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Heterocondensed 1,2,3-Diazaphosphorines

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ABSTRACT: *The reaction of phosphorus tribromide with phenylhydrazones of heterocyclic aldehydes leads to formation of a new phosphorus-containing heterocyclic system—heterocondensed 1,2,3-diazaphosphorines. Properties of the phosphorus-containing heterocyclic compounds that have been synthesized are described.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:658–664, 2001

INTRODUCTION

As we have previously shown, tervalent phosphorus halides in basic media are effective phosphorylating reagents with respect to π-excessive aromatic heterocycles such as pyrrole, furan, thiophene, indole, benzofuran, and phosphole [1–4]. The aim of this work is a study of phosphorylation of phenylhydrazones of pyrrolyl-, indolyl-, and furylcarboxaldehydes by tervalent phosphorus halides. These phenylhydrazones containe two nucleophilic centres in the molecule (the nitrogen atom of the hydrazone group and the carbon atom of the heterocycle) that influenced us to expect the formation of new heterocyclic systems—the heterocondensed 1,2,3-diazaphosphorines. It should be noted that, up to the present, only one example of the synthesis of the 1,2,3-diazaphosphorine cycle has been described [5]. Preliminary results of the investigation of this reaction have been given in a concise report [6].

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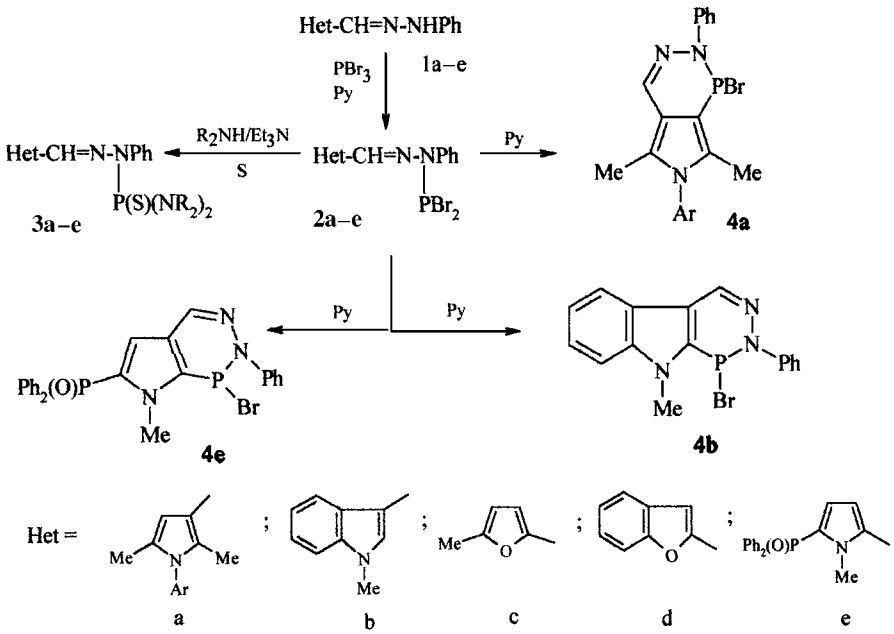
RESULTS AND DISCUSSION

As we have found, the reaction of hydrazones **1a–e** with phosphorus tribromide in pyridine at 20°C and with use of a 1:1 ratio of reagents proceeds at the nitrogen atom of the hydrazone group and leads to the formation of thermally unstable dibromophosphinohydrazides (**2a–e**) (δP = 155–165 p.m.), which are converted into the corresponding dimorpholinothiophosphonates (**3a–e**) when treated consecutively with morpholine in the presence of triethylamine and with sulfur. Compounds **2a,b,e** in a solution of pyridine at .20°C are converted into the heterocondensed 1,2,3-diazaphosphorines (**3a,b,e**) (Scheme 1).

The compound **2a** is the most active in the reaction of cyclization, and this is conditioned by enhanced nucleophility of the carbon atom of the pyrrole ring. However introduction of an electron-acceptor phosphorus-containing substituent into position 5 increases the time of cyclization of **2e** by several hours.



SCHEME 1

Phenylhydrazone (**2b**), containing an indole residue, is less active in the reaction of cyclization. Thus, the time of its reaction, compared with hydrazone **1a**, is increased to 48 h. Heterocyclization of dibromophosphinoamides, (**2c**) containing much less active heterocycles with respect to electrophilic phosphorylation, such as furan and benzofuran, as monitored by the ^{31}P NMR spectroscopy, does not occur even during a period of a month.

