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Formation of three-membered phosphorus heterocycles via ligand-exchange reactions in mono-adducts of the phosphenium ion: an ab initio investigation

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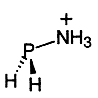
Abstract

The formation of ionic three-membered phosphorus heterocycles from unsaturated hydrocarbons and mono-adducts of the phosphenium ion has been investigated using ab initio molecular orbital calculations at the G2 level. In appropriate cases, these so-called exchange reactions are exothermic with no overall barrier, and they should therefore be experimentally feasible. Thus, we suggest that phosphenium ions with one lone-pair donor ligand may represent a valuable new reagent in the synthesis of ionic three-membered phosphorus heterocycles. In addition, we discuss the nature of the electronic interactions in the bis-adducts of the phosphenium ion with two lone-pair donors, two π donors, or with one lone-pair donor and one π donor. (Int J Mass Spectrom 201 (2000) 205–213) © 2000 Elsevier Science B.V.

Keywords: G2 theory; Three-membered heterocyclic ions; Mono-adducts of the phosphenium ion; Exchange reactions

1. Introduction

A substantial number of reagents have been employed as precursors for phosphenium ions (PH_2^+) [1], including phosphenium ions coordinated by Lewis bases. Such species have been isolated and spectroscopically characterized by several workers [2]. We have recently employed high level ab initio calculations to study ligand-exchange reactions between adducts of the phosphenium ion with Lewis bases (e.g. **1**) and simple lone-pair donors (e.g. NH_3) [3].



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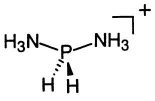

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These reactions were found to proceed via a bis-adduct of the phosphenium ion (e.g. **2**) and predicted to be experimentally feasible in appropriate cases. Our calculations suggested, in addition, that phosphenium ions coordinated by two such lone-pair donors should be observable under appropriate conditions, which is consistent with experimental observations on related systems [4].

The impetus for our investigation had been provided by the experimental observation of facile and

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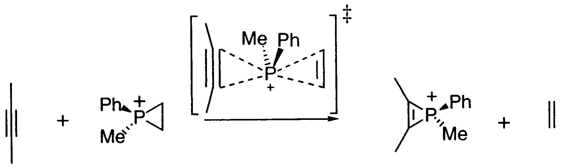
exclusive exchange reactions between certain phosphiranium ions and alkynes, for example [5]:

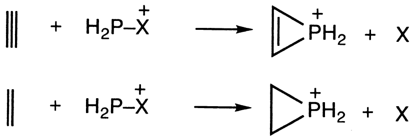


This reaction has been referred to as a π-ligand-exchange reaction [6]. In a subsequent ab initio study we found that π-ligand exchange is a very low energy process, and that it proceeds via a transition structure in which the principal electronic interaction resembles the bonding interaction in phosphenium ions coordinated by two lone-pair donors [3,6].

A tantalizing question arises as to whether a phosphenium ion coordinated by one π donor and one lone-pair donor represents a transition structure or an experimentally observable equilibrium structure. In addition, it is of interest to investigate whether the reactions between unsaturated hydrocarbons (π donors) and phosphenium ions coordinated by one lone-pair donor are low energy processes, since these reactions may provide a novel synthetic route to phosphirenium and phosphiranium ions. These matters are addressed in the present systematic ab initio investigation of model systems. Specifically, we examine the displacement of the ligand in mono-adducts of the phosphenium ion, such as **1**, by unsaturated hydrocarbons to form ionic three-membered phosphorus heterocycles.

