The Gas-Phase Route from $Cp^*{}_2P_6$ to Neutral Hexaphosphorus

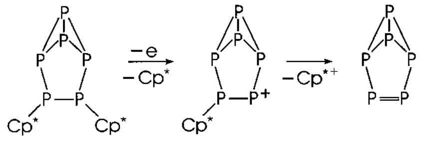
Markus Reiher*[a] and Detlef Schröder*[b]

Abstract: Density functional theory has been applied to gain insight into the fragmentation and redox behavior of $Cp_nP_6{}^{+/0}$ and $Cp^*{}_nP_6{}^{+/0}$ cations and neutral species ($n = 1, 2$) in the gas phase. Particular attention is paid to the previously reported generation of neutral hexaphosphorus upon high-energy collisions of the $Cp^*P_6{}^+$ cation. Theory provides an explanation for the experimentally observed effect that collisional electron transfer to the $Cp^*P_6{}^+$ cation is negligible in that the associated Franck–Condon factors are predicted to be unfavorable. In contrast, dissociation of $Cp^*P_6{}^+$ into $Cp^{*+} + P_6$ has a relatively low energy demand, thereby accounting for the efficient formation of neutral P_6 in the gas phase. Theoretical exploration of the parent compound Cp_2P_6 reveals that the unsubstituted cyclopentadienyl ligand is much less suitable in this respect, thereby sustaining the previous suggestion that Cp* is a particularly good leaving group.

Keywords: cyclopentadienyl ligands · density functional calculations · electron transfer · hexaphosphabenzvalene · mass spectrometry · phosphorus

Introduction

The disubstituted hexaphosphabenzvalene $Cp^*{}_2P_6$,[1] (**1***), a P_6 unit that has a benzvalene skeleton with two η^1-bound Cp* ligands (Cp* = pentamethylcyclopentadienyl), has recently been used as a precursor for the generation of neutral hexaphosphorus P_6 in the gas phase.[2] To this end, **1*** was subjected to electron ionization (EI), and the resulting ions were examined by various mass-spectrometric methods, including neutralization–reionization (NR)[3] experiments with the $Cp^*P_6{}^+$ fragment, which permit the generation of neutral hexaphosphorus in the gas phase (Scheme 1).



1* **2***

Scheme 1.

The major fragmentation of the molecular ion $Cp^*{}_2P_6{}^{\cdot+}$ corresponds to the loss of a Cp* ligand [Eq. (1)]. High-energy collisions of the resulting $Cp^*P_6{}^+$ fragment with different target gases T lead to predominant fragmentations according to Equations (2a) and (2b), whilst collisional neutralization either to the intact neutral species [Eq. (3a)] or to dissociation products (e.g. [Eq. (3b)]) is negligible. The neutral P_6 molecule formed according to Equation (2b) can then be detected by mass spectrometric means via collisional reionization [Eq. (4)].[2]

$$Cp^*{}_2P_6{}^{\cdot+} \rightarrow Cp^*P_6{}^+ + Cp^{*\cdot} \tag{1}$$

$$Cp^*P_6{}^+ \rightarrow Cp^*P_2{}^+ + P_4 \tag{2a}$$

$$\rightarrow Cp^{*+} + P_6 \tag{2b}$$

$$Cp^*P_6{}^+ + T \rightarrow Cp^*P_6{}^{\cdot} + T^{\cdot+} \tag{3a}$$

$$\rightarrow Cp^{*\cdot} + P_6 + T^{\cdot+} \tag{3b}$$

$$P_6 \rightarrow P_6{}^{\cdot+} + e \tag{4}$$

Accordingly, the NR spectrum of mass-selected $Cp^*P_6{}^+$ is dominated by $P_n{}^+$ fragments ($n = 1-6$). Quite surprising, however, is that hardly any hydrocarbon fragments from to the Cp* ligand are observed. Although not unprecedented,[4] the essential absence of collisional neutralization according to Equation (3) is exceptional in NR experiments.[3]

Here, we report a computational study of the dissociative ionization of $Cp^*{}_2P_6$ as well as the parent system Cp_2P_6 (Cp = cyclopentadienyl) including all relevant fragmentation and redox processes en route to the generation of the neutral P_6 molecule in the gas phase.

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Computational Methods

All calculations employed density functional programs provided by the TURBOMOLE 5.1 suite;[5] specifically, the hybrid functional B3LYP[6, 7] and the Becke–Perdew functional dubbed BP86[8] as implemented in TURBOMOLE. The BP86 functional was also used for the resolution of the identity (RI) technique.[9] All structures were optimized in all-electron Kohn–Sham calculations by using Ahlrichs' valence triple-zeta basis sets with polarization functions on all atoms (TZVP).[10] The two different functionals used (B3LYP and BP86) give good agreement for relative energies for the species examined in this study (mean deviation: 0.14 ± 0.20 eV), thereby lending confidence to the appropriate description of all species treated by these two methods. For the sake of brevity, only B3LYP energies are reported here because this hybrid functional shows a somewhat better performance in the prediction of thermochemical data;[11] the BP86/RI results are given in the Supporting Information. Vibrational frequencies were determined from the second derivatives of the total electronic energy computed as numerical first derivatives[12] to analytical energy gradients obtained from TURBOMOLE. The optimized structures were visualized with the program Molden.[13]

