Organometallics **2005,** *24,* 3125−3135

Gas-Phase Synthesis, Characterization, and Reactivity Studies of the Prototype Aromatic Phosphirenylium Ion

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Received March 3, 2005

The unsubstituted phosphirenylium ion, cyclo-$C_2H_2P^+$, was generated in the gas phase via an addition−ablation strategy employing a modified quadrupole ion-trap mass spectrometer. The reaction of gas-phase PBr^+ with acetylene affords $H_2C_2P^+$ as the sole product ion. Its structure is that of the phosphirenylium cation (**1**). Experimental results find support from density functional theory calculations at the B3LYP/6-31G* and G3//B3LYP/6-31G* levels. The reaction of PBr^+ with acetylene is predicted to be exothermic with respect to the formation of two isomers, the phosphirenylium cation (**1**) and the ethenylidenephosphenium cation (**2**), whereas formation of eight other isomers is endothermic. Reactions of **1** with acetylene and ethylene do not lead to observable products, but **1** does react with 1,3-butadiene as a phosphenium ion via formal 1,4-addition to give the 3-phosphaspiro[2,4]-hepta-1,5-diene phosphonium ion. The formation of this *P*-spiro adduct is predicted to be a stepwise process. An isotopic labeling experiment supports this structure, which is predicted by computational modeling to be kinetically favored over a lower energy structure that could arise from a Diels-Alder-like reaction of the phosphirenylium ion.

Introduction

The structure and energetics of the cyclopropenium ion ($C_3H_3^+$) and its isomers have attracted extensive study.[1−15] The parent cyclopropenyl cation, $C_3H_3^+$, represents the simplest Hückel aromatic system, with two delocalized π-electrons. Theoretical studies find that the cyclopropenyl cation is the lowest energy structure on the $C_3H_3^+$ potential energy surface; its resonance energy, as estimated by Pople and co-workers from high-level ab initio calculations, exceeds 60 kcal/mol.[8] In 1957 Breslow and co-workers synthesized the first derivative of this system, the triphenylcyclopropenyl cation,[14] and in 1970 Breslow and Groves prepared the parent cyclopropenyl cation in solution.[1] Electronic and infrared spectra of cyclo-$C_3H_3^+$ in neon matrixes were also reported recently.[15]

Substituted phosphorus analogues were only recently observed in solution[16] and as part of a complex.[17] The unsubstituted phosphirenylium cation, $C_2H_2P^+$, however, has not been generated in solution.

In the gas phase Smith and co-workers,[18] using a selected ion flow tube (SIFT), found that $C_2H_2P^+$ ions are the product of the reactions of acetylene, methylacetylene, and ethylene with PH_n^+ (n = 0−2). They interpreted its facile formation as indicating a phosphirenylium structure for $C_2H_2P^+$. The reaction of P_2^+ with acetylene also gives $C_2H_2P^+$, as determined in an FTICR study by Eyler and co-workers.[19] Although they found an upper limit of 256 kcal/mol for ΔH_f of $C_2H_2P^+$, they did not determine its structure. $C_2H_2P^+$ can form in the reactions of P^+ with ethylene and react further with ethylene to yield $(C_2H_2)_2P^+$ ions.[19] The authors considered the likelihood that these $C_2H_2P^+$ products might be either complexes or covalently bonded molecules, but they also proposed no detailed structures.

Although experimental studies are inconclusive about the structure of the $C_2H_2P^+$ ions, theory does give structural perspective. Maclagan[20] suggested that at least three isomers of $C_2H_2P^+$ can form from the

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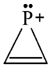
10.1021/om050155l CCC: $30.25

reactions of PH_n^+ ($n = 1-2$) with ethylene:[18] **2** and **3** in addition to the phosphirenylium ion, **1**.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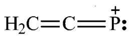
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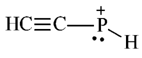
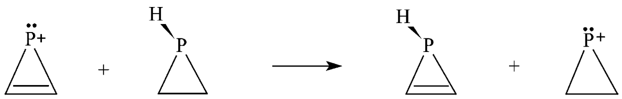

(3)

In SIFT experiments the reaction of $P^+(^3P)$ with acetylene was found to give two product ions, C_2HP^+(95%) and $C_2H_2P^+$ (5%).[18] On the basis of theoretical calculations, Largo et al.[21] suggested that the minor product $C_2H_2P^+$ formed in the experiments of Smith et al.[18] most likely had the vinylidene-type structure CH_2CP^+ ($^3A_2$). The cyclic π-complex, $PC_2H_2^+$ ($^3A_2$), was also a possible candidate because its energy was predicted to be only 7.3 kcal/mol higher than that of the former.

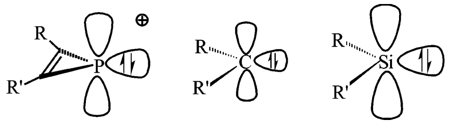
Calculations on the $C_2H_2P^+$ isomers at the HF/6-31G* level of theory[20] indicated that the global minimum on the $C_2H_2P^+$ potential energy surface is the singlet phosphirenylium cation, and this conclusion found support in later studies at the MP4/MC-311G*//MP2/6-31G* levels.[21] From ab initio calculations of the energetics of the following homodesmotic reaction, it was predicted that the resonance energy of the parent phosphirenylium cation is ca. 38 kcal/mol.[22]



The same method yielded an estimate for the resonance energy of the cyclopropenium ion of 59 kcal/mol.[12] The stabilization energy of the phosphirenylium cation, while much smaller than that of the cyclopropenyl cation, is still significant, indicating that the phosphirenylium cation is aromatic. The reduced stabilization arises because the overlap of valence shell p orbitals between phosphorus and carbon atoms is less than the overlap between two C_{2p} atomic orbitals.

Recently, studies of the gas-phase chemistry of 2-*tert*-butyl-3-phenylphosphirenylium ion, the sole phosphirenylium ion prepared in solution,[16] were reported.[23] The *m/z* 189 cation formed in abundance upon 70 eV electron ionization and chlorine atom loss from 1-chloro-2-*tert*-butyl-3-phenyl-1*H*-phosphirene in a pentaquadrupole mass spectrometer was assigned a phosphirenylium ion structure. The basis for this structure assignment seems to have been the variety of product ions formed upon 15 eV collision-induced dissociation with argon, suggesting a fairly stable ion. The reaction of the *m/z* 189 ion with oxygen nucleophiles (Et_2O, propylene oxide, THF), sulfur nucleophiles (diethyl sulfide, ethyl phenyl sulfide, thiolane, thiane, thiirane), and nitrogen nucleophiles (pyridine, aniline) led to adducts that mainly dissociated back to *m/z* 189 under CID conditions.[23] These reactions were all interpreted as occurring by attack of the nucleophilic heteroatom centers at the P atom, readily reversible due to the stability of the substituted phosphirenylium ion.

Scheme 1



With support from computational studies, reactions of *m/z* 189 with 1,3-dienes (butadiene, isoprene, 1-methoxy-3-trimethylsilyloxybutadiene) were interpreted as formal 1,4-addition of the dicoordinate phosphorus center to form *P*-spiro bicyclic phosphonium ions that dissociate back to *m/z* 189 upon CID (vide infra). The butadiene and isoprene adducts were observed to react with a second molecule of diene in what was presumed to be a Diels-Alder reaction.[23]

Considering the experimental difficulties in generating the parent phosphirenylium cation and the sparse experimental evidence for its reactions, we set two goals for this study: to establish a new route to generate the phosphirenylium ion, and to examine its reactivity. As a class, phosphirenylium ions are rather poorly characterized relative to similar reactive intermediates such as carbenes and silylenes. This alone is sufficient to motivate fundamental studies of their structures and reactivity.