2. Computational methods

Standard ab initio molecular orbital calculations [7] were carried out using a slightly modified form of G2 theory [8] with the GAUSSIAN 94 [9] and MOLPRO 96 [10] suites of programmes. G2 theory effectively corresponds to a QCISD(T)(fc)/6-311+G(3*df*,2*p*) energy calculation on MP2(full)/6-31G(*d*) optimized geometries and includes scaled HF/6-31G(*d*) zero-point vibrational energies (ZPVEs) and a so-called higher-level correction. G2 theory has been shown to perform well in the calculation of thermodynamical properties such as heats of formation and reaction barriers [8,11]. In the present work, we have substituted the standard ZPVEs by ZPVEs calculated using MP2(full)/6-31G(*d*) harmonic vibrational frequencies scaled by 0.9646 [12]. This modified version of G2 theory is formally referred to as G2(ZPE = MP2) [13] but we use the G2 label here for the sake of brevity. We have deviated from standard G2 theory in order to be consistent with our other recent studies of ligand-exchange reactions involving the phosphenium ion and related isoelectronic species [3,6,14]. The transition structures reported in the present work have been confirmed in each case by the calculation of vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate analysis. Calculated G2 total energies and GAUSSIAN 94 archive entries for the MP2(full)/6-31G(*d*) optimized geometries are presented in Tables S1 and S2 of the Supporting Information. Relative energies within the text correspond to G2 values at 0 K.



X = NH_3, H_2O, HF, PH_3, H_2S or HCl

Scheme 1.

3. Results and discussion

In the present work we have investigated two series of prototypical exchange processes (Scheme 1). First, we examine reactions between acetylene and phosphenium ions coordinated by simple first- or second-row lone-pair donors ($H_2P–X^+$). These reactions lead to the formation of a phosphirenium ion and a free donor molecule (X). Second, we investigate the corresponding reactions involving ethylene which lead to a product phosphiranium ion. MP2(full)/6-

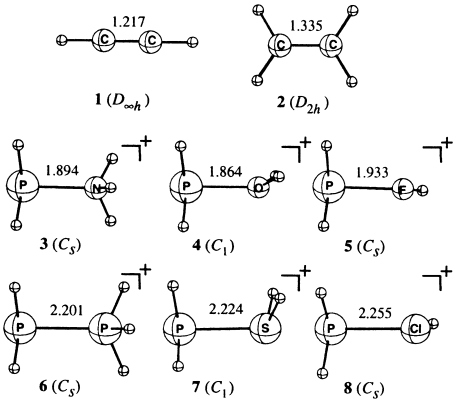


Fig. 1. Optimized [MP2(full)/6-31G(d)] geometries of the reactant species in the exchange reactions. Bond lengths in angstroms.

31G(d) optimized structures, including selected optimized geometrical parameters, of the species involved in these reactions are presented in Figs. 1–4.

In the following sections, we discuss in detail the energetics of these exchange reactions and the possible experimental consequences of the results. We also make comparisons with our previously investigated exchange reactions involving the phosphenium ion, unsaturated hydrocarbons and first- or second-row lone-pair donors [3,6,14].

3.1. Exchange reactions involving acetylene (formation of a phosphirenium ion)

Both the HF/6-31G(d) and the MP2(full)/6-31G(d) levels of geometry optimization predict that acetylene and the phosphenium ions coordinated by ammonia, phosphine or hydrogen sulfide initially combine to form a C_s complex [Figs. 3 and 5(a)], and that this reactant complex is connected to a C_s product complex by a C_s transition structure. At the HF/6-31G(d) level, a similar reaction profile [i.e. that of Fig. 5(a)] is also obtained when the weaker donors, water or hydrogen chloride, are involved in the exchange reaction. However, at MP2(full)/6-31G(d), the product complex in these two cases is formed directly from the reactants without a barrier [Fig.

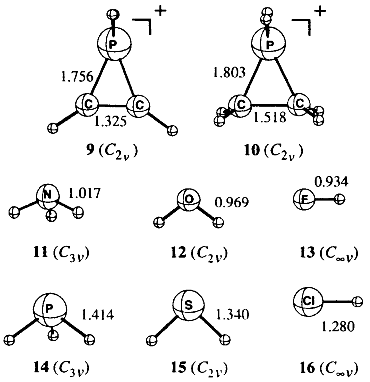


Fig. 2. Optimized [MP2(full)/6-31G(d)] geometries of the product species in the exchange reactions. Bond lengths in angstroms.