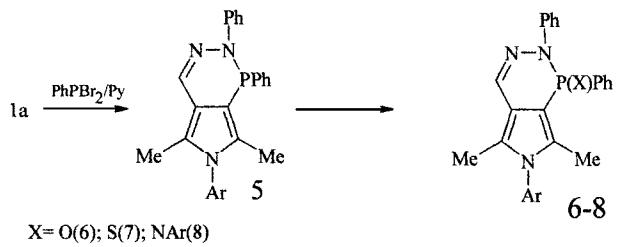
Cyclic bromoanhydrides are bright-yellow crystalline substances, which are highly soluble in benzene and chloroform and are stable in the absence of atmospheric moisture. Their structures were confirmed by ^{1}H and ^{31}P NMR spectral data.

Reaction of the most active hydrazone **1a** with a less active phosphorylating reagent—diphenylbromophosphine, as monitored by ^{31}P NMR spectroscopy, also leads to the formation of the 1,2,3-diazaphosphorine ring (Scheme 2). Amidophosphine **5** was converted into the corresponding oxide (**6**), thiooxide (**7**), and imine (**8**).

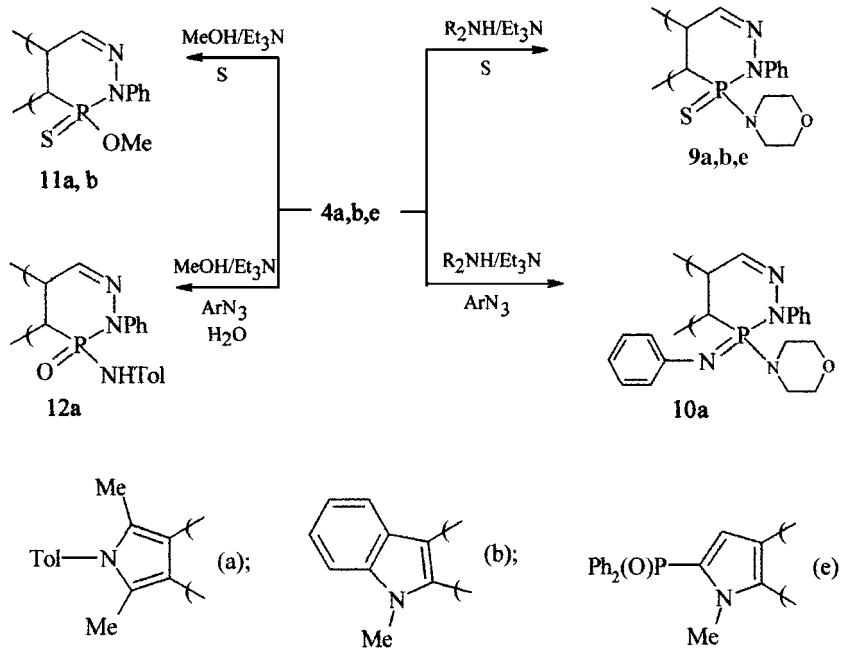
The bromine atom present in the heterocondensed 1,2,3-diazaphosphorines is reactive in nucleophilic substitution, which allowed us to realize, in good yields, syntheses of different derivatives **9–12** with a four-coordinated phosphorus atom (Scheme 3).

Diazaphosphorines **10–12** are bright-yellow crystalline substances that are very soluble in benzene and chloroform. Their structures were confirmed by ^{1}H and ^{31}P NMR spectral data.

Peculiarities of the molecular and crystal structure of **10a** have been studied by the x-ray diffraction method. The perspective view of molecule **10a** is shown in Fig. 1, the main geometrical parameters being given in Table 1. The P(1)N(1)N(2)N(3)C (1–5) central bicyclic system is approximately planar: deviations of atoms from the least-squares plane do not exceed 0.081 Å^3; the dihedral angle between the 6-membered heterocycle P(1)N(1)N(2) C(1)C(2)C(5) and 5-membered cycle N(3)C(1–4) is only 4.3(1)°. Benzene rings C(8–13) and C(15–20) form with the central plane dihedral angles of 61.71(6)° and 78.74(7)°, respectively. Both N(1) and N(3) nitrogen atoms have trigonal planar bond configurations (the sum of bond angles, 360.0(3.0)° and 359.7(6)°). The geometrical parameters of the N(3)C(1–4) heterocycle indicate significant delocalization of electron density [7]. Bond lengths and angles around the phosporus atom are unexceptional [8,9].



SCHEME 2



SCHEME 3

EXPERIMENTAL

^{31}P and ^{1}H, NMR spectra were recorded on a Varian- VXR 300 spectrometer TMS being used as an internal standard for ^{1}H and 85% H_3PO_4 as an external standard for ^{31}P signals. All manipulations were carried out in anhydrous solvents.

