Heteroatom Chemistry
Volume 10, Number 3, 1999

Structural Changes in a 1,2λ^5-Azaphosphole/Nitrilimine Cycloaddition

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Received 7 August 1998; revised 13 October 1998

ABSTRACT: *Diphenylnitrilimine adds to the phosphazene bond of the azaphosphole* **1**. *A single-crystal X-ray investigation of the cycloadduct* **3** *shows a planar bicyclo[3.3.0]octane skeleton meridional to the trigonal bipyramidal phosphorus. The structural data are compared to those of the starting compound* **1**, *to those of the trifluoroacetone adduct* **2**, *and to the change from ideal tetrahedral to ideal tbp geometry.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:243–245, 1999

PHOSPHAZENE CYCLOADDITIONS

1,2λ^5-Azaphospholes such as **1** contain a phosphazene unit as part of a five-membered ring. They show a reactivity considerably higher than that of acyclic, six-membered, or larger ring phosphazenes. The difference is best demonstrated by a variety of cycloaddition reactions of **1** and related compounds [1] and becomes visible in particular by the high stability of the cycloadducts of **1**. The difference can be explained by geometrical considerations [2]: The five-membered ring necessitates a relatively small endocyclic angle at phosphorus (98.5° for **1**, Table 1) meaning some distortion of the tetrahedral coordination in the starting compound. The two small endocyclic angles at phosphorus as a bridgehead of the bicyclo[3.2.0]heptane skeleton resulting from a [2 + 2] cycloaddition of **1** or of the bicyclo[3.3.0]octane skeleton resulting from a [3 + 2] cycloaddition of **1**, however, fit well between axial and equatorial bonds of a trigonal bipyramidal five-coordinate phosphorus atom. For the [2 + 2] ketone adduct **2**, the molecular structure is known from an X-ray investigation, and the structural changes connected to the cycloaddition have been discussed [2]. Now we present the structure analysis (Table 3) of the nitrilimine adduct **3** [3] as an example of a [3 + 2] cycloaddition.

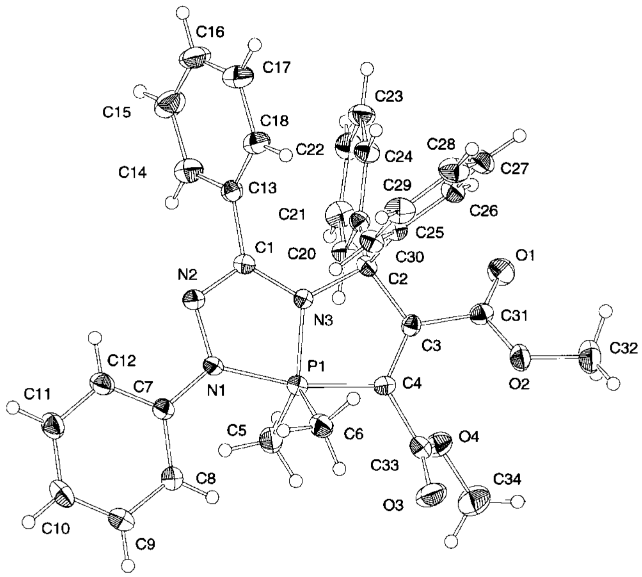

FIGURE 1 Molecular structure of **3** in the crystal (thermal ellipsoids with 30% probability).

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TABLE 1 Relevant Bond Lengths [pm] and Angles [°] for **3** and for Comparison of the Corresponding Data of **2** and **1** [2]