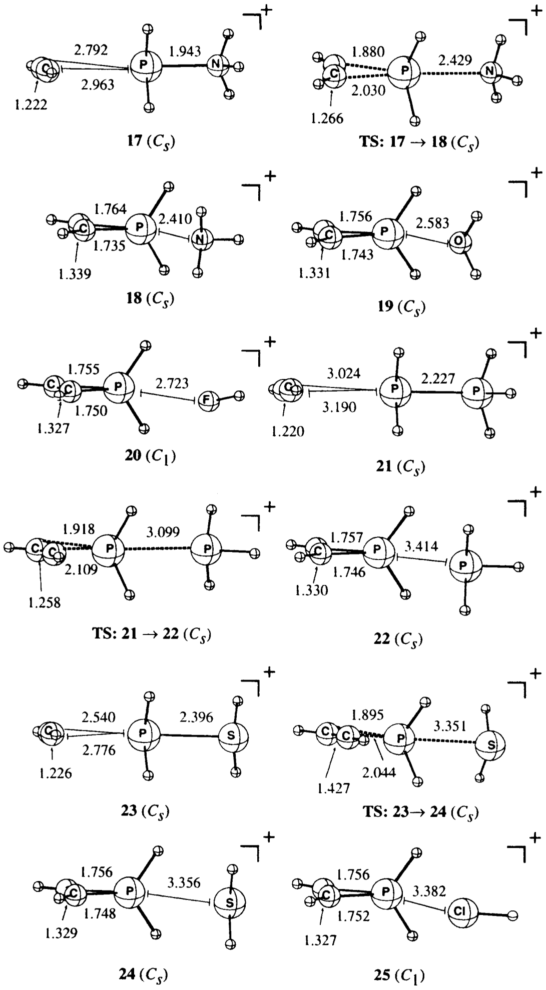


Fig. 3. Optimized [MP2(full)/6-31G(d)] geometries of the species involved in the exchange reactions between mono-adducts of the phosphenium ion and acetylene. Bond lengths in angstroms.

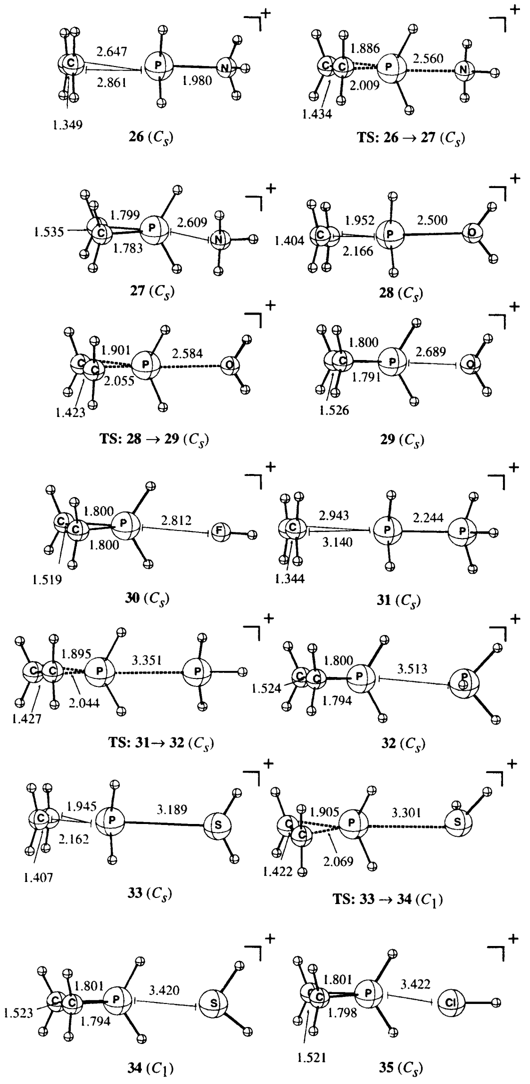


Fig. 4. Optimized [MP2(full)/6-31G(*d*)] geometries of the species involved in the exchange reactions between mono-adducts of the phosphenium ion and ethylene. Bond lengths in angstroms.

