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Novel Pi−Ligand Exchange and Insertion Reactions Involving Three-Membered Phosphorus Heterocycles: An ab Initio Investigation

Theis I. Sølling,[†] Mark A. McDonald, S. Bruce Wild,* and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

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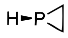
Abstract: Ab initio molecular orbital calculations at the G2 level of theory have been used to characterize the potential energy surface for the reactions of phosphirenium or phosphiranium ions with acetylene or ethylene. Comparisons between two competing pathways for π-ligand exchange are discussed along with comparisons between the lower energy exchange pathway and a competing insertion reaction. The lower energy exchange reactions have barriers (4−39 kJ mol^{-1}) much smaller than those of the insertion reactions (215−234 kJ mol^{-1}), despite the fact that the insertion products are strongly preferred thermodynamically. This is consistent with the exclusive observation of exchange experimentally. The transition structures for the preferred exchange reactions contain PH_2^+ moieties that are rotated so that they are almost parallel to the CC bond of the ring and the CC bond of the incoming hydrocarbon, leading to the prediction that the reactions are stereospecific with respect to the configuration at phosphorus.

Introduction

Whereas aziridine is a small heterocycle that has commercial importance as a precursor of polymers and as a high-energy intermediate in organic synthesis,[1] its phosphorus analogue phosphirane (**1**) is a very reactive substance,[2] which precludes serious investigations of its chemistry.[3] The *P*-phenyl derivative **2**, however, is readily isolated,[4−6] and some of its chemistry has been explored. Oxidation of **2** by a dithiete[7] and a dioxetane[8] leads to unstable pentacoordinate phosphiranes, and with transition metals, **2** yields complexes that are potential precursors of crown phosphines by cyclooligomerization.[4] Further evidence of the nucleophilicity of **2** is provided by its reaction with methyl trifluoromethanesulfonate (methyl triflate), which furnishes **3**, the first phosphiranium salt to be isolated and structurally characterized.[9,10]



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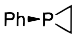

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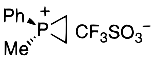

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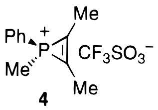

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A remarkable feature of the phosphiranium salt **3**, and the aspect of its chemistry that inspired the present investigation, is its reaction with dimethylacetylene to give cleanly by displacement of ethylene the phosphirenium salt **4**.[10] A related phosphirenium salt had been characterized previously.[11] In addition, we have recently observed that **4** undergoes alkyne exchange with other alkynes to give thermodynamic mixtures of phosphirenium salts.[12]

The behavior of **3** and **4** toward alkynes is reminiscent of π-ligand exchange in organometallic chemistry, and it is tempting to consider these salts as π-complexes of the six-electron methylphenylphosphenium ion. Salts containing phosphenium ions lacking strong π-donor substituents have yet to be isolated, however.[13] To our knowledge, the π-ligand exchange observed in the reactions of **3** and **4** with alkynes is unprecedented in heterocyclic chemistry. Various theoretical investigations of neutral and cationic three-membered phosphorus heterocycles have been reported previously.[14] In the present work, we use ab initio molecular orbital theory to examine prototypical examples of the π-ligand exchange

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[†] Present address: Kemisk Laboratorium II, H. C. Ørsted Institutet, Universitetsparken 5, 2100 København Ø, Denmark.

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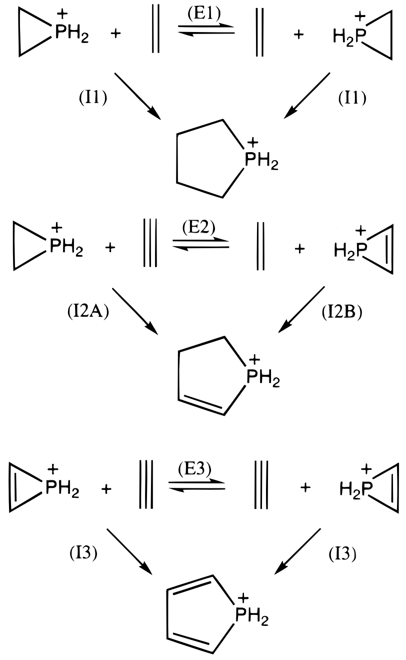
Scheme 1



reactions. In addition, we present results for a parallel set of competing insertion reactions forming five-membered heterocycles.

