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Reaction of Phosphaethene with Hydrogen Isocyanide: [2+1] versus [2+2] Cycloaddition

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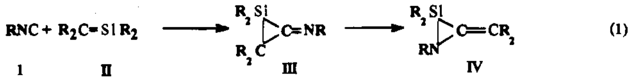
Abstract: The model reactions of hydrogen isocyanide plus phosphaethene and its protonated form have been studied by ab initio MO methods. The energy potential surfaces have been explored using MP2/6-31G(d,p) calculations while relative energies between stationary points have been estimated using QCISD(T)/6-31G(d,p) and CISDQ/6-311G(d,p) wave functions in conjunction with zero-point corrections. The $HN{\equiv}C + CH_2{=}PH$ system is also considered at a higher level by means of the CASPT2/ANO method. With regard to the [2+1] cycloaddition giving phosphiranimine (**1**), the initial C-attack with an energy barrier of 25 kcal/mol is slightly favored over the P-attack. Two transition structures for [2+2] cycloaddition have also been found, but this approach is much less favored than the [2+1] approach with a difference of at least 30 kcal/mol in the barrier heights. Two four-membered carbene rings resulting from the [2+2] cycloadditions exist; the most stable of the two adducts lies 29 kcal/mol above **1** and is also an intermediate in the rearrangement of **1** to phosphaziridine **2** having an exocyclic C=C double bond (6 kcal/mol above **1**). The isomer with an exocyclic C=P bond (**3**) lies 16 kcal/mol above **1**. Overall our results suggest that the [2+1] approach is the dominating mechanism of the $HN{\equiv}C + H_2C{=}PH$ reaction. The participation of the [2+2] cycloaddition in the transformation can be ruled out. The [2+1] cycloaddition giving **1** is also the rate-determining step. Owing to the fact that the rearrangement **1** → **2** requires a smaller activation energy and that the energy difference between **1** and **2** is small (6 kcal/mol), **2** could be formed as a minor product. Thus, the reaction differs fundamentally from that involving the isoelectronic $HN{\equiv}C + H_2C{=}SiH_2$ system where a four-membered carbene has been found to have a high stability. Protonating the phosphorus atom substantially stabilizes the cyclic structures. The four-membered carbene is stabilized by about 9 kcal/mol relative to the neutral structure **1a**. Nevertheless, the only thermodynamically favored process in the $HN{\equiv}C + H_2C{=}PH_2^+$ system is a C-nucleophilic addition giving an open nitrilium cation which is by far the most stable protonated species.

Introduction

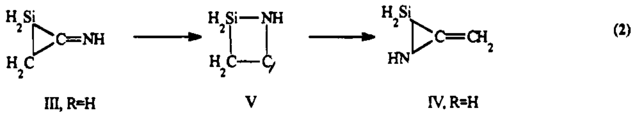
Isocyanides are versatile building blocks in organic synthesis. Owing to the presence of a monocoordinated carbon atom, these compounds are well suited as 1,1-dipolar partners in diverse addition reactions whose primary products are expected to undergo further rearrangements or ring expansions. Although isocyanides have been known to add to dipolarophiles containing second-row atoms such as disilenes ($R_2Si{=}SiR_2$),[1] diphosphenes (RP=PR),[2,3] and silenes ($R_2C{=}SiR_2$),[4] yielding different heavier analogues of methylenecyclopropanes, their reactivity toward other doubly-bonded compounds is not yet known.

Brook and co-workers[5] showed that an isocyanide (**I**) undergoes a formal [2+1] cycloaddition to a stable silene (**II**) yielding an unstable siliranimine (**III**) which rapidly rearranges to form the isomeric silaziridine **IV** (eq 1). The isomerization **III** → **IV** is intriguing in many aspects, in particular as concerns the relative stability of both products as well as the reaction mechanism.



(1)

In a recent theoretical study[6] on the model $HN{\equiv}C + H_2C{=}SiH_2$ system, using ab initio molecular orbital calculations, we have shown that the unimolecular rearrangement **III** → **IV** occurs preferentially in two distinct steps involving a four-membered cyclic carbene (**V**) as the intermediate (eq 2). Surprisingly, the relative stabilities of **V** and **III** (R = H) are of comparable magnitude and the formation of **V** constitutes the rate-determining step of the entire transformation.



(2)

From a geometrical viewpoint, **V** could formally be regarded as a product of a [2+2] cycloaddition of HN≡C plus $H_2C{=}SiH_2$. Although the relevant [2+2] transition structure could not be located in our earlier study, the cyclic carbene establishes a genuine bridge between both [2+1] and [2+2] approaches. These theoretical results raise the question as to whether the existence of a stabilized carbene intermediate is merely a particularity of the silicon system or rather represents a more general phenomenon. In an attempt to tackle this question, we have considered the phosphorus analogue $HN{\equiv}C + CH_2{=}PH$. In this work, particular attention has been paid to both [2+2]

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(1) Yockelson, H. B.; Millevolte, A. J.; Haller, K. J.; West, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1605.

(2) Baudler, A. M.; Simon, J. *Chem. Ber.* **1987**, *120*, 421.

(3) Lentz, D.; Marshall, R. *Z. Anorg. Allg. Chem.* **1992**, *617*, 53.

(4) Brook, A. G.; Kong, Y. K.; Saxena, A. K.; Sawyer, J. F. *Organometallics* **1988**, *7*, 2245.

(5) Brook, A. G.; Saxena, A. K.; Sawyer, J. F. *Organometallics* **1989**, *8*, 850.

(6) Nguyen, M. T.; Vansweevelt, H.; De Neef, A.; Vanquickenborne, L. G. *J. Org. Chem.* **1994**, *59*, 8015.

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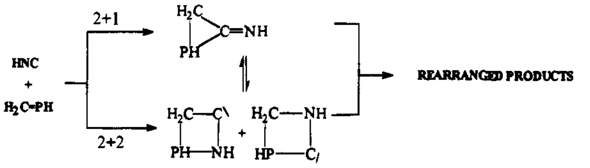
and [2+1] cycloaddition pathways, the interconversion between cycloadducts, and the formation of other rearranged adducts (eq 3).



(3)

For the purpose of comparison with $H_2C{=}SiH_2$, the reactions involving the protonated phosphaethene $HN{\equiv}C + H_2C{=}PH_2^+$ have also been examined. As far as we are aware, no experimental study on these reactions has been reported even though the reactions of isocyanides with diphosphenes (RP=PR) are known experimentally.[2,4]

