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Structure and Ring Cleavages of the Phosphirane Cation: A Theoretical ab Initio SCF-CI Study

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The structure of phosphirane cation 1 ($PC_2H_4^+$) and the relative stabilities of 1 and some isomeric structures have been investigated by using ab initio SCF-CI calculations. The C–C disrotatory ring opening giving bis(methylene)phosphorane cation 2 has a 15.2 kcal·mol^{-1} activation energy, and 2 is 17.5 kcal·mol^{-1} more stable than 1. Ethylene plus P^+, in their ground states, lie 60.7 kcal·mol^{-1} above 1. The lowest vertical excitation energies of 1 and 2 have been calculated. The linear phosphallene cation $CH_2{=}P{=}CH_2^+$ and $CH_2CH_2P^+$ cation are not minima on the potential energy surfaces (PES). However, a C_{2v} triplet exciplex having rather long P–C bonds is found only 7.9 kcal·mol^{-1} above 1. The preceding data together with semiquantitative calculated PESs provide a background for a general discussion of the thermal and photochemical reactivity of cation 1.

Introduction

The chemistry of three-membered ring carbon–phosphorus heterocycles has been studied widely during recent years.[1] Theoretical studies of phosphirane,[2] its protonated form,[3] and diphosphirane and related cations and anions[4] are available. As far as we know, no systematic calculations have been done concerning the structure and reactivity of phosphirane cation 1. This species is of interest for several reasons. First, though this cation is expected to have a singlet closed-shell ground state, the presence of a low-lying empty 3p-type MO on the phosphorus atom allows us to predict the existence of a low-energy triplet state. Second, several isomers of this cation, which result from the breaking of one bond of the ring, are possible: bis(methylene)phosphorane planar allyl-like open structure 2 and allene-like structure 3. The existence of these isomers has not been proven, and their relative stabilities are unknown. In addition, we considered the possible products of an extrusion reaction yielding ethylene and phosphorus cation. Third, from a theoretical point of view, it may be asked whether compound 1 obeys the Woodward–Hoffmann rules[5] in its thermal and photochemical ring openings, as do the three-membered rings of the second-period elements.

Experimentally, phosphirane cation derivatives can be generated, as intermediates, during nucleophilic substitution reactions of chlorophosphiranes.[6] An attempt to get a phosphirane cation from the reaction of $AlCl_3$ and a substituted chlorophosphirane led to a rearrangement involving ring substituents,[7] but the ring opening was not observed as is true for cyclopropyllium cation.[8]

We present here an investigation of various $C_2H_4P^+$ isomers resulting from ring opening of 1 and of their possible interconversions in their ground states. In addition, the calculation of semiquantitative PESs of excited states provides a background for a general qualitative discussion of the photochemical reactivity of the phosphirane cation and its stable isomers. Further transposition processes have not been explored.

Calculation Methods

The SCF step was achieved by using the MONSTERGAUSS series of programs.[9] The Davidson RHF Hamiltonian[10] was used for triplet species; the closed-shell Roothaan–Fock Hamiltonian[11] was used in the other cases. The structure optimizations (stable species and transition states) were carried out at the SCF 6-31G**[12] level with the full gradient technique. Energy values were calculated at the SCF 6-31G** level and at the SCF-CI level according to methods I and II, respectively.

Method I. After the 6-31G SCF calculation, a space of about 100 selected configurations was diagonalized. The active space typically included the four highest occupied MOs and the seven lowest unoccupied ones. In this space, we considered all the monoexcitations and, for singlet states, pair-excitations. Other diexcited configurations were included in a space restricted to the two highest occupied and the five lowest unoccupied MOs. In a few cases, other configurations were added to describe the lowest states of the system. This method provides exploratory runs and semiquantitative potential energy surfaces (PESs).

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Table I. Calculated Energies at 6-31G SCF-CI (Method II) and 6-31G** SCF Levels**

species	energy SCF+CI *a*	energy SCF+CI *b*	energy SCF[c]	energy SCF+CI[d]
1 (GS)	0.0		−418.443 33	−418.811 42
$^3A_2$	29.3			−418.764 61
$^1A_2$	45.9			−418.738 12
$^3B_1$	37.3			−418.751 79
$^1B_1$	54.9			−418.723 82
2 (GS)	−17.5	0.0	−418.424 48	−418.839 55
$^3B_2$	18.6	36.1		−418.781 75
$^1B_2$	71.2	88.7		−418.697 99
$^3A_2$	24.7	42.2		−418.772 11
$^1A_2$	25.9	43.4		−418.770 09
3	25.9		−418.386 56	−418.770 13
TS1	15.3		−418.413 03	−418.787 10
TS2			−418.400 99	
4 (GS)	60.7	0.0	−417.581 20	−418.714 76
$^1D+^1A_{1g}$	61.2	0.5		−418.713 86
$^1S+^1A_{1g}$	91.7	31.0		−418.665 31
1a ($^3A_2$)	7.91	0.0	−418.394 76	−418.798 82
$^1A_2$		24.8		−418.759 30

[a] All the energies (kcal·mol^{-1} are relative to the GS of cation 1. [b] Vertical excitation energy for each species is referred to its GS. [c] 6-31G** SCF absolute energies (au). [d] 6-31G** SCF-CI absolute energies (au).