Computational Methods

Ab initio molecular orbital calculations[15] were carried out using a modified form of G2 theory[16] with the GAUSSIAN 94[17] and MOLPRO 96[18] systems of programs. G2 theory corresponds effectively to energy calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2(full)/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point vibrational energies (ZPVEs) and a so-called higher level correction. It has been shown to perform well for the calculation of atomization energies, ionization energies, electron affinities, bond energies, proton affinities, acidities, and reaction barriers.[16,19,20] In the present work, we have used a slightly modified version of G2 theory in which the ZPVEs were calculated using MP2(full)/6-31G(d) harmonic vibrational frequencies scaled by 0.9646[21] rather than the standard scaled HF/6-31G(d) frequencies because of an occasional symmetry discrepancy between the optimized geometries at the two levels. This is formally the G2(ZPE=MP2) method,[22] but we use the G2 label here for the sake of brevity. The transition structures for the reactions reported in this 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 are presented in Table S1 of the Supporting Information. Relative energies within the text correspond to G2 values at 0 K, unless otherwise specified.

Table 1. Calculated Barriers and Reaction Energies for Exchange (E) and Insertion (I) Reactions[a]

reaction	pathway	barrier	reaction energy
E1	A	3.6	0.0
	B	151.3	0.0
E2	A	28.0	0.4
	B	168.8	0.4
E3	A	39.4	0.0
	B	207.9	0.0
I1		234.0	−258.7
I2A		229.2	−310.5
I2B		214.5	−310.9
I3		216.9	−342.4

[a] G2 values in kJ mol^{-1} at 0 K.

Results and Discussion

A schematic representation of the model exchange (E1−E3) and insertion (I1, I2A, I2B, and I3) reactions investigated in the present work is displayed in Scheme 1.

Two pathways were characterized for the exchange reaction, and one pathway was characterized for the insertion reaction. The results for the two exchange pathways, the pathway for insertion, and comparisons between them are discussed separately in the sections that follow. Figures 1, 2, 4, and 6 depict MP2(full)/6-31G(d) optimized structures, including optimized values of selected geometric parameters for all species investigated. Complete geometries in the form of GAUSSIAN archive entries are presented in Table S2 of the Supporting Information. Barriers and reaction energies for the reactions in Scheme 1, calculated at the G2 level at 0 K, are given in Table 1. Schematic energy profiles are displayed in Figures 3, 5, and 7.

Exchange Reactions. Pathway A. In the identity reaction E1, the phosphiranium ion **7** reacts with ethylene. Although reaction E1 has not been observed in the laboratory, it should nevertheless be feasible, since 1-methyl-1-phenylphosphiranium triflate (**3**) liberates ethylene on heating and in solution.[9,10]

Pathway A of the E1 reaction (see Figures 2 and 3) involves the initial formation of a C_s complex (**10**) between the reactant phosphiranium ion and ethylene, which is bound relative to the reactants by 25.9 kJ mol^{-1}. Concerted rotation of the PH_2^+ moiety toward the ring carbon atoms and stretching of the PC bonds of the phosphiranium ion leads to another C_s complex **11**, which is bound relative to the reactants by 2.3 kJ mol^{-1}. As can be seen from Figure 2, the transition structure (**TS-E1A-1**) in the transformation of **10** to **11** has a geometry very similar to that of **11**. The reaction of **11** to give **11**' occurs via the C_{2v} transition structure **TS-E1A-2** and involves further rotation of the PH_2^+ moiety and further stretching of the PC bonds. The most notable geometric feature of **TS-E1A-2** is that the PH_2^+ moiety is almost parallel to the two CC bonds (Figure 2).

