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Synthesis and Characterization of 4,5-Dihydro-1H-pyrazolo[3,4b][1,4]azaphosphinines

Andrei A. Tolmachev,[1] Sergei I. Dovgopoly,[1] Aleksandr N. Kostyuk,[1] Ernest S. Kozlov,[1] Aleksei O. Pushechnikov,[1] and Wolfgang Holzer[2]

[1]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya 5, Kiev-94, 253660, Ukraine*

[2]*Institute of Pharmaceutical Chemistry, University of Vienna, Pharmaziezentrum, Althanstrasse 14, A-1090 Vienna, Austria*

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ABSTRACT: *1,3,3-Trimethyl-2-(1-R-3-methyl-5-pyrazolyliminoethylidene)indolines were shown to undergo phosphorylation with phosphorus(III) halides at the two nucleophilic carbon centers to give fused 1,4-azaphosphinine ring systems. Chemical properties of the synthesized compounds were characterized. For some representative compounds, detailed NMR spectroscopic investigations were performed, including the determination of* ^{31}P, ^{1}H *and* ^{31}P, ^{13}C *coupling constants.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 391–398, 1999

INTRODUCTION

1,4-Azaphosphinines were first obtained by reacting bis-β-carbonylsubstituted phosphine oxides with ammonia [1,2]. Similar cyclizations were later realized with phosphine oxides containing other unsaturated groups [3–5]. The reactions of phosphorus pentachloride with enamides [6] were also used to prepare 1,4-azaphosphinines. The simplest approach to the heterocyclic system seems to be the phosphorylation of enamines with phosphorus (III) halides [7].

Correspondence to: Andrei A. Tolmachev
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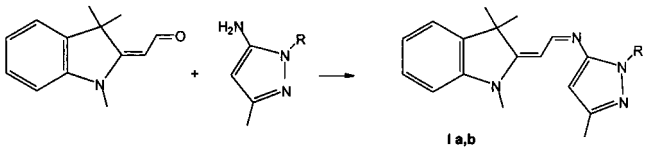
In the present work, we report on the design of the 1,4-azaphosphinine ring using enamine substrates such as 1,3,3-trimethyl-2-(1-R-3-methyl-5-pyrazolyliminoethylidene)indolines (**Ia,b**). The supposed suitability of such compounds for the intended heterocyclization relies on the basis of our previous experience of phosphorylating pyrazoles [8] and 1,3,3-trimethyl-2-methyleneindoline derivatives [9] and synthesis of a range of novel phosphorus-containing heterocyclic systems on their basis [10,11]. 1,4-Azaphosphinines fused to heterocycles, in particular to pyrazoles, are hitherto unknown.

RESULTS AND DISCUSSION

The starting pyrazolyliminoethylideneindolines **Ia,b** were obtained by condensation of 2-formylmethylene-1,3,3-trimethylindoline with appropriate aminopyrazoles.