Method II. The 6-31**G step was followed by a Møller-Plesset[13] second-order (MP2) treatment using the CIPSI method:[14] a set of 100–150 reference configurations was taken as a basis for the multireference perturbation scheme involving 10^6–10^7 terms depending on the state under scrutiny. This method afforded reliable energy values for fundamental and excited states of the crucial structures.

Results and Discussion

Study of the $PC_2H_4^+$ Isomers. The calculation results are reported in Table I.

Parent Phosphirane Cation 1. The dominant configuration in the ground state (GS) is closed-shell: (core) $5a_1^2\,3b_2^2 6a_1^2 2b_1^2 7a_1^2 1a_2^2 8a_1^2 4b_2^2$. The two HOMOs, schematically drawn in Figure 1, are very close in energy (about 0.01 au). The $8a_1$ MO is predominantly a nonbonding phosphorus lone pair with a weak bonding character along the C–C bond. The $4b_2$ MO is the antisymmetrical Walsh MO (15); it is strongly bonding along both P–C bonds and antibonding along the C–C bond. The LUMO is essentially a phosphorus $3p_x$ nonbonding orbital. From these data, we can expect two vertical excitations close in energy of A_2 and B_1 symmetry. The vertical excitation energies GS → $^1A_2$ (symmetry forbidden) and GS → $^1B_2$ (symmetry allowed) are equal to 1.99 and 2.38 eV, respectively; these energies correspond to ca. 500–600-nm radiation. The vertical singlet–triplet separation is 0.72 eV for A_2 and 0.77 for B_1.

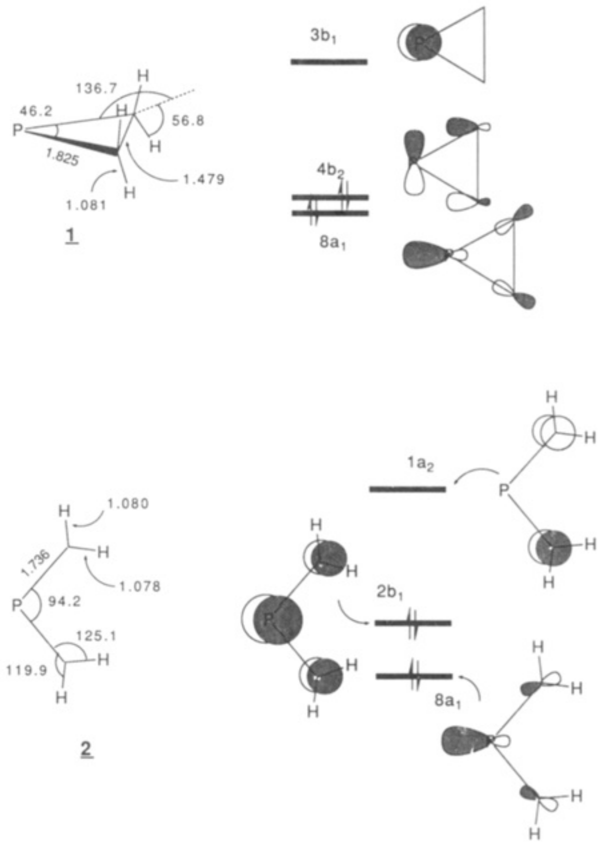

Figure 1. Optimized geometries (6–31G**, bond lengths in Å and angles in deg) and schematic drawings of the relevant MOs of cations 1 and 2 (minor AO contributions, i.e., those with coefficients less than 0.15, have been omitted).