Calculations and Results

Ab initio molecular orbital calculations were carried out making use of local versions of the Gaussian 92 and Molcas-3 sets of programs.[7,8] Stationary points on the $[C_2H_4NP]$ and $[C_2H_5NP]^+$ surfaces were initially determined at the Hartree–Fock (HF) level with the 6-31G(d,p) basis set and characterized by harmonic vibrational analysis at this level. Geometries of the relevant points were fully reoptimized using second-order Møller–Plesset perturbation theory (MP2/6-31G(d,p)). Relative energies were then computed using the quadratic configuration interaction method QCISD(T)/6-31G(d,p) as well as the configuration interaction method CISDQ with a larger 6-311G(d,p) basis set and MP2 optimized geometries. In order to assess further the influence of electron correlation on relative energies, we have also constructed multireference wave functions using the CASSCF-CASPT2 method[9,10] for all structures involving the $HN{\equiv}C + CH_2{=}PH$ system. In these calculations, generally contracted atomic natural orbital type basis sets (ANO) were used. The starting primitive sets of functions (13s10p4d) for P, (10s6p3d) for C and N, and (7s3p) for H were contracted to the following final basis sets: [5s4p2d] for P, [4s3p1d] for C and N, and [3s1p] for H.[11] Only the pure spherical harmonic components of the d-functions were used, yielding a total of 105 contracted ANO functions. Each of the CASPT2 calculations is performed in two steps: the CASSCF wave function determined in the first step is used to the second step as the reference function for a second-order perturbation calculation. The CASPT2 method computes the first-order wave function and the second-order energy in the full space of configurations generated by the basis set. The zero-order Hamiltonian is constructed from a Fock-type one-electron operator that is reduced to the second-order Møller–Plesset operator in a single-reference closed-shell case. The "nondiagonal" approach, which consists of taking the full Fock matrix (with all nondiagonal elements), is used in constructing the zero-order Hamiltonian. In the CASSCF calculations, 10 electrons were correlated in an active space of 10 molecular orbitals. This choice was based on the consideration that the active space should be large enough to include the most important nondynamical correlation effects for all structures considered. The population analysis of the natural orbitals resulting from the CASSCF calculations indicates that, in all cases, all orbitals with a population lying between 0.02 and 1.98 are included. In both MP2 and CASPT2 calculations, all valence electrons were correlated whereas core orbitals were kept frozen. Selected geometrical parameters are displayed in Figures 1 and 2 for $[C_2H_4NP]$ and in Figure 6 for $[C_2H_5NP]^+$. The corresponding total, zero-point and relative energies are recorded in Tables 1–3. As for the notation, A/B denotes a transition structure (TS) connecting both equilibrium structures A and B. The indentity of each TS is determined by intrinsic reaction coordinate (IRC) calculations. The schematic potential energy profiles for $HN{\equiv}C + CH_2{=}PH$ showing the cycloadditions and rearrangements are illustrated in Figures 3 and 5.

Throughout this paper, total energies are given in hartrees, zero-point vibrational and relative energies in kilocalories per mole, bond lengths in angstroms and bond angles in degrees.

Discussion

Cycloadducts and Isomers. Formally, phosphiranimine (**1**) and both cyclic carbenes **4** and **5** are the [2+1] and [2+2] primary cycloadducts, respectively, of the addition of phosphaethene to hydrogen isocyanide. In the [2+2] cycloaddition two distinct approaches giving two regioisomers (**4** and **5**) are in fact possible. Phosphaziridine **2** and exocyclic phosphaalkene derivative **3** are the alternative structures of **1** through ring-opening whereas the cyclobutene derivative **7** could be formed from **4** by a 1,2-hydrogen shift (Figure 1).

As seen in the first half of Table 1, the different methods and basis sets used essentially lead to the same energy ordering for the equilibrium structures **1**–**7**. The effect of going from the segmented 6-311G(d,p) basis to the ANO basis is in some cases significant (up to 3 kcal/mol), as indicated by the MP2 results obtained with both basis sets. The differences between the relative energies obtained by MP2 and CASPT2 methods are smaller, less than 2 kcal/mol for all structures. This is an indication that nondynamical correlation effects are only of minor importance and reliable results on equilibrium structures can be obtained from single-reference HF-based methods. An additional confirmation of this fact comes from the weights ω of the reference wave functions in the final wave functions which are similar for all structures already at the MP2 level. Unless otherwise noted, the relative energies quoted hereafter refer to the CASPT2 + ZPE values.

The *syn* form **1a** of phosphiranimine in which both atoms P and H(N) are disposed in a *cis* conformation with respect to the C=N bond is marginally more stable than *anti*-**1b** (0.8 kcal/mol). A similar situation has previously been found for the sulfur and silicon analogues.[6,12,13] Both molecules **2a** and **2b** containing a phosphaziridine cyclic structure and an exocyclic C=C double bond have essentially a planar configuration of the four heavy atoms. The *syn* form **2a** is about 1 kcal/mol less stable than *anti*-**2b**, in part due to the repulsion between the N and P lone pairs. The third alternative ring system **3** with an exocyclic C=P bond is calculated to have an almost planar heavy atom skeleton, but the nitrogen atom remains pyramidal.

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(7) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. G.; Gompert, R.; Andres, J. L.; Raghavachari, R.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(8) Andersson, K.; Blomberg, M. R. Å.; Fühscher, M. P.; Karlström, G.; Kellö, V.; Lindl, R.; Malmqvist, P. Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P. O. *MOLCAS-VERSION 3*; Lund, 1994.

(9) Andersson, K.; Malmqvist, P. Å,; Roos, B. O.; Sadlej, A. J.; Wollinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.

(10) Andersson, K..; Malmqvist, P. Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(11) Pierloot, K.; Dumez, B.; Widmark, P. O.; Roos, B. O. *Theor. Chim. Acta*, **1995**, *90*, 87.

(12) Nguyen, M. T.; Vansweevelt, H.; Vanquickenborne, L. G. *J. Org. Chem.* **1991**, *56*, 5651.

(13) Vanquickenborne, L. G.; Vansweevelt, H.; Coussens, B.; Hajnal, M. R.; Delvaux, I.; Hendrickx, M. *J. Phys. Chem.* **1990**, *54*, 1335.

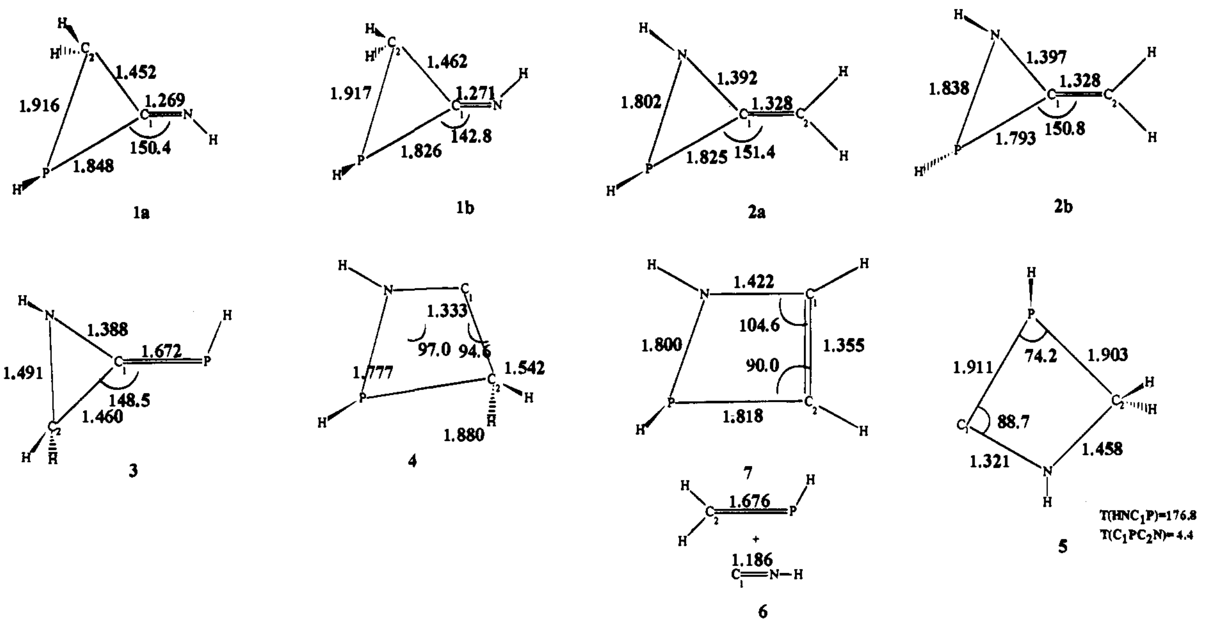

Figure 1. Selected MP2/6-31G(d,p) geometrical parameters of the [C_2H_4NP] equilibrium structures considered.