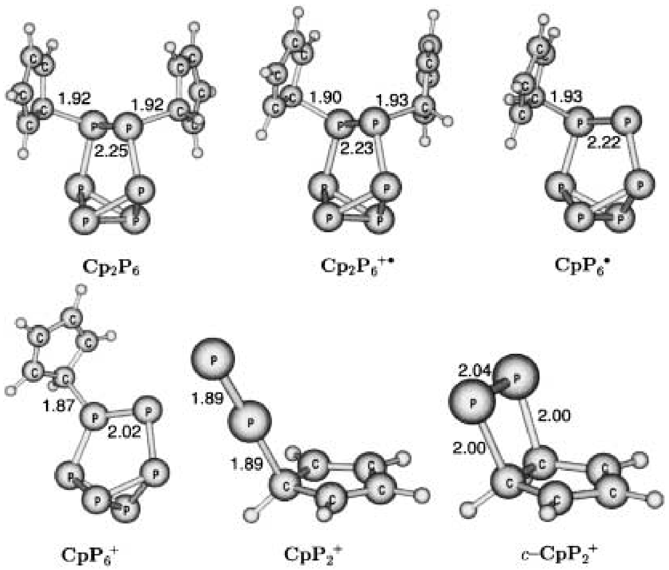
Results

The metastable ion and high-energy collision experiments to be analyzed here involve adiabatic as well as vertical transitions. Specifically, the unimolecular dissociation of metastable ions with kinetic energies in the keV region samples typical lifetimes in the microsecond range, and can therefore be considered to proceed to the relaxed geometries of the relevant fragments, that is, the occurrence of adiabatic processes. Similarly, ion dissociation of polyatomic molecules following collisional activation is most likely to proceed adiabatically, although prompt dissociations may contribute to some extent. In marked contrast, the neutralization of cations in high-energy collisions requires close contact of the projectile cation with the neutral target gas in order to allow electron transfer (ET) from the target (here: He and Xe)[2] to the fast-moving ionic species. For example, if we consider a distance of 10 Å[14] as a rough guess for an effective collision parameter of $Cp^*_2P_6^{\cdot+}$, the interaction time of the projectile and the quasistationary target is in the order of 10^{-14} s at 8 keV kinetic energy. Hence, collisional ET can be assumed to occur vertically and is therefore governed by Franck–Condon effects.[3, 15, 16] Consequently, a concise analysis of the mass-spectrometric fragmentation patterns in NR experiments requires both the knowledge of adiabatic and vertical redox properties.[4b, 17]

These considerations define the guidelines for the present theoretical study. In the following, we discuss the way from the neutral precursor $Cp^*_2P_6$ to the generation of neutral hexaphosphorus upon collisional activation of mass-selected $Cp^*P_6^+$ in the gas phase. The unsubstituted Cp variants are considered in addition to the fully methylated Cp* system.

According to the B3LYP/TZVP calculations, the neutral compounds Cp_2P_6 and $Cp^*_2P_6$ have rather similar, C_2-symmetrical structures (Figures 1 and 2); representative bond lengths are $r_{CP} = 1.92$ Å and $r_{PP} = 2.25$ Å for Cp_2P_6 compared with $r_{CP} = 1.96$ Å and $r_{PP} = 2.25$ Å for $Cp^*_2P_6$.[18] The sequential homolytic bond strengths are computed as $D_0(CpP_6–Cp) = 1.57$ eV and $D_0(Cp–P_6) = 0.79$ eV compared with $D_0(Cp^*P_6–Cp^*) = 1.10$ eV and $D_0(Cp^*–P_6) = 0.54$ eV, respectively (Table 1).

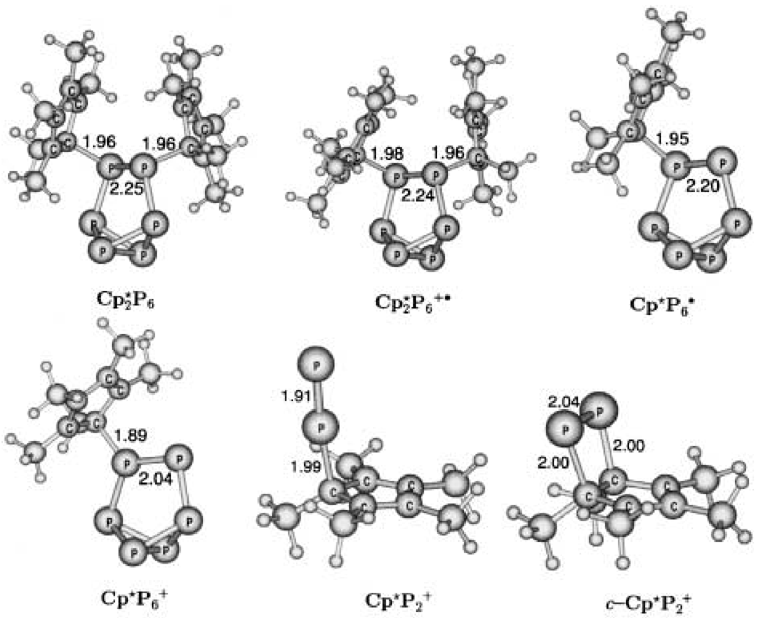
The adiabatic ionization energies to the corresponding monocations are predicted as $IE_a(Cp_2P_6) = 7.26$ eV and



Cp_2P_6 $Cp_2P_6^{+\cdot}$ $CpP_6^{\cdot}$

CpP_6^+ CpP_2^+ c–CpP_2^+

Figure 1. Fully optimized B3LYP/TZVP structures of Cp_2P_6, $Cp_2P_6^{\cdot+}$, $CpP_6^{\cdot}$, CpP_6^+, CpP_2^+, and c-CpP_2^+ (selected bond lengths in Å).