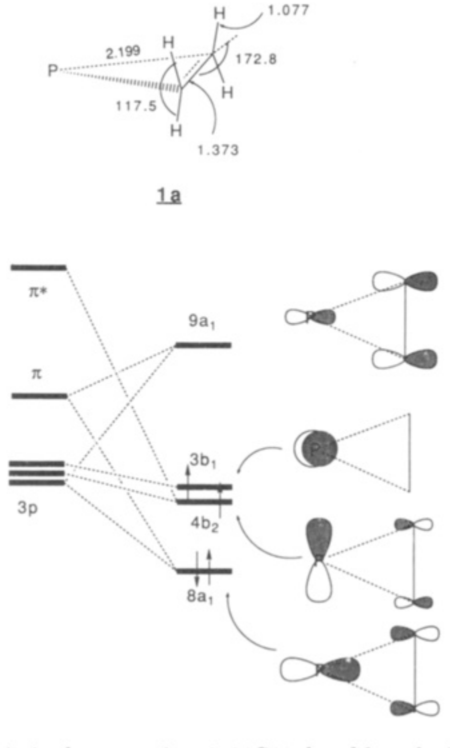

Figure 2. Optimized geometries (6–31G**, bond lengths in Å and angles in deg) and relevant MOs of triplet exciplex **1a** (see also the caption of Figure 1).

Relaxed Structure 1a. Structure **1a** (Figure 2), the lowest $^3A_2$ triplet ($\ldots 8a_1^2\,4b_2^1\,3b_1^1$) has rather long P–C bonds (2.20 Å) and a short C–C bond (1.37 Å), as expected considering that one electron has been removed from a strongly bonding MO along the P–C bonds. The C_2H_4 group is nearly planar, and the molecule resembles more a P^+–ethylene exciplex, with π donation from ethylene toward the empty $3p_z$ AO of phosphorus. Indeed, the atomic charge on phosphorus (from Mulliken populations, at the 6–31G** SCF level) is lowered from 0.87 in **1** to 0.57 in **1a**. Structure **1a** lies at 0.15 eV below **1** at the SCF level

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but is found 0.34 eV above for the CI calculation (method II). The vertical singlet–triplet separation is 1.05 eV (the $^1A_2$ structure has not been optimized). This value, which is close to the calculated ^3P-^1D separation for P^+ cation, shows that there is relative weak mixing of the P^+ AOs with the ethylene MOs. The resulting MOs are schematically drawn in Figure 2. The $8a_1$ MO arises from the $3p_z$ of P^+ with a minor in-phase contribution of the ethylene π MO. Its antibonding counterpart is the $9a_1$ LUMO. The $4b_2$ MO is predominantly the $3p_y$ of P^+, slightly stabilized by a weak in-phase participation of the π^* MO of ethylene. The $3b_1$ MO is nearly the pure $3p_x$ orbital of phosphorus.

Bis(methylene)phosphorane Cation 2. Open structure 2 possesses the classical electronic structure of the allyl cation: $^1A_1$ symmetry within the C_{2v} point group (Figure 1). This species appears (after the CI calculation according to method II) as the absolute minimum energy of the investigated $PC_2H_4^+$PES. It should be noted that, at the SCF 6-31G** level, 2 is found at higher energy than 1 and that, at the 6-31G + CI level of method I, both entities lie at almost the same energy (see the PESs of Figure 4 or 5). The P–C bond lengths (1.74 Å) lie between the values expected for the true double bonds and the values for single bonds. The HOMO, $2b_1$, is similar to the π_1 MO of the allyl cation, but the σ lone pair of phosphorus, $8a_1$, lies very close to this HOMO. The lowest vertical excited state is the triplet $\pi \rightarrow \pi^*$ state ($2b_1 \rightarrow a_2$), lying at 1.58 eV. Then are found, very close to each other, the singlet and triplet $n \rightarrow \pi^*$ transitions ($8a_1 \rightarrow a_2$), at 1.84 and 1.89 eV, respectively, and finally the singlet $\pi \rightarrow \pi^*$, at 3.85 eV.

Phosphallenium Cation 3. When the C–P–C angle is frozen at 180° and the remaining parameters are optimized, an entity similar to allene with D_{2d} symmetry, π-degenerate HOMOs, and π^*-degenerate LUMOs is obtained (Figure 6). This structure is actually unstable and undergoes a spontaneous bending. It has been shown (at the SCF level) that a monotonous potential energy curve links structure 3 to TS2, the transition state for a methylene rotation in the bis(methylene)phosphorane cation 2 (vide infra, path e).

Ethylene + Phosphorus Cation 4. The various relevant states of P^+ were calculated using method II (Table I). The ^3P–^1D separation is 1.32 eV (expl: 1.10 eV (16)), and the ^3P–^1S separation is 3.00 eV (expl: 2.68 eV (16)). The GS ($^1A_{1g}$) energy of ethylene was calculated with the following geometrical parameters: $r(CC) = 1.326$ Å, $r(CH) = 1.076$ Å, (HCH) = 113.6°.

Interconversions between the $PC_2H_4^+$ Isomers. The following reaction paths were studied (Figure 3): (1) ring opening by C–C bond cleavage ($1 \rightarrow 2$), conrotatory (path a) and disrotatory (path b); (2) methylene rotation in bis(methylene)phosphorane cation 2 (path e); (3) P^+ extrusion with ethylene formation ($1 \rightarrow 4$, path c); and (4) ring opening by P–C bond cleavage (path d).

