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A 1,5-Diaza-2,4-(λ^4P^+, λ^6P^-)-Diphosphorinane**

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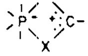
ABSTRACT

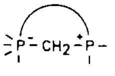
The oxidation of the 1,3-diaza-4,6-diphosphorine **1** *with tetrachloroorthobenzoquinone* **2** *led, unexpectedly, to the formation of 1,5-dimethyl-2,2-bis(dimethylamino)-4,4,4,4-bis-(tetrachloro-o-phenylenedioxa)-1,5-diaza-2,4-*λ^4*,* λ^6*-diphosphorinane-6-one* **4***, containing two phosphorus atoms of opposite formal charge and different coordination number. The X-ray crystal structure analysis of* **4** *revealed the presence of a six-membered ring with an unusual conformation.*

INTRODUCTION

Cyclic compounds of hexa-coordinate phosphorus with intracyclic charge separation are represented in the literature mainly by four-membered ring systems of type I. The positive part in these compounds is the $-N \mathrel{\dot{=}} \overset{(+)}{C} \mathrel{\dot{=}} N-$ unit (X = N) [1, 2]. In two cases, X is O and S [3].

A phosphonium group may also serve as a counterion for a negatively charged six-coordinate phosphorus atom. Thus, it is well known that some fluorophosphoranes undergo facile transformation with formation of $\lambda^6P^{(-)}\lambda^4P^{(+)}$ species [4–9]. However, heterocyclic compounds containing two phosphorus atoms of opposite charge ($\lambda^4P^{(+)}$ $\lambda^6P^{(-)}$) are a rarity [10, 11]


I
(X = N,O,S)

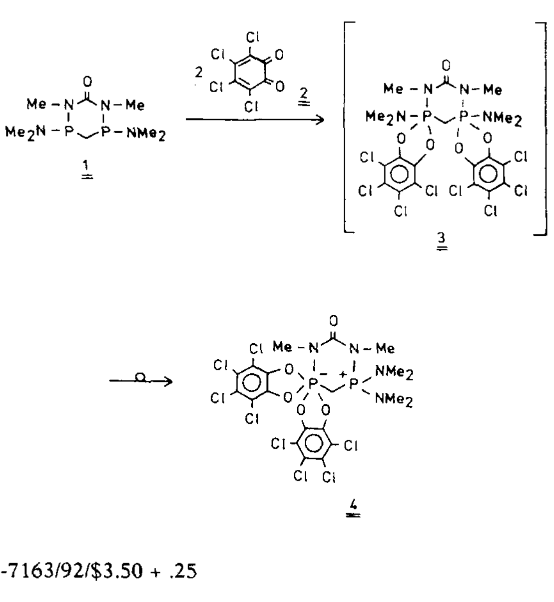

II

In this article we describe a new compound of type II containing the structural unit $\lambda^6P^{(-)}-CH_2-\lambda^4P^{(+)}$ as part of a ring. The presence of the methylene group with two mobile hydrogen atoms makes this compound a potential model for further investigations.

DISCUSSION

We have found that the 1,3-diaza-4,6-diphosphorine **1**, consisting of a mixture of cis-and trans-isomers (1: 9), is readily oxidized by tetrachloroorthobenzoquinone (TOB) **2** to compound **4**, containing two phosphorus atoms of opposite charge and different coordination number. The reaction is believed to proceed via the formation of an intermediate phosphorane **3**, which rearranges into the thermodynamically more stable reaction product, **4**.

Compound **4** is a colorless, high-melting crystalline product, which, owing to its zwitterionic struc-



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**Dedicated to Professor Academician Alexander V. Kirsanov on the occasion of his 90th birthday.