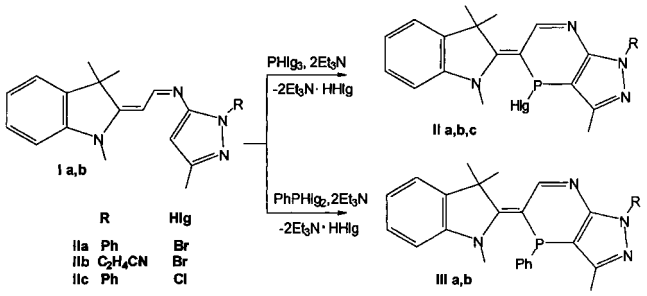
I a,b

a: R=-Ph; b: R=-CH_2CH_2CN

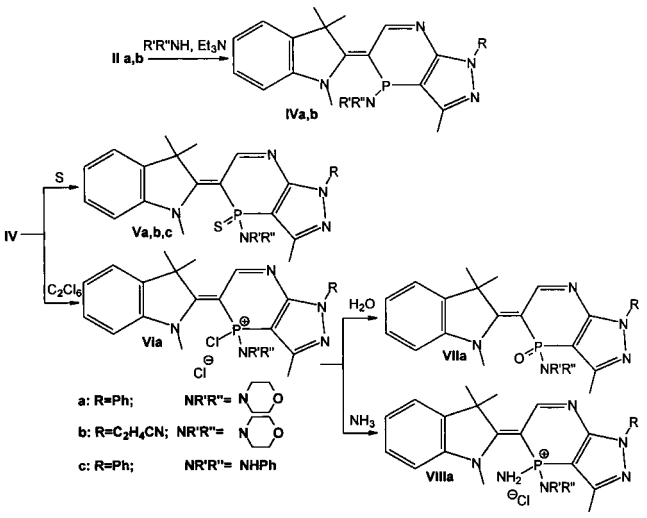
The C-phosphorylation of **Ia,b** with phosphorus(III) halides proceeds simultaneously at the two nucleo-

philic carbon centers and results in pyrazole-fused 1,4-azaphosphinines **IIa–c**. The cyclization is most effective when conducted in dichloromethane in the presence of triethylamine as the base. Under these conditions, the reaction is complete in 1 hour with phosphorus tribromide and in 18 hours with phosphorus trichloride. The substitution of the aryl for the *β*-cyanoethyl group at the pyrazole nitrogen atom has no effect on the reaction rate in contrast to the previously described phosphorylation of pyrazoles [8].

With less reactive dibromo(phenyl)phosphine and dichloro(phenyl)phosphine, the reaction requires 16 and 24 hours, respectively, for completion under the same conditions. No intermediate acyclic phosphorylation products were detected even by ^{31}P-NMR spectroscopy in both cases. The structures of the high-melting solid compounds **IIa–c** and **IIIa,b** were confirmed by ^{31}P- and ^{1}H-NMR spectral evidence.

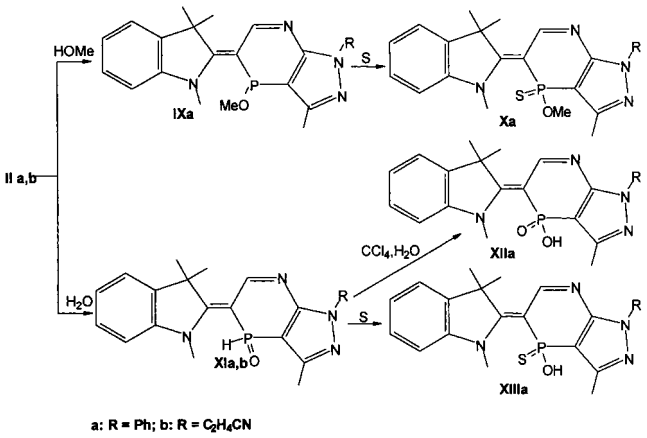


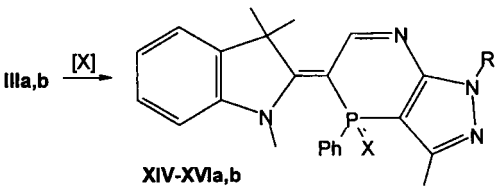
The cyclic bromo phosphines **IIa,b** easily react with secondary amines and anilines to give unstable aminophosphines IV identified by NMR spectra and the transformation to stable thioxo V and oxo VII derivatives or to the imine hydrochloride VIII, via phosphonium salts VI. The classical Staudinger reaction of IV with aryl azides, however, failed to give individual iminophosphoranes.



Bromophosphines **IIa,b** smoothly react with alcohols to yield phosphinites **IX** identified, without isolation, by ^{31}P-NMR spectra and characterized in the form of stable thiophosphinates **X**.

In contrast to acyclic C-phosphorylated enamines [9], the P–C bond in compounds **11a,b** is fairly strong and is not cleaved by dry hydrogen chloride, excess phosphorus(III) halides, or water. Owing to this, bromides **IIa,b** can be preparatively hydrolyzed to phosphinous acids XI. They were converted by the Atherthon–Todd reaction and sulfurization into phosphinic acids **XII** and **XIII**. Acids **XI** failed, however, to give amides **VII** under Atherthon–Todd reaction conditions perhaps due to steric congestion around the phosphorus.





XIV:X=S; XV:X=O; XVI: X=NAr
a: R = Ph; b: R = C_2H_4CN

Unlike compounds **XI**, phosphines **IIIa,b** are easily oxidized with hydrogen peroxide, sulfur, or aryl azides into the corresponding derivatives **XIV–XVI**.