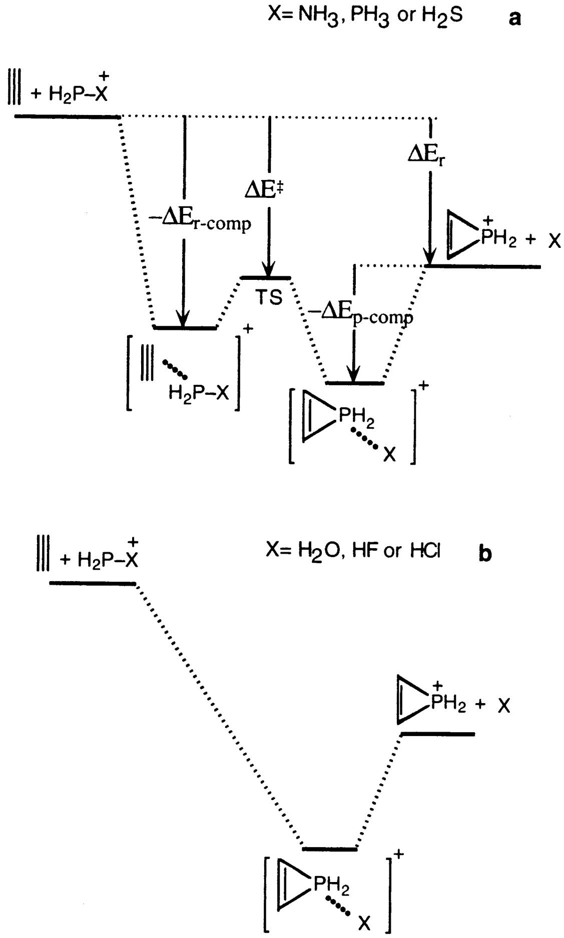


Fig. 5. Generalized schematic presentation of the two possible potential energy profiles for exchange reactions involving acetylene and mono-adducts of the phosphenium ion. The appearance does not change significantly for the corresponding reactions involving ethylene (see text).

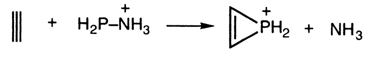
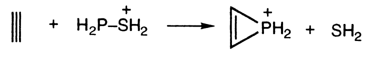
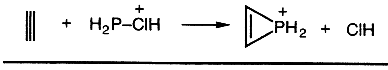
5(b)]. At both HF/6-31G(*d*) and MP2(full)/6-31G(*d*), the exchange reaction between acetylene and H_2P–FH^+ (**5**) follows the pattern of Fig. 5(b). The barriers and the reaction energies for exchange and the binding energies of the associated reactant and product complexes are presented in Table 1.

The exchange reactions are endothermic when H_2P–NH_3^+ (**3**) and H_2P–PH_3^+ (**6**) react with acetylene (by 32.4 and 25.6 kJ mol^{-1}, respectively). In the remaining cases, however, the reactions are exothermic by substantial amounts, and take place without an overall barrier. The exothermicity is most pronounced when the weak donors, hydrogen fluoride or hydrogen chloride, are involved (−204.7 and −155.8 kJ mol^{-1}, respectively).

3.2. Exchange reactions involving ethylene (formation of a phosphiranium ion)

The results for the exchange reactions between ethylene and mono-adducts of the phosphenium ion

Table 1
Overall barriers ($\Delta E^{\ddagger}$), reaction energies (ΔE_r), and binding energies of reactant complexes ($\Delta E_{r\text{-comp}}$) and product complexes ($\Delta E_{p\text{-comp}}$) in exchange reactions involving acetylene[a]

reaction	$\Delta E_{\text{r-comp}}$[b]	$\Delta E^{\ddagger}$[b,c]	$\Delta E_{\text{p-comp}}$[b]	ΔE_r[b]
	33.7	23.3	64.6	32.4
	d	d	50.9	−84.9
	d	d	34.2	−204.7
	25.8	46.7	33.3	25.6
	40.8	−31.2	29.2	−51.7
	d	d	20.9	−155.8

[a] G2 values in kJ mol^{-1} at 0 K.
[b] See Fig. 5.
[c] A positive value indicates that the TS lies higher in energy than the entrance channel.
[d] Reaction proceeds directly from reactants to product complex without a barrier.