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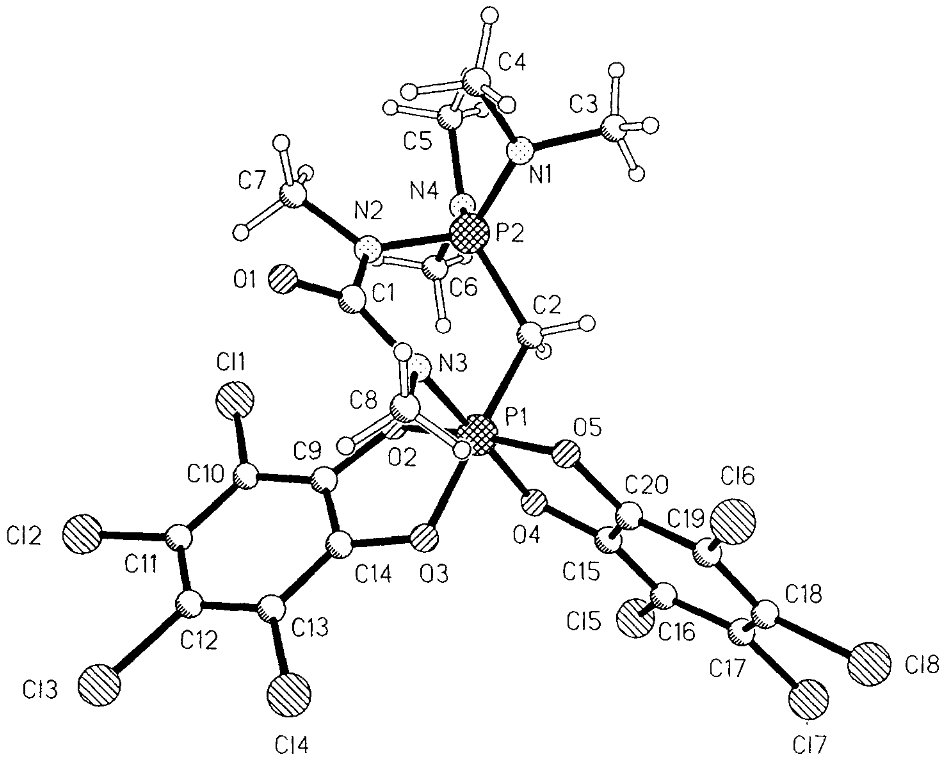

FIGURE 1 Molecular Structure of **4** in the Crystal.

ture, is insoluble in nonpolar and poorly soluble in polar organic solvents. The ^{31}P-NMR-spectrum of the compound **4** shows two doublets with chemical shifts of $\delta = +55$ and -115, which are characteristic of λ^4P and λ^6P, respectively. The value of the $^2J_{PP}$ coupling constant is very small, amounting to only 4.3 Hz.

The analysis of the ^{1}H-NMR-spectrum of compound **4** leads to the conclusion that the molecule is asymmetric. Two dimethylamino groups bonded to λ^4P were found to give rise to two doublets.

The structure of **4** and its asymmetry were confirmed by a single crystal X-ray analysis of the acetonitrile solvate. The structure of **4** is shown in Figure 1. Bond lengths and angles are presented in Table 1.

All bond angles at the six-coordinate phosphorus atom P(1) are very close to 90° or 180°; the angle N(3)-P(1)-C(2) is 94°, which can be realized only by assuming distortion of the six-membered heterocyclic ring. The resulting strain at P(1) is reflected in a marked increase of the bond lengths. For example, the P(1)-C(2) bond (186.0(4) pm) is significantly longer than the C(2)-P(2) bond (177.5(3) pm). The six-membered ring displays an unusual conformation, with the atoms N(2), P(2), C(2) and P(1) essentially coplanar and N(3) and C(1) on the same side of the plane (displacements 107 pm and 76 pm, respectively). The P ... P distance is 311 pm.

The mass spectrum [12] of compound **4** (FAB) showed the presence of the molecular peak, M + 1 = 743. The measurements were carried out in a matrix of m-nitrobenzyl alcohol. Under the experimental conditions m-nitrobenzyl alcohol and compound **4** form a stable 1:1 complex, giving rise to the corresponding peak at M = 895.

EXPERIMENTAL

All the experiments were carried out with exclusion of air and moisture. The solvents were purified and dried, according to the usual methods [13, 14]. ^{1}H- and ^{31}P-NMR-spectra were recorded on the spectrometer BRUKER AC-200 with working frequencies of 200 and 81 MHz, respectively.

Synthesis of 1,5-dimethyl-2,2-bis(dimethylamino)-4,4,4,4-bis(tetrachloro-o-phenylenedioxa)-1,5-diaza-2,4-λ^4, λ^6-diphosphorinane-6-one **4**

To a solution of methylene-bis(dimethylaminochlorophosphine) [15] (1.5 g; 6.4 mmol) in 15 mL of methylene chloride was added N,N′-dimethyl-N,N′-bis-(trimethylsilyl)urea (1.49 g; 6.4 mmol), and the mixture was stirred at room temperature for 20 min. The solvent was removed *in vacuo*, and 10 mL of ether were added. To this ether solution, decanted from an undissolved residue, a solution of tetrachloroortho-benzoquinone (2.2 g; 9.0 mmol) in 15 mL ether was added dropwise in the temperature region