As a first step, exploratory scans of paths a–d were performed using method I (see Calculation Methods). For this purpose, the processes were simulated by linear variation of the geometrical parameters from their optimized value in cation 1 up to their value in the final species (6 points for paths a, b, d and 12 points for path c, with polynomial interpolations). The C–H bond lengths were frozen at their initial value. Clearly, the PESs calculated according to this method are not minimum energy paths.

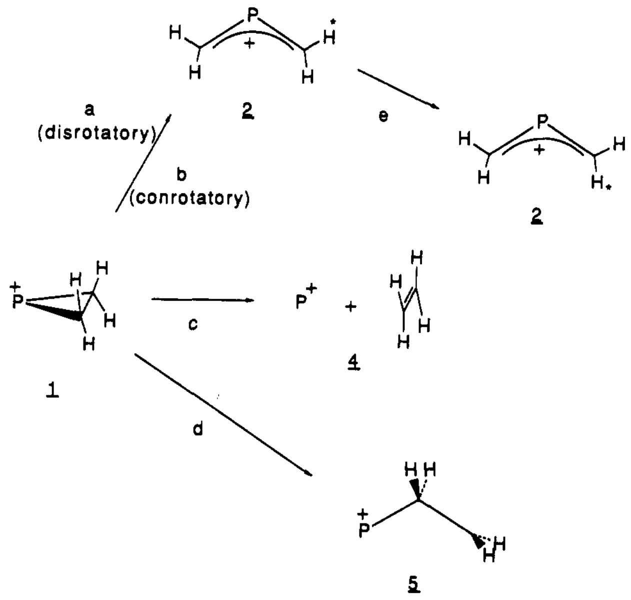


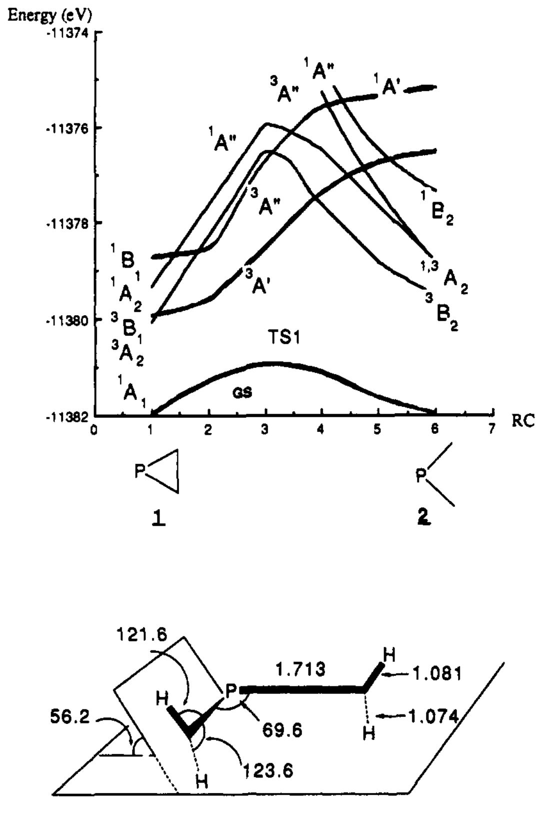
Figure 3. Reaction paths studied.

Nevertheless, they provide a good qualitative comparison of similar reaction paths (such as conrotatory or disrotatory ring openings); they can indicate the presence of minima (exciplexes) and the existence of a monotonous reaction coordinate (RC). More generally, they constitute useful starting points for a selection of the most relevant reaction paths for a further optimization of TS or stable species. Path e has been studied at the SCF 631G** level by optimizing the TS between the two rotamers. We have to point out that there may be some discrepancies between the semiqualitative results of these calculations and the results previously reported with method II.

Ring Opening by C–C Bond Cleavage 1 → 2. The PESs corresponding to the C–C ring opening are displayed in Figure 4 (disrotatory) and Figure 5 (conrotatory). In the disrotatory ring opening, the C_s point group is preserved along the reaction coordinate, and the C_2 group is preserved in the conrotatory ring opening. We report, in each case, the evolution of the ground state $^1A_1$ (GS) and of the lowest triplet and singlet excited states $^{1,3}A_2$ and $^{1,3}B_1$ of phosphirane cation 1. The Woodward–Hoffmann rules[5] predict that the thermal reaction should occur through a disrotatory process: on the corresponding PES, the energy barrier is only about 1 eV vs about 3.5 eV for the conrotatory PES. The optimized transition state (TS1) geometry for the allowed reaction is displayed in Figure 4, and it should be noted that the TS is symmetrical (within 0.1° for angles and 10^{-3} Å for bond lengths), as expected for a disrotatory synchronous ring opening. The activation energy is 0.82 eV at the SCF level and 0.55 eV at the SCF-CI (method II) level.

