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The CH by N Replacement Effects on the Aromaticity and Reactivity of Phosphinines

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Geometries, aromatic character, Mulliken charge distribution, and MO diagrams of 1,2-aza-, 1,3,2-diaza-, 1,3-aza-, and 1,3,5-diazaphosphinines have been calculated and compared to those of phosphinine and pyridine. This study reveals that the introduction of nitrogen atoms at the position adjacent to phosphorus significantly reduces the aromatic delocalization and induces a [1,4] dipolar character through an increase of the positive charge on the P atom. This phenomenon does not occur in 1,3-aza- and 1,3,5-diazaphosphinines, which exhibit a poor dipolar character. This comparison confirms the high reactivity of 1,3,2-diazaphosphinines toward alkynes. A [4 + 2] cycloaddition reaction between these two types of diazaphosphinines and acetylene has been modelized. Calculated geometries of the resultant [4 + 2] diazabarrelene cycloadducts and that of their respective transition states reveal that, especially with 1,3,2-diaza isomers, the cycloaddition proceeds via a disymmetrical pathway that involves the preliminary formation of the P−C bond.

Introduction

Since their discovery, phosphinines have been the subject of a number of theoretical investigations.[1] These studies were motivated by the need for phosphorus chemists to have a good understanding of the electronic factors that render phosphinines so different from their nitrogen counterparts (pyridines) with regard to their chemical reactivity[2] and their coordinating properties.[3] A second important point is that this heterocycle and its derivatives constitute an ideal model for studying the ability of the −P═C double-bond system to participate in conjugative interactions.[4] More recently, the discovery of 1,3-di-[5] and 1,3,5-triphosphinines[6] has furnished a new interesting field of research for theoretical chemists since these sytems allow assess to the effects of perturbations induced by the successive replacements of CH units by P atoms.[7] On the other hand, it appears that only little attention has been paid to the study of mixed nitrogen−phosphorus heteroaromatic systems. Some studies refer to the electronic structure of azaphospholes[8] and their benzannulated derivatives,[9] but to the best of our knowledge, azaphosphinines have not been studied. Meanwhile, several experimental results indicate that the replacement of CH units by nitrogen atoms in phosphinines considerably enhances the ring reactivity. A number of possible isomers of aza- and diazaphosphinines are known. Historically, the first isomer to be discovered was 1,4-azaphosphinine synthesized by Märkl.[10] Later, the same group reported on the synthesis and the reactivity of 1,3-aza- and 1,3,5-diazaphosphinines.[11,12] They showed that this new class of compounds could be used as precursors of polyfunctional phosphinines through their thermal reactions with alkynes. Although no intermediates were isolated, these transformations are reasonably thought to consist of a [4 + 2] cycloaddition/cycloreversion sequence involving the formation of a transient aza and diazaphosphabarrelenne and the concomitant release of one molecule of nitrile (Scheme 1).

Unfortunately, despite of their undeniable interest, these transformations suffer from severe limitations that reduce their applicability. Indeed, 1,3-aza- and 1,3,5-

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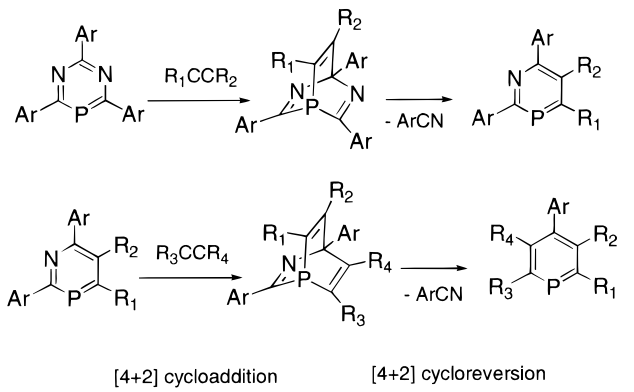
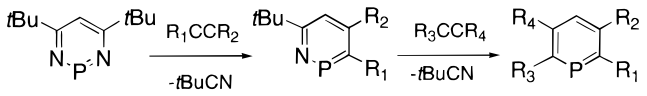
Scheme 1



