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X-ray Crystal Structure, ab Initio Calculations, and Reactivity of 1,3,$2\lambda^5$-Diazaphosphetes: A New Type of 4-π-Electron 4-Membered Heterocycle

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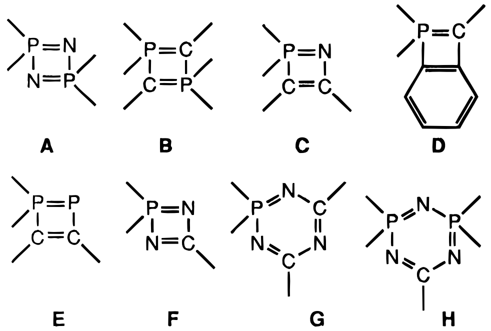
The structure of *P,P*-bis(diisopropylamino)-4-phenyl-1,3,$2\lambda^5$-diazaphosphete, **1a**, has been determined by a single-crystal X-ray diffraction study ($C_{19}H_{33}N_4P$, monoclinic system, space group $P2_1$, $a = 9.482(1)$ Å, $b = 11.374(3)$ Å, $c = 9.668(2)$ Å, $\beta = 97.16(1)°$, $Z = 2$). According to quantum chemical calculations at an RHF level of optimization utilizing the 6-31g(d,p) basis set, **1a** has a zwitterionic structure with the negative charge delocalized on the NCN allylic fragment and the positive charge localized at the phosphorus. Heterocycle **1a** reacts with water and benzaldehyde affording *N*-phosphoranylbenzamidine **3** (95% yield) and the expected aza-Wittig adduct **4** (85% yield), respectively. Addition of 1 equiv of methyl trifluoromethanesulfonate and of 2 equiv of BH_3•THF to **1a** affords cyclic phosphonium salt **5** (94% yield) and the bis(borane) adduct **6a** (90% yield), respectively. Dimethyl acetylenedicarboxylate slowly reacts with **1a** giving rise to 1,3,$4\lambda^5$-diazaphosphinine, **9**, in 70% yield. The X-ray crystal structures of products **2**, **3**, and **6a** are reported (**2**: $C_{26}H_{38}N_5P$, monoclinic system, space group *C*2/*c*, $a = 16.337(8)$ Å, $b = 19.810(2)$ Å, $c = 8.800(2)$ Å, $\beta = 117.68(2)°$, $Z = 4$. **3**: $C_{19}H_{35}N_4OP$, orthorhombic system, space group $P2_12_12_1$, $a = 9.090(1)$ Å, $b = 12.955(2)$ Å, $c = 17.860(3)$ Å, $Z = 4$. **6a**: $C_{19}H_{39}B_2N_4P$, orthorhombic system, space group $P2_12_12_1$, $a = 10.340(1)$ Å, $b = 13.247(1)$ Å, $c = 16.996(1)$ Å, $Z = 4$).

Introduction

In a recent paper, Barton et al.[1] underlined that the bonding in cyclic phosphazenes and related compounds is not adequately described by the concept of aromatic or antiaromatic hydrocarbon systems in which the extensive electron delocalization is via $p_\pi-p_\pi$ bonding. On the other hand, from calculations by Dewar,[2] Maier[3] emphasized in his 1988 outstanding review, that the "excess energy" of cyclobutadiene can be divided in two components namely strain energy and electronic destabilization which counts for 40% and 60%, respectively. It is thus clear, that 4-π-electron 4-membered ring systems possessing heteroatoms with no available p-orbital, although they are not antiaromatic, should be rather unstable due to the ring strain. Indeed, so far, only one 1,3,$2\lambda^5$,$4\lambda^5$-diazadiphosphete (cyclodiphosphazene) (**A**),[4] a couple of $1\lambda^5$,$3\lambda^5$-diphosphetes (**B**),[5] two 1,$2\lambda^5$-azaphosphetes (**C**),[6] and recently a naphto-λ^5-phosphete (**D**),[7] and a $1\lambda^5$,$2\lambda^3$-diphosphete (**E**),[8] have been isolated (Chart 1). Like cyclobutadienes, all these compounds are extremely reactive, and the use of bulky substituents is required for their isolation.

Chart 1



The synthesis of the title compound, namely the 1,3,$2\lambda^5$-diazaphosphete **F** has been claimed in 1973;[9] however, soon after Glemser[10] demonstrated that it was in fact a mixture of 6-membered rings **G** and **H**. Although the mechanism of the reaction has not been elucidated, it seemed quite possible that the observed products **G** and **H** resulted from a disproportionation of the 4-π-electron 4-membered ring **F**, arguing again for the high instability of the 4-π-electron 4-membered heterocycles.