The conrotatory process for the excited states is displayed in Figure 5. The fact that the four lowest excited states reported are strongly repulsive and display energy barriers of more than 2 eV makes the reaction forbidden, as expected. However, the reaction coordinate is not optimized.

The disrotatory process is displayed in Figure 4. The excited ^1A and ^3A PESs, arising from the $^{1,3}A_2$ states of 1, also exhibit steep slopes and energy barriers of more than 3 eV, which makes the reaction very unlikely. The most favored path corresponds to the ^1A PES. This PES is slightly attractive at the beginning of the RC which



TS1

Figure 4. Disrotatory ring opening of cation 1. Upper part: semiquantitative calculated PESs obtained using method I (see Calculation Methods). Lower part: optimized transition state (TS1) at the SCF 6-31G** level.

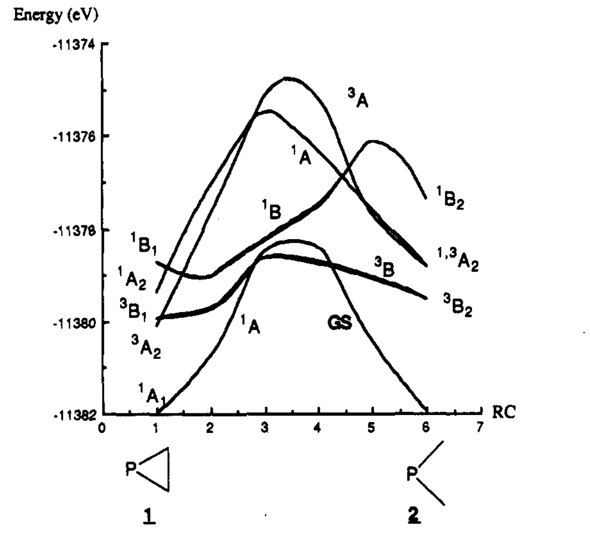
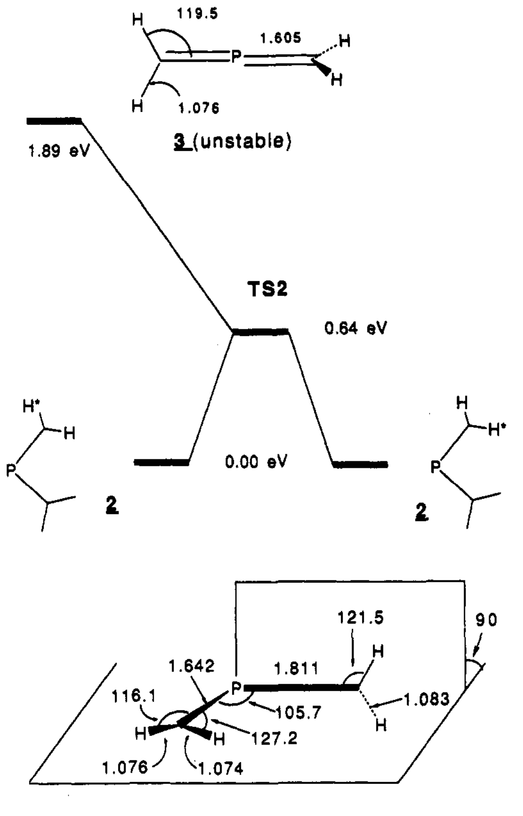


Figure 5. Conrotatory ring opening of cation 1: semiquantitative PESs calculated using method I (see Calculation Methods).

indicates that the relaxed structure arising from the $^1B_1$ excited state of 1 possesses a stretched C–C bond (about 1.75 Å) and C_2 rather than C_{2v} symmetry. This result can be expected when one considers that one electron has been removed from the $8a_1$ MO, which is weakly bonding along the C–C bond. A photochemical reaction from this state can occur if the system reaches the region of points 3–4 of the RC (i.e., a CPC angle of about 70°), the "product side" of the GS PES, before deactivation. This requires about 0.8 eV with respect to the initial $^1B_1$ energy of 1. This would correspond to a poor quantum yield, although the amount of energy required could be lowered by optimizing the RC. Another possible photochemical ring opening might arise from a "hot" GS through a disrotatory process. As a matter of fact, excited A_2 or B_1 cation 1 possesses enough internal energy to overcome, after deactivation, the GS energy barrier. The paths are nevertheless unlikely in condensed media because of efficient vibronic intermolecular energy transfers but could be considered in the gas phase.