$Cp^*_2P_6$ $Cp^*_2P_6^{+\cdot}$ $Cp^*P_6^{\cdot}$

$Cp^*P_6^+$ $Cp^*P_2^+$ c–$Cp^*P_2^+$

Figure 2. Fully optimized B3LYP/TZVP structures of $Cp^*_2P_6$, $Cp^*_2P_6^{\cdot+}$, $Cp^*P_6^{\cdot}$, $Cp^*P_6^+$, $Cp^*P_2^+$, and c-$Cp^*P_2^+$ (selected bond lengths in Å).

Table 1. Relative free energies E_{rel} at 0 K and 298 K (in eV)[a] for neutral and ionized Cp_2P_6, $Cp^*_2P_6$, and relevant dissociation asymptotes calculated with B3LYP/TZVP.

	$E_{\text{rel, 0 K}}$	$E_{\text{rel, 298 K}}$	derived properties
Cp_2P_6	0.00	0.00	
$CpP_6^{\bullet} + Cp^{\bullet}$	1.57	1.01	$D_0(CpP_6{-}Cp) = 1.57$ eV
$CpP_6^{\bullet}$ (v)[b] $+ Cp^{\bullet}$	2.45[c]		$RE_v(CpP_6^+) = 6.21$ eV
$2\,Cp^{\bullet} + P_6$	2.36	1.26	$D_0(Cp{-}P_6) = 0.79$ eV
$Cp_2P_6^{\bullet +}$	7.26	7.27	$IE_a(Cp_2P_6) = 7.26$ eV
$Cp_2P_6^{\bullet +}$ (v)[d]	7.66[c]		$IE_v(Cp_2P_6) = 7.66$ eV
$CpP_6^+ + Cp^{\bullet}$	8.66	8.09	$D_0(CpP_6^+{-}Cp) = 1.40$ eV $IE_a(CpP_6) = 7.09$ eV
$c\text{-}CpP_2^+ + P_4 + Cp^{\bullet}$	9.00	7.91	$\Delta_rH(Cp^*P_6^+ \rightarrow c\text{-}Cp^*P_2^+ + P_4) = 0.34$ eV
CpP_6^+ (v)[d] $+ Cp^{\bullet}$	9.20[c]		$IE_v(CpP_6) = 7.63$ eV
$CpP_2^+ + P_4 + Cp^{\bullet}$	10.05	8.89	$D_0(CpP_2^+{-}P_4) = 1.39$ eV
$CpP_6^{\bullet} + Cp^+$	10.16	9.60	$D_0(CpP_6^{\bullet}{-}Cp^+) = 2.89$ eV $IE_a(Cp) = 8.59$ eV
$P_6^+ + 2\,Cp^{\bullet}$	10.42	9.34	$IE_a(P_6) = 8.06$ eV
$Cp^+ + P_6 + Cp^{\bullet}$	10.95	9.85	$D_0(Cp^+{-}P_6) = 2.29$ eV
$Cp^+ + P_4 + P_2 + Cp^{\bullet}$	11.06	9.47	$D_0(Cp^+{-}P_2) = 1.01$[e]/2.06 eV[f]
$Cp^*_2P_6$	0.00[g]		
$Cp^*P_6^{\bullet} + Cp^{*\bullet}$	1.10[g]		$D_0(Cp^*P_6{-}Cp^*) = 1.10$ eV
$Cp^*P_6^{\bullet}$ (v)[b] $+ Cp^{*\bullet}$	1.97[g]		$RE_v(Cp^*P_6^+) = 5.69$ eV
$2\,Cp^{*\bullet} + P_6$	1.64[g]		$D_0(Cp^*{-}P_6) = 0.54$ eV
$Cp^*_2P_6^{\bullet +}$	6.51[g]		$IE_a(Cp^*_2P_6) = 6.51$ eV
$Cp^*_2P_6^{\bullet +}$ (v)[c]	6.70[g]		$IE_v(Cp^*_2P_6) = 6.70$ eV
$c\text{-}Cp^*P_2^+ + P_4 + Cp^{*\bullet}$	7.66[g,h]		$\Delta_rH(Cp^*P_6^+ \rightarrow c\text{-}Cp^*P_2^+ + P_4) = -0.03$ eV
$Cp^*P_6^+ + Cp^{*\bullet}$	7.70[g,i,j]		$D_0(Cp^*P_6^+{-}Cp^*) = 1.19$ eV $IE_a(Cp^*P_6) = 6.60$ eV
$Cp^*P_6^{\bullet} + Cp^{*+}$	8.02[g]		$D_0(Cp^*P_6^{\bullet}{-}Cp^{*+}) = 1.51$ eV $IE_a(Cp^*) = 6.92$ eV
$Cp^*P_6^+$ (v)[c] $+ Cp^{*\bullet}$	8.14[g]		$IE_v(Cp^*P_6) = 7.04$ eV
$Cp^{*+} + P_6 + Cp^{*\bullet}$	8.56[g]		$D_0(Cp^{*+}{-}P_6) = 0.86$ eV
$Cp^{*+} + P_4 + P_2 + Cp^{*\bullet}$	8.67[g]		$D_0(Cp^{*+}{-}P_2) = 0.13$[k]/1.01[l] eV
$Cp^*P_2^+ + P_4 + Cp^{*\bullet}$	8.80[g,m]		$D_0(Cp^*P_2^+{-}P_4) = 1.11$ eV
$P_6^+ + 2\,Cp^{*\bullet}$	9.70[g]		$IE_a(P_6) = 8.06$ eV