(Fig. 4 and Table 2) are very similar to those obtained for the corresponding reactions involving acetylene. However, the binding energies for the reactant complexes are slightly greater and the overall barriers slightly smaller for the reactions involving ethylene, consistent with ethylene being a better donor than acetylene. One minor qualitative difference is that the reaction between ethylene and $H_2P\text{–}OH_2^+$ (**4**) now involves the initial formation of a reactant complex (**28**), although it should be noted that this complex lies only 3.5 kJ mol^{-1} below the transition structure for the reaction and has significant product character. Again, the reactions that involve the weakest donors, hydrogen fluoride or hydrogen chloride, proceed directly from the reactants to the product complex without a barrier at MP2(full)/6-31G(*d*). However, the HF/6-31G(*d*) level of geometry optimization predicts these reactions to proceed via a central transition structure [i.e. surfaces equivalent to Fig. 5(a)].

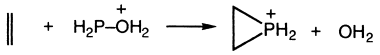
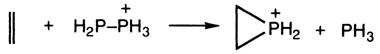
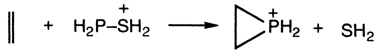
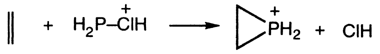
The exchange reactions with ethylene that involve $H_2P\text{–}NH_3^+$ (**3**) and $H_2P\text{–}PH_3^+$ (**6**) are again endothermic, whereas the remainder are exothermic by substantial amounts (Table 2). In the latter cases, there is no overall barrier. As found for the reactions with acetylene, the exothermicity is most pronounced for the reactions involving the phosphenium ion coordinated by the weakest donors, hydrogen fluoride or hydrogen chloride (−205.1 and −156.2 kJ mol^{-1}, respectively).

3.3. Reactant and product complexes

The reactant complexes in the cases where they are formed generally have quite similar structures (cf. **17**, **21**, **23**, **26**, and **31** in Figs. 3 and 4). They basically represent an unsaturated hydrocarbon weakly bound to the mono-adduct. In two cases (**28** and **33**), however, there appears already to be significant product character. The binding energies of the reactant complexes increase as the electronegativity of the ligand in the reactant mono-adduct increases (Tables 1 and 2). This is consistent with the fact that increasing the electronegativity of X makes $H_2P\text{–}X^+$ a better acceptor and hence improves the binding to the unsaturated hydrocarbon.

Most of the reactant complexes reside in quite

Table 2
Overall barriers ($\Delta E^{\ddagger}$), reaction energies (ΔE_r), and binding energies of reactant complexes ($\Delta E_{r\text{-comp}}$) and product complexes ($\Delta E_{p\text{-comp}}$) in exchange reactions involving ethylene[a]

reaction	$\Delta E_{r\text{-comp}}$[b]	$\Delta E^{\ddagger}$[b,c]	$\Delta E_{p\text{-comp}}$[b]	ΔE_r[b]
	39.8	6.5	56.1	32.0
	105.4	−101.9	46.6	−85.3
	d	d	33.3	−205.1
	28.4	24.3	30.2	25.2
	56.0	−51.3	27.4	−52.1
	d	d	19.7	−156.2

[a] G2 values in kJ mol^{-1} at 0 K.
[b] The various relative energiers are defined for the corresponding reactions involving acetylene in Fig. 5.
[c] A positive value indicates that the TS lies higher in energy than the entrance channel.
[d] Reaction proceeds directly from reactants to product complex without a barrier.

shallow potential wells, their binding energies and the barriers for their further decomposition generally being low. The observation of such complexes will therefore present a challenge to experimental chemists. The complex formed from $H_2P–NH_3^+$ (**3**) and ethylene is perhaps the best candidate for experimental observation since this complex is relatively strongly bound (by 39.8 kJ mol^{-1}) and the barrier for its further decomposition is relatively high (46.3 kJ mol^{-1}).

A comparison of the product complexes reveals that they also have very similar structures (Figs. 3 and 4). They may be described as weak complexes between the phosphirenium or phosphiranium ion and the Lewis base. Their binding energies decrease as the donor ability of the Lewis base decreases along a period (Tables 1 and 2).

3.4. Transition structures

The motion that takes the reactant complex into the region of the transition structure is a slight rotation of the PH_2^+ moiety (Figs. 3 and 4), coupled of course with changes in distances between the interacting species.