Phosphenium ions $R_2P:^+$ are isolobal with carbenes.[24] A structure for a singlet phosphirenylium ion resembling that of singlet carbenes and silylenes is shown in Scheme 1, with a phosphorus lone pair as the HOMO and an empty p orbital as the LUMO. Partial delocalization of the C=C π-electrons into the phosphorus 3p orbital may cause the phosphirenylium ion to behave differently than most carbenes and silylenes. The nearest analogue is the cyclopropenylidene carbene, whose carbenic reactivity is attenuated by its cyclic π-electron system.[25,26]

Experimental Section

Materials. Phosphorus tribromide, pentane, and 1,3-butadiene were obtained from Aldrich Chemical Co. (Milwaukee, WI). Ethylene (C_2H_4) and acetylene were from Matheson Gas Products (Parsippany, NJ), and labeled acetylene ($^{13}C_2D_2$) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). All chemicals were used without further purification, except pentane, which was distilled under nitrogen prior to use.

Mass Spectrometry. Ion−molecule reactions were studied with a Thermo Finnigan PolarisQ quadrupole ion-trap mass spectrometer (San Jose, CA) to which a gas inlet system had been added. Briefly, the neutral acetylene was introduced into the trap as a part of the helium background gas flow. The flow of the acetylene was restricted by a 200 mm × 10 μm i.d. restrictor column at a pressure of 200 Torr. The fine capillary column controls the acetylene flow rate. The pressure of acetylene in the ion trap was estimated to be $\sim 10^{-6}$ Torr, and the molar mixing ratio of helium/reagent was $\sim 10^3$:1 for all experiments reported here.

The reactant ion PBr^+ was generated by electron ionization (70 eV) of PBr_3, which had been introduced into the ion source as an eluent from a gas chromatograph (ThermoFinnigan Trace GC 2000, San Jose, CA) equipped with a 30 m × 25 μm i.d. Rtx-5MS column (Restek Corp., Bellefonte, PA). For each experiment, 1 μL of a solution of 1 μL of PBr_3 in 25 mL of dry

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pentane was injected into the chromatograph. The injector was held at 200 °C, and the initial oven temperature was 50 °C, with a hold time of 4 min. The temperature was then ramped to 250 °C at 15 °C/min and held at that temperature for 5 min. While PBr_3 eluted from the chromatographic column (the retention time of PBr_3 was ca. 7.3−7.5 min), the mass spectrometer electron beam was turned on to ionize the PBr_3. Ions formed in the ion source were extracted and focused into the ion trap. Unwanted ions were ejected from the ion trap by ramping the rf potential and applying a negative dc pulse potential, and the desired ion was mass selected for further studies. Ion−molecule reactions were examined after the precursor ion was isolated and allowed to undergo collisions with the He gas in an effort to thermalize the ions. The PolarisQ's Xcalibur software was used for parameter control and data acquisition.

High-energy collision-induced dissociation (CID) product-ion spectra were obtained using a triple-sector Kratos MS-50 TA mass spectrometer (Kratos Analytical, Ramsey, NJ) of EBE geometry.[27] The ion beam was accelerated to 8 keV and selected by using the first electrostatic analyzer (ESA) and the magnetic sector. The selected ions were activated by collision with helium in the third field-free region. The collision pressure was adjusted to give 50% main-beam attenuation, and the β-slit width (after the second ESA) was maintained at 0.50 mm. A CID spectrum was obtained by scanning the voltages applied to the second ESA; each spectrum was an average of forty 20 s scans.

Theory. The Spartan'02 (version 1.0.1) and Spartan'04 (version 1.0.1) Windows program suites from Wavefunction Inc. (Irvine, CA)[28] were used for all the theoretical studies. Compared to high-level ab initio molecular orbital procedures, density functional theory (DFT) is substantially simpler and requires less computational resources to give similar results. DFT has, therefore, become the theory of choice in an increasing number of the gas-phase ion chemistry studies,[29,30] and the electronic structure calculations reported here were carried out using DFT methods unless otherwise indicated. Optimized geometries, energies, and harmonic vibrational frequencies for all species were obtained by using Becke's three-parameter (B3) exchange functional[31] in conjunction with the Lee−Yang−Parr (LYP) correlation functional.[32] For all calculations the split-valence plus polarization 6-31G* basis set, which incorporates a set of d functions for heavy atoms and includes all electrons in the calculation, was used. All stationary points were verified through computation of their vibrational frequencies. The energies reported in this work include zero-point vibrational energy (ZPVE) corrections, which were scaled by a factor of 0.9806.[33] For bromine-containing species,[34] energies were also obtained employing B3LYP/6-311+G**//B3LYP/6-31G* and G3//B3LYP/6-31G*.[35−37] When the level of calculation is not indicated, it was B3LYP/6-31G*.

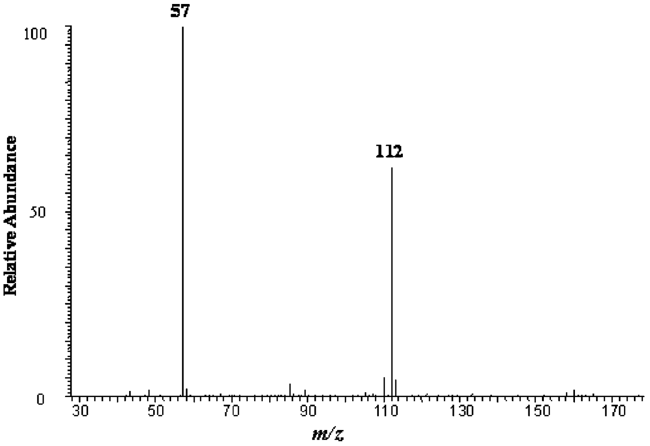

Figure 1. Reaction of $P^{81}Br^+$ (*m/z* 112) with C_2H_2 to form the *m/z* 57 ion $C_2H_2P^+$.

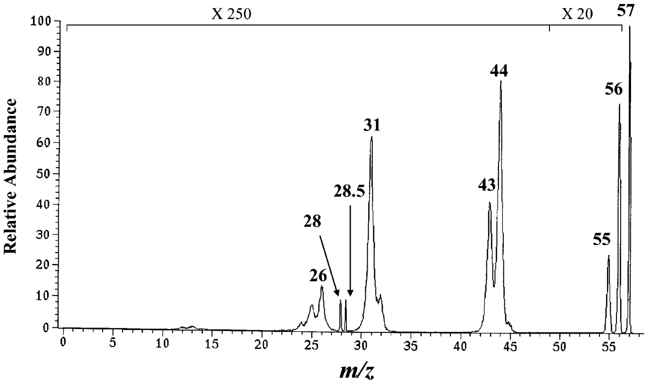

Figure 2. High-energy CID spectrum of the product ion $C_2H_2P^+$ (*m/z* 57) generated in the reaction of $PBr^+ + C_2H_2$. Two doubly charged species *m/z* 28.5 and 28 correspond to $C_2H_2P^{2+}$ and C_2HP^{2+}, respectively.

Results and Discussion

Reaction of PBr^+ with Acetylene. It was anticipated that a monovalent phosphorus cation $X{-}P^+$ could act as a "P^+-oid", allowing transfer of P^+ to acetylene, while the X-moiety functions as a sacrificial ligand. In this addition−ablation strategy, the X−P bond would undergo homolysis to dissipate some of the exothermicity of the reaction of XP^+ with the substrate acetylene. Because the bond energy of Br−P is not high (~65 kcal/mol), the BrP^+ species seemed to be a promising choice. For an open-shell species with low-lying SOMO and LUMO orbitals, such as XP^+, several product structures can form, even from a reaction partner as simple as acetylene. Hence we chose to study the reaction of PBr^+ with acetylene by using a modified quadrupole ion-trap mass spectrometer, anticipating that tandem mass spectrometric methods could be employed to characterize the product ions. The reaction gives only the one product ion, $C_2H_2P^+$, and we sought to identify this product ion and investigate its reactivity by both experimental and theoretical studies.