The barrier for the formation of complex **11** from phosphiranium ion and ethylene is 3.6 kJ mol^{-1}, while the transition structure (**TS-E1A-2**) for the reaction of **11** to give **11**' lies just

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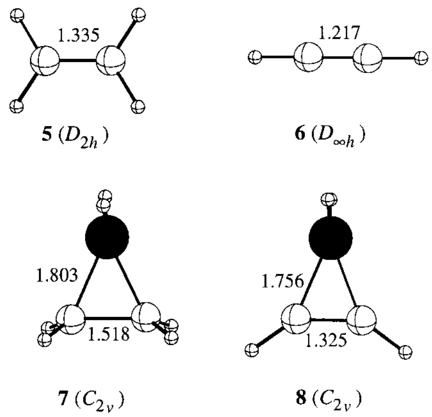


5 (D_{2h}) **6** ($D_{\infty h}$)

7 (C_{2v}) **8** (C_{2v})

Figure 1. Selected MP2(full)/6-31G(d) geometrical parameters of reactant molecules involved in the E1−E3 exchange and I1−I3 insertion reactions. Bond lengths in angstroms.

1.6 kJ mol^{-1} above the reactants (Table 1). Because of the shallowness of the potential well in which **11** resides (Figure 3), it is not clear whether it plays a significant role in reaction E1.

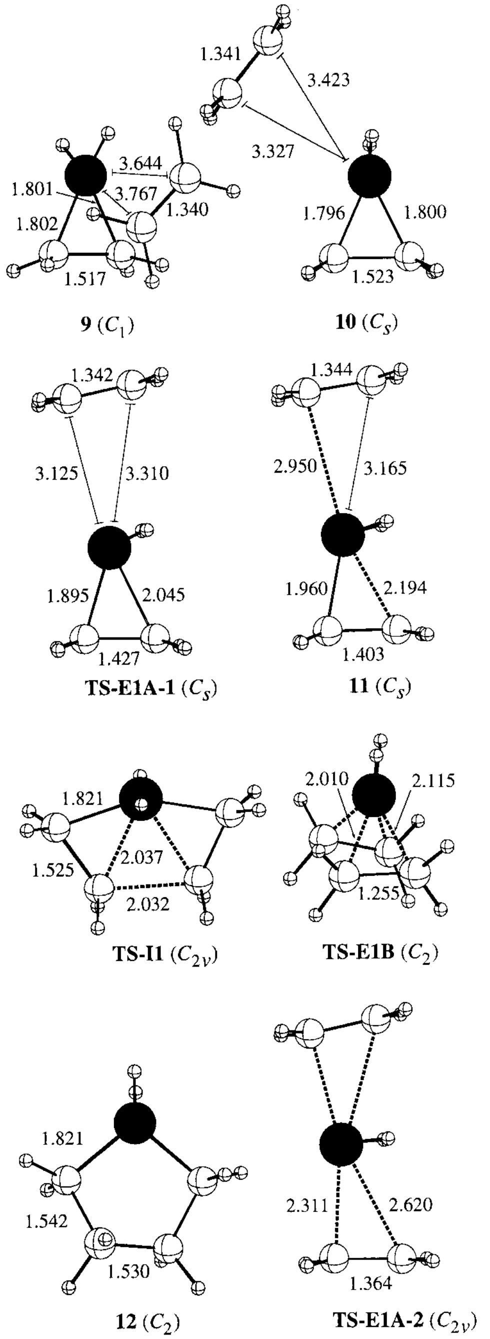
In reaction E2, the phosphiranium ion **7** reacts with acetylene, forming the phosphirenium ion **8** and ethylene. Reaction E2 models the experimentally observed reaction of 1-methyl-1-phenylphosphiranium triflate with dimethylacetylene to form 1,2,3-trimethyl-1-phenylphosphirenium triflate (**4**).[9,10]

In a manner similar to reaction E1, acetylene and phosphiranium ion initially form the C_{2v} complex **13**, which is bound relative to acetylene and phosphiranium ion by 23.8 kJ mol^{-1} (Figures 4 and 5). In the reverse reaction, ethylene and phosphirenium ion give the C_s complex **14**, which is bound relative to ethylene and phosphirenium ion by 28.1 kJ mol^{-1}. In contrast to the E1 reaction, the E2 reaction occurs via one transition structure only (**TS-E2A**), which directly connects the reactant and product complexes **13** and **14**. The C_s transition structure **TS-E2A** is very similar to **TS-E1A-2**, and represents a concerted rotation of the PH_2^+ moiety and stretching of the PC bonds. Interestingly, the HF/6-31G(d), B3LYP/6-31G(d), and MP2(fc)/6-31G(d) surfaces have two distinct transition structures along this pathway. These connect the reactant and product complexes via a central complex similar to the situation pertaining to the E1 reaction. In the case of the MP2(fc)/6-31G(d) surface, the central complex lies 7.5 kJ mol^{-1} above the reactants and is separated from **13** by a barrier of only 0.5 kJ mol^{-1} when ZPVEs are included.