[a] 1 eV = 96.485 kJ mol^{-1}. Rounding errors of < 0.01 eV have been removed. A compilation of all computed energies is provided as Supporting Information. [b] Single-point calculation of the neutral species at the optimized geometry of the cation. [c] *ZPE* of the optimized structure used for $E_{0\,K}$. [d] Single-point calculation of the cation at the optimized geometry of the neutral species. [e] Relative to CpP_2^+. [f] Relative to $c\text{-}CpP_2^+$. [g] *ZPE*s estimated, see Supporting Information. [h] 7.70 eV with the computed *ZPE*. [i] 7.72 eV with the computed *ZPE*. [j] The prismane isomer of the $Cp^*P_6^+$ analogue to structure **3** of the CpP_6^+ system (Figure 3) is computed to be 0.12 eV higher in energy than $Cp^*P_6^+$ with a hexaphosphabenzvalene skeleton. [k] Relative to $Cp^*P_2^+$. [l] Relative to $c\text{-}Cp^*P_2^+$. [m] 8.82 eV with the computed *ZPE*.

$IE_a(Cp^*_2P_6) = 6.51$ eV. While the differences in bond lengths of the neutral and monocationic species are small (< 0.04 Å),[19] distortion of the Cp substituents leads to C_1 symmetry in the corresponding molecular cations. Accordingly, vertical ionizations of the neutral species are somewhat more demanding than the adiabatic ones: $IE_v(Cp_2P_6) = 7.66$ eV and $IE_v(Cp^*_2P_6) = 6.70$ eV, resulting in differences $\Delta IE_{v/a}$ of 0.40 and 0.19 eV, respectively. Further on, we use the term $\Delta IE_{v/a}$ as a qualitative measure for the energy deposition in the species formed upon vertical ET. Considering the size of the systems, the increases of internal energies resulting from vertical ionizations are not unusually large and appear unlikely to induce rapid isomerizations or dissociations. In fact, the computed bond strength $D_0(CpP_6^+{-}Cp) = 1.40$ eV is only 0.17 eV lower than that of the neutral compound and the $D_0(Cp^*P_6^+{-}Cp^*)$ of 1.19 eV even slightly exceeds that of the neutral counterpart, $D_0(Cp^*P_6{-}Cp^*) = 1.10$ eV. Resuming these results, ionization of Cp_2P_6 and $Cp^*_2P_6$ is likely to yield the corresponding intact molecular ions.

The lowest dissociation channels of the $Cp_2P_6^+$ and $Cp^*_2P_6^+$ cations correspond to C–P bond cleavages to afford CpP_6^+ and $Cp^*P_6^+$, respectively, as ionic fragments along with the corresponding neutral cyclopentadienyl radicals. According to the time-honored Stevenson rule, formation of cyclopentadienyl cations is less likely to occur because the computed *IE*s of the phosphorus fragments are significantly lower than those of the corresponding hydrocarbon ligands: $IE_a(CpP_6) = 7.09$ eV and $IE_a(Cp^*P_6) = 6.60$ eV versus $IE_a(Cp) = 8.59$ eV[20] and $IE_a(Cp^*) = 6.92$ eV.

In contrast to Cp_2P_6 and $Cp^*_2P_6$, the monosubstituted phosphorus compounds show pronounced differences both with respect to the type of Cp ligand and the net charge. For example, the C–P bond strength of the neutral radical $CpP_6^{\bullet}$, $D_0(Cp{-}P_6) = 0.79$ eV, is much lower than the $D_0(Cp^+{-}P_6) = 2.29$ eV of the cation; note that the positive charge is assumed to remain on the Cp fragment in this case. The charge-permuted bond strength $D_0(Cp{-}P_6^+) = 1.76$ eV is somewhat smaller, because the $IE_a(P_6) = 8.06$ eV[21] is lower than $IE_a(Cp) = 8.59$ eV. In contrast, $D_0(Cp^*{-}P_6) = 0.54$ eV and $D_0(Cp^{*+}{-}P_6) = 0.86$ eV are of comparable magnitude, whereas the charge-permuted bond cleavage $D_0(Cp{-}P_6^+) = 2.00$ eV is more energy demanding, because $IE_a(P_6) = 8.06\ \text{eV} > IE_a(Cp^*) = 6.92$ eV. In addition to these changes in the dissociation behavior, the adiabatic and vertical redox properties differ substantially. Thus, $IE_v(CpP_6) = 7.63$ eV is considerably larger than $IE_a(CpP_6) = 7.09$ eV ($\Delta IE_{v/a} = 0.54$ eV), and likewise, the vertical recombination energy of the cation, $RE_v(CpP_6^+) = 6.21$ eV, is much lower than IE_a ($\Delta IE_{v/a} = 0.88$ eV). Similar conclusions apply to the Cp* substituent with the vertical values $IE_v(Cp^*P_6) = 7.04$ eV and $RE_v(Cp^*P_6^+) = 5.69$ eV compared with $IE_a(Cp^*P_6) = 6.60$ eV ($\Delta IE_{v/a} = 0.44$ and 0.91 eV, respectively). These changes are also reflected in the calculated elongation of the relevant bond lengths upon neutralization, that is, $r_{CP} = 1.87$ Å/$r_{PP} = 2.02$ Å and $r_{CP} = 1.89$ Å/$r_{PP} = 2.04$ Å for the cationic species CpP_6^+ and $Cp^*P_6^+$ compared with $r_{CP} = 1.93$ Å/$r_{PP} = 2.22$ Å and $r_{CP} = 1.95$ Å/$r_{PP} = 2.20$ Å for the neutral radicals. In a simple picture of binding mnemonics, these changes in bond lengths imply significant P–P double bond character in the cationic species (small r_{PP}) compared with single bonds in the neutral species (larger r_{PP}).