Electron ionization (EI) of gaseous PBr_3 was the source of the precursor ion, PBr^+. EI of PBr_3 at 70 eV gave PBr_3^+, PBr_2^+, PBr^+, Br^+, and P^+. The most abundant was that of *m/z* 191 ($P^{79}Br^{81}Br^+$); the relative abundance of PBr^+ (of *m/z* 110 or 112) was ca. 20% of that of the most abundant ion. After ejecting all unwanted ions from the ion trap, the $P^{81}Br^+$ ion (*m/z*

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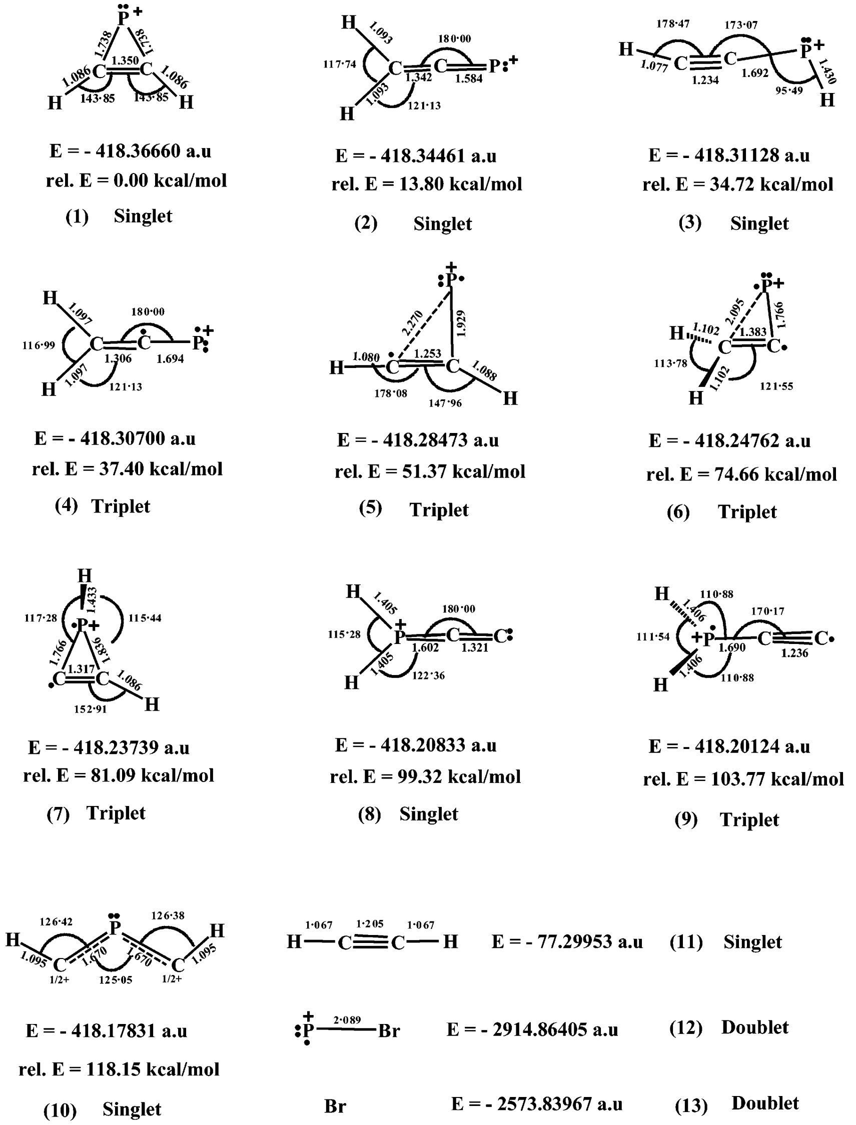


Figure 3. Optimized geometries and energies of 10 isomers (**1** to **10**) of $C_2H_2P^+$ as well as of PBr^+, C_2H_2, and Br atom at the B3LYP/6-31G* level. Distances are given in Å and angles in deg.

112) was isolated and allowed to collide with helium in an effort to thermalize it. The reaction time for PBr^+ with acetylene (eq 1) was 100 ms, and typical results are illustrated as a mass spectrum in Figure 1.

$$PBr^+ + C_2H_2 \rightarrow C_2H_2P^+ + Br^\bullet \qquad (1)$$

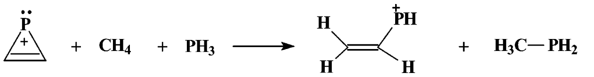
The only product ion that forms in this reaction is $C_2H_2P^+$ (of *m/z* 57), which is believed to result (vide infra) from the elimination of a bromine atom from an initially formed adduct, $C_2H_2PBr^+$. We were unable to detect the adduct $C_2H_2PBr^+$, and this is not surprising given the exothermicity of the reaction (see below), the small number of the vibrational modes of the system, and the relatively weak P−Br bond.

Identification of the Product Ion $C_2H_2P^+$. Although the structure of $C_2H_2P^+$ had not been determined experimentally, several theoretical studies on isomers of $C_2H_2P^+$ showed that the singlet species **1** is the global minimum.[20,21] Low-energy collision-induced dissociation (CID) of the $C_2H_2P^+$ product ions failed. Under high-energy CID conditions in a tandem magnetic sector mass spectrometer, the product-ion spectrum of $C_2H_2P^+$ (Figure 2) shows that loss of C_2H_2 is a major process, but at least four structures are compatible with this observation (see structural considerations below). A doubly charged species $C_2H_2P^{2+}$ also forms under these high-energy conditions, which indicates a low second ionization energy of neutral C_2H_2P. One often sees doubly charged ions in the mass spectra of aromatic compounds, as a second ionization is relatively facile. Note that another doubly charged species C_2HP^{2+} is also formed.

To obtain more structural information for the $C_2H_2P^+$ formed in eq 1, we carried out a detailed theoretical investigation of this reaction by employing density function theory at the B3LYP/6-31G* and G3//B3LYP/6-31G* levels. The optimized geometries and energies of the 10 lowest energy isomers (**1** to **10**) of $C_2H_2P^+$ are given in Figure 3. Others have also carried out ab initio calculations on structures **1**,[20,21] **2**,[20,21] **3**,[20,21] and **5**,[20] and our results agree reasonably with those from the previous studies. The best agreement is with those from the MP2/6-31G* calculations of Lopez et al.,[21] and less so with those from the HF/6-31G* calculations of Maclagan.[20] The DFT employed in this work is more comparable with MP2, in that both the DFT and MP2 models take into account the correlation of electron motions, whereas HF treats the motions of individual electrons as independent of one another and overestimates electron−electron repulsion energy. The optimized structures and energies for PBr^+, C_2H_2, and Br are also illustrated in Figure 3.

The results at all three levels of calculation employed in this work predict that the phosphirenylium ion, **1**, is the lowest energy isomer, which is consistent with conclusions from previous studies at the HF/6-31G* and MP2/6-31G* levels.[20,21] The ΔH_f of **1** is predicted to be 249 kcal/mol at G3//B3LYP/6-31G*.

The thermodynamic stability of the phosphirenylium ion is due to its significant resonance energy, 38 kcal/mol (vide supra),[22] and low ring-strain energy. An isodesmic reaction (eq 2) was used to calculate the strain energy of phosphirenylium ion **1**.[38]



(2)

The strain energy of the phosphirenylium ion was found to be only 2.0 kcal/mol at the B3LYP/6-31G* level. The lowest energy π-bonding orbital (i.e., HOMO-2) of **1** holds two π-electrons that are completely delocalized in the three-membered CCP ring.