Scheme 2



diazaphosphinines are obtained in low yields from the reaction of $P(SiMe)_3$ with the corresponding aza- and diazapyriliums salts precursors, only available when aryls groups are present at the ortho and para positions. Phosphinines thus obtained always bear, at least, one aryl group at the C_4 position (para to P). Furthermore, the reaction of these azaphosphinines with alkynes often requires drastic conditions (high temperatures and several kbar of pressure). To circumvent this limitation, in 1996, we investigated the synthesis of the 1,2-aza and 1,3,2-diaza isomers.[13] We postulated, as seen for 1,3,2-diazaphospholes,[14] that the incorporation of nitrogen at the α position at phosphorus would dramatically enhance the 1,4-dipolar character of phosphinines by increasing the positive charge at the P atom. This assumption turned out to be valid, and we showed that these aza and diazaphosphinines more readily react with alkynes than their 1,3-aza and 1,3,5-diaza isomers. Furthermore, the substitution scheme of their diazatitanacyclohexadiene precursor keeps the para position unsubstituted. In most transformations so far studied, both [4 + 2] cycloaddition/cycloreversion sequences proceed under mild conditions at atmospheric pressure (between 80 and 100 °C for the 1,3,2-diaza to 1,2-azaphosphinine conversion and in toluene under reflux for the final transformation into phosphinine). Recently, this strategy was successively exploited to synthesize a number of tetrafunctional phosphinines, bis- and trisphosphinines,[15a,b] diazaphosphabarrelennes,[15c] and the first examples of phosphinine-based macrocycles[15d] (Scheme 2).

The difference observed between the reactivity of 1,3,5-diaza- and 1,3,2-diazaphosphinines prompted us to investigate in depth the electronic structure of these two systems. With the concern of understanding the factors that govern the reactivity of the [1,4] formal PCH dipoles in these molecules,[16] we deliberately excluded the 1,4-azaphosphinine structure of this study.

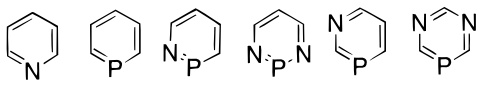
Table 1. Calculated Geometries, at the B3LYP/6-31G* Level, of Compounds 1−6[a]

	1	2	3	4	5	6
d (1-2)	1.339	1.747	1.745	1.654	1.749	1.760
d (2-3)	1.396	1.393	1.396	1.333	1.390	1.332
d (3-4)	1.394	1.398	1.395	1.400	1.399	1.337
d (4-5)			1.403		1.338	
d (5-6)			1.328		1.333	
d (6-1)			1.660		1.759	
α	117.1	100.0	103.7	107.7	98.0	95.7
β	123.8	125.4	122.4	121.0	124.0	128.0
χ	118.4	123.2	122.2	124.9	122.3	119.4
δ	118.5	122.8	121.8	120.5	126.2	129.4
ε			126.0		120.1	
φ			124.0		129.3	

[a] Bond lengths are given in Å and intramolecular bond angles in deg.

Results and Discussion

Geometry and Electronic Structure of 1−6. All calculations were performed on the six model structures presented below using the DFT/B3LYP method (Gaussian 94):[17] pyridine **1**, phosphinine **2**, 1,2-aza- and 1,3,2-diazaphosphinines **3** and **4** and their isomers where the nitrogen atom is located at the *β* position at phosphorus, and 1,3-aza- and 1,3,5-diazaphosphinines **5** and **6**.