X-ray Structure Determination of **10a**

Crystal data: $C_{30}H_{32}N_5OP$, M = 509.6 triclinic, a = 9.015 (1), b = 10.599 (2), c = 15.317 (2) Å, α = 104.73 (1)°, β = 100.88 (1)°, γ = 99.76 (1)°, V = 1353.1 (3)° Å^3, Z = 2, d_{calc} = 1.25 g cm^{-1}, space group P$\bar{1}$

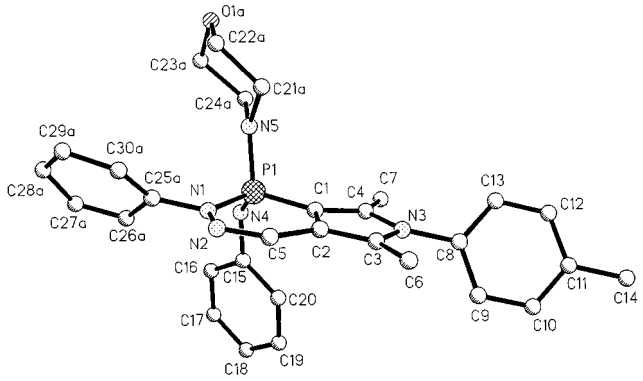


FIGURE 1

TABLE 1 Selected Bond Lengths (E) and Angles (deg) in **10a**

Bond lengths	
P(1)–N(1)	1.712(2)
P(1)–N(4)	1.542(2)
P(1)–N(5)	1.642(2)
P(1)–C(1)	1.753(2)
N(1)–N(2)	1.408(2)
N(2)–C(5)	1.279(3)
N(3)–C(3)	1.384(3)
N(3)–C(4)	1.380(3)
N(3)–C(8)	1.436(3)
N(4)–C(15)	1.392(3)
C(1)–C(2)	1.429(3)
C(1)–C(4)	1.372(3)
C(2)–C(3)	1.375(3)
C(2)–C(5)	1.428(3)
Bond angles	
N(4)–P(1)–N(5)	104.77(9)
N(1)–P(1)–N(4)	116.16(11)
N(1)–P(1)–N(5)	106.16(10)
N(4)–P(1)–C(1)	120.40(10)
N(5)–P(1)–C(1)	110.41(10)
N(1)–P(1)–C(1)	98.28(9)
P(1)–N(1)–N(2)	130.3(1)
N(1)–N(2)–C(5)	119.3(2)
C(3)–N(3)–C(4)	110.5(2)
P(1)–N(4)–C(15)	130.9(2)
P(1)–C(1)–C(2)	122.6(2)
C(2)–C(1)–C(4)	107.6(2)
C(1)–C(2)–C(3)	108.2(2)
C(1)–C(2)–C(5)	122.3(2)
N(3)–C(3)–C(2)	106.6(2)
N(3)–C(4)–C(1)	107.2(2)
N(2)–C(5)–C(2)	126.5(2)

(N2), $\mu = 11.5$ cm^{-1}, $F(000) = 540$, crystal size ca. $0.22 \times 0.41 \times 0.53$ mm. All crystallographic measurements were performed at 18°C on a CAD-4-Enraf-Nonius diffractometer operating in the $\omega - 2\theta$ scan mode (the ratio of the scanning rates $\omega/2\theta = 1.2$). Intensity data were collected within the range $3 < \theta < 62°$ ($0 < h < 10$, $-12 < k < 11$, $-17 < l < 17$) using graphite monochromated Cu -K_α radiation ($\lambda = 1.54178$ Å). Intensities of 4566 reflections (4261 unique reflections, $R_{int} = 0.014$) were measured. Data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods [10] and refined by the full-matrix least-squares technique in the anisotropic approximation [11]. In the refinement, 4041 reflections with $I > 2\sigma(I)$ were used. All hydrogen atoms were placed in calculated positions and were included in the final refinement with fixed positional and thermal parameters. Convergence was obtained at $R_1(F) = 0.044$ and $R_w(F^2) = 0.128$, GOF = 1.065 (411 refined parameters; obs./variabl. 9.8; the largest and minimal peaks in the final difference map, 0.21 and −0.23 e/Å^3). The weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.079P)^2 + 0.356P)]$ with P = $(Fo^2 + 2Fc^2)/3$ was used. The final atomic coordinates are listed in Table 2.

Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 156084.