	3	**2**	**1**[a]
P1-N3	173.2(2)	168.4(3)	158.7(5)
P1-C6	181.3(2)	180.5(8)	176.7(7)
P1-C5	182.2(2)	181.2(6)	177.3(8)
P1-N1[b]	183.6(2)	181.1(3)	
P1-C4	189.8(2)	188.8(3)	180.4(5)
N1-N2	138.3(2)		
N1-C7	140.2(2)		
N1-C1	128.5(2)		
N3-C1	140.2(2)		
N3-C2	148.3(2)	147.2(5)	146.4(6)
C1-C13	148.9(3)		
C2-C3	152.6(3)	155.1(6)	155.7(7)
C2-C25	154.3(3)	153.4(7)	154.8(8)
C2-C19	154.6(3)	155.3(7)	153.4(7)
C3-C4	132.2(3)	133.8(5)	133.8(8)
C3-C31	149.4(3)	150.5(6)	149.3(7)
C4-C33	148.8(3)	148.8(7)	147.2(7)
N3-P1-C6	118.8(1)	122.8(2)	117.0(3)
N3-P1-C5	124.6(1)	125.8(3)	115.1(3)
C6-P1-C5	116.6(1)	109.9(3)	104.2(3)
N3-P1-N1[b]	82.9(1)	74.2(1)	
C6-P1-N1[b]	95.7(1)	93.7(3)	
C5-P1-N1[b]	93.5(1)	92.0(3)	
N3-P1-C4	85.0(1)	86.0(2)	98.5(3)
C6-P1-C4	92.4(1)	99.7(3)	110.3(3)
C5-P1-C4	91.3(1)	97.2(3)	112.1(3)
N1-P1-C4	167.6(1)	159.9(2)	
N2-N1-C7	114.8(2)		
N2-N1-P1	115.6(1)		
C7-N1-P1	129.5(1)		
C1-N2-N1	109.5(2)		
C1-N3-C2	123.9(2)	136.3(4)	
C1-N3-P1	115.0(1)	97.2(2)	
C2-N3-P1	121.0(1)	123.2(3)	111.5(3)
N2-C1-N3	116.1(2)		
N2-C1-C13	116.3(2)		
N3-C1-C13	127.6(2)		
N3-C2-C3	102.9(1)	101.2(3)	107.7(4)
N3-C2-C25	111.7(2)	110.0(4)	108.5(4)
C3-C2-C25	106.3(2)		
N3-C2-C19	110.3(2)	112.4(3)	111.3(4)
C3-C2-C19	109.5(2)		
C25-C2-C19	115.3(2)		
C4-C3-C31	123.5(2)	126.0(4)	122.8(5)
C4-C3-C2	116.2(2)	116.3(3)	114.6(4)
C31-C3-C2	120.4(2)	117.7(3)	122.6(5)
C3-C4-C33	122.2(2)	125.3(4)	125.7(3)
C3-C4-P1	114.3(2)	112.6(3)	106.6(4)
C33-C4-P1	123.5(1)	122.0(3)	127.6(3)

[a] Average values of two independent molecules.

[b] For **2**: O in place of N1

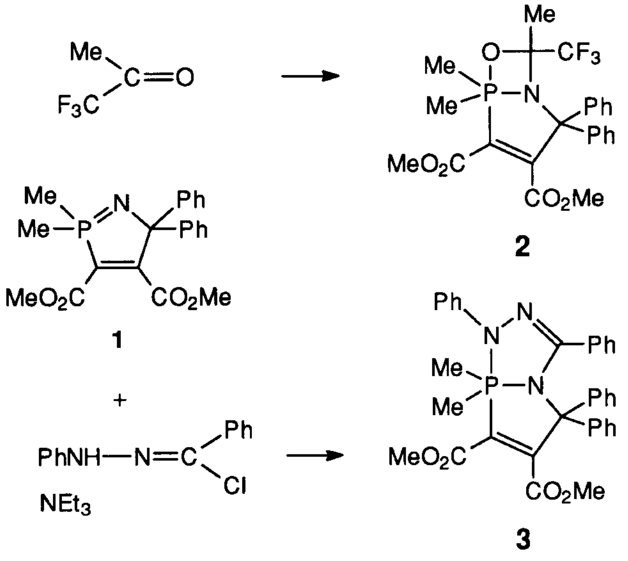
TABLE 2 Structural Changes from the Azaphosphole **1** to Its Cycloadducts **2** and **3** and from Ideal Tetrahedral to Ideal Tbp Coordination