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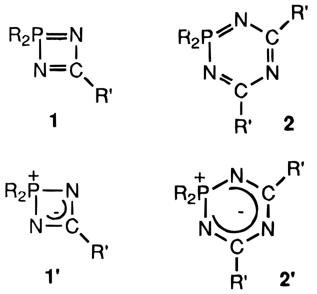
Table 1. Crystallographic Data for **1a**, **2**, **3**, and **6a**

	1a	**2**	**3**	**6a**
formula	$C_{19}H_{33}N_4P$	$C_{26}H_{38}N_5P$	$C_{19}H_{35}N_4OP$	$C_{19}H_{39}B_2N_4P$
fw	348.46	451.6	366.50	376.13
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$ (No. 4)	$C2/c$ (No. 15)	$P2_12_12_1$(No. 19)	$P2_12_12_1$(No. 19)
a, Å	9.482(1)	16.337(8)	9.090(1)	10.340(1)
b, Å	11.374(3)	19.810(2)	12.955(2)	13.247(1)
c, Å	9.668(2)	8.800(2)	17.860(3)	16.996(1)
β, deg	97.16(1)	117.68(2)		
V, Å^3	1034.5(4)	2522.1(13)	2103.4(5)	2328.0(3)
Z	2	4	4	4
d_{calcd}, g.cm^{-3}	1.12	1.19	1.16	1.07
μ, mm^{-1}	1.22	1.13	1.26	1.10
F(000)	380	976	800	824
diffractometer	Enraf-Nonius CAD4			
λ, Å (Cu-Kα)	1.54184			
T, K	200(2)	193(2)	193(2)	193(2)
max 2θ, deg	120	120	130	120
no. of data	3249	2018	3937	5717
no. of unique data	2999	1879	3565	3452
no. of variables	226	149	237	239
R^a	0.082	0.047	0.034	0.034

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

Chart 2



1 2 1' 2'

1a,**2** : R = (i-Pr)$_2$N, R' = Ph

1b : R = R' = H

1c : R = NH$_2$, R' = H

In the course of our study concerning the mechanism[11] of the substitution reaction of bromophenyldiazirine,[12] we discovered that the use of bis(diisopropylamino)(trimethylstannyl)phosphine, as the nucleophile, allowed the synthesis of the 1,3,2λ^5-diazaphosphete **1a** (26% yield) and the 1,3,5,2 λ^5-triazaphosphinine **2** (3% yield).

Here we report the results of an X-ray crystal study of **1a** and ab initio calculations on the parent compound **1b** and P-amino-substituted derivative **1c**, as well as some examples of reactivity of the intriguing 1,3,2λ^5-diazaphosphete derivative **1a** (Chart 2).

Results and Discussion

Structure Determinations. The crystallographic data for **1a**, **2**, **3**, and **6a** are summarized in Table 1. The structures were solved by direct methods (SHELXTL-Plus).[13] The non-hydrogen atoms were refined anisotropically of F (**2**, and **3**, SHELXTL-Plus), and F^2 (**1a**, and **6a**, SHELXL-93),[14] respectively. H atoms were refined isotropically using a riding model.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1a**

P(1)−N(1)	1.670(4)	C(1)−N(1)	1.368(7)
P(1)−N(2)	1.675(4)	C(1)−N(2)	1.377(6)
P(1)−N(3)	1.625(4)	C(1)−C(2)	1.471(6)
P(1)−N(4)	1.644(3)		
N(1)−P(1)−N(2)	86.0(2)	N(2)−P(1)−N(4)	111.8(2)
N(1)−P(1)−N(3)	112.2(2)	N(3)−P(1)−N(4)	105.9(2)
N(1)−P(1)−N(4)	120.5(2)	P(1)−N(1)−C(1)	81.1(3)
N(2)−P(1)−N(3)	120.4(2)	P(1)−N(2)−C(1)	80.6(3)
N(1)−C(1)−N(2)	112.4(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

