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A Bridgehead Pentaamino Phosphorus Atom in an Aminodiazadiphosphetospirobi[triazaphosphole]. The First PN_5 Structure[1,2]

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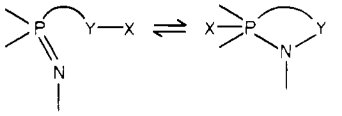
The aminodiazadiphosphetospirobi[triazaphosphole] (7) forms by simple amine substitution on 6. The latter results from a phosphazene–azaphosphetidine tautomerism of the (chlorophosphonyl)spirobi[triazaphosphole] (5). The crystal structure of 7 reveals a nearly trigonal-bipyramidal phosphorus atom and a tetrahedral phosphorus atom. The structural determination of 7 represents the first example of a pentacoordinated compound containing the PN_5 unit. ^1H, ^{13}C, and ^{31}P NMR data verify the structural similarity between 6 and 7. 7 crystallizes as the 1:1 benzene solvate in the monoclinic space group $C2/c$ with a = 25.386 (8) Å, b = 9.636 (1) Å, c = 28.640 (8) Å, β = 126.50 (3)°, and Z = 8. Refinement led to the values of R = 0.046 and R_w = 0.054 for the 3043 reflections having $I \geq 2\sigma_I$. 7 contains both a very long and a very short P–N bond as well as being the first example of phosphorane having an unsubstituted amino group. The plane of the equatorial amino group is nearly perpendicular to the equatorial plane, thus supporting the presence of P–N π bonding. The generality of the proposed tautomerism leading to 7 is discussed for a reaction sequence yielding the related triazaphosphole 3 as well as a possible role in the formation of cyclophosphazenes.

Introduction

Pentacoordinated phosphorus is greatly stabilized in bridgehead positions of oligocyclic systems containing triazaphospholes fused to diazadiphosphetidine rings. For example, when 2-methyl-5-phenyl-1,2,4,3-triazaphosphole (**1**) is exhaustively chlorinated (Scheme I), dimer **2** of its 3,3-dichloro derivative is the sole product.[4] We determined that the crystal structure of **2** and its fluoro analogue contain pentacoordinated phosphorus in a cis-facial arrangement halfway between the idealized trigonal bipyramid and square pyramid.[5]

If less than 1 mol of chlorine is added to **1**, complex mixtures of products are obtained.[6] One of the isolated products **3** results when **1** is reacted with chlorine in the ratio of 3:2. The reaction is accompanied by loss of PCl_3. **3** also results from the reaction of equimolar amounts of **1** and **2**. We have shown that the X-ray structure of **3**[7] contains two triazaphosphole rings condensed to a diazadiphosphetidine as in **2** but to adjacent edges rather than to opposite ones. The two diazaphosphole rings thus have one phosphorus atom of the diazadiphosphetidine ring in common while the other phosphorus atom is shared with a third triazaphosphole ring as a spirocenter.

As an aid in elucidating the mechanism by which **3** forms, a series of derivatives of the spirobi[triazaphosphole] (**4**) were prepared (Scheme II).[8] Among these, the chorophosphinyl derivative **5** is instructive. It, in fact, spontaneously undergoes rearrangement to **6** in which the spiro center phosphorus atom has become pentacoordinate. The rearrangement of **5** to **6** illustrates the possible existence of a phosphazene–azaphosphetidine tautomerism



which might prove general in describing the mechanism of formation of **3** and related diazadiphosphetidines.

To establish the structure illustrated for **6**, the amino derivative **7** was subjected to X-ray analysis. The formation of **7** represents a simple substitution of **6** with no major structural change expected.

Experimental Section

The X-ray crystallographic study was done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[9]

A sample of **7** was recrystallized from a 50:50 mixture of $CHCl_3$ and benzene. Large, colorless lath-shaped crystals of **7** were obtained, which proved to be the 1:1 benzene solvate. A roughly triangular-prismatic crystal (edge length 0.37 mm, height 0.25 mm), cut from a larger crystal and mounted inside a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray studies.