1 **2** **3** **4** **5** **6**

Relevant B3LYP/6-31G*-optimized geometry parameters are given in Table 1. The geometries for **1** and **2** deserve no special comments since they are in good agreement with experimental values and earlier calculations.[1e] The geometries of compounds **3**−**6** are, by far, more interesting. First, it appears that they all display a planar-type structure and a strong conjugative character as indicated by the bond distances, which are intermediate between those of singly or doubly bonded analogues, as shown in Table 2 (calculated at the same level of theory). With respect to average values, a contraction is always observed for aromatic compounds.[1h]

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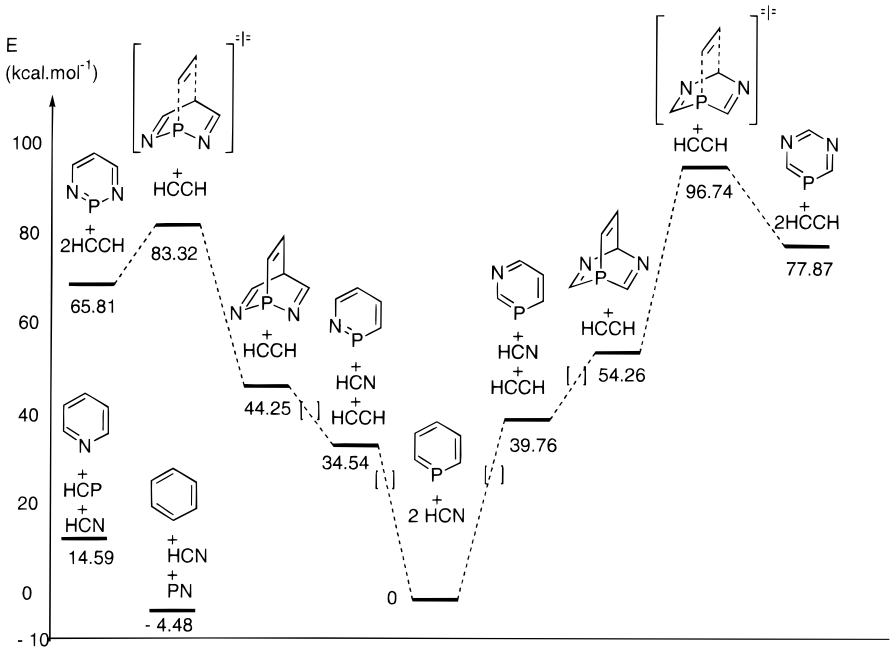

Figure 1. Relative energies of transformations from **4** to **2** and from **6** to **2** at the B3LYP/6-31G* level + ZPE corrected. Similar transformations involving C_6H_6 and C_5H_5N **1** are indicated as references.

Table 2. Typical Single and Double Bond Lengths (Å) and Their Average Values at the B3LYP/6-31G* Level

XH_n-YH_p		$XH_{n-1}=YH_{p-1}$		average
H_3C-CH_3	1.531	$H_2C=CH_2$	1.331	1.431
H_3C-PH_2	1.877	$H_2C=PH$	1.675	1.776
H_3C-NH_2	1.466	$H_2C=NH$	1.270	1.368
H_2P-NH_2	1.727	$HP=NH$	1.594	1.660

This contraction remains weak, ≤0.01 Å for PN bonds in **3** and **4**, about 0.02 Å for PC bonds in **5** and **6**, and close to 0.03−0.04 Å for all other bonds in **1**−**6**. These data seem to indicate a weaker aromaticity for **3**−**6** compared to **1** and **2**, nevertheless without giving a quantitative estimation of this phenomenon. Another interesting remark concerns the values of the internal angle at phosphorus (between 95.7 and 107.7°). These values appear to be quite short compared to that of pyridine **1** (117.1°). This phenomenon, which has already been rationalized, is common for other doubly bonded systems such as phosphaalkenes.[18] It reflects both the difficulty of phosphorus to achieve sp^2-hybridization compared to elements of the first long row (C and N) and the lengthening of the X=P bond distances. Thus, whereas the opening of this angle decreases in **5** and **6** (longer P=C bond lengths than in **2**), it significantly increases in **3** and **4** as a result of adjacent shorter P=N bond lengths.

Another significant set of data concerns the thermodynamic stability of the different isomers of azaphosphinines **3**−**6**. As shown in Figure 1, the introduction of nitrogen at the α or the β position tends to destabilize the ring compared to phosphinine. It can also be noted that 1,2-aza and 1,3,2-diaza derivatives are more stable than their 1,3-aza and 1,3,5-diaza isomers from 5.21 and 12.06 kcal·mol^{-1}, respectively. As we will see later, this difference in stability can be ascribed to the σ skeleton.