P(1)−N(1)	1.630(2)	C(1)−N(1)	1.330(2)
P(1)−N(1a)	1.630(2)	C(1)−N(2)	1.345(2)
P(1)−N(3)	1.644(2)	C(1a)−N(2)	1.346(2)
P(1)−N(3a)	1.644(2)		
N(1)−P(1)−N(1a)	110.0(1)	N(1a)−P(1)−N(3a)	112.9(1)
N(1)−P(1)−N(3)	112.9(1)	N(3)−P(1)−N(3a)	104.3(1)
N(1)−P(1)−N(3a)	108.4(1)	P(1)−N(1)−C(1)	117.3(1)
N(1a)−P(1)−N(3)	108.4(1)	N(1)−C(1)−N(2)	128.5(2)
C(1)−N(2)−C(1a)	118.5(2)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

P(1)−O(1)	1.498(1)	C(1)−N(1)	1.294(2)
P(1)−N(1)	1.654(1)	C(1)−N(2)	1.338(2)
P(1)−N(3)	1.656(1)	C(1)−C(2)	1.503(2)
P(1)−N(4)	1.653(2)		
N(1)−P(1)−O(1)	115.9(1)	N(1)−P(1)−N(4)	102.0(1)
N(3)−P(1)−O(1)	109.7(1)	N(3)−P(1)−N(4)	104.8(1)
N(4)−P(1)−O(1)	115.7(1)	P(1)−N(1)−C(1)	125.6(1)
N(1)−P(1)−N(3)	107.7(1)	N(1)−C(1)−C(2)	117.1(1)
N(1)−C(1)−N(2)	126.1(2)		

An absorption correction (**2** and **3**, DIFABS; **1a** and **6a**, Ψ-scans) and an extinction correction (**1a**) were applied. The absolute structure cannot be determined reliably in **3**. In **1a** and **6a** the absolute structure was determined by Flack's x-parameter [**1a**, $x = 0.05(4)$; **6a**, $x = 0.00(3)$].[15] Tables 2−5 summarize selected interatomic distances and angles for **1a**, **2**, **3**, and **6a**.

Quantum Chemical Calculations. These were performed at an RHF level of optimization,[16] utilizing the 6-31g(d,p) basis set.[17] They are of double-ζ quality with polarization functions at all atoms. Electron correlation correction at the RHF

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for **6a**

P(1)−N(1)	1.694(2)	C(1)−N(1)	1.359(3)
P(1)−N(2)	1.689(2)	C(1)−N(2)	1.354(2)
P(1)−N(3)	1.608(2)	C(1)−C(2)	1.456(3)
P(1)−N(4)	1.613(2)		
N(1)−P(1)−N(2)	79.8(1)	N(3)−P(1)−N(4)	110.4(1)
N(1)−P(1)−N(3)	118.7(1)	N(2)−P(1)−N(4)	120.4(1)
N(1)−P(1)−N(4)	112.7(1)	P(1)−N(1)−C(1)	86.8(1)
N(2)−P(1)−N(3)	112.3(1)	P(1)−N(2)−C(1)	87.2(1)
N(1)−C(1)−N(2)	106.2(2)		

Table 6. Relevant Bonding Parameters (Bond Lengths in Å, Bond Angles in deg) as Obtained from Experiment (**1a**, **6a**) in Comparison with Theory (**1b**, **1c**, **6c**)

	PN_{en}	PN_{ex}	$N_{en}PN_{en}$	$N_{en}PN_{ex}$	PNC	CN	θ^a
1a	1.670(4) 1.675(4)	1.625(4) 1.644(3)	86.0(2)	112.2(2) 120.5(2) 111.8(2) 120.4(2)	81.1(3) 80.6(3)	1.368(7) 1.377(6)	8.6
1b[b]	1.655		85.4		80.7	1.343	0.0
1c[c]	1.653	1.640	85.0	110.7 125.0	81.1	1.341	12.0
6a	1.694(2) 1.689(2)	1.608(2) 1.613(2)	79.8(1)	112.7(1) 118.7(1) 112.3(1) 120.4(1)	86.8(1) 87.2(1)	1.359(3) 1.354(2)	8.0
6c[d]	1.668	1.607	80.1	107.9 126.5	86.0	1.329	16.0

[a] Twisting angle between $\angle[(N_{ex}PN_{ex})(N_{en}PN_{en})] - 90°$. [b] C_2 equilibrium geometry. [c] C_2 equilibrium geometry. [d] With NH_2 substituents at phosphorus and H at carbon.