While ionization of Cp_2P_6 and $Cp^*_2P_6$ can safely be assumed to yield the intact molecular ions (see above), the dissociative ionization may also afford isomeric fragments. Therefore, the potential-energy surface of the unsubstituted CpP_6^+ system is explored briefly. In addition to isomer **2** having a hexaphosphabenzvalene skeleton, four other isomers **3**–**6** are found

(Figure 3) of which the hexaphosphaprismane derivative **3** is very close in energy to **2** ($E_{rel} = 0.10$ eV); a very similar difference of 0.12 eV is computed for the benzvalene and prismane isomers of $Cp^*P_6^+$ (Table 1).[22] Nevertheless, **2** and **3** are separated by a significant barrier (computed as 0.91 eV relative to **2**). With the reasonable assumption that the barrier associated with the internal rearrangement of the P_6 skeleton is similar for the Cp* system, we may neglect isomerization of $Cp^*P_6^+$, particularly because direct C–P bond cleavage with $D_0(Cp^{*+}{-}P_6) = 0.86$ eV is expected to compete efficiently.

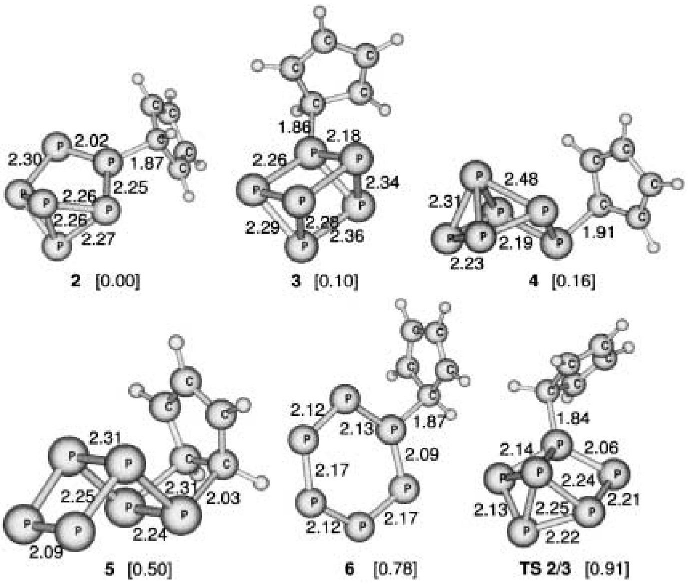


Figure 3. Fully optimized B3LYP/TZVP structures of the CpP_6^+ isomers **2**–**6** with selected bond lengths in Å and relative energies in eV (in square brackets); P_6 skeletons: benzvalene (**2**), prismane (**3**), envelope (**4**), sheet-like (**5**), benzene (**6**). **TS2/3** denotes the optimized saddle point connecting **2** and **3**. Except for the methyl substituents, the computed structure of the Cp* variant of **3** is more or less superimposable on that of **3** and therefore omitted.

Experimentally, one major dissociation channel of $Cp^*P_6^+$ corresponds to the loss of neutral tetraphosphorus P_4 concomitant with a cationic $Cp^*P_2^+$ fragment [Eq. (2a)]. For the ionic product, two different structures are located as minima. The first, more obvious one is best described as an *end-on* cationized P_2 unit (structures CpP_2^+ and $Cp^*P_2^+$ in Figures 1 and 2). For these *end-on* isomers, the calculations predict similar energetics to the corresponding fragmentations for Cp and Cp*, that is, $D_0(CpP_2^+{-}P_4) = 1.39$ eV and $D_0(Cp^*P_2^+{-}P_6) = 1.11$ eV. The computed bond lengths ($r_{CP} = 1.89$ Å and $r_{PP} = 1.89$ Å for CpP_2^+, $r_{CP} = 1.99$ Å and $r_{PP} = 1.91$ Å for $Cp^*P_2^+$) are consistent with η^1 coordination of a P_2 unit by Cp^+ and Cp^{*+} cations, respectively. However, the bicyclic structures c-CpP_2^+ and c-$Cp^*P_2^+$ are more stable than the *end-on* isomers by 1.05 and 1.14 eV, respectively. Considering the pyramidalization of the bridgehead carbons, c-CpP_2^+ and c-$Cp^*P_2^+$ are best described as covalently bound 6,7-diphosphabicyclo-[3.2.0]-heptadi-3,6-en-2-yl cations.[23, 24] Note that intramolecular strain leads to somewhat increased bond lengths as compared with the *end-on* isomers, that is, $r_{CP} = 2.00$ Å and $r_{PP} = 2.04$ Å for both c-CpP_2^+ and c-$Cp^*P_2^+$. Due to the larger stability of the bicyclic isomers, the formal bond strengths of their predecessors CpP_6^+ and $Cp^*P_6^+$ decrease to only 0.34 eV for the former and even to a slightly negative value (−0.03 eV) for the latter.[25]

In order to evaluate the possible role of thermal contributions in the dissociation behavior of Cp_nP_6, the energetics at 0 K are compared with the relative free energies at 298 K. However, consideration of the data compiled in Table 1 reveals no particular entropic effects other than the obvious preference of all dissociation channels at 298 K. We can safely adopt this result to the $Cp^*_2P_6$ system as well.