The aromaticity of **1**−**6** has been estimated through their calculated NICS values (nucleus-independent chemical shifts)[19,20] and compared to that of benzene. These values are collected in Table 3. In good agreement with previous reports, **2** is found to be less aromatic than **1**.[1e] As expected from experimental observations, the introduction of nitrogen atoms in the phosphinine ring significantly reduces the aromatic character. Thus, diazaphosphinines always show lower NICS (absolute values) than their monoaza derivatives (compare **4** to **3** and **6** to **5**). Apparently, the degree of aromaticity does not correlate with the order of thermodynamic stability since 1,2-aza- **3** and 1,3,2-diazaphosphinine **4** show lower NICS values than their 1,3-aza- **5** and 1,3,5-diaza **6** counterparts.

Table 3. NICS Values (ppm) at Points 0.5 Å above the Ring Centers at the GIAO-SCF/6-31+G*//B3LYP/6-31G* Level[a]

compound	NICS	compound	NICS
benzene	−11.5	1,3,2-diazaphosphinine **4**	−7.5
pyridine **1**	−10.6	1,3-azaphosphinine **5**	−9.3
phosphinine **2**	−10.2	1,3,5-diazaphosphinine **6**	−8.4
1,2-azaphosphinine **3**	−8.9		

[a] Negative (NICSs) denote aromaticity; positive, antiaromaticity.[19,20]

Very likely, the weaker aromatic character of α-substituted derivatives results from the difference of electronegativity between the concerned elements (C, P, N). A large difference in electronegativity between the two neighboring atoms increases the π electron density on the more electronegative atom, thus limiting electronic delocalization within the ring. As we will see later, this

(18) Schoeller, W. In ref 2, p 5.

(19) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Eikema Hommes, N. J. R. v. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(20) NICS values have been used to estimate aromaticity of various systems; see, for example: (a) Jiao, H. Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383. (b) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2638. (c) Jiao, H. Schleyer,; P. v. R.; Mo, Y.; Allister, M. A.; Tidwell, T. *J. Am. Chem. Soc.* **1997**, *119*, 7075. (d) Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951.

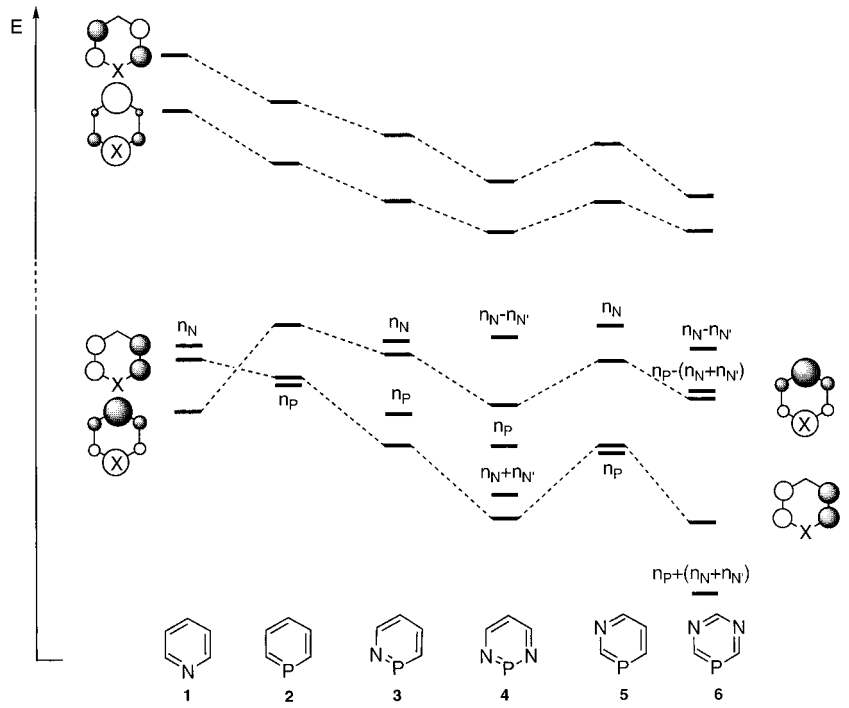

Figure 2. MOs for **1**−**6** and their relative levels, at the B3LYP/6-31G* level. n_N, $n_{N'}$, and n_P mean lone pair at nitrogen and/or phosphorus.

phenomenon can be measured in a quantitative way by using the NBO method,[21] which yields the population of π orbitals ($2p_z$ for C and N and $3p_z$ for P) (vide supra).