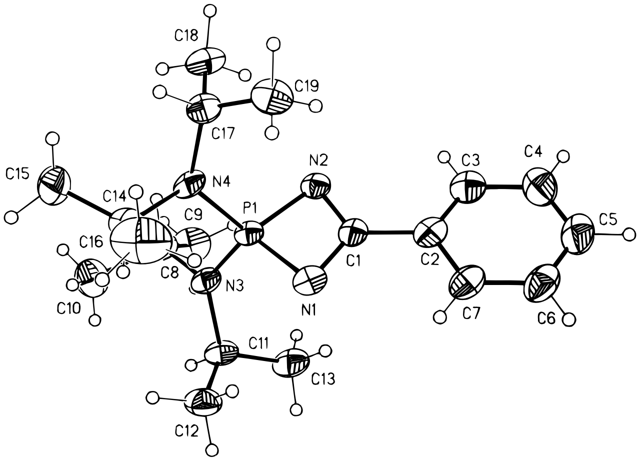

Figure 1. ORTEP plot of the diazaphosphete **1a** showing the numbering scheme used.

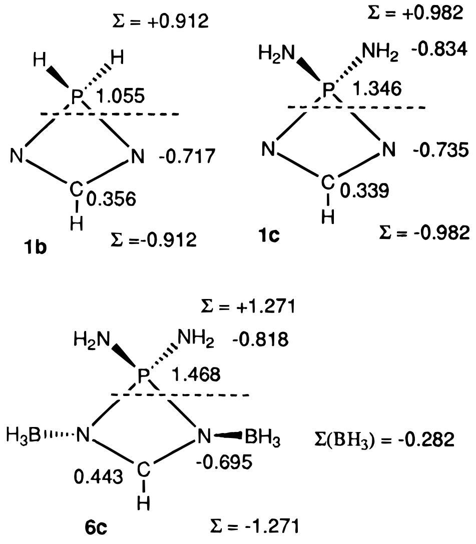

Figure 2. Electron density populations (Mulliken charges) in **1b**, **1c**, and **6c**.

optimized geometries were computed with the MP4(SDTQ(fc)) approximation.[18] All stationary points on the energy hypersurface were characterized by a vibrational analysis within the harmonic approximation. From Table 6 it is obvious that the computed structural parameters for **1c** are in good accord with the experimental results of the crystallographically determined structure of **1a**. A drawing of the molecule is shown in Figure 1, and important bond lengths and angles are given in Table 2. The four-membered ring is nearly planar as shown by the mean deviation from the best plane (0.0063 Å). A remarkably short diagonal P1···C1 distance [1.987(4) Å] is observed. It is the consequence of a strong rhomboidal distortion due to: (a) the lone pair repulsion of the endocyclic negatively charged nitrogens and (b) the strong valence angle strain at the ring carbon atom [112.4(3)°]. The exocyclic P−N bond lengths [1.625(4) and 1.644(3) Å] are shorter than the endocyclic P−N bond lengths [1.670(4) and 1.675(4) Å], which is probably due to the ring strain. Indeed, a delocalization of the positive charge towards the exocyclic amino groups by a mesomeric interaction seems unpronounced, the amino groups play rather an acceptor role via *σ*-inductive interactions as indicated by the electron density populations (Mulliken charges); the positive charge at phosphorus increases from **1b** to **1c** (from 1.055 to 1.346) (Figure 2). The C−N bond lengths [1.368(7) and 1.377(6) Å] are halfway between single and double bonds. The tetrahedral geometry around the phosphorus atom is slightly distorted (N−P−N bond angles: 86.0−120.5°). This is due to the ring strain and to the different steric environments of the lone pairs at the amino nitrogens with respect to the lone pairs of the endocyclic nitrogen atoms.[19] Moreover, the values of the N_{en}−P−N_{ex} bond angles vary from 111.8 to 120.5°. As a consequence of a facile distortional mode, which reduces the molecule from C_{2v} to the lower C_2 symmetry, a mixing of the *π*-orbitals of the endocyclic allyl anionic system with the (formal) *π*-orbitals of the diaminophosphenium unit is allowed.[20] Therefore, the zwitterionic form **1′** can be considered as the major canonical structure for 1,3,2λ^5-diazaphosphetes (Chart 2).