Calculations were carried out on several excited states. Triplet **5** is predicted to be 51 kcal/mol higher in energy than singlet **1** at B3LYP/6-31G*. This result is in good agreement with that of Maclagan, who found an energy difference of 53 kcal/mol at MP4SDQ/6-31G*//HF6-31G*.[20] At HF/6-31G* Maclagan did not locate a minimum for a triplet state corresponding to structure **2**.[20] We, however, found triplet species **4** and **6** corresponding to **2**, with energies higher by 37 and 61 kcal/mol, respectively.

High-energy triplet H_2PCC^+ (**9**) is predicted to lie only 5 kcal/mol above corresponding singlet **8**. The formation of each of these triplets is endothermic from BrP^+ and acetylene and is therefore likely to be too slow to be observable under the reaction conditions employed. Optimization of a singlet corresponding to triplet cyclo-$(HCCPH)^+$ **7** led to ring-opened $HCCPH^+$ (**3**), lower in energy by 46 kcal/mol.

Attempts to optimize a singlet H_2CPC isomer, with a linear CPC unit, led to species **2**. Singlet species $HCPCH^+$ **10** has the highest calculated energy of the $C_2H_2P^+$ isomers considered in this work.

The energy calculations predict that the formation of $C_2H_2P^+$ isomers **1** and **2** from PBr^+ and acetylene in eq 1 is exothermic by 20 and 2 kcal/mol, respectively, at G3//B3LYP/6-31G* (by 23 and 8 kcal/mol, respectively, at B3LYP/6-311+G**//B3LYP/ 6-31G*, and by 27 and 13 kcal/mol, respectively, at B3LYP/6-31G*). The formation of any of the other eight isomers (**3** to **10**) from eq 1 is unlikely because the reactions are all endothermic, ranging from 17 to 90 kcal/mol at G3//B3LYP/6-31G* and from 8 to 91 kcal/mol at B3LYP/6-31G*, and should therefore be too slow to be observed under our experimental conditions.

Because isomers **1** and **2** are the only two $C_2H_2P^+$ species whose formation from PBr^+ and acetylene is "thermodynamically allowed", detailed reaction path studies were carried out for the formation of these two isomers to determine whether a distinction between them can be made on the basis of "kinetic allowedness" (i.e., can they both be formed from reactions of PBr^+ with acetylene via low-energy barriers?). Figure 4 displays the important intermediates and transition structures in those portions of the potential energy surface shown in Figure 5. We examined the nature of the transition structures by computing the second derivatives of the energy; there is one imaginary frequency for each case, corresponding to a saddle point on the potential energy surface. The imaginary vibration was also examined to ensure that each transition structure led to the anticipated product.

According to the B3LYP/6-31G* doublet potential energy surfaces, formation of both **1** and **2** is possible both thermodynamically and kinetically, but formation of **2** is less favored as the level of calculation is raised. The B3LYP potential energy surface suggests that from initially formed, open-chain adduct **14** two feasible pathways afford either **1** or **2**. The odd electron in the doublet species **14** is located almost completely (∼95%) on the terminal carbon atom.

However, the very low energy barrier (a 1.4 kcal/mol energy difference between intermediate **14** and transition structure **15**) associated with the movement of the P−Br bond outside the molecular plane of **14** to give a more stable cyclic intermediate **16** disappears at higher levels of calculation. The barrier height changes from +1.4 kcal/mol at B3LYP/6-31G* to + 0.5 kcal/mol at B3LYP/6-311+G**// B3LYP/6-31G* and −0.6 kcal/mol at G3//B3LYP/6-31G*. Attempts to optimize transition structure **15** at B3LYP/6-311+G** and MP2/6-311+G** returned structure **14**, and thus, the intermediacy of **14** in the formation of **16** from **1** plus acetylene must be doubted.

Formation of intermediate **16** appears to be a barrierless process favored kinetically over the formation of **18** via intermediate **14**. In **16** the odd electron is widely distributed: at P (∼46%), at Br (∼32%), and at both carbon atoms (11% each).

No transition structure was found for doublet species **16** expelling Br and dissociating to singlet **1**, implying that there is no barrier for the reverse process, addition of Br to **1**.

Transition structure **17** for conversion of **14** to **18** involves a hydrogen atom migration from the middle to the terminal carbon atom. The height of the barrier connecting **14** to **18** is predicted to be 4.5 kcal/mol at G3//B3LYP/6-31G*, 7.7 kcal/mol at B3LYP/6-311+G**//B3LYP/6-31G*, and 6.7 kcal/mol at B3LYP/6-31G*, respectively (see Figure 5). At B3LYP/6-311+G** and MP2/6-311G** the barrier is 7.6 and 7.1 kcal/mol, respectively.

The odd electron in the doublet species **18** is distributed at P (∼30%), Br (∼30%), and the middle carbon (∼40%). We found no transition structure for the elimination of the bromine atom from **18** to give **2**, and this is in accord with a barrierless addition of Br to **2**.

The results from these calculations suggest that the formation of **1** is favored over **2** both thermodynamically and kinetically. The energy difference between products **1** and **2** is 18 kcal/mol at G3//B3LYP/6-31G*, 15 kcal/

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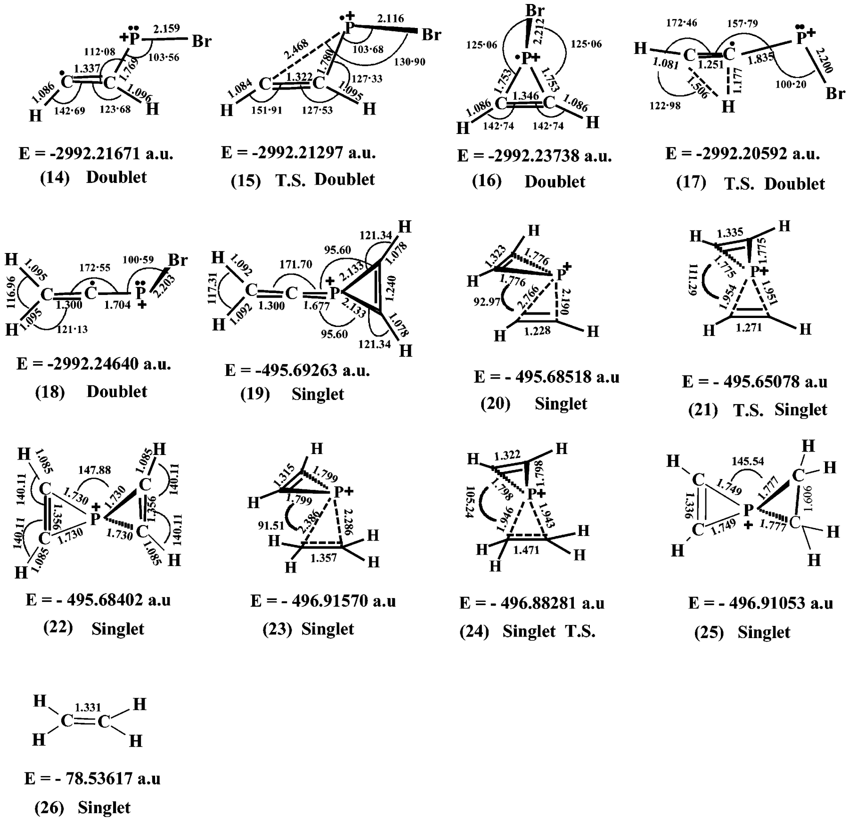
(38) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419.