	2	**3**	*Ideal*
Total increase of the three angles at P to become diequatorial	22.2°	23.7°	31.5°
Total decrease of the three angels at P to become axial-equatorial	38.0°	52.2°	58.5°
Increase of PN bond length	9.7 pm	14.5 pm	
Increase of endocyclic PC bond length	8.4 pm	9.4 pm	
Total increase of the two exocyclic PC bond lengths	8.3 pm	9.5 pm	

TABLE 3 Crystal Data and Structure Refinement for **3**

Empirical formula	$C_{34}H_{32}N_3O_4P$
Formula weight	577.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 10.1891(11)$ Å $b = 15.045(2)$ Å $c = 19.679(3)$ Å $\beta = 98.828(11)$ °
Volume	2980.9(7) Å^3
Z	4
Density (calculated)	1.287 Mg/m^3
Absorption coefficient	0.135 mm^{-1}
$F(000)$	1216
Crystal size	0.53 × 0.40 × 0.27 mm
Θ range for data collection	2.42–23.98°.
Index ranges	$0 \leq h < 11$, $0 \leq k \leq 17$, $-22 \leq l \leq 22$
Reflections collected	4956
Independent reflections	4665 [R(int) = 0.0114]
Observed reflections ($I > 2\sigma I$)	3842
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.9996 and 0.9809
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	4665 / 0 / 383
Goodness-of-fit on F^2	1.067
Final R indices ($I > \sigma I$)	$R1 = 0.0407$, $wR2 = 0.0970$
R indices (all data)	$R1 = 0.0530$, $wR2 = 0.1070$
Largest diff. peak and hole	0.235 and −0.370 eÅ^{-3}

Additional information of the crystal structure determination are deposited at the Cambridge Crystallographic Data Center (CCDC 102625, E-mail: deposit@ccdc.cam.ac.uk).



MOLECULAR STRUCTURE OF 3

The chemical shift $\delta^{31}P = -62.4$ [3] clearly indicates the pentacoordination of phosphorus in **3**, and the ^1H NMR spectroscopic equivalence of the two *P*-methyl groups [3] point to a meridional placement of the bicyclic system in a trigonal bipyramidal coordination of phosphorus. This is confirmed by the X-ray structure analysis (Figure 1).

The bicyclic system is planar: The sum of angles (Table 1) in the azaphosphole ring is 539.4°, and in the triazaphosphole ring is 539.1°; the sum of angles at the bridgehead N3 is 359.9°. Both endocyclic angles at the bridgehead P1 are smaller than 90°, and their sum of 167.9° is equal to the diaxial angle 167.6°. The axis is bent in an "anti-Berry" mode (toward the anellating PN bond), and the angle between the exocyclic equatorial bonds in accord is smaller than 120°. The equatorial plane of the trigonal bipyramid is undistorted. As expected, the axial PN bond is somewhat longer (6%) than the equatorial.

COMPARISON TO THE STRUCTURES OF 1 *AND* 2

In the course of the cycloaddition reactions, the azaphosphole **1** undergoes structural changes that generally are more pronounced for the nitrilimine adduct **3** than for the ketone adduct **2** (Tables 1 and 2).

The endocyclic angle N3-P1-C4 becomes in **3** still a bit smaller than in **2**, and this also applies to the other two angles that become axial-equatorial in the cycloadduct. The total angular reorganization for **3** is considerably larger than that for **2**; it is still smaller, however, than that from a perfect tetrahedral to a perfect tbp geometry (Table 2).

All the phosphorus bonds become longer when the coordination increases from 4 to 5, and they lengthen more in **3** than in **2**. As expected, this is most pronounced for the phosphazene bond P1–N3.

As it has been observed for **2**, the changes of the endocyclic angles in the azaphosphole ring from **1** to **3** also add up to zero.

CONCLUSION

1,2λ^5-Azaphospholes such as **1** generally give more stable cycloadducts than acyclic phosphazenes. In case of the [2 + 2] cycloadduct **2** from **1** and a ketone, this was explained by the relatively small structural reorganization necessary in the addition reaction of **1**. The structure analysis of **3** now shows this explanation to hold also for the [3 + 2] cycloadduct from **1** and a nitrilimine, although the structural changes relative to **1** are not as small in **3** as in **2**.

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