Though noteworthy, these results (geometry, aromaticity, and thermodynamic stability) do not really explain why 1,2-aza- and 1,3,2-diazaphosphinines are more reactive than 1,3-aza and 1,3,5-diaza derivatives. An examination of the molecular orbital diagram of each compound affords a clear answer to this question (see Figure 2). A word of caution is necessary prior the use of Kohn−Sham MOs in terms that have been widely used for Hartree−Fock MOs. Previous works by Parr,[22] Baerends,[23] and very recently by Hoffmann and co-workers[24] have shown that both types of MOs bear the same qualitative explanatory power, and moreover, a very good linear relationship is found between both types of MO energies, in such a way that an $ax + b$ scaling may be used.

The inversion of the highest occupied π orbitals sequence between pyridine and phosphinine does not deserve comment since it has already been discussed in several reports.[1e] A first interesting remark concerns the comparison between phosphinine and its aza derivative. If we exclude the different combinations of the lone pairs at P and N atoms, it appears that the orbital sequence of phosphinine is maintained whatever the number and the localization of the nitrogen atoms included. In all cases, the second π orbital in energy presents a node at P and C_4, whereas the highest occupied π orbital exhibits the largest coefficients at these positions. A first consequence of the replacement of CH by N concerns the position of the LUMO and LUMO + 1, which both decrease in energy as the number of nitrogen atoms increases. The same phenomenon is also observed for the relative position of the two highest occupied π orbitals (HOMO and HOMO-1 in **2**), which experience a dramatic decrease in energy. In all azaphosphinines studied, the HOMO now mostly describes the lone pair at N (for **3** and **5**) or an antisymmetric combination of the two associated AOs in the case of diaza derivatives **4** and **6**.

Table 4. Coefficients of the Highest π and Lowest π^* MO of 2−6

π MO	2	3	4	5	6
π LUMO					
P ($3p_z$)	0.45	0.47	0.52	0.44	0.45
C_4 ($2p_z$)	0.31	0.29	0.28	0.33	0.35
π HOMO					
P ($3p_z$)	0.42	0.40	0.38	0.42	0.45
C_4 ($2p_z$)	−0.31	−0.31	−0.35	−0.29	−0.28

Though the localization of the nitrogen atoms does not notably influence the relative level of the HOMO's in **3**−**6**, it significantly modifies the coefficients of the π orbitals, especially at P and C_4 (see Table 4). Thus, when one or two nitrogen atoms are incorporated at the α position at phosphorus (**3** and **4**), the LUMO is more clearly localized on the P atom whereas the weight of C_4 increases in the highest π HOMO. The opposite phenomenon is observed when the nitrogen atoms are incorporated at the β position (**5** and **6**).

Two kinds of qualitative arguments support these trends. The first one is provided by the evolution of Mulliken charges (see Scheme 3), the second by the analysis of the NBO π population (see Table 5). This allows one to assess that the introduction of nitrogen atoms at the α position increases the electrophilic character of the P atom and, consequently, the dipolar

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Scheme 3. Mulliken Charge Distribution for 1-6 at the B3LYP/6-31G* Level