Discussion

The computed data can be combined in terms of schematic potential-energy surfaces for the Cp and Cp* systems; here we limit ourselves to the benzvalene skeleton of the hexaphosphorus unit (see above). Before entering this discussion, the experimental results of the mass spectrometric experiments are summarized briefly. Unimolecular decay of $Cp^*_2P_6^{\bullet+}$ gives almost exclusive loss of one Cp* ligand to afford $Cp^*P_6^+$ [Eq. (1), 100%] along with a trace of Cp^{*+} being formed as ionic fragment (2%). The major fragmentations of $Cp^*P_6^+$ lead to $Cp^*P_2^+$ and Cp^{*+} as ionic fragments according to Equations (2a) and (2b). It is important to note that the ratio of $Cp^*P_2^+$ to Cp^{*+} changes quite significantly from about 10:1 in metastable ion decomposition to about 1.5:1 upon collisional activation of $Cp^*P_6^+$. Reionization of the P_6 fragment concomitantly formed as in Equation (2b) can then be used to demonstrate the existence of the neutral hexaphosphorus molecule in the gas phase.[2]

Let us first analyze the $Cp^*_2P_6$ system (Figure 4) in order to rationalize the experimental findings. Considering the size of the neutral precursor, as well as the relatively small difference between vertical and adiabatic transitions, it can safely be

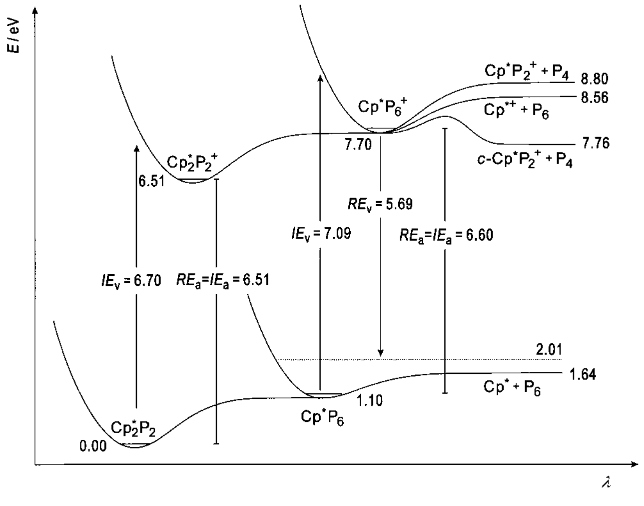


Figure 4. Schematic potential-energy surface describing the fragmentation and redox processes involved in the generation of neutral P_6 upon ionization of $Cp_2^*P_6$. While the transition structure en route from $Cp^*P_6^+$ to the c-$Cp^*P_2^+$ + P_4 products has not been examined theoretically, the experimental data[2] suggest it to be situated below the energy demand of the Cp^{*+} + P_6 exit channel (see text).

concluded that the electron ionization of $Cp^*_2P_6$ affords the intact molecular ion (see above). Nevertheless, with some excess energy imparted by the ionizing electrons, $Cp^*_2P_6^{\bullet+}$ can easily dissociate by C–P bond cleavage to afford $Cp^*P_6^+$ + $Cp^{*\bullet}$ and $Cp^*P_6^\bullet$ + Cp^{*+}; here the two channels only differ by the location of the positive charge. The experimentally observed preference for $Cp^*P_6^+$ formation from metastable $Cp^*_2P_6^{\bullet+}$ is consistent with the computed ionization energies of the fragments, $IE_a(Cp^*P_6) = 6.60$ eV versus $IE(Cp^*) = 6.92$ eV. In terms of Cooks' kinetic method,[26] the approximate 50:1 ratio of $Cp^*P_6^+$ and Cp^{*+}, in conjunction with the computed ΔIE of 0.32 eV, suggests an effective temperature $T_{eff} \approx 900$ K. This appears reasonable for a metastable ion of this size when further considering that temperatures of about 450 K are already required for the evaporation of neutral **1***. Likewise, the dissociation of the $Cp^*P_6^+$ fragment is consistent with the computed energetics. For the metastable ion, loss of P_4 [Eq. (2a)] leads to the rearranged product c-$Cp^*P_2^+$ by a more or less thermoneutral process, whereas direct C–P bond cleavage [Eq. (2b)] is 0.86 eV endothermic. Competition of both processes implies that a significant barrier is associated with loss of P_4 when accompanied by rearrangement to the bicyclic c-$Cp^*P_2^+$ isomer.