The barrier for the E2 reaction (28.0 kJ mol^{-1}) is significantly higher than that found for the E1 reaction. No strong thermodynamic driving force is affecting the barrier for the E2 reaction, since the reaction energy is very small (0.4 kJ mol^{-1}).

Reaction E3 also models an experimentally observed process, namely, the facile alkyne exchange equilibrium between simple phosphirenium salts.[9,10]

The results for the E3 reaction (see Figures 6 and 7) are very similar to those found for the E2 reaction. The initial C_s complex (**19**) is bound by 26.6 kJ mol^{-1} relative to the reactants. Again, MP2(full)/6-31G(d) optimization predicts one transition structure, the C_{2v} species **TS-E3A**, which reflects concerted rotation of the PH_2^+ moiety and stretching of the PC bonds. The HF/6-31G(d) and B3LYP/6-31G(d) calculations again predict two distinct transition structures with the central complex lying in a shallow potential well, i.e., surfaces similar to Figure 3. Again the PH_2^+ moiety is close to parallel to the two CC bonds.



9 (C_1) **10** (C_s)

TS-E1A-1 (C_s) **11** (C_s)

TS-I1 (C_{2v}) **TS-E1B** (C_2)

12 (C_2) **TS-E1A-2** (C_{2v})

Figure 2. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the E1 and I1 reactions. Bond lengths in angstroms.

The calculated barrier for this last exchange reaction is 39.4 kJ mol^{-1}, which is the largest of the barriers that we have found for an exchange reaction proceeding via pathway A.

The main characteristic of pathway A for all the exchange reactions is the rotation of the PH_2^+ moiety to an orientation almost parallel to the CC bond, accompanied by the approach of the reactant hydrocarbon and elimination of a hydrocarbon moiety from the ring. The arrangement of π-ligand−PH_2^+−π-ligand found in the pathway A transition structures closely resembles the triple-ion arrangement (e.g., $X^- \cdots CH_3^+ \cdots X^-$) found in S_N2 transition structures.

The exchange reaction via pathway A becomes energetically more expensive in the order E1 < E2 < E3, which implies that rotation of the PH_2^+ moiety and stretching of the PC bonds are energetically less feasible for the phosphirenium ion than for the phosphiranium ion (E1 < E3). This can be rationalized in

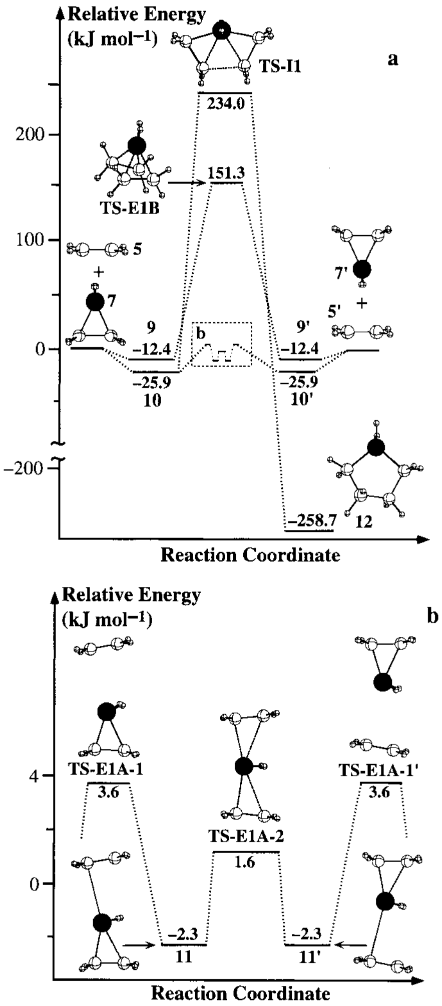


Figure 3. (a) Schematic energy profiles for the E1 and I1 reactions and (b) inset from part a showing in more detail the central part of pathway A of the E1 reaction.