TABLE 2 Coordinates of Atoms and Equivalent Isotropic Thermal Parameters B_{eq} (Å) in **10a**

Atom	*x*	*y*	*z*	U_{eq}
P(1)	4201(1)	9750(1)	7289(1)	47(1)
N(1)	5436(2)	11135(2)	7241(1)	56(1)
N(2)	5351(2)	11823(2)	6565(1)	54(1)
N(3)	1255(2)	8305(2)	4826(1)	46(1)
N(4)	4971(2)	8711(2)	7635(1)	58(1)
N(5)	3250(2)	10299(2)	8067(1)	55(1)
C(1)	3002(2)	9302(2)	6163(1)	47(1)
C(2)	3129(2)	10118(2)	5556(1)	44(1)
C(3)	2029(2)	9490(2)	4734(1)	45(1)
C(4)	1837(2)	8184(2)	5694(1)	49(1)
C(5)	4296(2)	11328(2)	5806(1)	51(1)
C(6)	1591(3)	9927(2)	3895(1)	58(1)
C(7)	1268(3)	6991(3)	5988(2)	75(1)
C(8)	119(2)	7295(2)	4081(1)	46(1)
C(9)	543(2)	6710(2)	3279(1)	54(1)
C(10)	−555(3)	5763(2)	2551(2)	58(1)
C(11)	−2075(3)	5371(2)	2604(1)	55(1)
C(12)	−2461(3)	5963(2)	3422(2)	58(1)
C(13)	−1386(2)	6925(2)	4149(1)	53(1)
C(14)	−3262(4)	4332(3)	1812(2)	79(1)
C(15)	5787(3)	7825(2)	7218(2)	57(1)
C(16)	6917(4)	7453(4)	7793(2)	90(1)
C(17)	7709(5)	6529(4)	7424(3)	113(1)
C(18)	7429(4)	5959(3)	6493(3)	97(1)
C(19)	6338(4)	6304(3)	5920(2)	79(1)
C(20)	5512(3)	7225(2)	6274(2)	62(1)
O(1A)	2496(10)	11782(8)	9619(5)	82(2)
C(21A)	2212(9)	11219(6)	8013(5)	55(2)
C(22A)	2722(6)	12353(5)	8915(4)	57(1)
C(23A)	3516(8)	10916(8)	9688(5)	78(2)
C(24A)	2853(11)	9756(8)	8799(4)	71(2)
O(1B)	1872(16)	11543(14)	9495(8)	141(6)
C(21B)	2622(12)	11444(8)	7960(7)	56(3)
C(22B)	1770(25)	11944(23)	8687(11)	319(18)
C(23B)	2657(19)	10525(16)	9433(9)	98(3)
C(24B)	3595(14)	10029(22)	9595(10)	160(8)
C(25A)	6571(16)	11877(13)	8064(8)	64(3)
C(26A)	7590(14)	11248(11)	8498(6)	69(2)
C(27A)	8651(14)	11962(9)	9336(10)	92(3)
C(28A)	8694(17)	13304(9)	9740(6)	104(4)
C(29A)	7675(20)	13933(10)	9306(8)	101(3)
C(30A)	6614(19)	13219(14)	8468(9)	73(3)
C(25B)	6473(21)	12048(16)	8102(9)	73(4)
C(26B)	7454(19)	11583(11)	8699(9)	95(4)
C(27B)	8450(18)	12477(12)	9508(8)	106(4)
C(28B)	8465(20)	13835(11)	9719(8)	111(5)
C(29B)	7485(23)	14300(12)	9122(9)	114(5)
C(30B)	6488(22)	13406(17)	8313(10)	85(3)

The morpholine O(1)N(5)C(21-24) and benzene C(25)-C(30) cycles are disordered over two positions (A and B) with multiplicity 0.53 and 0.47.

*General Procedure for Synthesis of Thioamidophosphonates (**3a–e**)*

To a solution of each phenylhydrazone (**1a–e**) (0.03 mol) in pyridine (30 ml) a solution of phosphorus tribromide (0.03 mol) in pyridine (10 ml) was added and the reaction mixture was allowed to stand for 5 min. Then a solution of morpholine (0.06 mol) and triethylamine (0.06 mol) in benzene was added and, an 1 h later, sulfur (0.03 mol) was added to the reaction mixture. The reaction mixture was heated at 80°C for 1 h and, after cooling, was filtered. The filtrate was evaporated in a vacuum, and the product was crystallized from hexane.

*N′-[2,5-Dimethyl-1-(4-methylphenyl)-1H-pyrrol-3-yl]methylidenedi(4-morpholinyl)-N-phenylphosphinothioic hydrazide (**3a**).* Yield 82%; m.p. 132–133°C. ^{31}P NMR ($CHCl_3$): $\delta = 65$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.95$ (s, 1H, C^5—CH_3), 2.14 (s, 1H, C^2—CH_3), 2.43 (s, 3H, Ar—CH_3), 3.1–3.25 (m, 8H, N—CH_2), 3.68 (t, 8H, $J_{HH} = 4.1$ Hz, O—CH_2), 6.21 (s, 1H, Het), 6.85–7.21 (m, 2H, *m*-Ar, 5H, N—Ph), 7.32 (d, 2H, $J_{HH} = 5.8$ Hz, *o*-Ar), 7.74 (s, 1H, CH=N). Anal. calcd for $C_{28}H_{36}N_5O_2PS$: N, 13.03; P, 5.76. Found: N, 13.44; P, 5.78.