$$Cp^*P_6^+ \rightarrow c\text{-}Cp^*P_2^+ + P_4 \qquad (2a')$$

Strong support for this view is lent by the drastic change of the $Cp^*P_2^+/Cp^{*+}$ ratio upon collisional activation, because increased occurrence of Equation (2b) is in accordance with a rearrangement involved in the loss of P_4 according to Equation (2a′). At low energies (i.e., for the metastable ions), the energetically advantageous rearrangement (2a′) is preferred, whereas direct bond cleavage is entropically favored at higher energies (i.e., upon collisional activation). With respect to the formation of neutral P_6, the key aspect concerns the redox chemistry of the $Cp^*P_6^+$ cation. Specifically, the question why almost exclusively cation dissociation [Eq. (2)] rather than ET [Eq. (3)] is observed in the experiments. Unfavorable Franck–Condon effects in conjunction with low fragmentation thresholds of the cation provide a rationale for this behavior. Thus, vertical neutralization of $Cp^*P_6^+$ affords the neutral counterpart at an energy above its dissociation threshold and is hence unlikely to occur because predissociative states bear unfavorable probabilities for ET.[27] In contrast, the $Cp^*P_6^+$ cation can easily dissociate by loss of neutral P_4 and P_6, which are then selectively reionized in the NR experiments. Furthermore, the particular choice of helium as a collision gas in the neutralization step[2, 28] strongly disfavors ET because $IE(He) = 24.5$ eV is rather large.

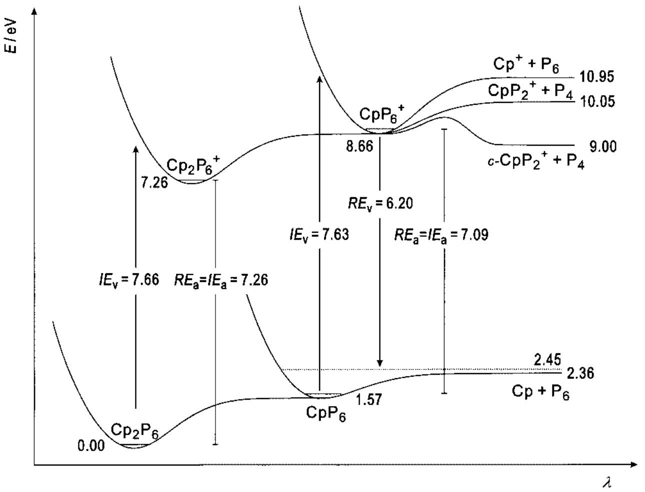


Figure 5. Schematic potential-energy surface describing the fragmentation and redox processes upon ionization of Cp_2P_6. The transition structure en route from CpP_6^+ to the c-$Cp^*P_2^+$ + P_4 products is qualitatively adopted from Figure 4.

Although the relative redox behavior is qualitatively similar for the Cp_2P_6 parent system (Figure 5), notable changes occur with respect to the absolute values as well as with respect to the exit channels. Both effects can be attributed to the different characters of the cyclopentadienyl substituents. Thus, the Cp ligand is considerably more strongly bound to phosphorus than the larger Cp* system for neutral as well as cationic species. Particularly with respect to a putative NR experiment on CpP_6^+, a rather different outcome than for $Cp^*P_6^+$ is expected. While vertical neutralization of CpP_6^+ also is associated with an unfavorable $\Delta IE_{v/a}$, the neutral $CpP_6^\bullet$ radical is bound more strongly, and hence the Franck–Condon factors may be preferable. The major difference, however, concerns the competitive dissociation of the cationic species that allowed the generation of neutral P_6 from $Cp^*P_6^+$ [Eq. (2b)]. As $IE_a(Cp)$ is significantly larger than $IE_a(Cp^*)$, the analogous reaction of the parent compound [Eq. (5b)] is unlikely to occur because the competing loss of P_4 [Eq. (5a)] is preferred energetically, even without invoking a rearrangement to the more stable bicyclic c-CpP_2^+ isomer.

$$CpP_6^+ \rightarrow CpP_2^+ + P_4 \qquad (5a)$$

$$\rightarrow Cp^+ + P_6 \qquad (5b)$$

Accordingly, even if the synthesis of the parent system Cp_2P_6 were achieved, this compound is deemed a poor precursor for the generation of neutral P_6, whereas the experiments were successful for $Cp^*_2P_6$.[2] This reasoning very much supports the suggestion of Jutzi that the Cp* substituent is particularly suitable as a leaving group in the generation of unusual molecules.[29]

Conclusion

The present theoretical results provide a consistent explanation for the mass-spectrometric generation of neutral hexaphosphorus by dissociative EI of $Cp^*_2P_6$ followed by neutralization–reionization experiments with the $Cp^*P_6^+$ fragment.[2] However, the computational prediction of the low-lying CpP_6^+ isomers **3** and **4** sheds some minor doubt on the structure of the neutral P_6 molecule formed upon collision-induced dissociation of mass-selected $Cp^*P_6^+$, because the latter is assumed to maintain the hexaphosphabenzvalene skeleton of the neutral precursor although no direct experimental evidence supporting this assumption is available. In this respect, independent synthesis of appropriate precursor molecules to deliberately generate the isomers **2**–**6** (or their Cp* analogues) in the gas phase would be desirable.

In a more general sense, the present study demonstrates that contemporary theoretical methods and computing technology allow reasonably large systems such as $Cp^*_2P_6$ (56 atoms) with adequate basis sets to be handled without applying any constraints to symmetry. Further, the pronounced differences between the Cp and Cp* systems studied here underline the fact that commonly applied simplifications of ligands in theoretical studies of coordination complexes (e.g., Cp* → Cp or even H)[30] may lead to inappropriate descriptions of the chemistry investigated experimentally. In the present case, for example, consideration of Cp_2P_6 as a model for the fragmentation behavior of $Cp^*_2P_6$ would not have led to a consistent explanation of the experimental observations.