terms of the tightness by which the unsaturated hydrocarbon is bound to the PH_2^+ moiety. The phosphirenium ion has the shorter PC bonds (Figure 1) and therefore the tighter binding; thus, the highest barrier is associated with the exchange reaction involving the phosphirenium ion alone. The fact that the barrier for the E2 reaction is closer to that of the E3 reaction than the E1 reaction may be rationalized by noting that the transition structure (**TS-E2A**) resembles more closely the product complex (**14**) between phosphirenium ion and ethylene than the reactant complex (**13**) between phosphiranium ion and acetylene.

Exchange Reactions. Pathway B. In pathway B of the E1 reaction, phosphiranium ion and ethylene initially form the C_1 complex **9**, bound by 12.4 kJ mol^{-1} relative to the reactants (see Figures 2 and 3). Product and reactant complexes are connected by a single transition structure (**TS-E1B**), which has C_2 symmetry at the MP2(full)/6-31G(d) level. Interestingly, the geometry optimized at the HF/6-31G(d) level for **TS-E1B** is more symmetrical (C_{2v}), but the energy difference between the C_{2v} and C_2 structures is only 0.2 kJ mol^{-1} at the MP2(full)/6-31G(d) level, with the MP2(full)/6-31G(d) C_{2v} structure having two imaginary frequencies. G2 theory predicts a barrier of 151.3 kJ mol^{-1} for the E1 reaction via pathway B (Table 1).

In the E2 reaction, acetylene and phosphiranium ion initially form the C_s complex **15**, which is bound relative to acetylene and phosphiranium ion by 40.8 kJ mol^{-1} (Figures 4 and 5). In the reverse reaction, ethylene and phosphirenium ion give the C_s complex **16**, which is bound relative to ethylene and phosphirenium ion by 37.7 kJ mol^{-1}. The C_s transition structure (**TS-E2B**), geometrically similar to that found for reaction E1, connects reactant and product complexes (**15** and **16**). The barrier for the E2 reaction via pathway B is 168.8 kJ mol^{-1}.

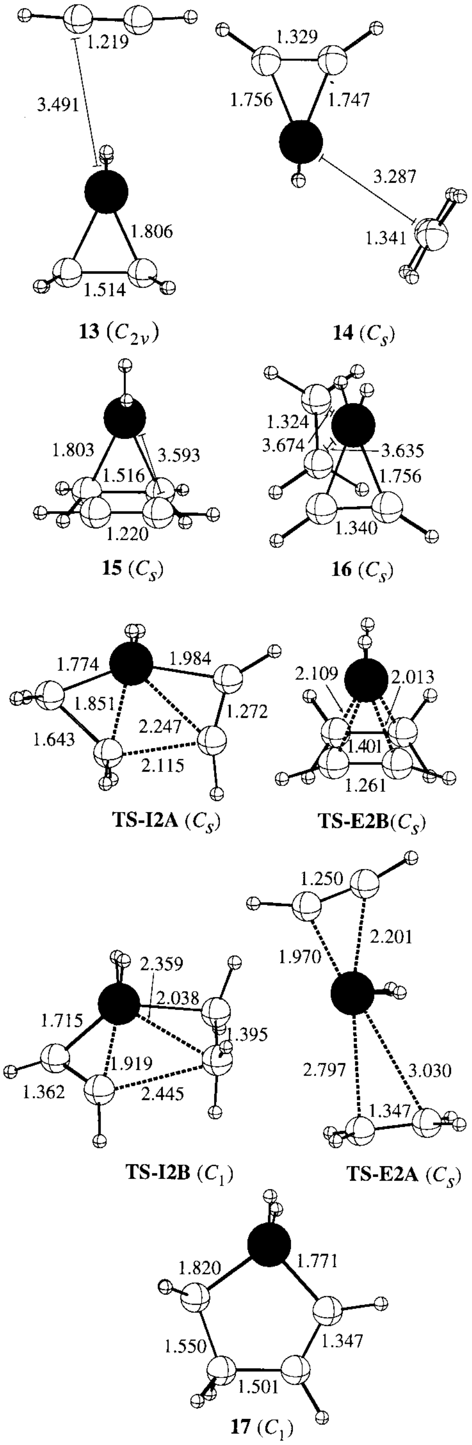


Figure 4. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the I2A and I2B insertion reactions and the E2 exchange reaction. Bond lengths in angstroms.