Crystal Data for $C_{22}H_{23}ON_7P_2 \cdot C_6H_6$ (7): monoclinic space group $C2/c$ [C_{2h}^6-No. 15][10] and Z = 8, from $2/m$ diffraction symmetry, extinctions, and successful solution and refinement; a = 25.386 (8) Å, b = 9.636 (1) Å, c = 28.640 (8) Å, β = 126.50 (3)°, and $\mu_{\mathrm{Mo}\,K\bar{\alpha}}$ = 0.194 mm^{-1}; 4925 independent reflections ($+h$, $+k$, $\pm l$) measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 50°$; no corrections made for absorption.

The structure was solved by using a combination of direct methods (MULTAN) and difference Fourier techniques and refined by using full-matrix least squares.[11] The 38 independent non-hydrogen atoms were refined anisotropically. Coordinates for only the two amino hydrogen atoms were refined, and isotropic thermal parameters for all hydrogen atoms were fixed. Coordinates for the 21 aromatic hydrogen atoms were calculated and updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Fixed coordinates for the six methyl hydrogen atoms and initial coordinates for the two amino hydrogen atoms were obtained from a difference Fourier

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(1) (a) Pentacoordinate Molecules. 48. (b) Previous paper in this series: Sau, A. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R., *Inorg. Chem.* **1983**, *22*, 1771.

(2) (a) Four- and Five-membered Phosphorus Heterocycles. 60. (b) Part 59: Karaghiosoff, K.; Majoral, J. P.; Meriem, A.; Navech, J.; Schmidpeter, A. *Tetrahedron Lett.* **1983**, *24*, 2137.

(3) (a) University of Massachusetts. (b) University of München.

(4) Schmidpeter, A.; Luber, J.; Tautz, H. *Angew. Chem.* **1977**, *89*, 554; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 546.

(5) Day, R. O.; Holmes, R. R.; Tautz, H.; Weinmaier, H.; Schmidpeter, A. *Inorg. Chem.* **1981**, *20*, 1222.

(6) Schmidpeter, A.; Nayibi, M.; Renoth, P.; Tautz, H. Abstracts, 3rd International Symposium on Inorganic Ring Systems, Graz, Austria, Aug 1981; p 30.

(7) Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 3916.

(8) Schmidpeter, A.; Nayibi, M.; Mayer, P.; Tautz, H. *Chem. Ber.* **1982**, *248*.

(9) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 101.

(11) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean scattering factors were taken from: Reference 10, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for O and P were taken from the same source, pp 149–150.

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Scheme I

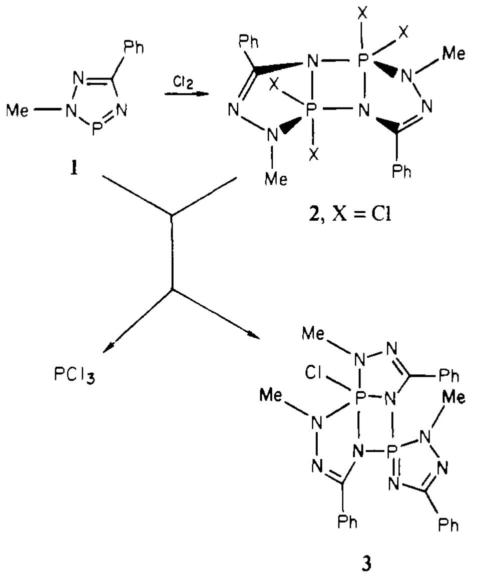

Table I. Atomic Coordinates in Crystalline $C_{22}H_{23}ON_7P_2{\cdot}C_6H_6$ (7)[a]