As mentioned above, beside the four-membered ring **1a**, a small amount of the 1,3,5,2λ^5-triazaphosphinine **2** (3%) was isolated from the reaction mixture. A similar heterocycle **G** was observed by Glemser[9] in the attempted synthesis of a 1,3,2λ^5-diazaphosphete (**F**). However, all the attempts to convert **1a** into **2** failed, even by photolysis or thermolysis in the presence of benzonitrile (**2** formally results from the insertion

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(20) As a consequence of this weak Jahn−Teller distortion the overall dipole moment is considerably reduced from C_{2v} symmetry (μ = 4.5 D, at RHF level) to C_2 (μ = 3.5 D). The energy difference between both geometries is −6.9 kcal mol^{-1} in favor of the C_2 symmetry.

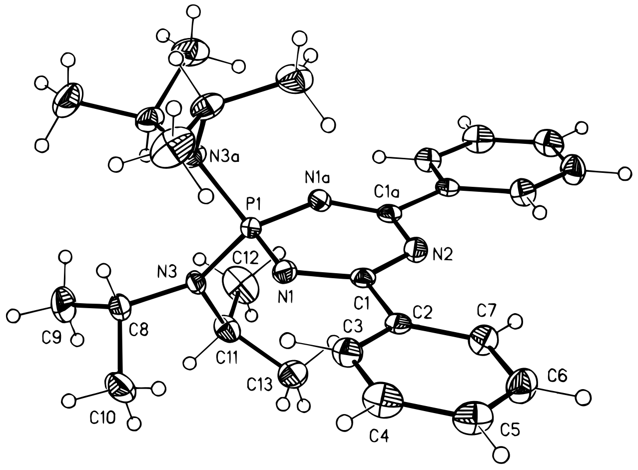
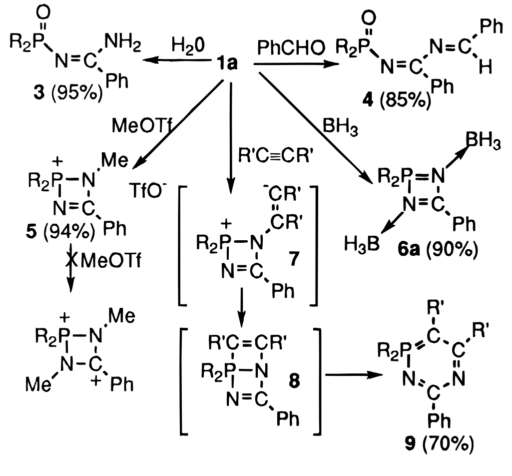


Figure 3. ORTEP plot of the triazaphosphinine **2** showing the numbering scheme used.

Scheme 1



R = (*i*-Pr)$_2$N, R' = CO$_2$Me, Tf = CF$_3$SO$_2$

of benzonitrile into a PN bond of **1a**). Although, the mechanism of the formation of **2** remains obscure, it was of interest to compare its structure with that of **1a**. The ORTEP view of the molecule is illustrated in Figure 3. Selected bond distances and angles are given in Table 3. As for the related four-membered heterocycle **1a**, the six-membered ring **2** is nearly planar as shown by the maximum deviation from the best plane (0.0052 Å), the values of the CN bond lengths (1.330−1.346 Å) are halfway between those of single and double bonds, and an almost ideal tetrahedral geometry around the phosphorus atom is observed. Here also, the zwitterionic form **2′** can be considered as being the major canonical structure for 1,3,5,2λ^5-triazaphosphinines (Chart 2).

Compound **1a** is extremely moisture sensitive; indeed a dichloromethane solution of **1a** in contact with air for a few minutes gave quantitatively the phosphine oxide **3** (95% yield) (Scheme 1), which was fully characterized, including an X-ray crystal analysis (Figure 4, Table 4). This reaction is analogous to that observed in the hydrolysis of linear iminophosphoranes.

In the same way, a classical aza-Wittig reaction[21] was observed on addition of benzaldehyde to **1a** (although the reaction is slow: 5 days at 50 °C) leading to **4** as a single isomer (85% yield) (Scheme 1).

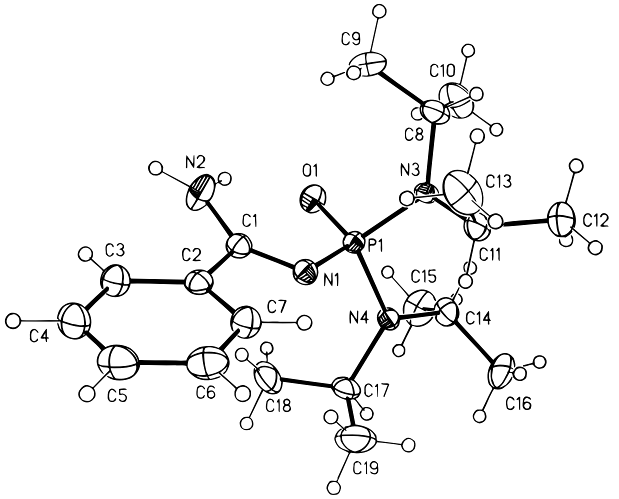


Figure 4. ORTEP plot of the phosphine oxide **3** showing the numbering scheme used.