In pathway B of reaction E3, phosphirenium ion and acetylene initially combine to give the C_s complex **18**, which is bound by 22.7 kJ mol^{-1} relative to the reactants (Figures 6 and 7). The transition structure **TS-E3B** is geometrically similar to the analogous structures found for reactions E2 and E1. As was the case for reaction E1, symmetry discrepancies between the

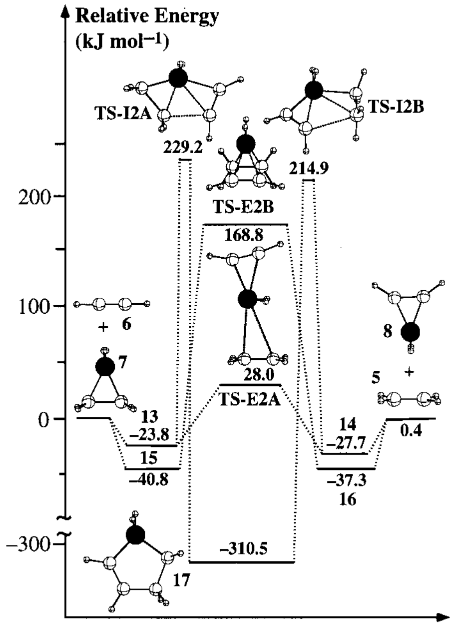


Figure 5. Schematic energy profiles for the E2, I2A, and I2B reactions.

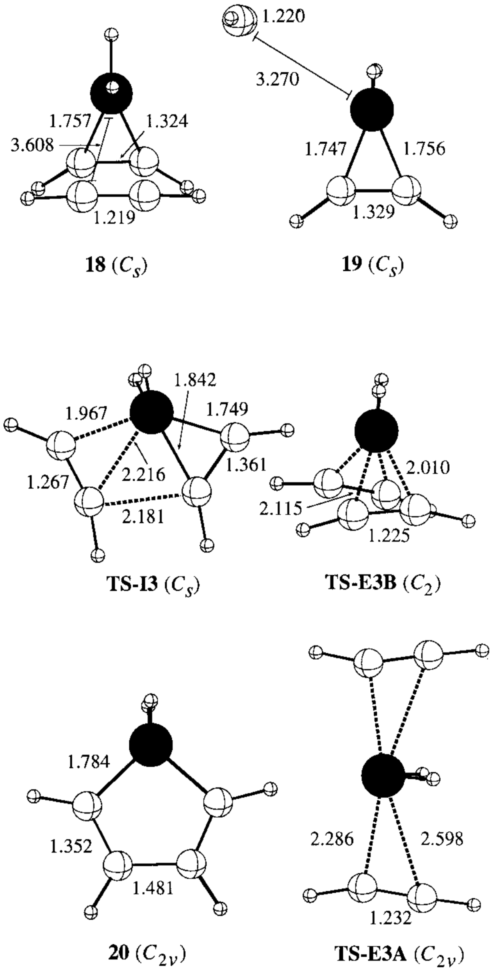


Figure 6. Selected MP2(full)/6-31G(d) geometrical parameters of species involved in the E3 and I3 reactions. Bond lengths in angstroms.

structures optimized at the HF/6-31G(d) and MP2(full)/6-31G-(d) levels are found; C_2 symmetry is predicted at the MP2(full)/6-31G(d) level, while HF/6-31G(d) again predicts a C_{2v} structure. As before, the energy difference between the C_{2v} and C_2 structures is very small (0.04 kJ mol^{-1} at MP2/6-31G(d)), with the MP2/6-31G(d) C_{2v} structure having two imaginary frequencies. Reaction E3 has the highest barrier for pathway B of the three exchange reactions investigated (207.9 kJ mol^{-1}).