atom type[b]	10^4x	10^4y	10^4z
P1	3632.7 (4)	3561 (1)	1247.2 (4)
P2	3726.3 (4)	1582 (1)	676.6 (4)
O	3397 (1)	1348 (3)	53 (1)
NP	2943 (2)	4402 (3)	872 (1)
NA1	4164 (1)	4953 (3)	1563 (1)
NA2	4601 (1)	5099 (3)	1422 (1)
NA4	4034 (1)	3167 (3)	952 (1)
NB1	3818 (1)	2795 (3)	1863 (1)
NB2	3457 (1)	1599 (3)	1783 (1)
NB4	3271 (1)	1883 (3)	910 (1)
CA1	4067 (2)	6252 (4)	1768 (2)
CA3	4530 (2)	4094 (3)	1089 (1)
CA4	4936 (2)	3944 (4)	885 (2)
CA5	5535 (2)	4637 (4)	1177 (2)
CA6	5911 (2)	4535 (6)	975 (2)
CA7	5700 (3)	3763 (6)	488 (2)
CA8	5114 (3)	3074 (5)	201 (2)
CA9	4728 (2)	3156 (4)	400 (2)
CB1	4104 (2)	3454 (5)	2428 (1)
CB3	3193 (2)	1088 (4)	1273 (1)
CB4	2817 (2)	−212 (4)	1077 (2)
CB5	2447 (2)	−593 (4)	498 (2)
CB6	2101 (2)	−1836 (5)	318 (2)
CB7	2111 (2)	−2680 (4)	707 (2)
CB8	2475 (2)	−2297 (5)	1288 (2)
CB9	2829 (2)	−1074 (4)	1472 (2)
CC1	4348 (2)	322 (4)	1108 (1)
CC2	4432 (2)	−767 (4)	837 (2)
CC3	4916 (2)	−1734 (4)	1159 (2)
CC4	5334 (2)	−1617 (4)	1756 (2)
CC5	5260 (2)	−559 (4)	2029 (2)
CC6	4765 (2)	415 (4)	1707 (2)
CS1	1338 (4)	5567 (6)	1518 (4)
CS2	1260 (3)	4830 (8)	1092 (3)
CS3	1677 (4)	3834 (8)	1197 (3)
CS4	2188 (3)	3555 (7)	1760 (3)
CS5	2273 (3)	4281 (9)	2201 (2)
CS6	1835 (4)	5308 (7)	2079 (3)
HN1	2566 (20)	3959 (44)	621 (17)
HN2	2931 (20)	5290 (44)	885 (18)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

Scheme II

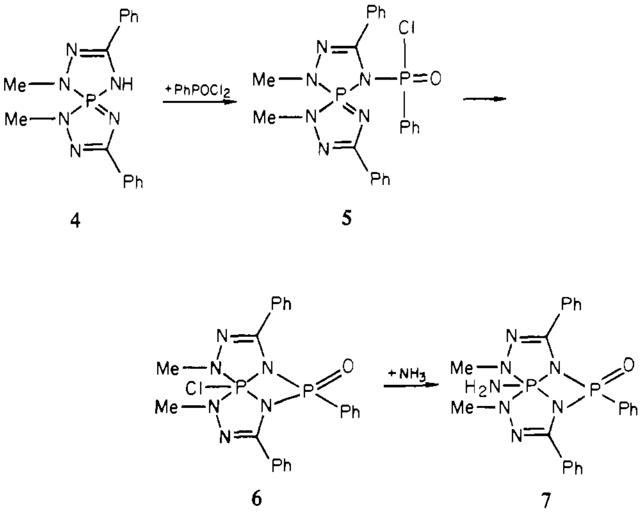

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $C_{22}H_{23}ON_7P_2{\cdot}C_6H_6$ (7)[a,b]