E = -2992.21671 a.u. (14) Doublet

E = -2992.21297 a.u. (15) T.S. Doublet

E = -2992.23738 a.u. (16) Doublet

E = -2992.20592 a.u. (17) T.S. Doublet

E = -2992.24640 a.u. (18) Doublet

E = -495.69263 a.u. (19) Singlet

E = - 495.68518 a.u (20) Singlet

E = - 495.65078 a.u (21) T.S. Singlet

E = - 495.68402 a.u (22) Singlet

E = - 496.91570 a.u (23) Singlet

E = - 496.88281 a.u (24) Singlet T.S.

E = - 496.91053 a.u (25) Singlet

E = - 78.53617 a.u (26) Singlet

Figure 4. Optimized geometries and energies at the B3LYP/6-31G* level of the important species on the potential energy surfaces for the reaction of PBr^+ with C_2H_2 (Figure 5), the reactions of **1** or **2** with C_2H_2 (Figure 6), and the reaction of **1** with C_2H_4 (Figure 7). Distances are given in Å and angles in deg.

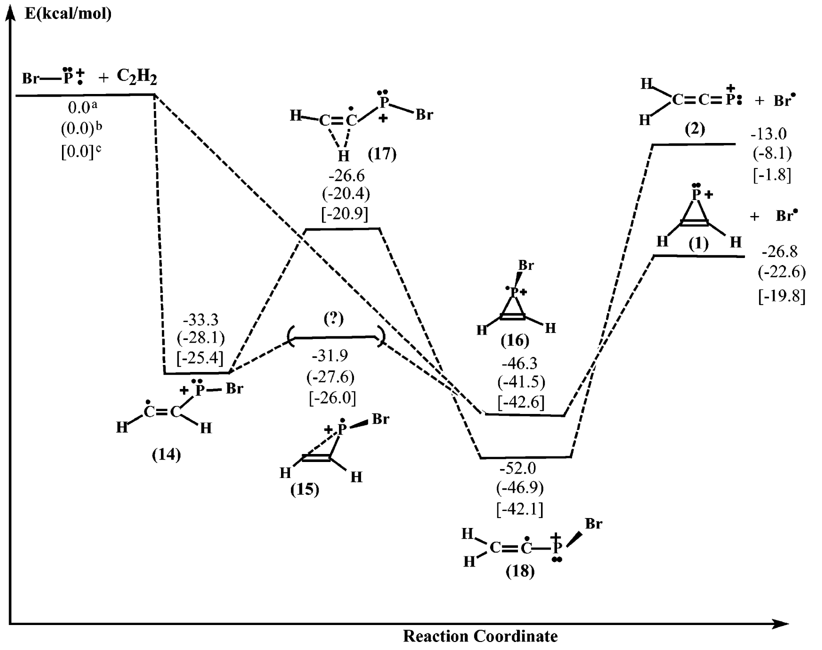


Figure 5. Doublet energy profiles for the formation of the two possible isomers, phosphirenylium ion (**1**) and vinylidenephosphenium ion (**2**), in the reaction of PBr^+ with C_2H_2. aB3LYP/6-31G* results; bB3LYP/6-311+G**//B3LYP/6-31G* results; cG3//B3LYP/6-31G* results.

mol at B3LYP/6311+G**// B3LYP/6-31G*, and 14 kcal/mol at B3LYP/6-31G*. **1** is thermodynamically favored over **2** at all computational levels employed, and at the highest levels employed, formation of **2** from PBr^+ is only slightly exothermic.

1 should also be formed more rapidly than **2**. The calculations suggest that formation of cyclic intermediate **16**, from which loss of Br yields **1**, is a barrierless carbene-like concerted addition. Formation of **2** involves conversion of initially formed radical-adduct **14** to a second intermediate **18**, from which loss of Br yields **2**. Thus, formation of intermediate **16** should be more rapid than that of intermediate **18**. Without barriers for the reverse processes, the greater predicted endother-

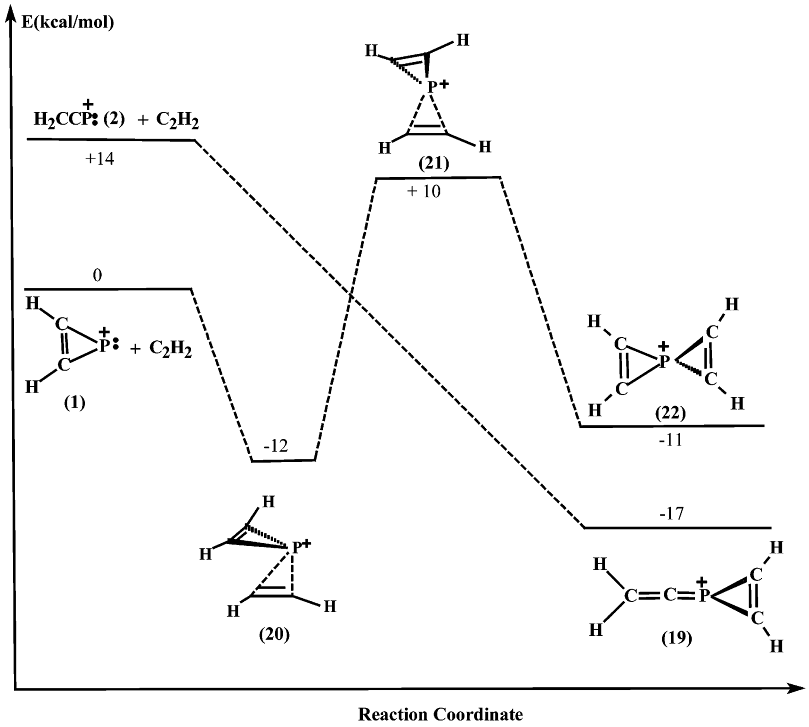


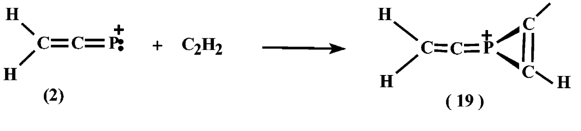
Figure 6. B3LYP/6-31G* singlet energy profiles for reactions of $H_2C_2P^+$ (**1**) + C_2H_2 and H_2CCP^+ (**2**) + C_2H_2.

micity of Br atom loss from **18** vs **16** to give **2** and **1**, respectively, supports the prediction that **1** is formed much more rapidly than **2**. The formation of **2** is, thus, predicted to be a minor process under the reaction conditions. Further mass spectrometric studies and theoretical calculations support the identification of **1** as the sole detectable product.

Reaction of $C_2H_2P^+$ with Acetylene. The reactivity of $C_2H_2P^+$ toward acetylene was examined by isolating $C_2H_2P^+$ and allowing it to interact with acetylene for 100 ms by using the MS^3 capabilities of the ion trap while turning off the excitation. The mass spectrum shows that $C_2H_2P^+$ formed from eq 1 is unreactive (eq 3), or, if it does react, the product of the ion–molecule reaction readily reverts to the starting materials (vide infra).

$$C_2H_2P^+ + C_2H_2 \rightarrow \text{no reaction} \qquad (3)$$

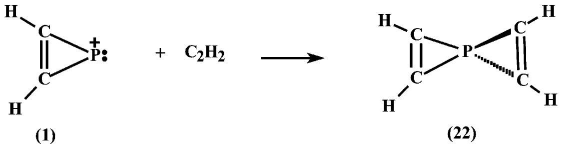
Would isomer **2** be expected to react with acetylene (eq 4)? The formation of adduct **19** is thermodynamically allowed by 30 kcal/mol. To probe its kinetic feasibility, we searched for a transition structure via a coordinate-driving analysis at the PM3, HF/6-31G*, and B3LYP/6-31G* levels. No barrier was found for the addition of **2** to acetylene depicted in eq 4 (see Figure 6 for a reaction-coordinate diagram).