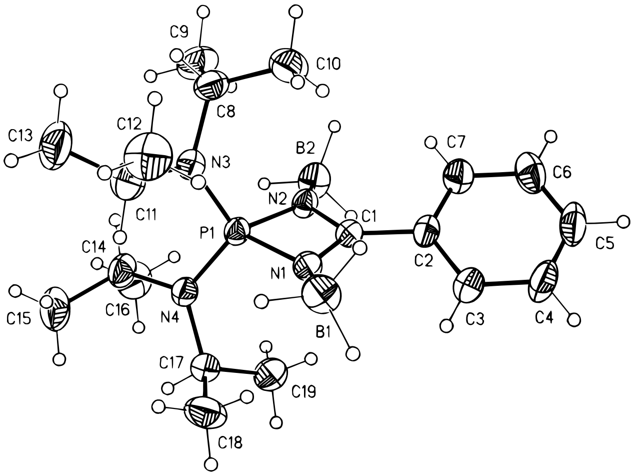


Figure 5. ORTEP plot of the bis(borane) complex **6a** showing the numbering scheme used.

The HOMO of the four-membered ring **1** is located at the endocyclic nitrogen atoms (for **1c** computed to be −8.7 eV); it is a mixture of the nonbonding lone pair orbitals of the endocyclic nitrogen atoms and the nonbonding allylic π-orbital within the ring system. Thus, methyl trifluoromethanesulfonate cleanly reacts with **1a**, affording the cyclic phosphonium salt **5** (94% yield). Note that the values of the ^{31}P NMR chemical shifts observed for **1a** (+54.2) and **5** (+51.6) are very close, confirming the cationic character of the phosphorus atom of **1a**. The use of excess alkylating reagent did not afford the bis-methylated derivative (Scheme 1).

In contrast, 2 equiv of a neutral Lewis acid, such as BH$_3$, reacted with diazaphosphete **1a** leading to the bis-adduct **6a** in 90% yield. From the spectroscopic data it seems that the 4π-electron 4-membered ring structure is only slightly disturbed by the complexation of the ring nitrogens. Indeed, the NMR spectra of **6a** [^{31}P NMR, +47.8; ^{13}C NMR, 186.1, $J_{PC} = 24.5$ Hz, NCN)] are comparable to those of **1a** [^{31}P NMR, +54.2 ppm; ^{13}C NMR, 194.7, $J_{PC} = 48.4$ Hz, NCN)]. This similarity was confirmed by an X-ray crystal analysis. The ORTEP view of **6a** is shown in Figure 5, and selected bond distances and angles are given in Table 5. The four-membered ring **6a** is nearly planar as shown by the mean deviation from the best plane (0.013 Å). Since the negative charge can now be delocalized onto the BH$_3$ fragments, the repulsion between the endocyclic nitrogen atoms decreases and thus, the diagonal P1···C1 distance [2.111(2) Å] in **6a** is longer than that observed in **1a** [1.987(4) Å] and the N1−P1−N2 angle is more accute [79.8(1)°]. The overal dipole moment calculated for **6c** is $\mu =$

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(21) Johnson A.W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993.

6.1 D, compared to 3.5 D for **1c** (Figure 2). Since overall the molecule of **6c** adopts C_2 symmetry, the nonbonding π-orbital (π_2-orbital of an allyl system) interacts with the nonbonding lone pair orbitals of the endocyclic nitrogen atoms. As a consequence, the BH_3 units will preferentially complex in a position which is out of the plane of the four-membered ring system. Indeed an out of plane tilting of BH_3 is observed in the experiment (mean deviation 0.42 Å) and is well reproduced by the quantum chemical calculations (Table 6).

Lastly, diazaphosphete **1a** reacts at room temperature with dimethyl acetylenedicarboxylate leading to the 1,3,4λ^5-diazaphosphinine **9** in 70% yield. Formation of this new type of heterocycle can easily be rationalized by the attack of the nitrogen atom on the electron-poor alkyne, leading to a zwitterionic intermediate **7**, which undergoes a ring closure affording a transient "hetero-Dewar-benzene", **8**, (Scheme 1).