*N′-(1-Methyl-1H-indol-3-yl)methylidenedi(4-morpholinyl)-N-phenylphosphinothioic hydrazide (**3b**).* Yield 87%; m.p. 183–184°C. ^{31}P NMR ($CHCl_3$): $\delta =$ 67. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 3.1–3.3$ (m, 8H, N—CH_2), 3.6–3.7 (m, 8H, O—CH_2), 3.9 (s, 3H, N—CH_3), 6.2 (s, 5H, Ph), 7.2–7.6 (m, 5H, Het), 8.25 (s, 1H, CH=N). Anal. calcd for $C_{24}H_{30}N_5O_2PS$: N, 14.33; P, 6.24. Found: N, 14.48; P, 6.41.

*N′-(5-Methyl-2-furyl)methylidenedi(4-morpholinyl)-N-phenylphosphinothioic hydrazide (**3c**).* Yield 81%; m.p. 211–212°C. ^{31}P NMR ($CHCl_3$): $\delta = 67$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.32$ (s, 3H, Het-Me), 3.06–3.11 (m, 8H, N—CH_2), 3.66–3.71 (m, 8H, O—CH_2), 5.87 (d, 1H, $J_{HH} = 1.7$ Hz, H^4), 5.95 (d, 1H, $J_{HH} = 1.7$ Hz, H^3), 7.41–8.04 (m, 6H, Ph, CH=N). Anal. calcd for $C_{20}H_{27}N_4O_3PS$: N, 12.31; P, 7.01. Found: N, 12.38; P, 7.19.

*N′-1-Benzofuran-2-ylmethylidenedi(4-morpholinyl)-N-phenylphosphinothioic hydrazide (**3d**).* Yield 78%; m.p. 239–240°C. ^{31}P NMR ($CHCl_3$): $\delta = 68$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 3.30–3.41$ (m, 8H, N—CH_2), 3.70–3.81 (m, 8H, O—CH_2), 6.74 (s, 1H, H^3 Het), 7.07 (s, 1H, CH=N), 7.11–7.50 (m, 9H, $H^{2,3,4,5}$ Ph). Anal. calcd for $C_{23}H_{27}N_4O_3PS$: N, 12.07; P, 6.34. Found: N, 12.11; P, 6.20.

*N′-[5-(Diphenylphosphoryl)-1-methyl-1H-pyrrol-2-yl]methylidenedi(4-morpholinyl)-N-phenylphosphinothioic hydrazide (**3e**).* Yield 65%; m.p. 173–174°C. ^{31}P NMR ($CHCl_3$): $\delta = 65$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.60–2.81$ (m, 8H, O—CH_2), 3.30–3.50 (m, 8H, O—CH_2), 3.84 (s, 3H, N—CH_3), 5.31 (dd, 1H, $J_{HP} = 4.2$ Hz, $J_{HH} = 3.4$ Hz, H^4, Het), 6.24 (dd, 1H, $J_{HP} = 1.8$ Hz, $J_{HH} = 3.4$ Hz, H^4, Het), 7.50–7.88 (m, 15H, Ph). Anal. calcd for $C_{23}H_{27}N_4O_3PS$: N, 11.05; P, 9.78. Found: N, 10.81; P, 9.86.

*1-Bromo-5,7-dimethyl-6-(4-methylphenyl)-2-phenyl-2,6-dihydro-1H-pyrrolo[3,4-d][1,2,3]diazaphosphinine (**4a**).* To a solution of phosphorus tribromide (0.01 mol) in pyridine (10 ml) with cooling and stirring, a solution of phenylhydrazone (**1a**) (0.01 mol) in pyridine (10 ml) was added dropwise. The reaction mixture was allowed to stand for 24 h and, after that, was evaporated in a vacuum. Then, it was purified by reprecipitation with hexane from benzene. Yield 62%; m.p. 176–177°C. ^{31}P NMR ($CHCl_3$): $\delta = 96.4$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.13$ (s, 3H, C_7—CH_3), 2.23 (d, 3H, $J_{HP} = 1.2$ Hz, C_5—CH_3), 2.46 (s, 3H, Ph—CH_3), 7.51 (m, 7H, *m*-H Tl, Ph), 7.64 (s, 1H, CH=N), 7.71 (d, 2H, $J_{HH} = 8.0$ Hz, *o*-H Tl). Anal. calcd for $C_{20}H_{19}N_3BrP$: N, 10.19; P, 7.51. Found: N, 10.22; P, 7.56.