(4)

The (π2s + π2s) cycloaddition of acetylene and the C=C double bond of the phosphirenylium ion (**1**) is forbidden by orbital symmetry as a thermal process. Therefore, we considered a carbene-like π-addition at P to give the *P*-spiro bicyclic phosphonium ion, **22** (eq 5), and computed that the reaction is exothermic by 11 kcal/mol. The reaction, however, is kinetically disfavored, with an energy barrier of 22 kcal/mol from a π-complex whose binding energy is predicted to be 12 kcal/mol (see Figure 6 for the reaction coordinate diagram). It is interesting that π-complex **20** has nearly the same energy as the spiro-product, **22**.

Since addition of isomer **2** to acetylene is predicted to proceed without a barrier, but no adduct of $C_2H_2P^+$ was observed, structure **2** is unlikely for the $C_2H_2P^+$ ion formed in eq 1. It appears that no products are observed from reactions of phosphirenylium ion **1** with acetylene because the loosely bound π-complex **20** that is formed from addition of **1** to acetylene can revert readily to reactants.



(5)

Reaction of $C_2H_2P^+$ with Ethylene. Eyler et al.[19] found that $C_2H_2P^+$ ions were formed in the reaction of P^+ with C_2H_4, and these reacted further with C_2H_4 to give $(C_2H_2)_2P^+$ with elimination of H_2 (eq 6). To assess whether the ion $C_2H_2P^+$ produced in eq 1 exhibits the same reactivity with ethylene, we carried out the reaction (eq 7) of doubly labeled $^{13}C_2D_2P^+$ with C_2H_4. No products were observed from the isotopically labeled phosphirenylium ions generated as in eq 1 and C_2H_4, indicating different structures for the $C_2H_2P^+$ ions produced by the two means (eq 6 vs eqs 1 and 7).

$$P^+ + C_2H_4 \xrightarrow{-H_2} C_2H_2P^+ \xrightarrow{+C_2H_4} (C_2H_2)_2P^+ + H_2 \qquad (6)$$

$$^{13}C_2H_2 + PBr^+ \xrightarrow{-Br} {}^{13}C_2D_2P^+ \xrightarrow{+C_2H_4} \text{no reaction} \qquad (7)$$

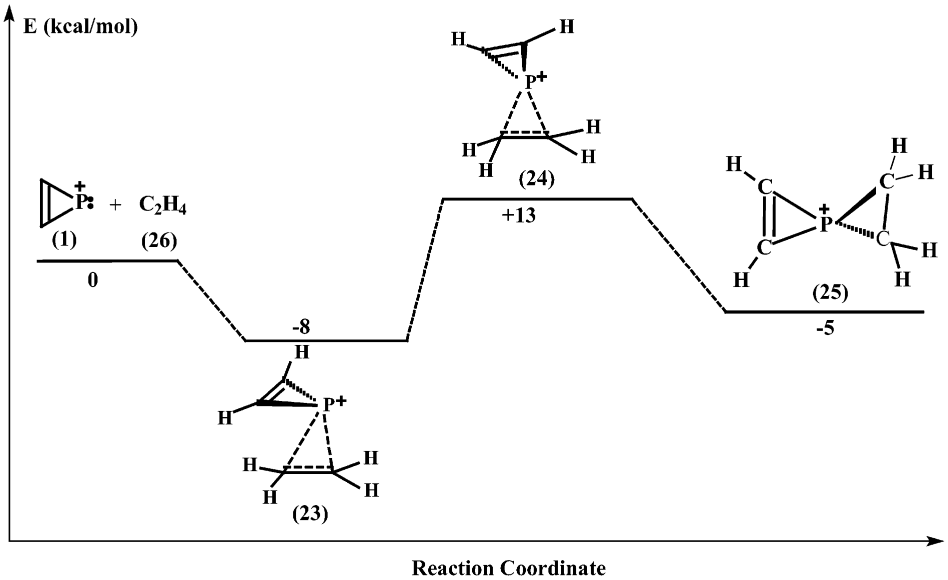


Figure 7. B3LYP/6-31G* singlet energy profiles for the reaction of $H_2C_2P^+$ (**1**) + C_2H_4.

Given the conclusion that the ion $C_2H_2P^+$ formed in eq 1 is the phosphirenylium ion (**1**) (vide supra), the lack of reactivity with C_2H_4 can be understood from the computationally predicted energy profile for this reaction (Figure 7). The addition to ethylene of the phosphirenylium ion that gives the *P*-spiro bicyclic phosphonium ion **25** is predicted to be exothermic by 5 kcal/mol. This process, however, is predicted to be kinetically disfavored, with an energy barrier of 21 kcal/mol. In a manner similar to the reaction with acetylene, interaction of **1** and C_2H_4 is predicted to afford a π-complex (**23**), with a calculated binding energy of 8.1 kcal/mol. Conversion of π-complex **23** to the *P*-spiro bicyclic product **25** traverses a calculated barrier of 20.6 kcal/mol, which is 13 kcal/mol higher than that for its reversion to **1** + C_2H_4.

Reaction of $C_2H_2P^+$ with 1,3-Butadiene. Although reactions of phosphirenylium ion **1** with acetylene and ethylene do not lead to observable products, **1** reacts readily with 1,3-butadiene to form an *m/z* 111 adduct ion. This may be the 3-phosphaspiro[2,4]hepta-1,5-diene phosphonium ion **28**. The structure of a formal 1,4-adduct is consistent with that of products reported for reactions of butadiene with the dimethoxyphosphenium ion $(MeO)_2P:^+$ [39,40] and the 2-*tert*-butyl-3-phenylphosphirenylium ion.[23]

To confirm the structure of the *m/z* 111 adduct of the parent phosphirenylium ion **1** and butadiene, we obtained the low-energy CID product-ion spectrum, which shows that the *m/z* 111 adduct dissociates to ions of *m/z* 109 (formed by loss of H_2), *m/z* 85 (formed by loss of C_2H_2), and *m/z* 57 (possibly arising by a retro-addition). The pathways illustrated in Figure 8 reflect the formation of a covalent adduct such as the *P*-spiro phosphonium ion (**28**) and not a loosely bound complex.

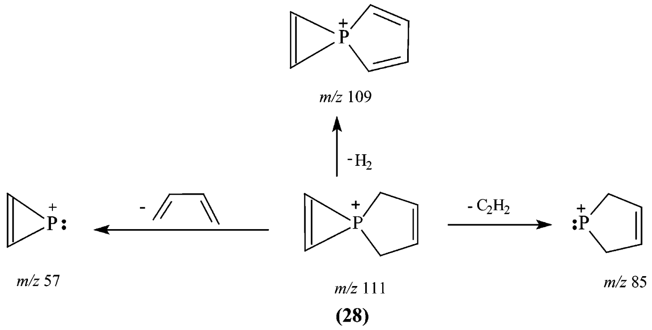


Figure 8. Proposed fragmentation pathways upon CID for the ion of *m/z* 111 which is generated in the reaction of the phosphirenylium ion (**1**) and 1,3-butadiene.

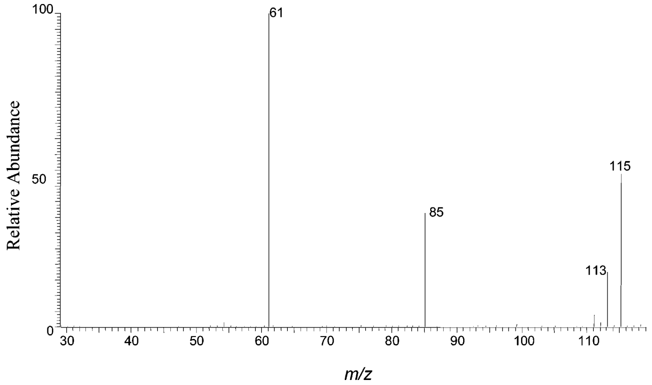


Figure 9. CID spectrum of *m/z* 115 which is formed in the reaction of the isotopically labeled phosphirenylium ion $^{13}C_2D_2P^+$ (**1**) (*m/z* 61) and 1,3-butadiene.