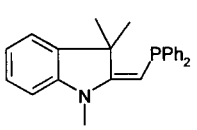
We have found previously that the 1,3,3-trimethyl-2-indolinylidenemethyl moiety exerts a strong stabilizing effect on phosphenium cations [10]. All attempts to generate the cations from **II** were, however, unsuccessful.

NMR Spectroscopic Investigations

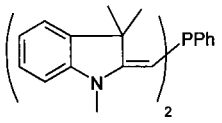
Complete and unambiguous assignments for all ^{1}H and ^{13}C resonances of compounds **Ia**, **VIIa**, **Xa**, and **XVa** could be achieved on the basis of chemical shift considerations, coupling information (APT [12] and

gated decoupled ^{13}C NMR spectra), NOE difference [13], COSY-45 [14], HMQC [15], and 1D-TOCSY [16] spectra as well as on 1D-HETCOR [17] and long-range INEPT experiments [18] with selective DANTE excitation. For compound **Ia**, the (E) configuration of the substituents attached to the -N=CH- moiety was deduced from NOE difference experiments (strong NOE on the signal of pyrazole H-4 upon irradiation of N=C*H*); the latter technique also allowed us to determine the stereochemistry of the exocyclic C=C double bond [through-space connections between N=C*H* (δ 8.78) and the six methyl protons (δ 1.63) attached to indole C-3 and between N=CH-C*H*= (δ 5.67) and indole-1-CH_3 (δ 3.22), respectively]. In a similar manner, for compounds **VIIa, Xa**, and **XVIa**, a strong NOE between the indole-3-CH_3 and H-6 of the pyrazolo[5,4b][1,4]azaphosphinine moiety (abbreviated as pyazph in the Experimental) unambiguously revealed the C=C bond connecting the two bicyclic ring systems to have a stereochemistry as displayed in the formulas.

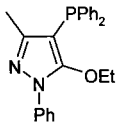
^{31}P-NMR signals of substances obtained appear in relatively high field due to the influence of electron-donating indole and pyrazole residues. We have already noted previously their influence for phosphorylated Fischer's bases and phosphorylated pyrazoles.



δ_p = -31,6; -29,1 [9]

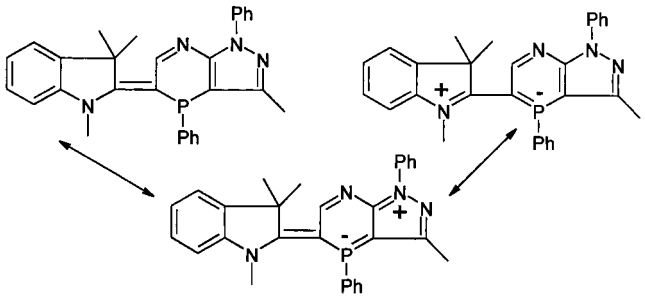


δ_p = -54,2; -52,5 [19]



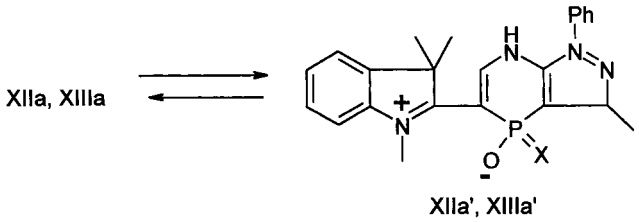
δ_p = -35,5 [8]

It is obvious that, in the substances synthesized, the electron-donating effects of both residues are summarized, for example.



It should be noted that six-membered unsaturated phosphorus-containing heterocyclic compounds are especially prone to formation of 1-R-phosphininyl anions [20].

^{31}P-NMR signals of the substances (**XIIa, XIIIa**) appear in unusually high field probably due to their existence in solutions as tautomeric forms (**XIIA′, XIIIa′**) or as an equilibrium of the two forms.



From literature data, it is well known that ^{31}P-NMR signals of substances of the 1,4-azaphosphinine type presented in this work occur in markedly high field [5].

EXPERIMENTAL

The ^{31}P-NMR spectra were taken on a Varian 300 spectrometer. Chemical shifts are reported relative to the external standard 85% H_3PO_4 (121 MHz).