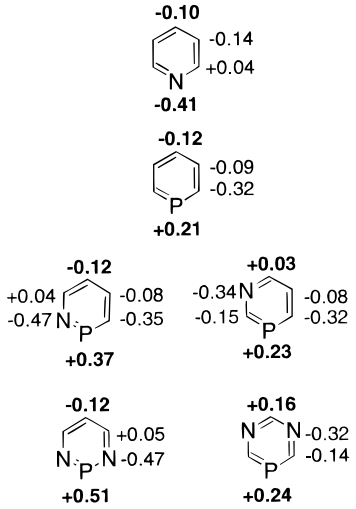


Table 5. nbo π Population Analysis for 1−6 and Percentage of s Character of the Lone Pairs at Nitrogen and/or Phosphorus at the B3LYP/6-31G* Level

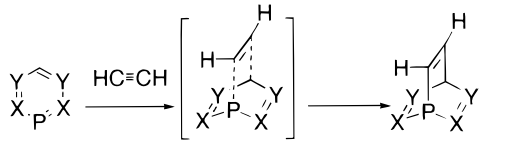
	1	2	3	4	5	6
P		0.95	0.87	0.77	0.96	0.96
N	1.15		1.22	1.23	1.13	1.15
C_2	0.93	1.05	1.06		1.01	0.94
C_3	1.01	0.97	0.93	0.87	0.98	
C_4	0.95	0.98	1.00	1.01	0.91	0.85
C_5	1.01	0.97	0.90	0.87		
C_6	0.93	1.05			0.98	0.94
P(%s)		63.8	67.2	70.5	65.1	66.4
N(%s)	29.1		29.2	31.2	28.3	29.1

character of 1,2- and 1,3,2-azaphosphinines. On the other hand, and in line with experimental observations, it is clear that the presence of one or two nitrogen atoms at the β position significantly increases the positive charge at the C_4 carbon but hardly modifies the electrophilic character of the P atom, compared to phosphinine. Consequently, 1,3-aza- and 1,3,5-diazaphosphinines cannot be considered as strong [1,4] P−C_4 dipoles (compare values for **4** and **6**).

Apart from this observation, we also examined the percentage of s character of lone pairs at P and/or N. As confirmed by experimental observations,[25] a weaker hybridization at phosphorus strongly decreases the basicity of the lone pair. We effectively observe a dramatic difference upon going from nitrogen (%s = 29.1 in **1**) to phosphorus (%s = 63.8 in **2**). To our knowledge, these

(25) (a) Oehling, H.; Schweig, A. *Phosphorus* **1971**, 203. (b) Hodges, R. V.; Beauchamp, J. L.; Ashe, A. J., III; Chan, W.-T. *Organometallics* **1985**, 457. (c) Ashe, A. J., III; Bohl, M. K.; Bomben, K. D.; Chan, W.-T. Gimzewski, J. K.; Sitton, P. G.; Thomas, T. D. *J. Am. Chem. Soc.* **1979**, *101*, 1764.

Scheme 4



4: X = N, Y = CH
6: X = CH, Y = N
9: X = N, Y = CH
10: X = CH, Y = N
7: X = N, Y = CH
8: X = CH, Y = N

values have not been reported for phosphinine and pyridine, so far. This effect is accentuated for azaphosphinines, especially when a nitrogen atom is present at the α position at phosphorus (compounds **3** and **4**). This phenomenon is easily rationalized by considering that the percentage of s character at phosphorus is weaker for P−N σ bonds (16.0% in **3** and 15.4% in **4**) than for P−C σ-bonds (18.6% in **2**, 17.9% in **5**, and 17.2% in **6**). Thus, a decrease of the s character at P in the two adjacent σ bonds will expand the s character in the lone pair.

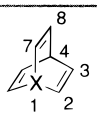
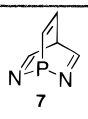
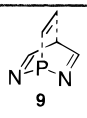
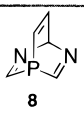
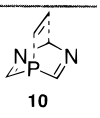
Reactivity. To confirm the higher reactivity of 1,2-aza- and 1,3,2-diazaphosphinines toward alkynes, we have examined the [4 + 2] cycloaddition between acetylene and diazaphosphinines **4** and **6**. Four structures have been optimized using the same method, phosphabarrelenes **7** and **8**, and the two corresponding transition states **9** and **10** (see Scheme 4).