*1-Bromo-9-methyl-2-phenyl-2,9-dihydro-1H-[1,2,3]diazaphosphinino[4,5-b]indole (**4b**).* To a solution of phosphorus tribromide (0.01 mol) in pyridine (30 ml) a solution of phenylhydrazone (**1b**) (0.01 mol) and methylene chloride (20 ml) was added. The reaction mixture was heated at 60°C for 12 h, then, cooled and evaporated. The product was purified by reprecipitation with hexane from benzene. Yield 68%; m.p. 179–180°C. ^{31}P NMR ($CHCl_3$): $\delta = 82$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 4.06$ (s, 3H, N—CH_3), 7.08–7.43 (m, 7H, 5H Ph, 2H Ind), 7.72 (d, 1H, $J_{HH} = 7.8$ Hz, H Ind), 7.87 (d, 1H, $J_{HH} = 7.8$ Hz, H Ind), 8.01 (s, 1H, CH=N). Anal. calcd for $C_{16}H_{13}N_3BrP$: N, 11.73; P, 8.65. Found: N, 11.86; P, 8.60.

*1-Bromo-6-(diphenylphosphoryl)-7-methyl-2-phenyl-2,7-dihydro-1H-pyrrolo [2,3-d][1,2,3]diazaphosphinine (**4e**).* This compound was obtained from phenylhydrazone (**1e**) analogously to **4a**. Yield 62%; m.p. 164–165°C. ^{31}P NMR ($CHCl_3$): $\delta = 86$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 4.06$ (s, 3H, N—CH_3), 6.87 (br s, 1H, Het), 7.03–8.01 (m, 10H, Ph), 8.80 (s, 1H, CH=N). Anal. calcd for $C_{24}H_{20}N_3BrP_2$: N, 8.27; P, 12.19. Found: N, 8.73; P, 12.11.

*5,7-Dimethyl-6-(4-methylphenyl)-1,2-diphenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinine-1-one (**6**).* To a solution of diphenylbromophosphine (0.01 mol) in pyridine (20 ml), a solution of hydrazone (**1a**) (0.01 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added; 48 h later, the reaction mixture was filtered and the filtrate evaporated to dryness. The oil obtained was dissolved in benzene and, then, Br_2 (0.01 mol) was added; 2 h later, a benzene solution was decanted. The obtained oil was dissolved in methylene chloride (30 ml) and washed with a 3% solution of NaOH. Then, the organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The product was crystallized from acetone. Yield 25%; m.p. 250–251°C. ^{31}P NMR ($CHCl_3$): $\delta = 8.1$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.97$ (s, 3H, C_7—CH_3), 2.20 (s, 3H, C_5—CH_3), 2.44 (s, 3H, Ph—CH_3), 7.04 (d, 2H, $J_{HH} = 5.4$ Hz, *m*-H T1), 7.17–7.36 (m, 10H, Ph), 7.55 (d, 2H, $J_{HH} = 5.4$ Hz, *o*-H T1), 7.81 (s, 1H, CH=N). Anal. calcd for $C_{26}H_{24}N_3OP$: N, 9.88; P, 7.28. Found: N, 7.64; P, 7.33.

*5,7-Dimethyl-6-(4-methylphenyl)-1,2-diphenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinine-1-thione (**7**).* To a solution of diphenylbromophosphine (0.01 mol) in pyridine (20 ml) a solution of hydrazone (**1a**) (0.01 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added; 48 h later sulfur (0.01 mol) was added and the

mixture was boiled for 1 h. A residue was filtered off, and the filtrate was evaporated in a vacuum. The product was crystallized from acetone. Yield 30%; m.p. 210–212°C. ^{31}P NMR ($CHCl_3$): $\delta = 40$, 30. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2,00$ (s, 3H, C_7—CH_3), 2.18 (s, 3H, C_5—CH_3), 2.43 (s, 3H, Ph—CH_3), 7.00–7.50 (m, 12H, *m*-H Tl, Ph), 7.77 (s, 1H, CH = N), 7.85 (d, 2H, sJ_{HH} = 8.1 Hz, *o*-H T1). Anal. calcd for $C_{26}H_{24}N_3PS$: N, 9.52; P, 7.03. Found: N, 9.28; P, 6.63.

*N-[5,7-Dimethyl-6-(4-methylphenyl)-1,2-diphenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinine-1-ylidene]-4-methylaniline(***8***).* To a solution of diphenylbromophosphine (0.01 mol) in pyridine (20 ml) a solution of hydrazone (**1a**) (0.01 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added. After 48 h the mixture was filtered and, then, to the filtrate a solution of *p*-tolyl azide (0.01 mol) in toluene (30 ml) was added. The mixture was boiled for 3 h and evaporated. The product was crystallized from methanol. Yield 28%; m.p. 221–223°C. ^{31}P NMR ($CHCl_3$): δ = −9.21. ^{1}H NMR ($CDCl_3$, TMS): δ = 1.98 (s, 3H, C_7—CH_3), 2.18 (s, 3H, C_5—CH_3), 2.24 (s, 3H, P=N—Ph—CH_3), 2.39 (s, 3H, N—Ph—CH_3), 6.97–7.63 (m, 14H, *m*-H T1, Ph), 7.82 (s, H, CH=N), 7.85 (m, 4H, *o*-H T1). Anal. calcd for $C_{33}H_{31}N_4P$: N,10.89; P, 6.03. Found: N, 10.67; P, 6.24.