TS2

Figure 6. Optimized geometry of the unstable phosphallenyl cation 3 (see text) and the optimized transition state (TS2) for the rotameric isomerization of cation 2 (SCF 6-31G** level).

Methylene Rotation in Bis(methylene)phosphorane Cation 2. Methylene rotation consists of a torsion of one CH_2 around the P–C axis. The transition state (TS2) has been optimized (Figure 6). In its structure, one P–C bond is clearly a double bond (1.64 Å), with coplanar $CP{=}CH_2$ atoms, and the second P–C bond is a single one (1.81 Å), with a CH_2 plane nearly perpendicular to the plane of the other CH_2 group. The energy barrier, at the SCF 6-31G** level, is 0.64 eV.

P^+ Extrusion with Ethylene Formation 1 → 4. The PESs for P^+ extrusion, within the C_{2v} point group, are reported in Figure 7. The $^1A_1$ GS is monotonously destabilized and correlated, at infinite separation, with ethylene in its GS plus P^+ in an excited ^1D state. The lowest triplet state, $^3A_2$, exhibits a deep well, previously ascribed to structure **1a**. The triplet state $^3A_2$ is correlated, together with the $^3B_1$ and $^3B_2$ states, to the GS of the products, namely ethylene (GS) plus P^+ (^3P). The PES for the lowest singlet $^1A_2$ also displays a deep well, but the corresponding structure was not independently optimized. Singlet state $^1A_2$ is correlated with one component ^1D state of P^+ and ethylene (GS).

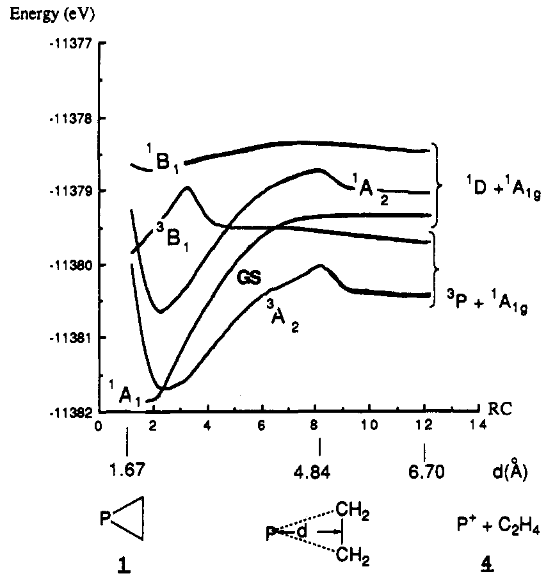


Figure 7. Extrusion reaction of P$^+$ from cation 2: semiquantitative PESs calculated using method I (see Calculation Methods), within the C_{2v} point group.

It is noteworthy that, in a nonsymmetrical extrusion, all crossings between states of the same multiplicity are forbidden. However, this fact could not significantly affect the PES pattern because, at least for the low-lying states, no crossings occur between states of the same multiplicity. Whatever the actual reaction coordinate may be the P$^+$ extrusion in the GS is strongly endothermic and, thus, remains very unlikely. One can see from Table I and Figure 10 that, starting from the lowest excited states, the initial energy is not sufficient to reach the GS of the products. However, starting from the $^{1,3}A_2$ states, a strong stretching of both PC bonds, yielding singlet or triplet exciplexes **1a**, is expected to be very efficient.

One puzzling point is the presence of energy barriers of ca. 0.5 and 0.3 eV, respectively, on both the singlet and triplet A_2 PESs, near point 8 of the RC (i.e., for a 4.85-Å P$^+$-ethylene separation). One may ask whether this maximum really has physical significance. It can be shown that these barriers do exist, at least conceptually, as a result of avoided crossings (Figure 8, upper part). Let us consider the lowest $^3A_2$ state of **1a**. Since the $8a_1$ MO is located mainly on phosphorus, this MO is diabatically correlated with the p_z AO of the phosphorus atom. The state of ...$8a_1^2 4b_2^1 3b_1^1$ dominant configuration is thus correlated to a highly excited P$^-$(3p^4) + C$_2$H$_4^{2+}$ (π^0) state of the products. The GS of the products is diabatically correlated with a doubly excited state ...$8a_1^0 4b_2^1 9a_1^2$ of **1a**. This state is intercepted by a lower A_2...$8a_1^1 4b_2^1 3b_1^1 9a_1^1$ state of **1a** correlated to the GS of neutral P plus ethylene cation.