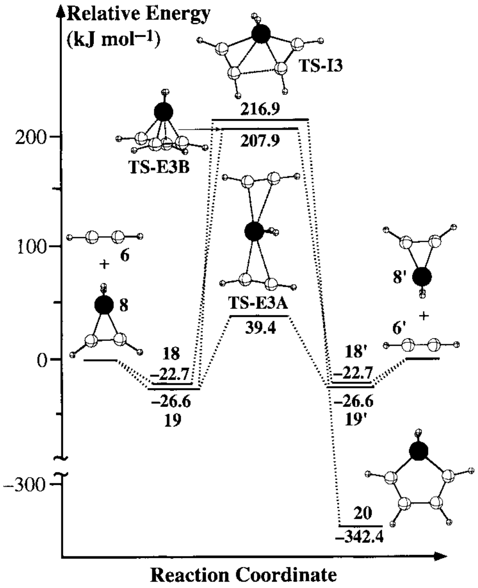


Figure 7. Schematic energy profiles for the E3 and I3 reactions.

Pathway B is consistently the higher energy exchange pathway, and the exchange reaction via pathway B becomes energetically more expensive in the order E1 < E2 < E3, as was the case for pathway A. This may be a reflection of the increasing strain along the series of transition structures **TS-E1B**, **TS-E2B**, and **TS-E3B** associated with the successively increased multiple-bond character in the CC bonds within the small rings.

Insertion Reactions. Since strained three-membered phosphorus heterocycles are very reactive molecules,[3] and the corresponding five-membered heterocycles are thermodynamically favorable,[23] it is of interest to ask why exchange takes place in preference to insertion, given that the latter would be a highly exothermic process. To this end, we have examined the I1, I2A, I2B, and I3 insertion reactions.

The insertion reactions are found to involve the same initial complexes as those for the corresponding pathway A exchange reactions.

Reaction I1 models insertion of ethylene into the three-membered ring of the phosphiranium ion **7**, yielding the C_2 saturated five-membered heterocycle **12** (see Figures 2 and 3). The transition structure that connects complexes **10** and **12** is the “end-to-end” type structure **TS-I1**, which is predicted at the MP2(full)/6-31G(d) level to have C_{2v} symmetry. In this case, optimization at the HF/6-31G(d) level predicts a transition structure of C_s symmetry; the energy difference between the C_{2v} and C_s structures is 15.1 kJ mol^{-1} at the HF/6-31G(d) level, with the HF/6-31G(d) C_{2v} structure having two imaginary frequencies.

The barrier for the I1 reaction is 234.0 kJ mol^{-1}, and the reaction exothermicity for the process is large (258.7 kJ mol^{-1}).

Reaction I2A represents insertion of acetylene into the three-membered ring of the phosphiranium ion **7**. The reaction proceeds from complex **13** via the C_s transition structure **TS-I2A** to the C_1 five-membered heterocycle **17** (Figures 4 and 5). Reaction I2B also yields **17**, but by insertion of ethylene into the three-membered ring of the phosphirenium ion **8**. The reaction involves initial formation of the complex **14**, which leads to **17** via the C_1 transition structure **TS-I2B**. The

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phosphorus−ethylene distance is larger in **TS-I2B** than in **TS-I2A**, which is expected since **TS-I2B** represents attack of ethylene on the phosphirenium ion.

The barrier for the I2A reaction (229.2 kJ mol^{-1}) is slightly larger than that for the I2B reaction (214.5 kJ mol^{-1}). Reactions I2A and I2B are exothermic by 310.5 and 310.9 kJ mol^{-1}, respectively.