P1-NA1	1.728 (3)	CA3-NA4	1.396 (4)
P1-NB1	1.700 (3)	CB3-NB4	1.397 (4)
P1-NA4	1.710 (3)	CA3-CA4	1.462 (5)
P1-NB4	1.826 (3)	CB3-CB4	1.470 (5)
P1-NP	1.625 (3)	P2-NA4	1.683 (3)
NA1-CA1	1.464 (4)	P2-NB4	1.667 (3)
NB1-CB1	1.468 (4)	P2-CC1	1.781 (4)
NA1-NA2	1.395 (4)	P2-O	1.471 (2)
NB1-NB2	1.403 (4)	NP-HN1	0.89 (4)
NA2-CA3	1.294 (4)	NP-HN2	0.86 (4)
NB2-CB3	1.290 (4)	HN1- - -O	2.04 (4)
NA1-P1-NB4	162.6 (1)	NA2-CA3-NA4	113.1 (3)
NB1-P1-NA4	122.6 (1)	NA2-CA3-CA4	123.1 (3)
NP-P1-NA4	120.5 (2)	CA4-CA3-NA4	123.8 (3)
NP-P1-NB1	115.3 (2)	CA3-NA4-P1	115.0 (2)
NA1-P1-NP	99.1 (2)	CA3-NA4-P2	143.3 (2)
NA1-P1-NA4	85.5 (1)	P1-NA4-P2	100.7 (1)
NA1-P1-NB1	98.4 (1)	P1-NB1-CB1	127.3 (3)
NB4-P1-NP	95.0 (1)	P1-NB1-NB2	115.9 (2)
NB4-P1-NB1	84.6 (1)	CB1-NB1-NB2	112.4 (3)
NB4-P1-NA4	78.5 (1)	NB1-NB2-CB3	110.2 (3)
O-P2-NA4	118.6 (1)	NB2-CB3-NB4	115.2 (3)
O-P2-NB4	118.9 (1)	NB2-CB3-CB4	122.7 (3)
O-P2-CC1	111.5 (2)	CB4-CB3-NB4	122.1 (3)
CC1-P2-NA4	108.7 (1)	CB3-NB4-P1	109.9 (2)
CC1-P2-NB4	112.3 (1)	CB3-NB4-P2	129.9 (2)
NA4-P2-NB4	83.9 (1)	P1-NB4-P2	96.7 (1)
P1-NA1-CA1	127.5 (3)	P1-NP-HN1	121 (3)
P1-NA1-NA2	115.7 (2)	P1-NP-HN2	121 (3)
CA1-NA1-NA2	112.5 (3)	HN1-NP-HN2	118 (4)
NA1-NA2-CA3	110.6 (3)	NP-HN1- - -O	160 (4)

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 1.

synthesis. The final agreement factors[12] were $R = 0.046$, $R_w = 0.054$, and GOF = 1.284 for the 3043 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.198 e/Å^3.

Results and Discussion

Structural Aspects. The atom-labeling scheme for **7** is shown in the ORTEP plot of Figure 1. Atomic coordinates for all non-hydrogen atoms and for the amino hydrogen atoms are given in Table I, and selected bond lengths and angles are given in Table II. Anisotropic thermal parameters and fixed hydrogen atom parameters are provided as supplementary material.

The geometry about the five-coordinated phosphorus atom, P1, lies between an idealized trigonal bipyramid (TP), having NP, NA4, and NB1 equatorially positioned and NA1 and NB4 in axial positions, and an idealized rectangular pyramid with NP in the apical position. It contains the same fused ring system as **3**.[7] In terms of the Berry coordinate[13] the geometry

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(12) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $N_o = 3043$ and $N_v = 349$.

Table III. NMR Data of the Chloro- and Aminodiazadiphosphetospirobi[triazaphospholes] **6** and **7** in $CDCl_3$ (J in Hz)

		6^a		7
$\delta(^1H)$	NMe (J_{PNCH})	3.22 (11.1)	3.33 (9.0)	3.30 (7.3)
	NH_2 (J_{PNH})			3.47 (9.4)
$\delta(^{13}C)$	NMe (J_{PNC})	37.1 (7.9)		36.4 (9.8)
	PPh, C_i (J_{PC}, J_{PNPC})	131.8 (103.8, 3.7)	131.2 (110.5, 3.7)	131.4 (80.6, 3.1)
	C_o (J_{PCC})	132.8 (12.2)	132.3 (12.2)	132.2 (11.6)
	C-5 (J_{PNC}, J_{PNC})	142.9 (19.9, 2.7)	142.9 (20.8, . . .)	141.2 (15.3, 1.8)
$\delta(^{31}P)$	σ^5P	−30.2	−25.7	−45.6
	σ^4P (J_{PNP})	1.0 (60.1)	5.5 (51.0)	5.7 (44.1)

[a] Two diastereomers.