The isotopically labeled phosphirenylium ion $^{13}C_2D_2P^+$ (*m/z* 61), prepared from the reaction of PBr^+ and $^{13}C_2D_2$, reacts with 1,3-butadiene to give an adduct ion of *m/z* 115. This adduct decomposes upon CID with loss of H_2 and also gives products of *m/z* 85 (with loss of $^{13}C_2D_2$) and *m/z* 61 (corresponding to retro-addition) (Figure 9), results that are consistent with the *P*-spiro bicyclic phosphonium ion structure (**28**) shown in Figure 8.

Electronic structure calculations also support the *P*-spiro bicyclic phosphonium ion structure (**28**). Figure 10 displays the important intermediates and transition structures in those portions of the potential energy surfaces shown in Figures 11 and 12. As shown in

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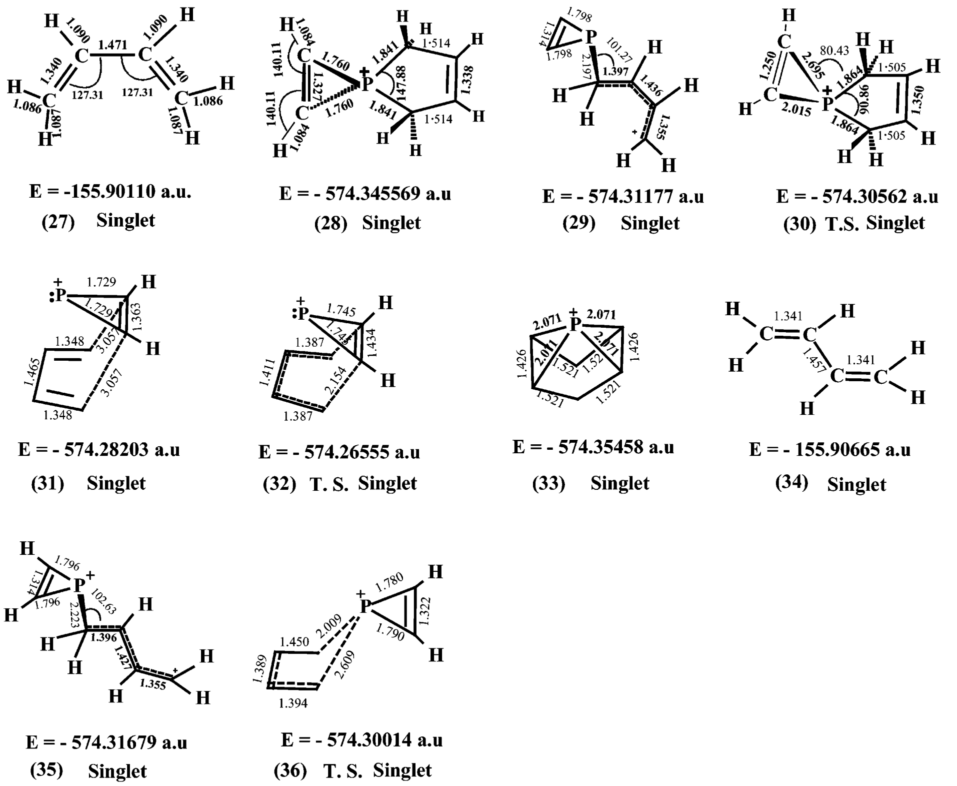


E = -155.90110 a.u.
(27) Singlet

E = - 574.345569 a.u
(28) Singlet

E = - 574.31177 a.u
(29) Singlet

E = - 574.30562 a.u
(30) T.S. Singlet

E = - 574.28203 a.u
(31) Singlet

E = - 574.26555 a.u
(32) T. S. Singlet

E = - 574.35458 a.u
(33) Singlet

E = - 155.90665 a.u
(34) Singlet

E = - 574.31679 a.u
(35) Singlet

E = - 574.30014 a.u
(36) T. S. Singlet

Figure 10. Optimized geometries and energies at the B3LYP/6-31G* level of the important species on the potential energy surfaces for the reaction of $C_2H_2P^+$ (**1**) with 1,3-butadiene (Figures 11 and 12). Distances are given in Å and angles in deg.

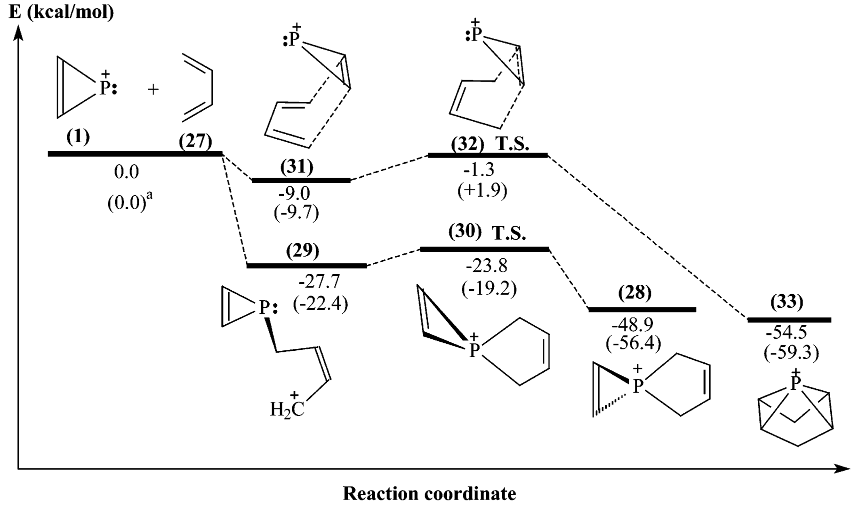


Figure 11. B3LYP/6-31G* energy profiles for the formation of the *P*-spiro bicyclic phosphonium ion (**28**) and the "cage-like" phosphorus cation (**33**) in the reaction of the phosphirenylium ion (**1**) and *cis*-1,3-butadiene (**27**). aG3//B3LYP/6-31G* results.

Figure 11, formation of **28** is exothermic by 56 kcal/mol at G3//B3LYP/6-31G* and 49 kcal/mol at B3LYP/6-31G*. The addition appears to be stepwise rather than concerted (Figure 11). Previous discussions of phosphenium ion−diene addition processes assumed concerted mechanisms.[40] The predicted energy profile (Figure 11) suggests that a complex (**29**) with a binding energy of 22 kcal/mol (G3//B3LYP/6-31G*) (28 kcal/mol B3LYP/6-31G*) results from a barrierless interaction between the phosphorus atom of **1** and 1,3-butadiene.

The three-membered ring adduct incorporating the P atom of ion **1** and one of the double bonds of *cis*-butadiene (**27**) was also considered, but this structure was not a local minimum, and optimization led to adduct ion **29**.

Dissociation of ion **29** to **1** and butadiene is predicted to be much slower than conversion of complex **29** to adduct **28** (barrier 3 kcal/mol at G3//B3LYP/6-31G*, 4 kcal/mol at B3LYP/6-31G*).