Taking into account the various forbidden crossings results in the actual adiabatic correlations displayed in Figure 8 (upper part). In the lower part of Figure 8 are reported the corresponding calculated curves. The presence of the energy barrier is of minor importance for reaction path 1 → 4, which, as has already been pointed out, is very unlikely. Nevertheless, this barrier is relevant for the reverse reaction of P$^+$ plus ethylene. Such a reaction may be achieved, for example, through an ion-molecule impact in a MS-MS spectrometer.

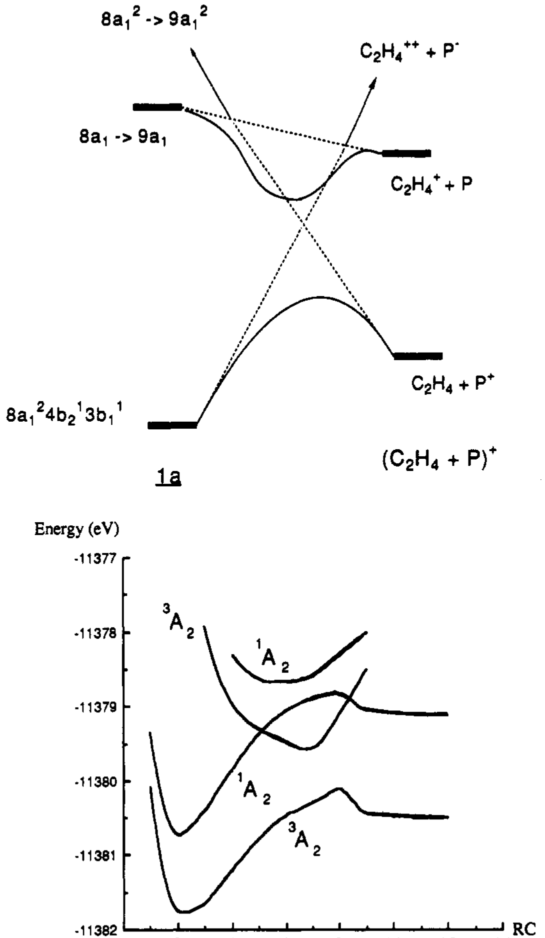


Figure 8. Topology of the lowest $^{1,3}A_2$ PESs in the P extrusion from exciplex 1a. Upper part: qualitative adiabatic (full lines) and diabatic (dotted lines) correlation diagram. Lower part: calculated adiabatic PESs.

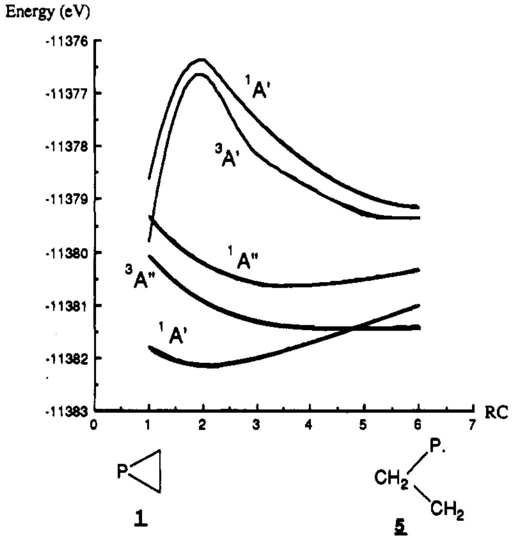


Figure 9. P–C ring opening of cation 1: calculated semiquantitative PESs calculated using method I (see Calculation Methods).

Ring Opening by P–C Bond Cleavage. The PESs for ring opening by P–C cleavage are reported in Figure 9. In this model reaction, one P–C–C angle is increased from its equilibrium value in 1 (67°) to the expected value (109.5°) for a tetravalent carbon, and the terminal CH$_2$ group becomes planar. In fact, though no attempt has been made to optimize the ring-opened structure, it does not appear as a potential energy minimum. Indeed, ring