*General Procedure for Synthesis of Thioamides (***9a,b,e***)*

To a solution of bromophosphine **4a–e** (0.01 mol) in benzene (20 ml), with cooling and stirring, a solution of morpholine (0.01 mol) and triethylamine (0.03 mol) in benzene (30 ml) was added; 2 h later, sulfur (0.01 mol) was added and the mixture was boiled for 1 h. After that, the mixture was filtered and the filtrate was evaporated. The product was crystallized from ethanol.

*5,7-Dimethyl-6-(4-methylphenyl)-1-(4-morpholinyl)-2-phenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinine-1-thione (***9a***).* Yield 55%; m.p. 191–195°C. ^{31}P NMR ($CHCl_3$): $\delta = 47.10$. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.15$ (s, 3H, C_7—CH_3), 2.46 (d, 3H, $J_{HP} = 1.0$ Hz, C_5—CH_3), 2.46 (s, 3H, Ph—CH_3), 2.90–3.10, 3.20–3.40 (m, 4H, N—CH_2), 3.48 (t, 4H, $J_{HH} = 4,8$ Hz, O—CH_2), 7.00–7.50 (m, 7H, *m*-H T1, Ph), 7.64 (s, 1H, CH=N), 7.70 (d,2H, $J_{HH} = 8.1$ Hz, *o*-H T1). Anal. calcd for $C_{24}H_{27}N_4OPS$: N, 12.44; P, 6.88. Found: N, 12.03; P, 6.84.

*9-Methyl-1-(4-morpholinyl)-2-phenyl-2,9-dihydro-1H-1λ^5-[1,2,3]diazaphosphinino[4,5-b]indole-1-thione (***9b***).* Yield 57%; m.p. 192–193°C. ^{31}P NMR ($CHCl_3$): $\delta = 41.01$. ^{1}H NMR ($CDCl_3$, TMS): $\delta =$ 2.70–3.10, 3.20–3.40 (m, 4H, N—CH_2), 3.41 (t, 4H, $J_{HH} = 4.0$ Hz, O—CH_2), 4.06 (s, 3H, N—CH_3), 7.10–7.55 (m, 7H, 5H Ph, 2H Ind), 7.75 (d, 1H, $J_{HH} = 7,8$ Hz, H Ind), 7.89 (d, 1H, $J_{HH} = 7.8$ Hz, H Ind), 8.05 (s, 1H, CH=N). Anal. calcd for $C_{20}H_{21}N_4OPS$: N, 14.11; P, 7.81. Found: N, 14.03; P, 7.85.

*6-(Diphenylphosphoryl)-7-methyl-1-(4-morpholinyl)-2-phenyl-2,7-dihydro-1H-1λ^5-pyrrolo[2,3-d][1,2,3]diazaphosphinine-1-thione (***9e***).* Yield 51%; m.p. 176–178°C. ^{31}P NMR ($CHCl_3$): $\delta = 43$, 62. ^{1}H NMR ($CDCl_3$, TMS): $\delta =$ 2.82–3.15, 3.22–3.45 (m, 4H, N—CH_2), 3.43 (t, 4H, $J_{HH} = 4.2$ Hz, O—CH_2), 4.12 (s, 3H, N—CH_3), 6.91 (d, 1H, $J_{HP} = 1.2$ Hz, Het), 7.05–8.10 (m, 10H, Ph), 8.82 (s, 1H, CH=N). Anal. calcd for $C_{28}H_{28}N_4O_2P_2S$: N, 10.25; P, 11.33. Found: N, 8.73; P, 12.11.

*N-[5,7-Dimethyl-6-(4-methylphenyl)-1-(4-morpholinyl)-2-phenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinin-1-ylidene]aniline (***10a***).* To a solution of bromophosphine **4a** (0.01 mol) in benzene (20 ml), with cooling and stirring, a solution of morpholine (0.01 mol) and triethylamine (0.03 mol) in benzene (30 ml) was added; 2 h later, phenylhydrazide (0.01 mol) in benzene (20 ml) was added. The reaction mixture was heated at 60°C for 1 h, cooled and, then, treated with a mixture of diethyl ether and acetone (1:1). The precipitated product was recrystallized from ethanol. Yield 72%; m.p. 208–210°C. ^{31}P NMR ($CHCl_3$): $\delta = -3$, 13. ^{1}H NMR ($CDCl_3$, TMS): $\delta = 2.35$ (s, 3H, C_7—CH_3), 2.39 (s, 3H, C_5—CH_3), 2.65 (s, 3H, Ph—CH_3), 3.08–3.20 (m, 4H, N—CH_2), 3.42 (m, 4H, O—CH_2), 6.89–7.56 (m, 2H, *m*-Tol, 5H, N—Ph, 5H, N=Ph), 7.82 (d, 2H, $J_{HH} = 6$ Hz, *o*-H, T1), 7.93 (s, 1H, CH=N). Anal. calcd for $C_{30}H_{32}N_5OP$: N, 13.74; P, 6.08. Found: N, 13.89; P, 6.06.