These results as a whole clarify the bonding situation in four-π-electron four-membered heterocycles with only one heteroatom possessing no available p-orbital, i.e., the case of an interrupted cyclic π-delocalization. It appears that these compounds are zwitterionic with the negative charge delocalized on an allylic fragment and the positive charge localized at the heteroatom. These compounds are very reactive and are therefore valuable building blocks in heterocyclic chemistry. In the case of 1,3,2λ^5-diazaphosphetes, the possibility of double complexation with Lewis acid is of primary interest and should open a route to polymers containing both a transition metal and the four-membered ring fragments.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points were obtained on a Electrothermal capillary apparatus and were not corrected. ^{1}H, ^{31}P, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P and ^{11}B downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and $BF_3.OEt_2$, respectively. Infrared spectra were recorded on a Perkin-Elmer 1725 X instrument. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Hydrolysis of 1a. A dichloromethane solution (1.5 mL) of diazaphosphete **1a** (0.20 g, 0.57 mmol) was stirred at room temperature, in contact with air. The reaction, monitored by ^{31}P NMR spectroscopy, was complete after 4 h. The solvent was removed under vacuum affording **3** as a white powder. Single crystals suitable for X-ray analysis have been obtained by recrystallization from a dichloromethane solution at −20 °C (0.2 g, 95% yield): mp 238−239 °C; ^{31}P NMR-{^{1}H} ($CDCl_3$) +23.1; ^{1}H NMR ($CDCl_3$) 1.16 (d, *J*(HH) = 6.7 Hz, 12 H, CH_3), 1.17 (d, *J*(HH) = 6.7 Hz, 12 H, CH_3), 3.52 (sept d, *J*(HH) = 6.7 Hz, *J*(PH) = 17.6 Hz, 4 H, NCH), 7.25−8.00 (m, 5 H, H_{arom}), 8.80 (s, 2 H, NH); ^{13}C NMR ($CDCl_3$) 22.6 (d, *J*(PC) = 1.8 Hz, CH_3), 22.9 (d, *J*(PC) = 1.7 Hz, CH_3), 45.1 (d, *J*(PC) = 5.2 Hz, NCH), 126.7 (d, *J*(PC) = 1.0 Hz, C_o), 128.4 (s, C_m), 130.9 (s, C_p), 136.6 (d, *J*(PC) = 22.6 Hz, C_i), 159.9 (d, J(PC) = 4.9 Hz, NCN). Anal. Calcd for $C_{19}H_{35}N_4OP$: C, 62.27; H, 9.63; N, 15.30. Found: C, 62.60; H, 9.65; N, 15.34.

Addition of Benzaldehyde to 1a. To a THF solution (3 mL) of diazaphosphete **1a** (0.85 g, 2.44 mmol) was added at room temperature benzaldehyde (0.26 g, 2.45 mmol). After the solution was stirred for 5 days at 50 °C, the solvent was removed under vacuum, and the residue was washed several times with pentane affording **4** as a yellow powder (0.94 g, 85% yield): mp 162−164 °C; ^{31}P NMR{^{1}H} ($CDCl_3$) +11.6; ^{1}H NMR ($CDCl_3$) 1.22 (d, *J*(HH) = 6.8 Hz, 24 H, CH_3), 3.67 (sept d, *J*(HH) = 6.8 Hz, *J*(PH) = 17.4 Hz, 4H, NCH), 7.30−8.00 (m, 10 H, $H_{arom.}$), 8.41 (s, 1 H, N═CH); ^{13}C NMR ($CDCl_3$) 22.8 (s, CH_3), 45.2 (d, *J*(PC) = 5.2, NCH), 128.0, 128.1, 128.2, 128.4, 128.7, 129.4 (s, C_{aro}), 131.6 (d, *J*(PC) = 17.7 Hz, C_i), 134.8 (s, C_i), 161.2 (s, PNCN═*C*), 166.1 (d, *J*(PC) = 5.7 Hz, PNC). Anal. Calcd for $C_{26}H_{39}N_4OP$: C, 68.69; H, 8.65; N, 12.33. Found: C, 68.80; H, 8.76; N, 12.11.