Finally, it is interesting to recognize that the energetics of the sequential Cp* losses do not differ largely for neutral $Cp^*_2P_6$ and the molecular cation. Thus, it is conceivable that thermolysis of the neutral compound might also yield the elusive P_6 modification.

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[1] P. Jutzi, R. Kroos, A. Müller, M. Penk, *Angew. Chem.* **1989**, *101*, 628; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 600.

[2] D. Schröder, H. Schwarz, M. Wulf, H. Sievers, P. Jutzi, M. Reiher, *Angew. Chem.* **1999**, *111*, 3723; *Angew. Chem. Int. Ed.* **1999**, *38*, 3513.

[3] a) N. Goldberg, H. Schwarz, *Acc. Chem. Res.* **1994**, *27*, 347; b) C. A. Schalley, G. Hornung, D. Schröder, H. Schwarz, *Chem. Soc. Rev.* **1998**, *27*, 91; c) D. V. Zagorevskii, J. L. Holmes, *Mass Spectrom. Rev.* **1998**, *18*, 87.

[4] Similarly pronounced Franck–Condon effects evolve in the NR spectra of the acetyl cation as well as $B(OH)_2^+$, see: a) A. A. Mommers, Proefschrift thesis, Rijksuniversiteit, Utrecht, The Netherlands, **1985**; b) R. Srinivas, S. Vivekananda, S. J. Blanksby, D. Schröder, H. Schwarz, L. M. Fell, J. K. Terlouw, *Int. J. Mass Spectrom.* **2000**, *197*, 105.

[5] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.

[6] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[7] P. J. Stephens, F. J. Derlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[8] a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[9] a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, 97, 119.

[10] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[11] See: W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**, p. 137.

[12] a) C. Kind, M. Reiher, J. Neugebauer, B. A. Hess, *SNF–A Program for Parallelized Vibrational Analyses*, University of Erlangen–Nürnberg, **1999**–**2001**; b) J. Neugebauer, M. Reiher, C. Kind, B. A. Hess, *J. Comp. Chem.* **2002**, *23*, 895.

[13] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.

[14] According to the B3LYP/TZVP calculations, the maximum interatomic separations in $Cp^*_2P_6$ are $r_{PH,max} = 7.75$ Å and $r_{HH,max} = 9.17$ Å.

[15] V. Q. Nguyen, F. Turecek, *J. Mass Spectrom.* **1996**, *31*, 843.

[16] For larger molecules, however, some rovibrational excitation is conceivable, see: D. Schröder, J. Loos, H. Schwarz, R. Thissen, D. V. Preda, L. T. Scott, M. V. Frach, D. K. Böhme, *Helv. Chim. Acta* **2001**, *84*, 1625; b) M. Kaczorowska, J. N. Harvey, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5227.

[17] a) J. N. Harvey, C. Heinemann, A. Fiedler, D. Schröder, H. Schwarz, *Chem. Eur. J.* **1996**, *2*, 1230; b) D. Schröder, S. Bärsch, H. Schwarz, *Int. J. Mass Spectrom.* **1999**, *192*, 125; c) D. Schröder, H. Schwarz, *Int. J. Mass Spectrom.* **2002**, in press.

[18] Throughout the paper we use a simplified notation, in which r_{CP} corresponds to the C(1)−P(1) bond length and r_{PP} describes the P(1)−P(2) bond length.

[19] It must be pointed out that consideration of bond lengths alone may be insufficient to evaluate Franck–Condon effects, see for example: a) Ref. [4b]; b) J. Hrušák, D. Schröder, S. Iwata, *J. Chem. Phys.* **1997**, *106*, 7541.

[20] The NIST homepage lists values between 8.41 and 8.69 eV, see: NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg MD, 20899, USA, **2000** (http://webbook.nist.gov).

[21] See also: R. O. Jones, G. Seifert, *J. Chem. Phys.* **1992**, *96*, 7564.

[22] The P_6 skeletons of Cp and Cp* are virtually identical for the prismane isomers **3** and **3***.

[23] For an introduction into phosphorus/carbon-cage compounds, see: R. Streubel, *Angew. Chem.* **1995**, *107*, 478; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 436.

[24] M. Sanchez, R. Réau, F. Dahan, M. Regitz, G. Bertrand, *Angew. Chem.* **1996**, *108*, 2386; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2228.

[25] Because the fragmentations $CpP_6^+ \rightarrow c\text{-}CpP_2^+ + P_4$ and $Cp^*P_6^+ \rightarrow c\text{-}Cp^+P_2^+ + P_4$ should be considered as rearrangements rather than direct bond cleavages, the formal bond strengths in fact correspond to reaction enthalpies for which negative values are acceptable; of course, some kind of barriers must be involved.

[26] R. G. Cooks, P. S. H. Wong, *Acc. Chem. Res.* **1998**, *31*, 379.

[27] In a strict sense, this is only true for diatomics. Tentatively, however, the low dissociation energy of the neutral radical $Cp^*P_6^{\bullet}$ suggests a direct coupling with the C−P bond length so that this approximation may hold true.

[28] M. J. Polce, S. Beranová, M. J. Nold, C. Wesdemiotis, *J. Mass Spectrom.* **1996**, *31*, 1073.

[29] P. Jutzi, *Comm. Inorg. Chem.* **1987**, *6*, 1.

[30] L. Maron, O. Eisenstein, F. Alary, R. Poteau, *J. Phys. Chem. A* **2002**, *106*, 1797.

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