neutral P_6, which is inter alia formed upon collision-induced dissociation of the $Cp^*P_6^+$ cation (Scheme 2). This scenario also accounts for the different signal-to-noise ratios in Figures 2a and 2b, because collision-induced dissociation of keV ions is much more effective for helium than for xenon in sector mass spectrometers. Further support for the presence of intact P_6 is provided by the fact that the P_n^+ signals for the even-numbered clusters ($n = 4$ and 6) are much more abundant than for the P_5^+ fragment, which would require loss of a phosphorus atom, even though the latter has a lower IE[2] and prevails over P_4^+ and P_6^+ upon direct laser vaporization of phosphorus.[22]

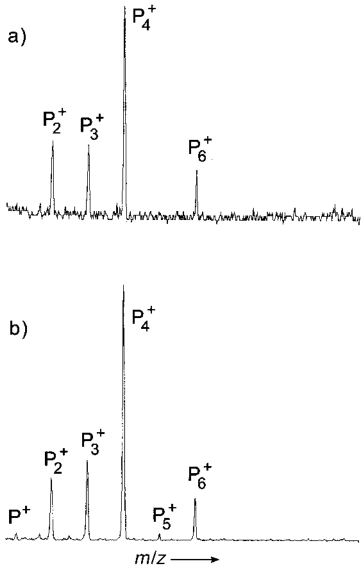
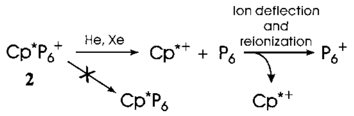


Figure 2. Neutralization–reionization mass spectra of B(1)/E(1)-mass-selected $Cp^*P_6^+$ generated by dissociative electron ionization of **1**; a) collision gases: xenon and oxygen, b) collision gases: helium and oxygen.



Scheme 2. Competition between fragmentation and electron transfer in high-energy collisions of $Cp^*P_6^+$.

These experiments provide firm evidence for the existence of neutral P_6 in the gas phase with a minimal lifetime on the order of microseconds. These experiments, however, cannot provide any information concerning the structure of the neutral species. Nevertheless, the use of **1** as a precursor suggests a benzvalene skeleton. Moreover, preliminary calculations using density functional theory indicate that the benzvalene structure of the P_6 unit remains intact in the $Cp^*P_6^+$ cation.[23] Last but not least, benzvalene structures were also predicted as the global minima in ab initio calculations of anionic,[5] neutral,[3, 7] and cationic hexaphosphorus.[7] Consequently, it appears reasonable to assume a benzvalene structure for the neutral P_6 species formed from $Cp^*P_6^+$, which is then monitored as a cation upon vertical electron transfer in the reionization step.

Returning to the conceptual description shown in Scheme 1, the presence of a P=P double bond suggests a high reactivity of neutral P_6, which is likely to prevent its isolation as bulk substance in the condensed phase. Besides the stabilization of the P_6 unit by covalent bonding to organic ligands, as realized in **1**, a dimerization of P_6 is also conceivable which could result in a polycyclic P_{12} allotrope which no longer possesses P=P double bonds,[3f] and may thus be less reactive and possibly stable towards dissociation into three P_4 molecules.

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[16] The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors).[17] The ions of interest were generated by electron ionization (electron energy 70 eV) of **1**; the latter compound was introduced as the solid probe. Because of a competition between evaporation and thermolysis of **1**, progressive heating[18] of the sample from 120 to 180 °C at a rate of about 5 °C min^{-1} was required to achieve reasonably constant ion fluxes. The ions having a kinetic energy of 8 keV were mass-selected using B(1) and E(1), and the respective mass spectra were recorded by scanning B(2). For collisional activation, helium was used as collision gas at 80 % transmission (T). In the NR experiments,[13, 17] neutralization was afforded by either xenon or helium (see text), while oxygen was used for reionization (each gas, 80 % T). All spectra were accumulated and on-line processed with the AMD/Intectra data system; 10 to 40 spectra were averaged to improve the signal-to-noise ratios.

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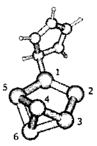
[23] All-electron density functional theory calculations were performed with Turbomole 5.1[24] on various isomers of $C_5H_5P_6^+$, which may serve as a model for the $Cp^*P_6^+$ cation. These isomers include inter alia Cp-substituted P_6 cations with a benzvalene skeleton (**2**), a prismane backbone (**3**), a Dewar-benzene structure (**4**), and a benzene-type P_6 unit (**5**). At all levels of theory, **2** corresponds to the most stable isomer. With B3LYP and a TZVP basis set,[25] the isomers **3**, **4**, and **5** are predicted to be 9, 48, and 75 kJ mol^{-1}, respectively, less stable than structure **2**.



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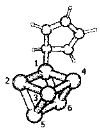

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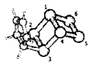

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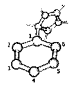

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