Table 1. Total (au) and Zero-Point Vibrational (kcal/mol) Energies for the [C_2H_4NP] Stationary Points Considered

structure[a]	MP2/6-311G(d,p)	CISDQ/6-311G(d,p)	QCISD(T)/6-31G(d,p)	MP2/ANO[b]	CASPT2/ANO[b]	ZPE[c]
1a	−473.789 18	−473.825 40	−473.772 90	−473.805 37(0.81)	−473.810 78(0.85)	34.5
1b	−473.786 08	−473.822 74	−473.769 87	−473.802 49(0.81)	−473.809 25(0.85)	34.3
2a	−473.776 05	−473.812 27	−473.759 97	−473.795 64(0.81)	−473.798 51(0.85)	34.2
2b	−473.777 23	−473.813 41	−473.762 01	−473.797 07(0.81)	−473.799 89(0.85)	34.1
3	−473.767 17	−473.802 95	−473.752 67	−473.781 79(0.81)	−473.786 19(0.85)	34.8
4	−473.743 50	−473.786 99	−473.730 22	−473.760 79(0.83)	−473.766 24(0.86)	34.6
5	−473.733 75	−473.777 88	−473.777 88	−473.751 40(0.82)	−473.758 01(0.85)	35.0
6	−473.759 53	−473.802 27	−473.747 69	−473.776 13(0.81)	−473.780 79(0.86)	29.3
7	−473.792 96	−473.828 89	−473.776 09	−473.812 87(0.82)	−473.816 76(0.85)	35.1
1a/1a	−473.706 03	−473.738 29	−473.713 38	−473.731 05(0.77)	−473.762 82(0.84)	33.1
1a/1b	−473.743 12	−473.777 08	−473.725 06	−473.762 52(0.81)	−473.766 32(0.85)	32.7
1a/2b	−473.717 96	−473.747 02	−473.713 28	−473.741 58(0.77)	−473.762 21(0.84)	32.9
1a/4	−473.701 44	−473.734 55	−473.683 45	−473.722 69(0.81)	−473.726 54(0.84)	33.9
2a/2b	−473.764 52	−473.800 16	−473.746 62	−473.783 47(0.82)	−473.786 67(0.85)	33.5
4/2b	−473.701 58	−473.735 25	−473.684 10	−473.724 92(0.81)	−473.726 15(0.85)	33.8
4/7	−473.682 66	−473.719 58	−473.663 57	−473.701 18(0.82)	−473.705 62(0.84)	32.0
6/4	−473.674 68	−473.711 98	−473.658 53	−473.695 19(0.81)	−473.698 92(0.85)	31.6
6/5	473.654 63	−473.691 51	−473.637 60	−473.675 98(0.80)	−473.680 73(0.85)	32.3
6/1a(C)	−473.718 17	−473.752 47	−473.708 05	−473.738 31(0.80)	−473.750 12(0.85)	31.7
6/1a(P)	−473.714 17	−473.747 64	−473.698 44	−473.737 03(0.80)	−473.743 09(0.85)	31.6
6/1b(P)	−473.716 33	−473.749 28	−473.699 40	−473.739 31(0.80)	−473.745 72(0.84)	31.6

[a] Based on MP2/6-31G(d,p) optimized geometries given in Figures 1 and 2. All core orbitals are kept frozen in CI and MP2 calculations. [b] See text for details of the ANO basis set. The weights ω of the zero-order wave functions in the final first-order wave functions are given in parentheses. [c] Zero-point vibrational energies, from the HF/6-31G(d,p) calculations and scaled by 0.9.

As would be expected, the C═N stretching wavenumber of **1a**, estimated to be centered at 1714 cm^{-1}, turns out to be slightly smaller than the corresponding values of 1780 cm^{-1} for cyclopropanimine, 1742 cm^{-1} for thiiranimine, and 1754 cm^{-1} for siliranimine,[6] but remains much larger than that of 1640 cm^{-1} for methanimine (CH_2═NH).[12] A similar trend is observed for the C═C and C═P stretching wavenumbers in **2** and **3**, respectively. The upward shift of the exocyclic double bond stretching wavenumber is a consequence of its coupling to a three-membered ring, irrespective of the nature of the ring atoms.[12]

The four-membered rings **4**, **5**, and **7** contain a quasi-planar geometry of the four heavy atoms. While the nitrogen atom has a planar configuration in the cycles, similar to that in aminocarbenes (with a short C−N distance of 1.333 Å) and vinylamines, the phosphorus atom remains strongly pyramidal.

Of the nine equilibrium structures considered, phosphaazacyclobutene (**7**) turns out to be the most stable isomer, lying about 3 kcal/mol below **1a**. The latter is the most stable among the five possible three-membered rings, followed by the endocyclic phosphaziridines **2a** and **2b** and finally the exocyclic phosphaalkene derivative **3**. While the fragments HN≡C + CH_2═PH (**6**) have an energetic content comparable to that of **3**, the cyclic carbene **5** is found to be the least stable isomer, being 34 kcal/mol higher in energy than **1a**. The other cyclic carbene **4** is also a high-energy isomer lying 29 kcal/mol above **1a**. This is in clear contrast with the situation of the silicon analogues where the endocyclic silaziridine **IV** was calculated to be the most stable species and where siliranimine **III** and the cyclic carbene **V** both have similar relative energies (eq 1 and 2).[6] Presumably repulsion between the lone pairs of the C, N, and P atoms is responsible for a certain destabilization of the structures **2**, **4**, and **5**. It is beyond doubt that the lower stability of **3** arises from the presence of the weaker exocylic C═P bond, relative to the C═C and C═N bonds.

Cycloadditions and Interconversions between Cycloadducts. Energies of the transition structures (TS) (Figure 2) for various processes are given in the second half of Table 1. The