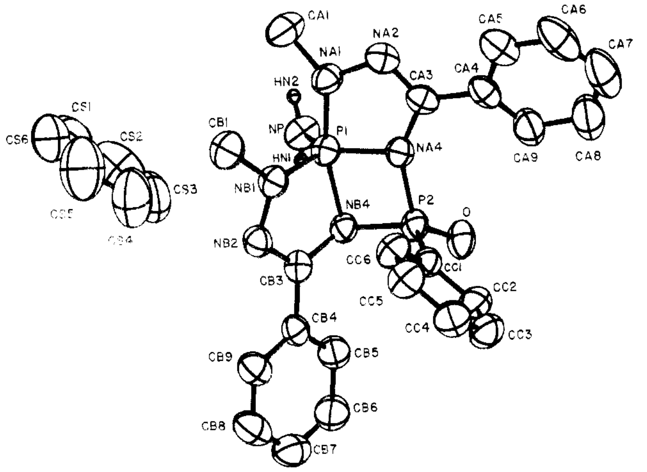
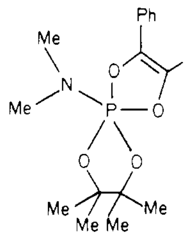


Figure 1. ORTEP plot of $C_{22}H_{23}ON_7P_2 \cdot C_6H_6$ (**7**) with thermal ellipsoids shown at the 50% probability level. All but the amino hydrogen atoms, which are shown as spheres of arbitrary radius, have been omitted for purposes of clarity.

is displaced, on the average, 26.2%[14] (23.8% using unit vectors) from the TP towards the RP. This compares with 34.1% (40.4%) for the related structure **3**.[7] Each of the three rings is attached to the TP phosphorus atom by an axial and an equatorial bond providing an endocyclic angle <90° for each of them (Table II).

The X-ray analysis of **7** not only represents the first pentacoordinated phosphorus crystal structure containing the PN_5 unit[15] but also is a rare example of a phosphorane structure with an unsubstituted amino group.[16] It is somewhat surprising that a five-coordinated phosphorus atom with only nitrogen-bonded substituents is stable and does not revert to the tetracoordinated state by tautomeric rearrangement.[15b] The fact that there is a 0.2-Å variation in the P–N bond lengths (Table II) suggests some potential instability.

The geometry about the equatorial amino nitrogen atom NP is essentially planar, as evidenced by the sum of the three angles about NP of 360°. The plane of the amino group is nearly perpendicular to the equatorial plane. The dihedral angle between the least-squares mean plane defined by NP, P1, HN1, and HN2 and that defined by P1, NP, NB1, and NA4 is 87.3°. X-ray analysis of the dimethylaminophosphoranes **8**[17] and **9**[18] shows that they also contain planar equatorially positioned amine nitrogen atoms. Here the planes of the dimethylamino groups make angles of 62 and 72°, respectively, with the equatorial plane. Planarity at nitrogen and orientation of the plane of the amino groups perpendicular to the equatorial plane are factors contributing to maximum P–N π bonding.[19] In view of the near 90° orientation found for the amine group in **7**, the presence of a steric effect largely between the amine methyl groups and axial atoms of **8** and **9**, previously cited,[20] is supported here.



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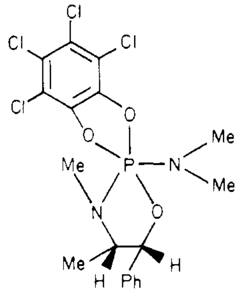

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Consistent with the orientation of the amino group in **7** is the length of the attached P1–NP bond, 1.625 (3) Å. This is a very short P–N bond,[21] close to that (1.590 (8) Å) for $H_2N\overline{P-[OC(CF_3)_2C(CF_3)_2O]}_2$.[16] The ring equatorial P–N bond lengths average 1.705 (3) Å while the axial P–N bond lengths are considerably longer, 1.777 (3) Å, as commonly observed.[21] The axial P1–NB4 bond length, 1.826 (3) Å is the longest P–N bond reported for a phosphorane.[21] Correspondingly, the tendency of the equatorial ring nitrogens to achieve trigonal planarity is greater than that of the axial nitrogens.