The ^1H and ^{13}C NMR spectra were recorded on a Varian Unity *Plus* 300 NMR spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C).

1,3,3-Trimethyl-2-(3-methyl-1-phenyl-5-pyrazolyliminoethylidene)indoline (**Ia**)

A mixture of 2-formylmethylene-1,3,3-trimethylindoline (50 mmol) and 5-amino-3-methyl-1-phenylpyrazole (50 mmol) in ethanol (100 ml) was refluxed for 12h. The precipitated product was filtered off and recrystallized from 2-propanol.

^1H NMR ($CDCl_3$) δ 1.63 (s, 6H, ind-3-CH_3), 2.35 (s, 3H, pyr-3-CH_3), 3.22 (s, 3H, ind-1-CH_3), 5.67 (d, ^3J = 10.4 Hz, 1H, N=CH-C*H*=), 5.95 (s, 1H, pyr H-4), 6.76 (d, 1H, ind H-7), 6.98 (t, 1H, ind H-5), 7.21 (d, 1H, ind H-4), 7.23 (t, 1H, ind H-6), 7.24 (t, 1H, Ph H-4), 7.41 (t, 2H, Ph H-3,5), 7.76 (d, 2H, Ph H-2,6), 8.78 (d, ^3J = 10.4 Hz, 1H, N=C*H*-CH=). ^{13}C NMR ($CDCl_3$) δ 14.1 (pyr-3-CH_3), 29.4 (ind-3-CH_3, ind-1-CH_3), 46.6 (ind C-3), 92.0 (pyr C-4), 96.6 (N=CH-*C*H=), 107.2 (ind C-7), 121.4 (ind C-5), 121.6 (ind C-4), 123.8 (Ph C-2,6), 125.9 (Ph C-4), 127.9 (ind C-6), 128.4 (Ph C-3,5), 139.0 (ind C-3a), 139.8 (Ph C-1), 144.0 (ind C-7a), 148.8 (pyr C-3), 153.3 (pyr C-5), 158.2 (N=*C*H-CH=), 167.7 (ind C-2).

1,3,3-Trimethyl-2-(3-methyl-1-(2-cyanoethyl)-5-pyrazolyliminoethylidene)indoline (**Ib**)

Prepared as described for **Ia**. ^1H NMR ($CDCl_3$ δ 1.63 (s, 6H, ind-3-CH_3), 2.25 (s, 3H, pyr-3-CH_3), 2.89 (t, 2H, NC-CH_2), 3.28 (s, 3H, ind-1-CH_3), 4.46 (t, 2H, N-CH_2), 5.63 (d, ^3J = 10.2 Hz, 1H, N=CH-C*H*=), 5.80 (s, 1H, pyr H-4), 6.79 (d, 1H, ind H-7), 7.00 (t, 1H,

ind H-5), 7.22 (d, 1H, ind H-4), 7.26 (t, 1H, ind H-6), 8.71 (d, ^3J = 10.2 Hz, 1H, N=C*H*-CH=).

4-Bromo-3-methyl-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphine (**IIa**)

To a stirred solution of Ia (4 mmol) and triethylamine (8 mmol) in dichloromethane (20 ml) was added phosphorus tribromide (4 mmol) under an argon atmosphere. After the mixture had been stirred for 1h, dichloromethane was evaporated, and the oily residue was dissolved in toluene (30 ml) and filtered after 30 min. The product was isolated by fractional precipitation with hexane and dried.

^{1}H NMR (C_6D_6) δ 1.31 (s, 6H, ind-3-CH_3), 2.25 (s, 3H, pyazph-3-CH_3), 3.39 (s, 3H, ind-1-CH_3), 6.52 (d, 1H, ind H-7), 6.67 (t, 1H, ind H-5), 6.73 (t, 1H, Ph H-4), 6.76 (d, 1H, ind H-4), 6.78 (t, 1H, ind H-6), 6.94 (t, 2H, Ph H-3,5), 7.69 (d, 2H, Ph H-2,6), 8.58 (d, $^3J_{H\text{-}6,P}$ = 9.6 Hz, 1H, N=C*H*-).