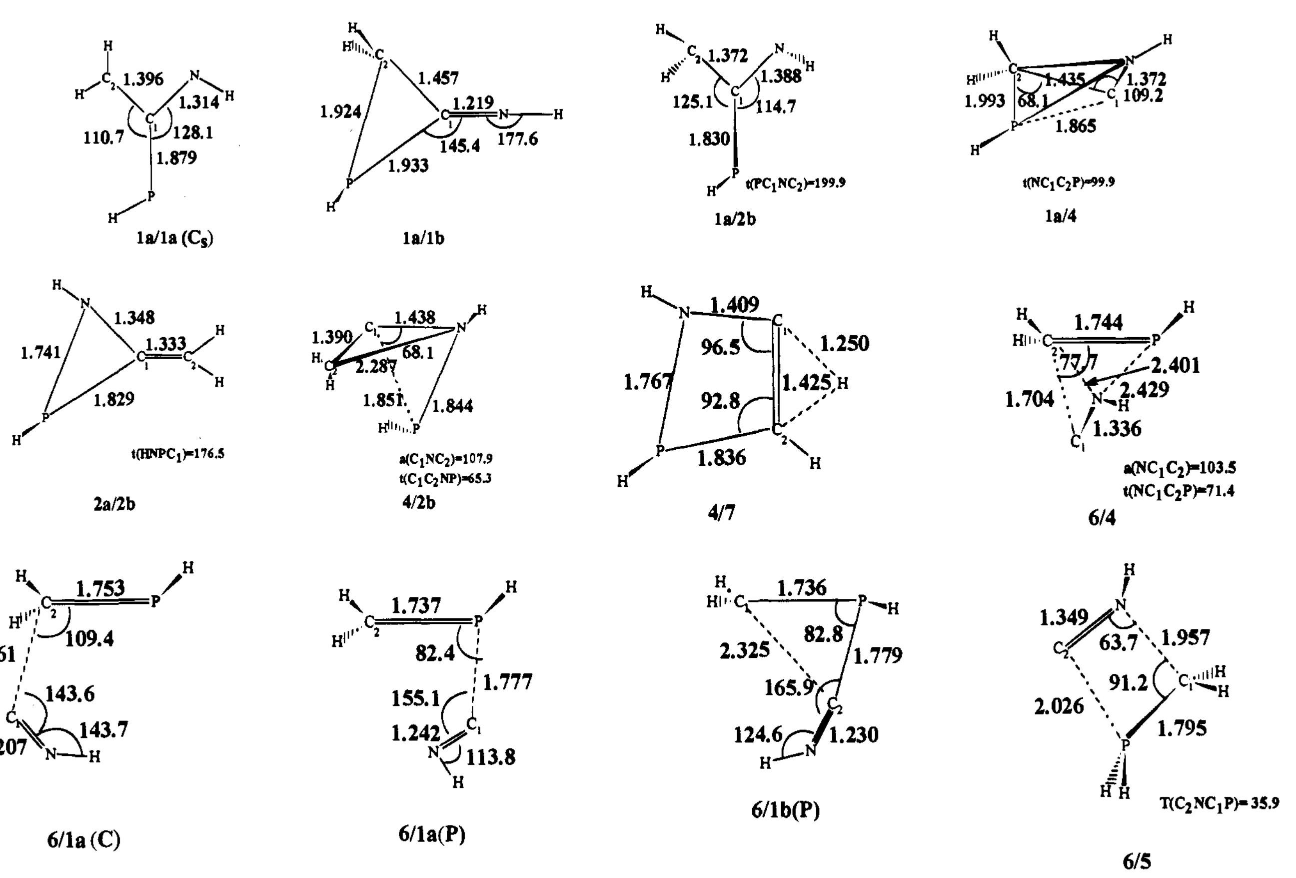

Figure 2. Selected MP2/6-31G(d,p) geometrical parameters of the transition structures for the isomerizations, cycloadditions, and rearrangements relevant to the $HN{\equiv}C + CH_2{=}PH$ system.

MP2 results are again subject to rather large basis set effects, which are, in most cases, more important than the effect of expanding from MP2 to CASPT2. In most cases, the SCF configuration clearly remains the dominating contributor to the CASSCF wave function, with a weight ranging from 0.83 to 0.94. There are however two cases, namely, the TSs **1a/1a** and **1a/2b**, where important nondynamical correlation effects could be observed. For both structures, the CISDQ method apparently does not improve the MP2 results whereas the QCISD(T) method, including a correction for triple substitutions, partially recovers the correlation energy. Thus, the QCISD(T) values are between the MP2 and CASPT2 results. Again our discussion will be based on CASPT2 relative energies.

Isomerization of 1 and 2. Both isomeric forms **1a** and **1b** are connected with each other by the TS **1a/1b**; the corresponding inversion barrier of 27.7 kcal/mol (Figure 3) is comparable to those of the sulfur and silicon analogues.[6,12] Phosphiranimines carrying poorer inverting groups at nitrogen are expected to be conformationally stable. With regard to phosphaziridine **2**, an inversion of configuration at nitrogen is a more facile motion; the TS **2a/2b** lies only 6.7 kcal/mol above **2a**.

[2+1] Cycloaddition. The [2+1] addition of $H_2C{=}PH$ + $HN{\equiv}C$ (**6**) giving phosphiranimine (**1**) is moderately exothermic, the reaction energy amounting to about −13.7 kcal/mol. As shown in Figure 2, three distinct transition structures have been located: **6/1a** (C) can be seen as the TS for an attack on the carbon center of phosphaethene, yielding **1a**, whereas **6/1a** (P) and **6/1b** (P) correspond to the TSs for attacks on the phosphorus center. Although the energy barriers are substantially reduced upon improvement of the wave functions, the C-addition is consistently favored over the P-addition (Figure 3). Our best estimate places **6/1a(C)** 4.4 and 2.6 kcal/mol below **6/1a(P)** and **6/1b(P)**, respectively, and 21.6 kcal/mol above the reactants **6**. This preference for a C-addition cannot be interpreted by the formal charge distribution nor by the frontier orbitals. In fact, the carbon center of phosphaalkenes is known to carry a negative charge and is a priori not attracted by a nucleophilic attack. In terms of frontier orbital interaction, the [2+1] addition of $HN{\equiv}C + CH_2{=}PH$ is mainly controlled by the HOMO(isocyanide)−LUMO(phosphaethene) interaction. The HOMO of isocyanide is the carbon lone pair while the LUMO of phosphaethene is a $\pi^*(C{=}P)$ orbital in which P bears a slightly larger MO coefficient.[14,15] This is due to the weak difference in electronegativity of C and P which, as a conse-

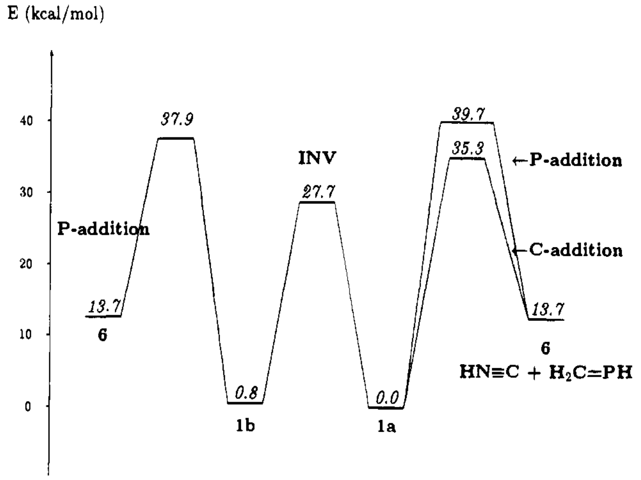

Figure 3. Schematic potential energy profile showing the [2+1] cycloaddition and isomerization of phosphiranimine. Energies were obtained from CASPT2 + ZPE calculations.

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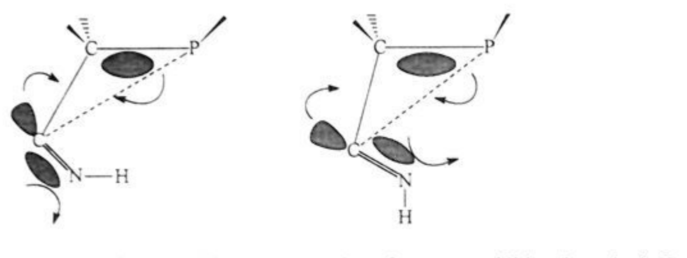
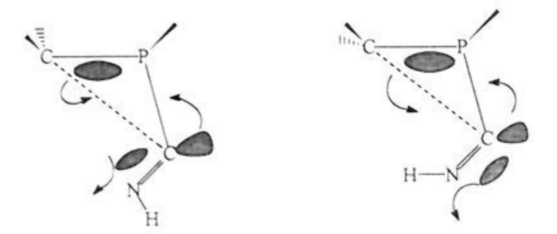
[14] Using the HF/6-31G(d,p) wave function, the MO coefficients of the LUMO of $H_2C{=}PH$ are $C_i(C)$ = 0.71 and $C_i(P)$ = −0.74. It seems that these coefficients are dependent on the basis set employed; for previous studies, see ref 15.