Electronically, the exchange transition structure can be characterized in terms of a principal and a secondary interaction. The principal interaction involves the empty *p* orbital on the PH_2^+ moiety, the filled π orbital of the unsaturated hydrocarbon and the (filled) donor lone pair [Fig. 6(a)]. The secondary interaction involves the π* orbital of the unsaturated hydrocarbon and the sp^2-type lone pair on the PH_2^+ moiety [Fig. 6(b)]. In the forward direction of the reaction coordinate, the displacement of the donor lone pair results in combination of the remaining orbitals to form the two C–P sigma bonds in the three-membered ring. In the reverse direction, the displacement of the hydrocarbon leaves the interaction between the empty *p* orbital on PH_2^+ and the (filled) donor lone pair.

3.5. Barriers and reaction energies

The strengths of the P–ligand bond in the monoadduct of the phosphenium ion decrease with decreas-

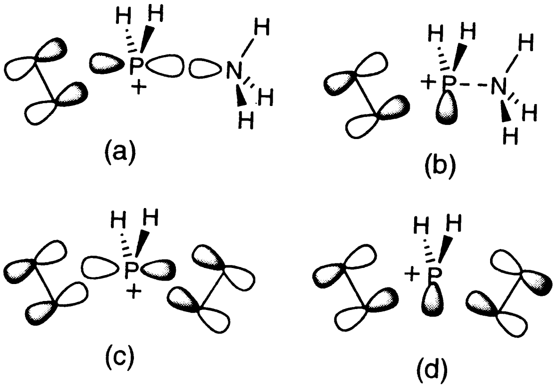


Fig. 6. Electronic interactions characteristic of exchange transition structures involving PH_2^+ and either a lone-pair donor and a π donor (a and b) or two π donors (c and d). The principal interaction involves the empty p orbital on the PH_2^+ moiety and the (filled) orbitals of the lone-pair donor or the π donor (a and c). The secondary interaction involves the (filled) sp^2-type orbital on the PH_2^+ moiety and the π* orbital(s) of the π donor(s) (b and d).

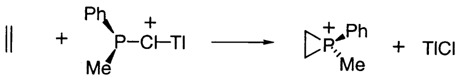
ing donor ability of the ligand [3]. Thus, the bond becomes weaker in the order $NH_3 > H_2O > HF$ or $PH_3 > H_2S > HCl$. The reaction energies parallel the strengths of the breaking P–ligand bond. This makes qualitative predictions of relative reaction energies possible from knowledge of donor abilities. The present results indicate that when there is a barrier for exchange it is related to the reaction energy and so qualitative predictions regarding relative exchange barriers can also be made.

Phosphine and ammonia are the most effective donors; thus $H_2P–NH_3^+$ (**3**) and $H_2P–PH_3^+$ (**6**) are the two most strongly bound mono-adduct of the phosphenium ion. The exchange reactions of both these species are endothermic (by between 25.2 and 32.4 kJ mol^{-1}). The remaining mono-adducts of the phosphenium ion undergo strongly exothermic exchange reactions with acetylene and ethylene without any overall barrier. The reaction energies in these cases fall between -51.7 and -205.1 kJ mol^{-1}.

3.6. Experimental consequences

The present investigation reveals that eight of the exchange reactions examined are exothermic and have no overall barrier. Thus, we predict that these exchange reactions should be experimentally feasible.

An important synthetic route to phosphirenium or phosphiranium ions has involved the reaction between a Lewis acid [e.g. thallium(I)] and a chlorophosphine in the presence of an alkyne or alkene [1,5,15]. The Lewis acid and the chlorophosphine can combine to form a species that can be considered as a mono-adduct of the phosphenium ion, and its reactions with unsaturated hydrocarbons can be regarded as exchange, e.g.



The present theoretical results allow us to predict that the formation of the ionic three-membered phosphorus heterocycles might be feasible with other, possibly more environmentally friendly, reagents. For example, the protonated form $H_2P–PH_3^+$ (**6**) of commercially available diphosphines might be utilized in an exchange reaction that, although endothermic, may be forced to completion by removing the product phosphine as it is formed. Alternatively, our calculations predict that *O*-protonated phosphinous acids, e.g. $H_2P–OH_2^+$ (**4**), will undergo exchange reactions with unsaturated hydrocarbons that are exothermic, and so no additional driving force is needed in such cases. However, to our knowledge, only *P*-alkyl derivatives of **4** have been isolated in the condensed phase [16].