4-Bromo-1-(2-cyanoethyl)-3-methyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinine (**IIb**)

Prepared as described for **IIa**.

4-Chloro-3-methyl-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinine (**IIc**)

Prepared as described for **IIa**. ^{1}H NMR (C_5D_5N) δ 1.52 (s, 6H, ind-3-CH_3), 2.39 (s, 3H, pyazph-3-CH_3), 3.58 (s, 3H, ind-1-CH_3), 6.85 (d, 1H, ind H-7), 6.96 (t, 1H, ind H-5), 7.06 (t, 1H, Ph H-4), 7.10 (d, 1H, ind H-4), 7.15 (t, 1H, ind H-6), 7.18 (t, 2H, Ph H-3,5), 8.18 (d, 2H, Ph H-2,6), 8.47 (d, $^3J_{H\text{-}6,P}$ = 15 Hz, 1H, N=C*H*-).

3-Methyl-1,4-diphenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinine (**IIIa**)

To a stirred solution of **Ia** (4 mmol) and triethylamine (8 mmol) in dichloromethane (20 mL) was added dibromo(phenyl)phosphine (4 mmol) under an argon atmosphere. After 24 hours, the solvent was evaporated, and the residue was redissolved in boiling toluene (30 mL) and filtered. The product that precipitated from the filtrate was reprecipitated from toluene with hexane.

^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, ind-3-CH_3), 1.73 (s, 3H, ind-3-CH_3), 2.25 (s, 3H, pyazph-3-CH_3), 3.78 (s, 3H, ind-1-CH_3), 6.89 (d, 1H, ind H-7), 7.22 (t, 1H, ind H-5), 7.26 (d, 1H, ind H-4), 7.28 (t, 1H, ind H-6), 7.29 (t, 1H, N-Ph H-4), 7.38 (m, 3H, P-Ph H-3,4,5), 7.45 (t, 2H, N-Ph H-3,5), 7.70 (m, 2H, P-Ph H-2,6), 7.86 (d, 2H, N-Ph H-2,6), 8.52 (d, $^3J_{H\text{-}6,P}$ = 18 Hz, 1H, pyazph H-6).

1-(2-Cyanoethyl)-3-methyl-4-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinine (**IIIb**)

This compound was prepared as described for **IIIa**. ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 6H, ind-3-CH_3), 2.38 (s, 3H, pyazph-3-CH_3), 2.88 (t,2H, CH_2-CN), 3.77 (s, 3H, ind-1-CH_3), 4.50 (t, 2H, N-CH_2-), 6.92 (d, 1H, ind H-7), 7.19 (t, 1H, ind H-5), 7.23 (d, 1H, ind H-4), 7.25 (t, 1H, ind H-6), 7.38 (m, 5H, P-Ph H-2,3,4,5,6), 8.49 (d, $^3J_{H\text{-}6,P}$ = 12.4 Hz, 1H, pyazph H-6).

3-Methyl-4-morpholino-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-4λ^5-pyrazolo[3,4-b][1,4]azaphosphinine-4-thione (**Va**)

To a stirred solution of **IIa** (2 mmol) and triethylamine (2 mmol) in dichloromethane (20 mL) was added morpholine (2 mmol) under an argon atmosphere. A ^{31}P-NMR signal δ_p = −3.9 was observed in the NMR spectrum of the reaction mixture. Finely divided sulfur (2 mmol) was added, and the suspension was stirred until sulfur had completely dissolved. The resulting solution was washed with water, dried over Na_2SO_4, filtered, and evaporated. The residue was crystallized from 2-propanol (20 mL).

^{1}H NMR ($CDCl_3$) δ 1.54 (s, 3H, ind-3-CH_3), 1.82 (s, 3H, ind-3-CH_3), 2.61 (s, 3H, pyrazph-3-CH_3), 3.37 (s, 3H, ind-1-CH_3), 3.58 (m, 4H, -CH_2-N-CH_2-), 4.10 (m, 4H, -CH_2-O-CH_2-), 7.30 (m, 7H, ind, Ph H-3,4,5), 7.85 (d, 2H, Ph H-2,6), 8.56 (d, $^3J_{H\text{-}6,P}$ = 24 Hz, 1H, N=C*H*-).