Chart 1



6/1a (C) - cis - addition
stereoelectronically allowed

6/1b (C) - trans - addition (hypothetical)
stereoelectronically forbidden



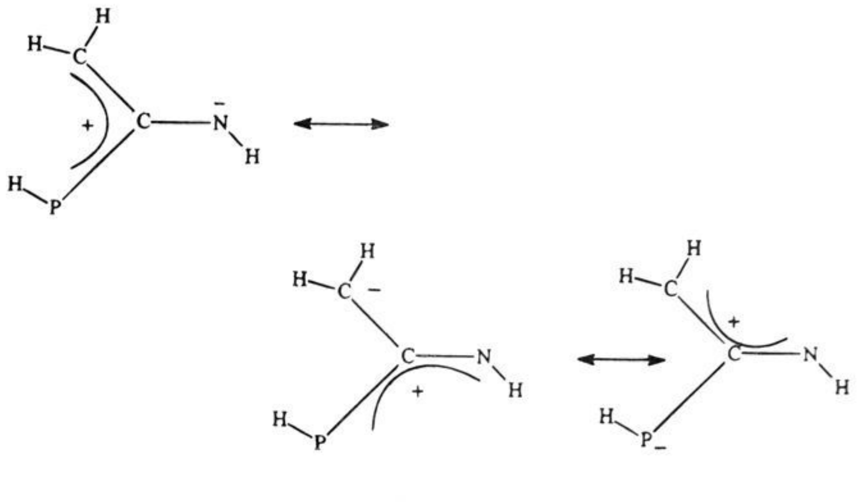
6/1a (P) - trans - addition
stereoelectronically forbidden

6/1b (P) - cis - addition
stereoelectronically allowed

quence, induces only a weak dissymmetry of the π-orbitals. Thus, both charge and orbital considerations would suggest a preference of P-addition over C-addition. The actual situation presumably arises from a subjacent control which consists in a destabilizing repulsion between both approaching lone pairs of P and C (isocyanide). However, in view of the rather small difference in activation energy, the preferred reaction path is expected to be strongly affected by the substituents which could reinforce the dissymmetry of the π^*-orbitals and/or modify the charge distributions. Thus, the [2+1] addition of isocyanide to phosphaethene markedly differs from that to silene where the Si-addition is clearly preferred (by 10 kcal/mol) over the C-addition.[6] In fact, on the one hand, the Si center is positively charged and exhibits the largest MO coefficient in the LUMO $\pi^*(C{=}Si)$ and, on the other hand, there is no unfavorable electron repulsion when both partners approach each other.

It is also interesting to note that the TS for C-addition leading to *anti*-phosphiranimine (**1b**) could not be located in spite of an extensive search. In contrast, both TSs for P-addition, yielding the isomers **1a** and **1b**, could be found (Figure 2). As seen in Figure 3, the C-addition gives preferentially the *syn* isomer **1a** whereas the P-addition favors the formation of the thermodynamically less stable *anti* isomer **1b**. This behavior could be rationalized simply in terms of a stereoelectronic effect related to the electronic movement during the reaction.[16,17] Accordingly, in an addition reaction, the electron pairs of the reaction partners involved in the formation of new chemical bonds have a natural tendency to migrate in the same direction in order to minimize the overlap between them. The resulting reaction path is favored because it is stereoelectronically allowed. In contrast, the path in which the electron pairs move in opposite senses, maximizing their overlap, is stereoelectronically forbidden.[16,17] The situation regarding the $HN{\equiv}C + CH_2{=}PH$ addition is summarized in Chart 1. Both TSs **6/1a(C)** and **6/1b(P)** can be termed as the TS for a *cis* addition in which the H(N) atom and the $H_2C{=}PH$ moiety are situated *cis* with repect to the C=N bond. Similarly, the **6/1a** (P) as well as the hypothetical structure **6/1b(C)** corresponds to a *trans* addition. It is clear that, in a *cis* addition, there is no opposition in the circulation of the electron pairs whereas, in the *trans* addition, a confrontation between the $\pi(C{\equiv}N)$ and $\pi(C{=}P)$ pairs occurs.

Scheme 1



1a/1a

The former gives the n(N) pair while the latter forms the σ-(C—C) or σ(C—P) pair in the cycloadduct. In other words, the *cis* additions via **6/1a(C)** and **6/1b(P)** are favored over the corresponding *trans* additions by the stereoelectronic effect.

[2+2] Cycloaddition. Two transition structures (**6/4** and **6/5**) for the [2+2] addition have been located. According to orbital symmetry considerations, a thermal and concerted [2+2] cycloaddition is only allowed in a suprafacial—antarafacial approach. TS **6/4** appears to satisfy this criterion more than TS **6/5**; in the former both partners approach each other in two quasi-perpendicular planes, thus allowing the best overlap between the interacting π^*(isocyanide) and $\pi(C{=}P)$ orbitals. The transition state structures suggest both asynchronous additions. The main difference between **6/4** and **6/5** concerns the bond which will be first formed. This bond is C—C in **6/4** and C—N in **6/5**. Both [2+2] cycloadditions are endothermic by 15 (giving **4**) and 20 (giving **5**) kcal/mol. In both cases, the resulting transition barriers are quite high, relative to the reactant fragments, namely, 53.6 kcal/mol via **6/4** and 70.1 kcal/mol via **6/5**. It is worth noting that the energies of both **6/4** and **6/5** are not particularly sensitive to the computational method. Single-reference wave functions are surprisingly well suited for the description of this type of transition structure. Because the addition mode giving **4** is much more pronounced over that giving **5**, only the former is displayed in Figure 5 and only **4** is considered in the following discussion.

Phosphiranimine—Phosphaziridine Rearrangement. We have located two TSs related to the ring-opening of phosphiranimine **1a**. The first TS is **1a/1a** possessing an open and planar geometry (Figure 2). Vibrational analysis at both HF and MP2 levels with the 6-31G(d,p) basis set indicates that **1a/1a** is characterized by only one imaginary vibrational wavenumber. The transition vector of the imaginary mode corresponds to a disrotatory ring-closing, giving **1a** in both directions. In other words, **1a/1a** is the TS for racemization of **1a**. As could be expected from its zwitterionic character (Scheme 1), **1a/1a** is not well described by HF-based methods. Its energy is substantially lowered by as much as 16.6 kcal/mol when going from MP2 to CASPT2. The presence of a strong nondynamical correlation effect is already apparent in the CASSCF wavefunction; the SCF contribution to the CASSCF wavefunctions of **1a/1a** is low, being only 0.61. The four electrons reside in the π-type orbital (Scheme 1), and the origin of the nondynamical correlation can be clearly identified as being connected to $\pi \rightarrow \pi^*$ excitations.

Similarly, the TS **1a/2b** describing the ring-opening of phosphiranimine **1a** along the C—P bond, giving phosphaziridine **2b**, is also subject to a large nondynamical correlation effect, even though the effect here is smaller than that in **1a/1a**. The reduction in relative energy amounts of 9.5 kcal/mol when going

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(15) (a) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1981**, 569. (b) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1985**, 2005.

(16) Nguyen, M. T.; Hegarty, A. F.; Sana, M.; Leroy, G. *J. Am. Chem. Soc.* **1985**, *107*, 4141.

(17) Nguyen, M. T.; Ha, T. K.; Hegarty, A. F. *J. Phys. Org. Chem.* **1990**, *3*, 697.