3.7. Comparisons with related exchange reactions

In a previous investigation, we found that the exchange reactions between mono-adducts of the phosphenium ion and first- or second-row Lewis bases proceed via an intermediate bis-adduct of the phosphenium ion [3]. We predicted these exchange reactions and the associated bis-adducts of the phosphenium ion with Lewis bases to be experimentally observable in appropriate cases. The principal bonding interaction in the bis-adducts involves the empty *p* orbital on the phosphorus atom and the two (filled)

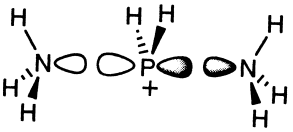


Fig. 7. The principal bonding interaction in bis-adducts of the phosphenium ion, occurring between the empty *p* orbital on the PH_2^+ moiety and the (filled) lone pairs of the two donors.

donor lone pairs (Fig. 7). Thus, the principal bonding interaction in bis-adducts are of the same type as the principal electronic interaction of the transition structures investigated in the present work [cf. Figs. 6(a) and 7].

In the case of exchange reactions between ionic three-membered heterocycles and unsaturated hydrocarbons, we have previously found that the reactant and product complexes are connected via an intermediate transition structure [6]. For the reactions investigated in the present work, we have found a similar surface in the case of the stronger donors [Fig. 5(a)], whereas the intermediate barrier disappears for weaker donors where the reaction becomes highly exothermic [Fig. 5(b)]. The electronic interactions in the transition structures in these two reactions are similar (Fig. 6), and the close resemblance of the principal interaction [Fig. 6(a) and (c)] to the triple-ion configuration ($X^- \cdots CH_3^+ \cdots X^-$) found in S_N2 transition structures [17] is noteworthy.

The nature of the bis-adduct of the phosphenium ion seems to play a central role in the appearance of the potential energy surfaces for exchange. It is therefore useful to summarize the relevant results for the two types of exchange reactions investigated previously [3,6] and the one investigated in the present study.

In the case of the reaction of a lone-pair donor with a mono-adduct of the phosphenium ion, there is a favorable donor–acceptor interaction. Accordingly, the resultant bis-adduct of the phosphenium ion with two Lewis bases represents an equilibrium structure [3].

On the other hand, in the case of the reaction of a π donor with an ionic three-membered phosphorus heterocycle, the electronic reorganization required in order to proceed from the reactants (or reactant complexes) to products results in there being a barrier for the reaction, i.e. there is an intermediate transition structure [6]. For degenerate reactions of this type, the transition structure can be considered to represent a phosphenium ion interacting symmetrically with two unsaturated hydrocarbons.

In the intermediate case of the reaction of a π donor with a mono-adduct of the phosphenium ion, the qualitative shape of the potential energy surface depends on the reaction energy. When the reaction is approximately thermoneutral, we find a surface with an intermediate transition structure, i.e. the barrier associated with the electronic reorganization required to form the three-membered heterocycle remains. The transition structure in this case resembles a phosphenium ion interacting with one lone-pair donor and one π donor. However, when the reaction is highly exothermic, there is a sufficient driving force that the barrier disappears.

4. Concluding remarks

Our calculations indicate that the formation of ionic three-membered phosphorus heterocycles from mono-adducts of the phosphenium ion and unsaturated hydrocarbons should be experimentally feasible in appropriate cases, and that mono-adducts related to those examined in the present study are potentially useful new reagents for the synthesis of such three-membered heterocycles.

The present investigation provides a valuable link between the exchange reactions involving mono-adducts of phosphenium ions plus Lewis bases on the one hand, and unsaturated hydrocarbons plus ionic three-membered phosphorus heterocycles on the other.

Our calculations provide information regarding the nature of bis-adducts of the phosphenium ion with (1) two lone-pair donor ligands, (2) two π-donor ligands and (c) one lone-pair donor plus one π-donor ligand. The results suggest that interaction of a phosphenium ion with two lone-pair donors will result in an equilibrium structure which should be experimentally observable in appropriate cases, whereas symmetric interaction with two π ligands is more likely to represent a transition structure. In the intermediate case of one lone-pair donor and one π donor, the shape of the potential energy surface is strongly influenced by reaction enthalpy effects.

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