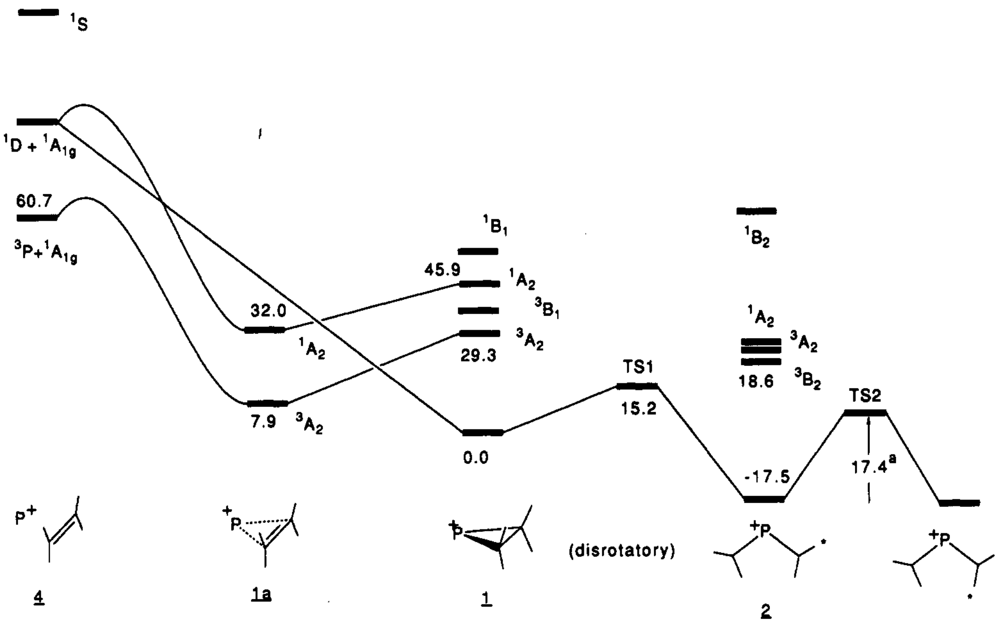


Figure 10. Overview of the reactivity of cation 1. 6-31G**-CI (method II, see Calculation Methods) energies are in kcal·mol^{-1}, relative to the GS of 1 taken as a reference. (a) SCF 6-31G* calculation level.

reclosure is spontaneous in the lowest 1A′ singlet state. The triplet A″ PES decreases in energy, indicating the possible existence of a diradical open structure; but the energy of this A″ PES lies above that of the C_{2v}^{3}A$_2$ exciplex **1a**, so that any attempt to open one of the P–C bonds would induce the system to "fall down" into this potential well. The same phenomenon is expected for the lowest A″ excited singlet state, which displays a minimum near point 3 of the RC (P–C–C = 85°). Since the geometry of the lowest singlet (arising from ^{1}A$_2$ of 1) has not been optimized, we cannot rule out the possibility of a non-symmetrical singlet exciplex in this region.

Conclusion: General Survey of the Reactivity of the Phosphirane Cation 1. The most salient features of the reactivity of 1 are reported in Figure 10 and can be summarized as follows. (i) The most stable of the $C_2H_4P^+$ structures studied is the open planar bis(methylene)-phosphorane cation 2, which lies 17.5 kcal mol^{-1} below 1.

(ii) The existence of a significant energy barrier (15.2 kcal mol^{-1}) between 1 and 2 agrees with the experimental result that *P*-halogenophosphiranes undergo nucleophilic substitutions and transpositions involving ring substituents without ring opening.[6,7] Compound 1 differs from both the diphosphirane cation, which is not a stable structure,[4] and the cyclopropyl cation, which is stable but undergoes an easy ring opening even at low temperature.[17] It can be expected that open bis(methylene)phosphorane cation 2 could be obtained in the same kind of experiments at a higher temperature, by a disrotatory process. In such an experiment, cation 2, which is a 1,3 dipole, could be trapped as a cycloadduct with an olefin. The existence of a noticeable energy barrier between the two rotamers of 2 allows the possibility of an experimental verification of the disrotatory stereochemistry of the ring opening from the structure of the cycloadducts of substituted species. The same cycloadducts might be obtained in MS–MS ion molecule reactions. Indeed, phosphirane cation 1 can be obtained by fragmentation of a *P*-halogenophosphirane ion radical

(iii) Phosphallenium structure 3 is not a minimum of the $PC_2H_4^+$PES.

(iv) Triplet species **1a**, which results from a charge transfer of the π electrons of ethylene toward the P$^+$ atom, lies only 7.9 kcal mol^{-1} above 1. Triplet **1a** could have a noticeable lifetime, since a vertical spin-allowed deactivation is not possible: the system must undergo an intersystem crossing to afford phosphirane ion 1.

(v) The extrusion reaction of phosphirane cation 1 from its GS, yielding P$^+$(^{1}D) plus ethylene (GS), is strongly endothermic and, thus, very unlikely, although it does not exhibit any activation barrier. Although we are aware that the photochemical reactivity of 1 is difficult to determine experimentally, our results clearly indicate that, upon irradiation, exciplexes might be spontaneously obtained from the lowest A$_2$ singlet and triplet excited states. However, the complete extrusion of P$^+$ remains very unlikely, since these states lie under the GS of the products. From another point of view, the reaction of P$^+$ (in its ^{3}P GS) with ethylene (^{3}A$_2$ PES) is expected to yield phosphirane cation through an activation barrier. Although, as far as we know, P$^+$–ethylene reactions have not yet been reported, this kind of experiment seems a priori feasible in a MS apparatus.

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