P-spiro phosphonium ion **28** can also be formed in the reaction of phosphirenylium ion **1** with *trans*-1,3-butadiene (**34**). As in the case of *cis*-butadiene, the computed energy profile, Figure 12, predicts that formation of **28** is a stepwise rather than a concerted process. The energy barrier for converting the loosely bonded complex **35** to the spiro product **28** is 6 kcal/mol at G3//B3LYP/

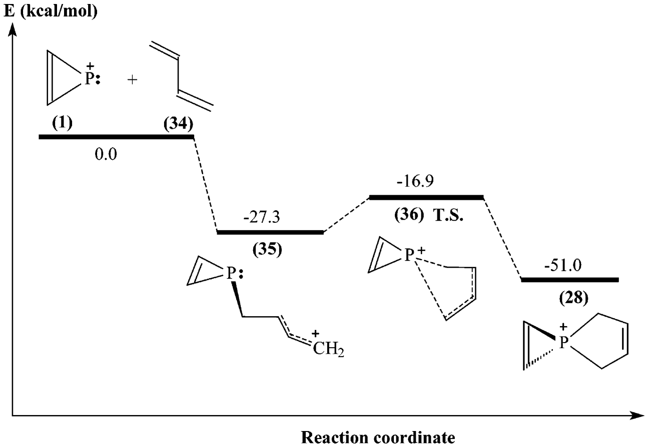


Figure 12. B3LYP/6-31G* energy profile for the formation of the *P*-spiro bicyclic phosphonium ion (**28**) in the reaction of the phosphirenylium ion (**1**) and *trans*-1,3-butadiene (**34**). [a]G3//B3LYP/6-31G* results.

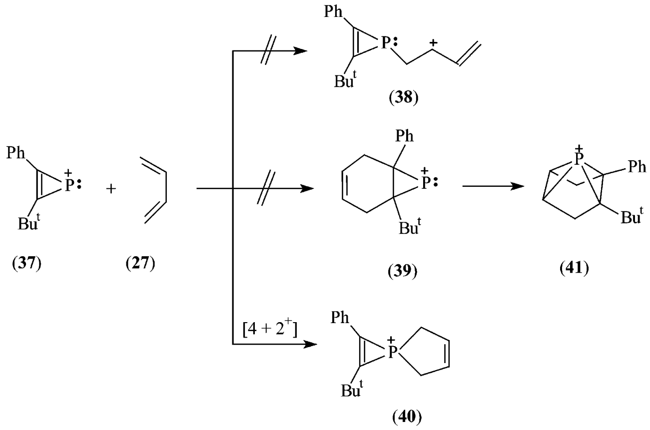
6-31G* (10 kcal/mol at B3LYP/6-31G*), higher than that for *cis*-1,3-butadiene due to the necessity for *anti*- to *syn*-epimerization of the allyl fragment. The three-membered ring adduct of **1** with one of the double bonds of *trans*-butadiene (**34**) was also examined, but this is also not a local minimum, and optimization led to adduct ion **35**.

We also considered an alternative addition to *S-cis*-1,3-butadiene involving both the C=C double bond *and* the P atom of the phosphirenylium ion. As shown in Figure 11, initial formation of a loosely bound complex (**31**) is predicted (binding energy 10 kcal/mol at G3//B3LYP/6-31G*, 9 kcal/mol at B3LYP/6-31G*). Conversion of **31** to adduct **33** traverses a predicted barrier of 12 kcal/mol at G3//B3LYP/6-31G* (8 kcal/mol at B3LYP/6-31G*). This barrier and the slight endothermicity at G3 of the formation of transition structure **32** from **1** and butadiene suggest that the formation of adduct **33** is kinetically disfavored, with dissociation of complex **31** to **1** favored over conversion to **33**.

A labeling experiment also speaks against formation of the thermodynamically favored "cage-like" phosphorus cation **33**. Loss of only labeled acetylene (see Figure 9) does not support the "cage-like" phosphorus cation structure but is consistent with the *P*-spiro bicyclic phosphonium ion structure **28**.

Comparison of Reactions 1,3-Butadiene with the Parent Phosphirenylium (1) and 2-*tert*-Butyl-3-phenylphosphirenylium (37) Ions. It is informative to compare the reactions of 1,3-butadiene with **1** and those with a bulky 2-*tert*-butyl-3-phenylphosphirenylium cation (**37**). Eberlin et al.[23] proposed that **37** reacts with *cis*-1,3-butadiene to yield the *P*-spiro bicyclic phosphonium ion **40** via a [4 + 2^+] cycloaddition at phosphorus (Scheme 2). The formation of **40** was predicted to be exothermic by 35 kcal/mol at B3LYP/6-31G**.[23] They also computed that the alternative cycloadduct **39** via a [4 + 2] cycloaddition across the CC double bond of **37** is unstable and isomerizes without a barrier to a "cage-like" phosphorus cation **41**. Formation of **41** is exothermic by 19.5 kcal/mol, but less favorable than formation of **40**. An open-chain adduct, **38**, is also unstable and would dissociate readily to reactants.

Scheme 2



Our studies of the reactions of the parent phosphirenylium cation (**1**) with 1,3-butadiene show both similarities with and differences from the reactions of 2-*tert*-butyl-3-phenylphosphirenylium cation **37**. The product ions formed from reactions with butadiene of both **1** and **37** have *P*-spiro structures, **28** and **40**, respectively. Calculations predict that addition of parent ion **1** occurs via a stepwise mechanism for both *cis*- and *trans*-1,3-butadiene to give initially the acyclic complex **29** or **35**, respectively. These complexes can isomerize to the *P*-spiro product **28** more readily than they can dissociate to reactants.

For formation of an analogous product (**40**) from the substituted phosphirenylium ion (**37**),[23] a concerted [4 + 2^+] cycloaddition has been proposed. This may be possible due to different steric effects in the two reaction systems. Another difference between the reactions of the unsubstituted (**1**) and substituted (**37**) phosphirenylium ions is that for **1** the formation of the "cage-like" product **33** is predicted to be thermodynamically favored over that of the *P*-spiro product **28** by approximately 4 kcal/mol at G3//B3LYP/6-31G* (6 kcal/mol at B3LYP/6-31G*), but kinetically disfavored. This is consistent with our conclusion that the *P*-spiro product is formed in the reaction of **1** with 1,3-butadiene. For **37** the spiro-product **40** is predicted to be more stable than cage-product **41**, but no barrier was predicted for the formation of **41**.[23]

Conclusions

The $H_2C_2P^+$ formed in the reaction of PBr^+ and acetylene is the aromatic phosphirenylium ion **1** and not vinylidene phosphenium ion **2**. The addition−ablation strategy for forming the phosphirenylium cation in the gas phase is the first reported reaction that can be used for its exclusive generation, and it may be a precedent for producing preparative quantities of heterocyclopropenium ions in the liquid phase.

Although the parent phosphirenylium ion **1** does not yield observable products from acetylene and ethylene, it does react with 1,3-butadiene to afford the *P*-spiro bicyclic phosphonium ion **28**, a structure supported by the fragmentation and isotopic labeling results. Calculations suggest that addition of **1** to *cis*- or *trans*-1,3-butadiene is stepwise rather than concerted and that the product has a kinetically rather than thermodynamically favored structure.

Acknowledgment. This work was supported by the NSF (CHE-9981715, CHE-0316124) and the National

Center for Research Resources of the NIH (Grant P41RR00954).

Supporting Information Available: A complete listing of Cartesian coordinates for each optimized structure without any constraints and computer-generated structures at the B3LYP/6-31G* level of theory, G3 energies, and relative energies of 10 $C_2H_2P^+$ isomers at G3//B3LYP/6-31G*, and energies of species involved in the potential energy surfaces of reactions of PBr^+/C_2H_2 and $C_2H_2P^+/C_4H_6$ at the G3//B3LYP/6-31G* level are available as Supporting Information free of charge via the Internet at http://pubs.acs.org.

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