Table 2. Relative Energies (kcal/mol) Including ZPE Corrections between the [C_2H_4NP] Stationary Points

structure	MP2/ 6-311G(d,p)	CISDQ/ 6-311G(d,p)	QCISD(T)/ 6-31G(d,p)	MP2/ ANO	CASPT2/ ANO
1a	0.0	0.0	0.0	0.0	0.0
1b	1.7	1.5	1.7	1.6	0.8
2a	7.9	7.9	7.8	5.8	7.4
2b	7.1	7.1	6.4	4.8	6.4
3	14.2	14.8	13.1	15.2	15.8
4	28.8	24.2	27.0	28.1	28.8
6	13.5	9.4	10.7	13.2	13.7
5	35.3	30.3	32.8	34.4	33.6
7	−1.8	−1.6	−1.4	−4.1	−3.2
1a/1a	50.9	53.1	36.8	45.4	28.8
1a/1b	28.7	34.4	29.8	26.7	27.7
1a/2b	43.1	47.6	35.8	38.4	28.9
1a/4	55.0	56.5	55.6	51.4	52.4
2a/2b	14.5	14.8	15.5	12.7	14.1
4/2b	54.4	50.3	55.1	49.9	52.3
4/7	64.5	64.0	66.2	63.0	63.6
6/4	69.0	68.3	68.9	66.2	67.3
6/5	82.3	81.8	82.7	83.4	83.8
6/1a(C)	41.8	43.0	37.9	39.3	35.3
6/1a(P)	44.3	46.0	43.8	40.1	39.7
6/1b(P)	42.8	44.9	43.2	38.6	37.9

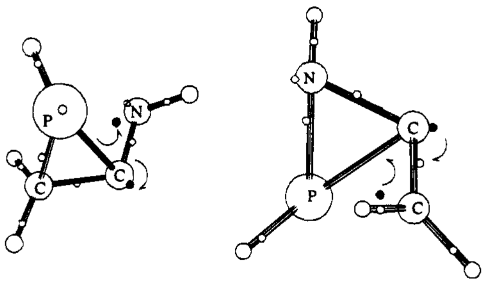


Figure 4. Localized orbitals (LMO) of the TSs (a, left) **1a/4** and (b, right) **4/2b** according to the Boys localization procedure. ○ are the centroids of charge; ● are the two electron pairs participating in the rearrangements of phosphiranimine and the cyclic carbene.

from MP2 to CASPT2 (Table 2). Analogous $\pi \rightarrow \pi^*$ excitations of the four delocalized electrons are also responsible for the large electron correlation. Our best estimates incidently place both structures **1a/2b** and **1a/1b** at comparable positions on the energy scale, namely, about 28.9 kcal/mol above **1a** (Figure 5). Nevertheless, since the geometrical parameters of both structures were not optimized using multireference wave functions, their structural identity remains doubtful. The above value can only be seen, at best, as an upper limit for their relative energies.

Phosphiranimine−Cyclic Carbene Rearrangement. The connection between both primary [2+1] and [2+2] cycloadducts can be made through the TS **1a/4** with an energy barrier of 52.4 kcal/mol relative to **1a** (Figure 5). Starting from **1a**, this rearrangement is apparently induced by a cleavage of the C−P bond and accompanied by an out-of-plane motion of the CNH moiety, finally giving **1a/4**, a bicyclic structure. In this manner, a new chemical bonding between P and N atoms could be established. It is of interest to examine the electronic reorganization along this rather unusual isomerization process. Figure 4a displays the centroids of charge of the localized orbitals of **1a/4** obtained from a Boys localization.[18] It is apparent that the rearrangement somehow starts with the migration of the $\sigma(C_1{-}P)$ bond of **1a** so as to form a novel $\sigma(N{-}P)$ bond; the other charge centroid of the former $\pi(C_1{=}N)$ also circulates in the same direction, finally forming the carbene lone pair. This is likely a manifestation of a stereoelectronic effect.

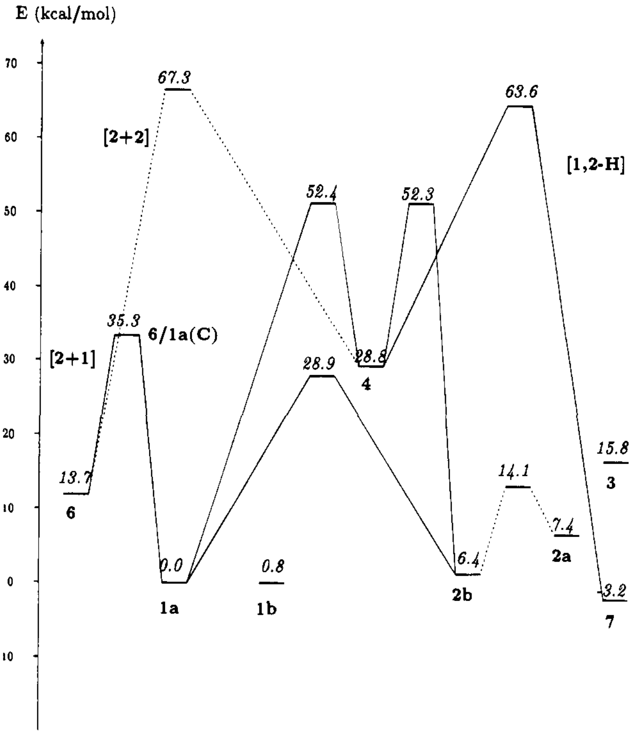
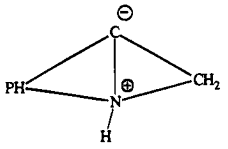


Figure 5. Schematic potential energy curves showing the various transformations of the HN≡C + $CH_2{=}PH$ system. Values were obtained at the CASPT2 + ZPE level.

Chart 2



TS 4/2b

Rearrangements of the Four-Membered Carbene 4. Having established the connection between both primary cycloadducts **1a** and **4**, we now examine the possible rearrangements of the carbene **4**. In fact the latter could be converted either to phosphaziridine **2** or to the cyclobutene derivative **7**. Energies of both relevant TSs **4/2b** and **4/7** are not particularly sensitive to the theoretical treatment (Table 2). Both rearrangements are characterized by significant barrier heights, namely, 23.5 kcal/mol for **4** → **2b** and 34.8 kcal/mol for **4** → **7** (Figure 5). Apparently the TS **4/2b** exhibits a tetrahedral zwitterionic structure having both carbanion and ammonium moieties at the bridgehead positions of a bicyclobutane derivative (Chart 2). **4/2b** is geometrically similar to the TS connecting both silicon analogues **II** and **IV** described in the Introduction. An analysis of the Boys localized orbitals along the reaction path suggests that the rearrangement via **4/2b** involves a number of different electron pairs (Figure 4b): the $\sigma(C_2{-}P)$ bond of **4** is broken, and its electron pair migrates to form the $\sigma(C_1{-}P)$ bond in **2b**. On the other hand, beyond the TS, the carbene lone pair moves so as to form a $\pi(C_1{-}C_2)$ bond of **2**. In **4/2b**, both lone pairs at carbon and nitrogen remain in the immediate neighborhood of these atoms.

The conversion of **4** to **7** occurs through a simple 1,2-hydrogen shift. The energy barrier via **4/7** is calculated to be 34.8 kcal/mol relative to **4**. On the energy scale, **4/7** lies slightly below **6/4** but significantly above **4/2b** and **1a/4** (Figure 5).