TABLE 1 Selected bond lengths (pm) and angles (°) for compound **4**

P(1)-O(2)	171.8 (2)	P(1)-O(3)	175.9 (3)
P(1)-O(4)	177.5 (2)	P(1)-O(5)	171.2 (2)
P(1)-N(3)	180.4 (2)	P(1)-C(2)	186.0 (4)
P(2)-N(1)	161.8 (3)	P(2)-N(2)	164.5 (3)
P(2)-N(4)	161.7 (2)	P(2)-C(2)	177.5 (3)
O(1)-C(1)	121.7 (3)	O(2)-C(9)	135.6 (4)
O(3)-C(14)	134.4 (3)	O(4)-C(15)	133.9 (3)
O(5)-C(20)	135.5 (3)	N(1)-C(3)	146.8 (5)
N(1)-C(4)	143.0 (5)	N(2)-C(1)	141.3 (4)
N(2)-C(7)	148.5 (3)	N(3)-C(1)	136.5 (3)
N(3)-C(8)	148.0 (4)	N(4)-C(5)	147.0 (5)
N(4)-C(6)	147.2 (4)		
O(2)-P(1)-O(3)	89.4 (1)	O(2)-P(1)-O(4)	87.3 (1)
O(3)-P(1)-O(4)	88.2 (1)	O(2)-P(1)-O(5)	175.6 (1)
O(3)-P(1)-O(5)	87.4 (1)	O(4)-P(1)-O(5)	89.6 (1)
O(2)-P(1)-N(3)	95.3 (1)	O(3)-P(1)-N(3)	89.0 (1)
O(4)-P(1)-N(3)	176.3 (1)	O(5)-P(1)-N(3)	87.7 (1)
O(2)-P(1)-C(2)	88.6 (1)	O(3)-P(1)-C(2)	176.4 (1)
O(4)-P(1)-C(2)	88.7 (1)	O(5)-P(1)-C(2)	94.4 (1)
N(3)-P(1)-C(2)	94.1 (1)	N(1)-P(2)-N(2)	108.1 (1)
N(1)-P(2)-N(4)	108.3 (1)	N(2)-P(2)-C(2)	111.9 (1)
N(1)-P(2)-C(2)	110.9 (1)	N(2)-P(2)-N(4)	108.4 (1)
N(4)-P(2)-C(2)	109.2 (1)	P(1)-O(2)-C(9)	111.5 (2)
P(1)-O(3)-C(14)	110.3 (2)	P(1)-O(4)-C(15)	110.8 (1)
P(1)-O(5)-C(20)	112.6 (1)	P(2)-N(1)-C(3)	119.7 (2)
P(2)-N(1)-C(4)	125.3 (2)	C(3)-N(1)-C(4)	114.3 (3)
P(2)-N(2)-C(1)	122.7 (2)	P(2)-N(2)-C(7)	119.7 (2)
C(1)-N(2)-C(7)	115.9 (2)	P(1)-N(3)-C(1)	125.5 (2)
P(1)-N(3)-C(8)	119.1 (2)	C(1)-N(3)-C(8)	112.0 (2)
P(2)-N(4)-C(5)	122.1 (2)	P(2)-N(4)-C(6)	120.6 (3)
C(5)-N(4)-C(6)	113.0 (2)	O(1)-C(1)-N(2)	118.8 (2)
O(1)-C(1)-N(3)	124.2 (3)	N(2)-C(1)-N(3)	117.0 (2)
P(1)-C(2)-P(2)	117.6 (2)		

TABLE 2 Atomic coordinates (×10^5) and equivalent isotropic displacement coefficients (pm^2) for compound **4**

	x	*y*	*z*	*U(eq)*
P(1)	23915(9)	28785(7)	78343(3)	236(3)
P(2)	32804(8)	55593(7)	75609(3)	216(3)
O(1)	−9527(22)	64891(20)	70685(10)	356(9)
O(2)	30672(22)	31737(19	69429(9)	250(7)
O(3)	12606(22)	19663(19)	76620(9)	276(8)
O(4)	41303(22)	12569(18)	79155(9)	280(7)
O(5)	17479(22)	24541(19)	87177(9)	272(7)
N(1)	26800(28)	65821(24)	81386(12)	321(10)
N(2)	17704(25)	60498(22)	70638(11)	234(9)
N(3)	5417(25)	44635(22)	77852(11)	249(9)
N (4)	49495(26)	57026(24)	70957(11)	290(9)
Cl(1)	34768(9)	41421(8)	53478(3)	354(3)
Cl(2)	12644(9)	33147(8)	45779(3)	362(3)
Cl(3)	−10375(11)	17740(9)	54906(4)	453(4)
Cl(4)	−11750(9)	10826(8)	71672(4)	374(3)
Cl(5)	68422(10)	−16301(8)	82279(4)	418(3)
Cl(6)	6622(11)	13248(9)	102267(4)	467(4)
Cl(7)	63132(11)	−31998(8)	98150(5)	535(4)
Cl(8)	31474(12)	−17309(10)	108113(4)	552(4)
C(1)	3532(32)	56888(28)	72979(13)	249(11)
C(2)	37049(33)	37652(27)	79894(13)	266(11)
C(3)	37334(49)	62984(38)	86954(19)	553(17)
C(4)	12973(58)	79014(55)	81015(27)	1007(27)
C(5)	52273(39)	70441(34)	69161(18)	455(15)
C(6)	59277(40)	47338(39)	66020(16)	475(15)
C(7)	16470(37)	71901(31)	64238(15)	345(12)
C(8)	−10717(33)	43507(31)	81038(15)	320(12)
C(9)	21727(32)	28962(27)	65493(13)	239(10)
C(10)	22169(32)	32583(27)	58218(13)	250(10)
C(11)	12143(34)	28973(28)	54914(13)	273(11)
C(12)	1901(35)	22136(29)	59007(14)	300(12)
C(13)	1458(33)	18717(28)	66429(14)	270(11)
C(14)	11625(32)	22066(26)	69597(13)	242(10)
C(15)	40582(34)	4758(28)	85696(14)	268(11)
C(16)	51828(35)	−8559(28)	88068(15)	301(12)
C(17)	49072(38)	−15297(29)	95103(16)	354(13)
C(18)	35355(39)	−8929(31)	99500(14)	345(13)
C(19)	23963(36)	4747(30)	97073(14)	305(12)
C(20)	27000(34)	11328(28)	90244(13)	265(11)
N(99)	33997(40)	92931(34)	52703(18)	618(17)
C(98)	39493(46)	98674(38)	38921(19)	523(17)
C(99)	36425(40)	95459(35)	46639(21)	465(16)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