There is a close similarity in bond parameters between the common structural parts of **7** and **3**.[7] The equatorial chlorine atom in **3** causes a general contraction of the bond lengths at the pentacoordinated phosphorus atom relative to those for **7**. In terms of electron pair repulsions,[22] P–N π bonding lessens these repulsions in **3**. The average contraction in length is 0.04 Å.

The molecules exist in the solid as hydrogen-bonded dimers. HN1 and O enter into hydrogen-bonding interactions with O and HN1, respectively, of a second molecule that is related to the first by an inversion center, where the HN1 to O dis-

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(13) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(14) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(15) (a) The synthesis of one other pentaaminophosphorane, a cyclen aminophosphorane, has been reported: Richman, J. E. (to E. I. du Pont de Nemours and Co.), U.S. Patent 3 987 128, 1976. (b) In another case, a PN_5 unit was originally cited as present in a diazadiphosphetidine similar to **7**: Appel, R.; Halstenberg, M. *Angew. Chem.* **1977**, *89*, 268; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 263; *Chem. Ber.* **1978**, *111*, 1815. However, X-ray analysis revealed an open-chain zwitterionic PN_4 structure instead: Halstenberg, M.; Appel, R.; Huttner, G.; v. Seyerl, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1491.

(16) The crystal structure of $H_2NP[O_2C_2(CF_3)_4]_2$ is reported in: Storzer, W.; Schomburg, D.; Röschenthaler, G.-V. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1071.

(17) Szobota, J. S.; Holmes, R. R. *Inorg. Chem.* **1977**, *16*, 2299.

(18) Weiss, R. In: Klaebe, A. D.Sc. Thesis, Paul Sabatier University, Toulouse, France, 1977, p 45.

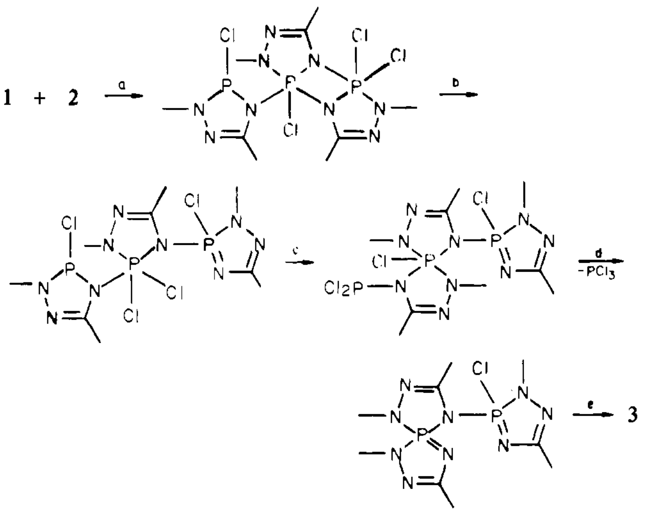
(19) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

(20) Holmes, R. R. *ACS Monogr.* **1980**, *No. 176*, 27.

(21) For structural results on other nitrogen-containing phosphoranes, see: Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*, 12-33.

(22) Gillespie, R. J. "Molecular Geometry"; Van Nostrand Reinhold: Princeton, NJ, 1972.

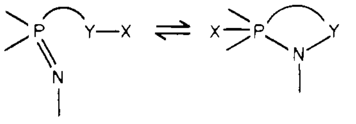
Scheme III



tance is 2.04 (4) Å as compared to the van der Waals sum of 2.6 Å.