[2+1] versus [2+2] Cycloadditions. We can now compare the different reaction pathways discussed above. The potential

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[18] Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

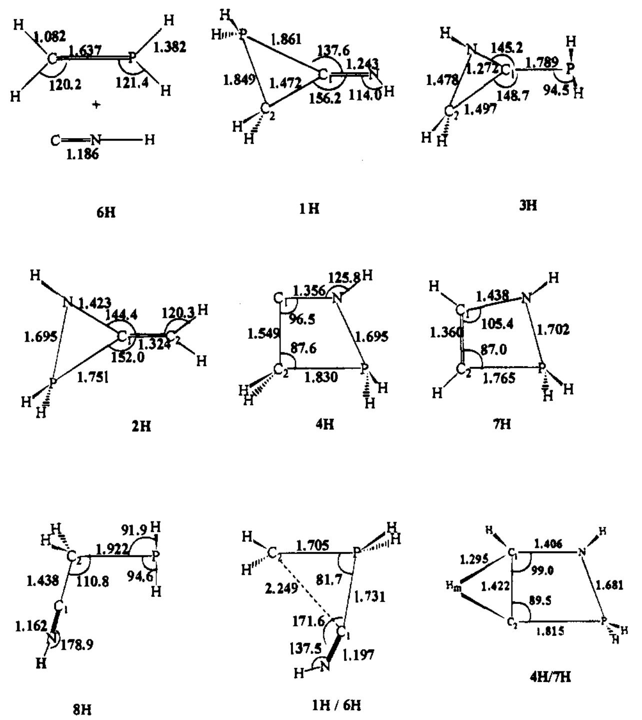
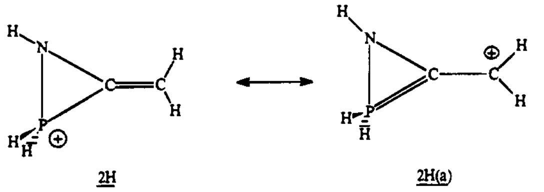


Figure 6. Selected MP2/6-31G(d,p) geometrical parameters of the $[C_2H_5NP]^+$ stationary points considered. Except for HNC, all structures are positively charged.

energy profile including all cycloadditions of HN≡C + CH_2=PH and the rearrangements of the cycloadducts, shown in Figure 5 (values at the CASPT2/ANO + ZPE level), clearly indicates that the [2+1] cycloaddition is by far the preferred mode of the reaction of phosphaethene and hydrogen isocyanide. The high energy content of the TS for [2+2] cycloaddition (6/4) renders this reaction mode hardly operative. The possible conversion of phosphiranimine (1), the [2+1] cycloadduct, to its isomer phosphaziridine 2 is likely to follow a direct concerted step rather than to proceed through the intermediacy of a cyclic carbene (4). In contrast to the situation in the silicon analogue,[6] the cyclic carbene does not seem to be involved at all in the entire process, irrespective of the starting point; this is due to its low thermodynamical stability. In the event that this carbene could be generated by other means, its existence as a discrete entity is however possible, thanks to its enclosure in rather deep potential wells. In this simplest case, the [2+1] cycloaddition turns out to be the rate-determining step, giving phosphiranimine (1) as the major product. Since the **1a**−**2b** interconversion requires a smaller activation energy, phosphaziridine 2 could eventually be formed as a minor product. In reality, the ratio between 2 and 1 should depend on the subtle balance of the effect of substituents attached at different centers.

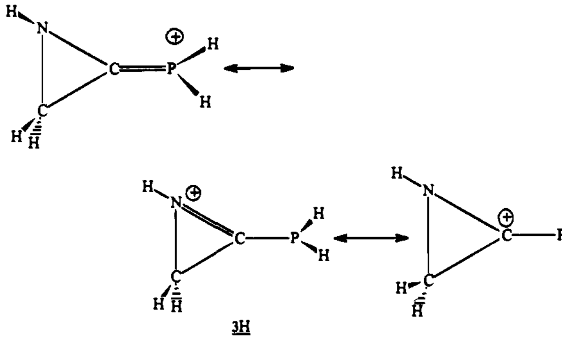
Protonated System HN≡C + H_2C=PH_2^+. As discussed above, the instability of the carbene 4 arises from the presence of the two vicinal lone pairs within a four-membered ring. Therefore, it is of interest to examine the relative stability of the protonated system in which the phosphorus lone pair is removed by protonation. Selected geometrical parameters obtained at the MP2/6-31G(d,p) level of the relevant stationary points are recorded in Figure 6. To facilitate comparison, the numbering of the neutral equilibrium structures has been used; in addition the letter **H** indicates the protonated form. Total and relative energies are summarized in Table 3. For this system our discussion is based on the values determined from QCISD-(T)/6-31G(d,p) + ZPE calculations.

Let us first mention a number of changes in geometrical parameters of the equilibrium structures following protonation. For phosphiranimine **1H**, the changes in bond length are rather small. Note that only **1H** which corresponds to the neutral **1b** can be located. All geometry optimizations starting from the **1a** conformation give rise to the open form **8H**. The shorter C−P distance in **2H** suggests a contribution of the resonance form **2H(a)** (eq 4).



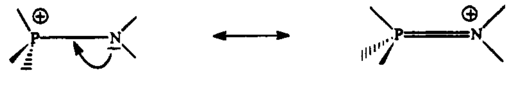
(4)

As for **3H**, this structure is better regarded as a phosphino derivative of the aziridinium cations (eq 5). While the short



(5)

carbon−nitrogen distance in **3H** (1.272 Å) is actually close to that of a C=N double bond, the C−P distance turns out to be much longer (1.789 Å) than that of a C=P double bond (1.637 Å in **6H**). In both four-membered cycles **4H** and **7H**, the N−P distance becomes shorter (up to 0.14 Å) than its counterpart in the neutral species. This is clearly due to the tendency of P to adopt a pentavalent state (eq 6). As such the nitrogen lone pair



(6)

also participates in the electron conjugation with the phosphorous moiety in 4, thus eliminating as a consequence the large electronic repulsion present in the neutral carbene 4. Nevertheless, as a negative consequence the carbenic structure loses the stabilization associated with the nitrogen lone pair. Overall, the stabilization effect remains clearly dominating, but it is expected to be less strong than in the case of its silicon counterpart. As a matter of fact, the calculated relative energies seen in Table 3 reveal only a moderate stabilization of **4H** which lies now only 18.4 kcal/mol above **1H**, as compared with the energy difference of 27.0 kcal/mol in the neutral **4**−**1a** (Table 2). The stabilization in **7H** is similar, namely, 15.2 kcal/mol relative to **7**. In any case **7H** remains more stable than **4H** by 35.0 kcal/mol. While the phosphaziridine **2** clearly does not benefit much from protonation, the isomer **3H** now becomes more stable than **1H** by 8.5 kcal/mol. A stabilization of 21.6 kcal/mol relative to the neutral forms at the QCISD(T)/6-31G-(d,p) level no doubt arises from the additional resonance forms seen in eq 5. As for a rationalization of the large stabilization by means of resonance, we have considered a series of isodesmic reactions of both neutral **3** and protonated **3H** forms. A rough estimate of the energy of these reactions obtained at the HF/6-31(d,p)+ZPE level is summarized in Figure 7. The negative sign of each of these reactions corresponds to a loss of ring strain. The differences in heats of reaction can be explained as

Table 3. Total (au) and Relative (kcal/mol) Energies for the Protonated Structures $[C_2H_5NP]^+$

structure[a]	MP2/6-311G(d,p)	CISDQ/6-311G(d,p)	QCISD(T)/6-31G(d,p)	ZPE[b]	MP2[c]	CISDQ[c]	QCISD(T)[c]
1H	−474.092 10	−474.132 73	−474.080 62	39.7	0.0	0.0	0.0
2H	−474.084 83	−474.124 33	−474.072 56	40.3	4.6	5.9	5.7
3H	−474.103 48	−474.146 16	−474.095 17	40.3	−6.5	−7.8	−8.5
4H	−474.061 46	−474.108 60	−474.053 04	40.8	20.3	16.2	18.4
6H	−474.060 35	−474.106 29	−474.031 28	34.8	15.0	11.7	26.1
7H	−474.124 01	−474.163 25	−474.109 79	41.4	−18.3	−17.5	−16.6
8H	−474.147 34	−474.187 10	−474.132 76	39.4	−35.0	−34.4	−32.3
6H/1H	−474.037 96	−474.072 53	−474.021 87	38.0	32.3	36.1	35.2
4H/7H	−474.001 42	−474.041 94	−473.987 20	38.1	55.3	55.4	57.0

[a] Based on the MP2/6-31G(d,p) geometry given in Figure 6. [b] From HF/6-31G(d,p) calculations and scaled by 0.9. [c] Relative energies, including ZPE corrections.