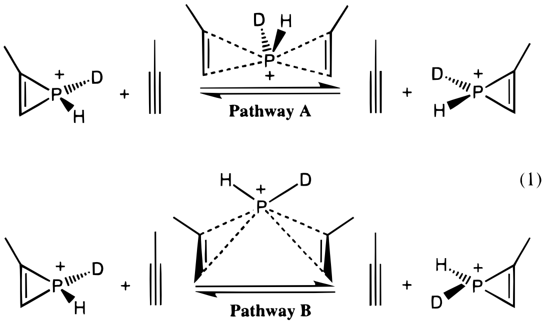
The final reaction considered (I3) is insertion of acetylene into the phosphirenium ion **8**, yielding the C_{2v} five-membered product **20**, which is formed from complex **19** via the C_s transition structure **TS-I3** (Figures 6 and 7). In this structure, the two acetylene molecules are unsymmetrically disposed around the PH_2^+ moiety (Figure 6), as opposed to the insertion of ethylene into phosphiranium ion, which proceeds via a C_{2v} transition structure (**TS-I1**, Figure 2).

The barrier for the I3 insertion reaction is 216.9 kJ mol^{-1}. The I3 reaction is the most exothermic (by 342.4 kJ mol^{-1}) of the four insertion reactions investigated.

The unifying theme of the insertion reactions is the end-to-end transition structure, in which terminal carbon atoms from each of the two unsaturated hydrocarbons involved in the reaction have approached one another to yield a five-membered ring by carbon−carbon bond formation.

The barrier for insertion increases in the order I2B < I3 < I2A < I1. Although there is effectively no thermodynamic preference for I2B over I2A, the barrier for formation of **17** from ethylene and the phosphirenium ion is 14.7 kJ mol^{-1} lower than the barrier for formation of **17** from acetylene and phosphiranium ion. This could be related to the release of strain in the transition structure, with more strain being released in the case of the opening of the unsaturated phosphirenium ion. This argument is consistent with the overall ordering of the insertion barriers; for example, I3 is energetically less expensive than I1 because I3 involves the unsaturated phosphirenium ion whereas I1 does not. Whether these differences are large enough to translate to experimental observations is unknown.

The Exchange Reaction: Pathway A versus Pathway B. The exchange reaction is predicted to be a stereospecific[24] process with respect to the configuration at phosphorus when proceeding via both pathways A and B. The stereochemical outcome, however, is opposite in the two cases. This is exemplified by reaction 1.



(1)

The difference between the energy barriers for the two pathways is significant, viz., 147.7 kJ mol^{-1} for E1, 140.8 kJ mol^{-1} for E2, and 168.5 kJ mol^{-1} for E3, with pathway A being favored in each case. Thus, we predict that the exchange reaction will *only* proceed via pathway A; hence, the major stereoisomer formed in the exchange reaction can be predicted by considering the pathway A type transition structure only. Confirmation of this hypothesis presents an interesting challenge to synthetic chemists.

Insertion versus Exchange. The differences in the energy barriers of the lowest energy exchange pathway and the energy barriers for insertion are very large, namely, 230.4 kJ mol^{-1} for E1 vs I1, 201.2 kJ mol^{-1} for E2 vs I2A, 186.9 kJ mol^{-1} for reverse E2 vs I2B, and 177.5 kJ mol^{-1} for E3 vs I3. These differences are sufficient to explain the failure to observe the insertion reaction experimentally. The lower barrier for exchange compared with insertion means that these reactions exemplify situations in which the thermodynamically preferred product is not kinetically preferred.

Concluding Remarks

The present investigation provides a fascinating insight into π-ligand exchange in three-membered organophosphorus ions, a reaction hitherto unobserved in main-group chemistry, but commonplace in transition metal chemistry. Detailed comparisons between competing exchange and insertion pathways confirm that the former is the kinetically favored process, despite a large thermodynamic preference for insertion. This is in agreement with experimental observations on related systems. The present theoretical investigation predicts that the exchange reaction is stereospecific with respect to the configuration at phosphorus.

A tantalizing question remains as to the utility of the π-ligand exchange reactions when applied to small rings containing other heteroatoms, or even carbon itself. Further work is in progress in this direction for a selection of related main-group heterocycles in order to determine the ubiquity of the π-ligand exchange process.

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Supporting Information Available: Total G2 energies (Table S1) and archive entries for the MP2(full)/6-31G(d) optimized geometries (Table S2) (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[24] The term “stereospecific” is used to denote a process which is “mechanistically constrained to proceeed in a stereochemically defined manner” as suggested by L. N. Mander in Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.