General Procedure for Synthesis of Thiophosphonates **11a,b**

To a solution **4a** (0.01 mol), with cooling and stirring, a solution of methanol (0.01 mol) and triethylamine (0.01 mol) in benzene (20 ml) was added; 0.5 h later, sulfur (0.01 mol) was added and, then, the mixture was boiled for 0.5 h. The reaction mixture was cooled, filtered and evaporated to dryness. The product was crystallized from ethanol.

*1-Methoxy-5,7-dimethyl-6-(4-methylphenyl)-2-phenyl-2,6-dihydro-1H-1λ^5-pyrrolo[3,4-d][1,2,3]diazaphosphinine-1-thione(***11a***).* Yield 43%; m.p. 163–164°C. ^{31}P NMR ($CHCl_3$): $\delta = 55,87$. ^{1}H NMR ($CDCl_3$,

TMS): $\delta = 2.17$ (s, 3H, C_7—CH_3), 2.38 (s, 3H, C_5—CH_3), 2.46 (s, 3H, Ph—CH_3), 6.61 (d, 3H, $J_{HP} = 1.5$ Hz, O—CH_3), 7.10–7.43 (m, 7H, *m*-H T1, Ph), 7.57 (d, 2H, $J_{HH} = 9.0$ Hz, *o*-H T1), 7.76 (s, 1H, CH=N). Anal. calcd for $C_{21}H_{22}N_3OPS$: N, 10.63; P, 7.83. Found: N, 10.21; P, 7.94.

*1-Methoxy-9-methyl-2-phenyl-2,9-dihydro-1H-1λ⁵ [1,2,3]-diazaphosphinino[4,5-b]indole-1-thione (***11b***).* Yield 51%; m.p. 174–173°C. ^{31}P NMR ($CHCl_3$): $\delta = 78.23$. ^1H NMR ($CDCl_3$, TMS): $\delta = 4.09$ (s, 3H, N—CH_3), 6.58 (d, 3H, $J_{HP} = 1.1$ Hz, O—CH_3), 7.11–7.54 (m, 7H, 5H Ph, 2H Ind), 7.71 (d, 1H, $J_{HH} =$ 7.0 Hz, H Ind), 7.89 (d, 1H, $J_{HH} = 7.0$ Hz, H Ind), 8.05 (s, 1H, CH=N). Anal. calcd for $C_{17}H_{16}N_3OPS$: N, 12.31; P, 9.07. Found: N, 12.74; P, 9.43.

*1-Anilino-5,7-dimethyl-6-(4-methylphenyl)-2-phenyl-2,6-dihydro-1H-1λ⁵-pyrrolo[3,4-d][1,2,3]diazaphosphinin-1-one(***12a***).* To a solution of **4a** (0.01 mol), with cooling and stirring, a solution of aniline (0.01 mol) and triethylamine (0.03 mol) in benzene (30 ml) was added; 1 h later, sulfur (0.01 mol) was added and the mixture was boiled for 1 h. After cooling the reaction mixture was filtered. The filtrate was evaporated to dryness. When treating the residue with ethanol, the product was precipitated. It was recrystallized from ethanol. Yield 72%; m.p. 195–196°C. ^{31}P NMR ($CHCl_3$): $\delta = 32.88$. ^1H NMR ($CDCl_3$, TMS): $\delta = 2.17$ (s, 3H, C_7—CH_3), 2.19 (s, 3H, C5—CH_3), 2.23 (s, 3H, Ph—CH_3), 5.59 (d, 1H, $J_{HP} =$ 9 Hz, NH), 6.61 (d, 2H, $J_{HH} = 9$ Hz, *o*-H, Ph—NH), 6.92–7.34 (m, 10H, 2H, *m*-H T1, 5H N—Ph, 3H, NH—Ph), 7.45 (d, 2H, $J_{HH} = 6.0$ Hz, *o*-H T1), 7.76 (s, 1H, CH=N). Anal. calcd for $C_{26}H_{25}N_4PS$: N, 12.28; P, 6.80. Found: N, 11.83; P, 7.01.

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