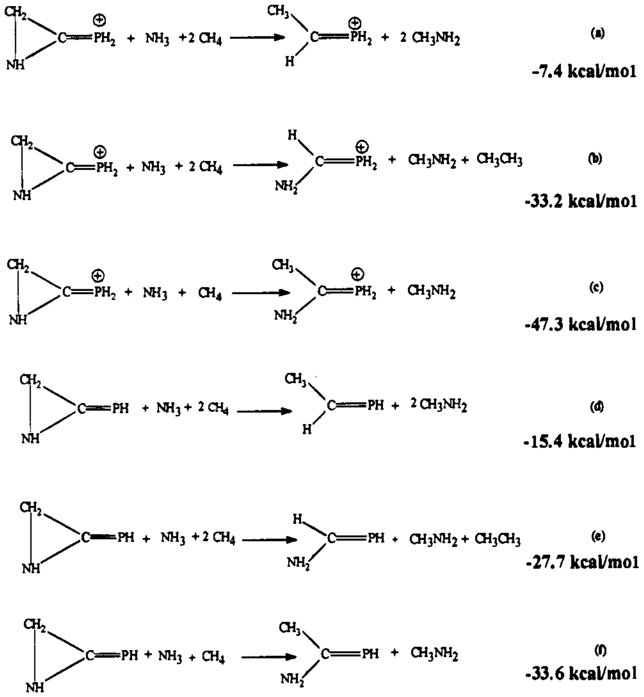


Figure 7. Some isodesmic reactions for **3** and **3H**. The values are the heats of reaction calculated at the HF/6-31G(d,p) + ZPE level.

follows. The least exothermic reactions are (a) in the protonated system and (d) in the neutral system. Because in these equations the products do not have an amino substituent on the $HC{=}PH_2-$ skeleton, the smaller exothermicity is for the greater part due to a resonance stabilization in the ring system. The smaller heat of reaction for the protonated system (a) compared to the neutral (d) arises from the larger ring resonance ability of **3H** compared to **3**. Reactions b and c and their counterparts e and f describe the influence of the resonance of the amino function on the exocyclic $C{=}PH(H^+)$ moiety. Indeed the larger exothermicity of these reactions is given by the resonance factor present on the right hand side of the equations. A combination of an alkyl group and an amino group stabilizes the $C{=}PH(H^+)$ entities, and the reactions c and f are therefore more exothermic. A comparison of the heats of the reactions (a−c) with their neutral counterparts d−f suggests that the protonated rings are much more stabilized through resonance. The difference between the heats of reactions c and e, for example, can—to a large extent—be traced back to the stabilization of **3H** relative to **3**.

Nevertheless, the most stable protonated forms turns out to be the open structure **8H** which is a phosphino derivative of the methylnitrilium cation. **8H** is 32.3 and 38.4 kcal/mol lower in energy than **1H** and the reactants $HN{\equiv}C + H_2C{=}PH_2^+$ (**6H**), respectively. Regarding the [2+1] cycloaddition, we have examined the attack on both C and P centers. Qualitatively, protonation tends to decrease the electronegativity of the C center and to lower the energy of the π^*-orbital. The LUMO of $CH_2{=}PH_2^+$ is actually associated with a quite low energy relative to that in the neutral $CH_2{=}PH$, and the C center now bears a larger MO coefficient. Such a change in the dominant character of the LUMO suggests that C-addition could be clearly favored upon protonation. As a matter of fact, at the HF level, we could locate two distinct transition structures for C- and P-addition of $HN{\equiv}C + H_2C{=}PH_2^+$; the TS for C-addition lies much lower in energy than the P-counterpart. At higher levels, the former no longer exists as a stationary point; only the latter, given now as TS **6H/1H**, remains. The corresponding P-addition, yielding **1H**, is prohibited by a large energy barrier of 35.2 kcal/mol, indicating that the C-addition is largely favored in the protonated case, in line with the orbital symmetry arguments. At the HF level, a TS for a C-addition giving the open-chain nitrilium cation **8H** has also been located, but this structure also disappears at higher levels of theory. In spite of an extensive search, the TS for [2+2] cycloaddition of the protonation reactants **6H** could not be found.

Another point of interest concerns the existence of **1H** as an equilibrium structure. As mentioned above, the protonated counterpart of **1a** does not exist, but instead the open form **8H** has been found. We have also attempted to locate a TS connecting **1H** and **8H**. The relevant TS, which essentially consists of a ring-opening along the C−P bond of **1H**, could be located at both HF and MP2 levels with a small barrier height; however, the barrier disappears almost completely at the CISDQ and QCISD(T) levels. This suggests that the **1H** → **8H** rearrangement is also a barrierless process. It seems reasonable to conclude that the $HN{\equiv}C + H_2C{=}PH_2^+$ addition straightforwardly leads to the formation of the open nitrilium cation **8H**.

We have also examined the 1,2-hydrogen shift connecting **4H** and **7H**. The barrier height calculated via the TS **4H/7H** (Figure 6) amounts to 38.6 kcal/mol, a value similar to that of 39.2 kcal/mol found earlier for the neutral **4** and **7** (Table 1, QCISD(T) + ZPE values.)

Conclusions

A number of results emerge from the present theoretical study on the cycloaddition of the model $HN{\equiv}C + CH_2{=}PH$ and $HN{\equiv}C + H_2C{=}PH_2^+$ systems.

(1) The [2+1] cycloaddition is the most favored mode of the $HN{\equiv}C + CH_2{=}PH$ reaction. This gives rise to phosphiranimine products **1a** and **1b** in which the reaction path via a C-attack leading to **1a** is slightly preferred by a stereoelectronic effect. Our best estimate predicts a classical barrier height of 35 kcal/mol.

(2) The most stable isomer among the possible three-membered rings resulting from the $HN{\equiv}C + CH_2{=}PH$ reaction is the phosphiranimine **1a**. Structure **2** with an exocyclic C=C

bond could be formed as a minor product through isomerization of **1**; the TS **1a/2b** lies in fact lower in energy than the TS **6/1a(C)** for [2+1] cycloaddition. Structure **3** with an exocyclic C=P bond is thermodynamically less stable (16 kcal/mol above **1a**).

(3) As far as the four-membered rings **4, 5,** and **7** are concerned, the latter is the most stable of all isomers considered while the former are the least stable isomers. Although the carbene ring **4** is in principle involved in the [2+2] cycloaddition, its low thermodynamical stability caused by electron pair repulsion renders the [2+2] cycloaddition hardly competitive with respect to the [2+1] reaction. However being surrounded by high potential wells, the cyclic carbene **4** might exist as a discrete species if it could be generated by other means.

(4) The effect of protonation at phosphorus results in an overall stabilization of the ring structures, but the most favored reaction mode of $HN{\equiv}C + H_2C{=}PH_2^+$ is a nucleophilic addition giving an open phosphino derivative of the methylnitrilium cation.

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