Synthesis of Alkylated Compound 5. To a toluene solution (5 mL) of diazaphosphete **1a** (0.52 g, 1.49 mmol) was added at room temperature methyl trifluoromethanesulfonate (0.24 g, 1.49 mmol). Immediately compound **5** precipitated as a white powder and was isolated by filtration (0.72 g, 94% yield): mp 93−95 °C; ^{31}P NMR-{^{1}H} ($CDCl_3$) +51.6; ^{1}H NMR ($CDCl_3$) 1.38 (d, *J*(HH) = 6.8 Hz, 12 H, CH_3), 1.39 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 3.45 (d, *J*(PH) = 16.5 Hz, 3 H, CH_3N), 3.88 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 20.5 Hz, 4 H, NCH), 7.50−8.10 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 21.9 (s, CH_3), 22.8 (s, CH_3), 33.3 (d, *J*(PC) = 8.1 Hz, CH_3N), 49.9 (d, J(PC) = 3.8 Hz, NCH), 129.9 (s, C_m), 130.0 (s, C_o), 136.4 (s, C_p), 184.5 (d, J(PC) = 23.5 Hz, NCN), C_i not observed. Anal. Calcd for $C_{21}H_{36}N_4O_3F_3PS$: C, 49.21; H, 7.08; N, 10.93. Found: C, 49.35; H, 6.89; N, 10.67.

Synthesis of the Bis-BH$_3$ Adduct 6a. To a toluene solution (5 mL) of diazaphosphete **1a** (0.30 g, 0.86 mmol) was added at room temperature 10 mL of a BH_3·THF solution (1 M). After the solution was stirred for 15 min at room temperature, the solvent was removed under vacuum, and complex **6a** was obtained as white crystals from a toluene solution at −20 °C (0.29 g, 90% yield): mp 133−134 °C; ^{31}P {^{1}H} NMR ($CDCl_3$) +47.8; ^{11}B {^{1}H} NMR ($CDCl_3$) −21.5;^{1}H NMR ($CDCl_3$) 1.25 (m, 6 H, BH_3), 1.46 (d, *J*(HH) = 6.9 Hz, 24 H, CH_3), 3.85 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 18.6 Hz, 4 H, NCH), 7.50−8.80 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 22.0 (d, *J*(PC) = 1.9 Hz, CH_3), 50.0 (d, *J*(PC) = 4.0 Hz, NCH), 124.9 (d, *J*(PC) = 18.9 Hz, C_i), 128.2 (s, C_m), 133.8 (s, C_o), 135.5 (s, C_p), 186.1 (d, *J*(PC) = 24.5 Hz, NCN). Anal. Calcd for $C_{19}H_{39}N_4B_2P$: C, 60.67; H, 10.45; N, 14.90. Found: C, 60.70; H, 10.44; N, 14.99.

Synthesis of Diazaphosphinine 9. To a THF solution (3 mL) of diazaphosphete **1a** (0.49 g, 1.40 mmol) was added at room temperature dimethyl acetylenedicarboxylate (0.20 g, 1.41 mmol). After the solution was stirred for 3 h at room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane. Evaporation of pentane afforded **9** as a brown powder (0.40 g, 70% yield): mp 149−151 °C; ^{31}P NMR{^{1}H} ($CDCl_3$) +27.8; ^{1}H NMR ($CDCl_3$) 1.12 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 1.29 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 3.70 (s, 3 H, CH_3O), 3.87 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 17.2 Hz, 4 H, NCH), 3.90 (s, 3 H, CH_3O), 7.30−8.40 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 23.2 (s, CH_3), 23.8 (s, CH_3), 47.3 (d, *J*(PC) = 5.2, NCH), 50.9 (s, CH_3O), 52.4 (s, CH_3O), 86.2 (d, *J*(PC) = 128.0 Hz, PC), 127.9 (s, C_m), 129.1 (s, C_o), 130.9 (s, C_p), 138.7 (d, *J*(PC) = 17.8 Hz, C_i), 165.8 (d, *J*(PC) = 3.2 Hz, NCN), 166.5 (d, *J*(PC) = 3.2 Hz, PC*C*), 167.2 (d, *J*(PC) = 5.9 Hz, CO), 168.7 (d, *J*(PC) = 15.7 Hz, CO); mass spectrum (FAB) m/z 491 (M+1); Anal. Calcd for $C_{25}H_{39}N_4O_4P$: C, 61.21; H, 8.01; N, 11.42. Found: C, 60.87; H, 7.81; N, 11.62.

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Supporting Information Available: Crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, and least-squares planes equations for componds **1a**, **2**, **3**, and **6a** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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