−10 to −20°C with stirring. Subsequently, the mixture was stirred for 2 hr at 20°C. The solution was decanted from a residue, the solvent removed *in vacuo* and 2 mL of toluene were added. In five days the crystals thus formed were recrystallized from acetonitrile. The residue was digested with 4 mL of hot acetonitrile. After the solution had been allowed to stand for 10 days, more product crystallized. Compound **4** is a colorless crystalline product, forming a crystallo-solvate with acetonitrile. Yield 0.8 g (24%); m.p. 182–184°.

^{1}H-NMR-Spectrum ($CDCl_3$, δ); 1.93 s (CH_3CN); 2.66 d, $^2J_{PH}$ 10.4 Hz ($PNMe_2$); 2.82 d, $^2J_{PH}$ 10.7 Hz ($P^{(+)}$NMe); 3.02 d, $^2J_{PH}$ 10.1 Hz ($PNMe_2$); 3.03 d, $^2J_{PH}$ 7.2 Hz $P^{(-)}$ NMe). A^{1}H-NMR resonance for the CH_2 group could not be discerned.

^{31}P-NMR-Spectrum ($CDCl_3$, δ): −115 d, $^2J_{PP}$ 4.3 Hz; +55 d, $^2J_{PP}$ 4.3 Hz, Mass spectrum: $M_{calc.}$ = 741.8. $C_{20}H_{20}Cl_8N_4O_5P_2$. M_{exp}(FAB) = 742 + H^+; M_{exp}.(EI) = 742.

X-Ray Structure Determination of Compound 4

Crystal Data: $C_{20}H_{20}Cl_8N_4O_5P_2 \bullet CH_3CN$, $M = 783.0$, triclinic, $P\bar{1}$, a = 885.8(3), b = 1049.0(3), c = 1952.1(6) pm, $\alpha = 75.52(3)$, $\beta = 78.63(3)$, $\gamma = 66.35(3)°$, U = 1.5991(6) nm^3, Z = 2, $D_x = 1.626$ Mg m^{-3}, λ(Mo K_α) = 71.069 pm, $\mu = 0.85$ mm^{-1}, $F(000) = 792$, $T = 178$ K.

Data Collection and Reduction: A colorless prism (0.5 × 0.45 × 0.4 mm) was mounted on a glass fibre with inert oil and transferred to the cold gas stream of the diffractometer (Siemens P3 with LT-2 low temperature attachment). 10855 reflections were collected to $2\Theta_{max}$ 55° using monochromated Mo $K\alpha$ radiation; of 7378 unique reflections (R_{int} 0.023), 5358 with $F > 4\sigma(F)$ were used for all calculations. Cell constants were refined from setting angles of 50 reflections in the range 2Θ 20–24°.

Structure Solution and Refinement: The program system SIEMENS SHELXTL PLUS was used. The structure was solved by direct methods and subjected to anisotropic full-matrix least squares refinement on F. Hydrogen atoms were included using a riding model. The final R value was 0.042, with wR 0.043; the weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 400 parameters, S 1.6, max. Δ/σ 0.2 for the methyl group at C(4) (probably indicating some rotational disorder), otherwise < 0.1, max $\Delta\rho$ 0.4×10^{-6} e pm^{-3}. Final atomic coordinates are given in Table 2.

Further details of the structure determination (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD55883.

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