Tautomeric Mechanism. From the similarity of the ^1H, ^{13}C, and ^{31}P NMR data listed in Table III, it may be concluded that replacement of the chloro group in **6** by an amino group occurs without any major structural change. However, **6** exists in soln. as a roughly 1:1 mixture of two diastereomers, whereas **7** is present entirely in one isomeric form, presumably that found in the crystalline state. The two diastereomers differ in positioning the amino group cis or trans to the phosphonyl oxygen atom attached to P2. For **7**, J_{PNH}, as expected, is smaller than the values found for fluoro-, chloro-, and oxyaminophosphoranes (16–19 Hz).[23]

The structures established for **6** and **7** tend to support the phosphazene–azaphosphetidine tautomerism



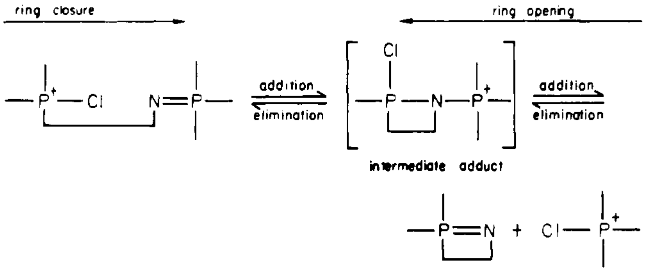
postulated for the rearrangement of **5** to **6** (Scheme II). This type of tautomeric rearrangement is also implicated in a reasonable multistep mechanism for the formation of the related fused-ring phosphetidine **3**. Scheme III shows a possible route of how the chlorine atom concentrates at the tervalent phosphorus. Substituents have been omitted for clarity. According to this scheme, the diazaphosphole ring of **3** would form in the final step (e) by an intramolecular addition of a P–Cl unit to a phosphazene bond. Step b, initiating the rearrangement, would be of a reverse type.

The PCl addition to the P═N bond apparent in the tautomeric rearrangement of **5** to **6** is based principally on the destabilization of phosphorus tetracoordination in the phosphazene or relative stabilization of phosphorus pentacoordination in the chlorophosphorane when the phosphorus atom is a member of a small ring.[24] This stabilization is enhanced if the phosphorus atom is at the spiro center of two small rings and even more so if it is at the bridgehead of two or three fused rings.[5,7]

In a broader application, the phosphazene–azaphosphetidine tautomerism supported in this paper may be relevant in understanding the mechanism of formation of cyclophosphazene rings from polyphosphazene chains[25]

$$Cl_3P(NPCl_2)_nNPCl_3^+ \rightleftharpoons (NPCl_2)_{n+1} + PCl_4^+$$

and the mechanism of ring opening of cyclic phosphazenes in the presence of PCl_5.[26]



The phosphorane tautomerism may be considered as an intramolecular version (with $-Y-X = {>}P^+-Cl$) of the individual steps in the latter mechanistic sequence (see ref 8). The key intermediate in this reaction sequence normally is not observed. In our case, the "adduct" is readily observed. In fact, it is so stable it is not an intermediate but becomes the product. In this sense, the phosphorane tautomers serve as useful models for the intermediate in the above mechanism.

In summary, the structure work presented here supports the presence of a phosphazene–azaphosphetidine tautomerism. In its simplest form, considerable potential exists for its utility in new synthetic applications and in understanding mechanistic features of some existing reactions.

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Registry No. **5**, 87517-61-1; **6** (isomer 1), 86213-73-2; **6** (isomer 2), 86259-16-7; **7**, 87583-17-3.

Supplementary Material Available: Thermal parameters (Table A), hydrogen atom parameters (Table B), and a listing of observed and calculated structure factor amplitudes for **7** (15 pages). Ordering information is given on any current masthead page.

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(23) Storzer, W.; Röschenthaler, G.-V.; Schmutzler, R.; Sheldrick, W. S. *Chem. Ber.* **1981**, *114*, 3609.

(24) Sheldrick, W. S.; Schomburg, D.; Schmidpeter, A.; von Criegern, T. *Chem. Ber.* **1980**, *113*, 55.

(25) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.

(26) Allcock, H. R.; Gardner, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.