A first remark concerns the striking similarity between the structures of **7** and **8**. The PC and CC bonds that are created have the same lengths as well as the C=C and C=N bonds. Considering that phosphabarrelenes display no π-conjugated character, we propose that σ effects are equivalent in both cases and do not influence the reactivity of the two diazaphosphinines (mainly governed by π-effects: delocalization, aromaticity). On the other hand, these σ effects are likely to play an important role in the difference of stability between the two diazaphosphinines since the energy difference calculated between **7** and **8** (10.01 kcal·mol^{-1}) compares with that calculated between **4** and **6** (12.06 kcal·mol^{-1}). A second important piece of data is the energy difference between the two transition states, which, respectively, lie 17.5 and 18.9 kcal·mol^{-1} higher than their precursors **4** and **6** (see Figure 1). Although quite weak, this difference confirms that [4 + 2] cycloadditions are facilitated in the case of 1,3,2-diazaphosphinines. Furthermore, we propose that the use of a polarized alkyne would reduce the energy of activation in the case of the formation of **9** on account of the important polarity of the P−C_4 dipole in **4**. The structures of the transition states **9** and **10** appear to be markedly different on examining the two formed bonds (PC and CC) (see Table 6). In **9**, the PC bond distance (2.358 Å, lengthening of 27% compared to **7**) is relatively short compared to the CC bond (2.382 Å, lengthening of 56.5%). This disymmetry clearly shows that the PC bond is formed earlier than the CC bond. Although less marked, the same phenomenon is also visible in the structure of **10**, the PC bond lying at 2.485 Å (lengthening of 34.1% compared to **8**) and the CC bond at 2.270 Å (lengthening of 49.6%).

Conclusion

On the basis of geometric and NICS criteria, we have demonstrated that the aza- and diazaphosphinines studied are aromatic. The higher reactivity of 1,3,2-diazaphosphinines and 1,2-azaphosphinines compared to their

Table 6. Calculated Geometries, at the B3LYP/6-31G* Level, of Compounds 7−10[a]

					
		7	**9**	**8**	**10**
d (1-2)		1.812	1.688	1.903	1.790
d (2-3)		1.267	1.307	1.266	1.305
d (3-4)		1.539	1.428	1.494	1.367
d (4-8)		1.521	2.382	1.517	2.270
d (7-8)		1.335	1.240	1.334	1.237
d (1-7)		1.856	2.358	1.853	2.485

[a] Bond lengths are given in Å.

1,3,5-diaza and 1,3-aza isomers mainly results from a strong polarization induced by the presence of two neighboring nitrogen atoms which dramatically increase the electrophilic character of the phosphorus atom. Although these results confirm experimental observations, we must keep in mind that steric effects would have to be taken into account. Thus, the presence of two tertiobutyl groups at the β position to phosphorus in aza and diazaphosphinines **3** and **4** is a factor which facilitates the interaction between the alkyne and the phosphorus atom by hampering the approach at the C_4 position. Steric hindrance also probably occurs in the case of Märkl's phosphinines, which always bear an aryl group at this position, but to a lesser extent. Furthermore, as we previously stated, the use of polar alkynes is also an important factor which accentuates the difference of reactivity since 1,3-aza and 1,3,5-diazaphosphinines **5** and **6** are weakly polarized.

Computational Methods

Geometries were optimized at the B3LYP/6-31G* density functional levels with the Gaussian 94 program package.[17] A vibrational analysis was done at the same level to characterize stationary points and transition structures and thereby to estimate their zero-point vibrational energies (ZPEs), whose calculated values were scaled by 0.98.[26] The aromatic character of azaphosphinine was evaluated by computing the nucleus independent chemical shift according to the method developed by Schleyer (NICS, GIAO-SCF/6-31+G*//B3LYP/6-31G*)[19,20] for **1**−**6** and benzene 0.5 Å above the ring center. Reed and Weinhold's NBO analysis[21] of **1**−**6** gave π-population and orbital hybridizations. The NBO representation of ab initio wave functions in terms of localized Lewis structures provides a quantitative interpretation of MO interactions.

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(26) (a) Bauschliger, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788. (b) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.