1-(2-Cyanoethyl)-3-methyl-4-morpholino-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-4λ^5-pyrazolo[3,4-b][1,4]azaphosphinine-4-thione (**Vb**)

This compound was prepared as described for **Va**. ^{1}H NMR (DMSO, D_6) δ 1.48 (s, 3H, ind-3-CH_3), 1.79 (s, 3H, ind-3-CH_3), 2.38 (s, 3H, pyrazph-3-CH_3), 2.96 (s, 4H, -CH_2-N-CH_2-), 3.05 (t, 2H, -CH_2-CN), 3.83 (m, 4H, -CH_2-O-CH_2-), 3.96 (s, 3H, ind-1-CH_3), 4.43 (t, 2H, -CH_2-N), 7.41 (m, 3H, ind, H-4,5,6), 7.57 (d, 1H, ind, H-7), 8.30 (d, $^3J_{H\text{-}6,P}$ = 8.6 Hz, 1H, N=C*H*-).

TABLE 1 Synthetic Data, Results of Elemental Analysis, and ^{31}P NMR Spectral Characteristics for Compounds **Ia–XVIa**

Compound	*M.p., °C*	*Yield, %*	*Molecular Formula*	δ_p *^{31}P NMR, ppm in CH_2Cl_2*	*Elmental Analysis Found (calculated)*		
					C	*N*	*P*
Ia	136–137	80	$C_{23}H_{24}N_4$		77.44(77.50)	15.76(15.72)	
Ib	146–148	75	$C_{20}H_{23}N_5$		72.11(72.04)	19.96(21.00)	
IIa	144–146	74	$C_{23}H_{22}BrN_4P$	61.4	59.29(59.37)	11.97(12.04)	6.58(6.66)
IIb	126–128	58	$C_{20}H_{21}BrN_5P$	79.1	54.26(54.31)	15.76(15.83)	6.92(7.00)
IIc	130–132	67	$C_{23}H_{22}ClN_4P$	51.3	65.67(65.64)	13.27(13.31)	7.29(7.36)
IIIa	180	40	$C_{29}H_{27}N_4P$	−70; −71	75.28(75.31)	12.06(12.11)	6.64(6.70)
IIIb	168	56	$C_{26}H_{26}N_5P$	−69; −76	70.98(71.06)	15.88(15.93)	7.11(7.05)
Va	253	52	$C_{27}H_{30}N_5OPS$	35.1	63.97(64.4)	13.85(13.91)	6.09(6,15)
Vb	214–216	63	$C_{24}H_{29}N_6OPS$	34.2; 34.4	59.92(59.98)	17.43(17.49)	6.38(6.45)
Vc	223	70	$C_{29}H_{28}N_5PS$	21	68.32(68.35)	13.78(13.74)	6.02(6.08)
VIa	166–167	72	$C_{27}H_{30}Cl_2N_5OP$	8.41	59.73(59.78)	12.78(12.91)	5.66(5.71)
VIIa	228–230	47	$C_{27}H_{30}N_5O_2P$	12.8	66.43(66.52)	14.38(14.36)	6.29(6.35)
VIIIa	243–245	36	$C_{27}H_{32}ClN_6OP$	19.7	61.89(62.01)	16.13(16.07)	5.97(5.92)
Xa	188	52	$C_{24}H_{25}N_4OPS$	5.2	64.21(64.27)	12.53(12.49)	7.03(6.91)
XIa	242	67	$C_{23}H_{23}N_4OP$	−17.2 (532 Hz)	68.58(68.65)	14.03(13.92)	7.65(7.70)
XIb	136	35	$C_{20}H_{22}N_5OP$	−15 (484 Hz)	63.26(63.32)	18.52(18.46)	8.10(8.16)
XIIa	210–212	45	$C_{23}H_{23}N_4O_2P$	8.15; 8.86	65.99(66.02)	13.43(13.39)	7.36(7.40)
XIIIa	262	68	$C_{23}H_{23}N_4OPS$	15	63.52(63.58)	12.81(12.89)	7.18(7.13)
XIVa	228	60	$C_{29}H_{27}N_4PS$	13	70.44(70.43)	11.26(11.33)	6.31(6.26)
XVa	162–164	32	$C_{29}H_{27}N_4OP$	23.4	72.72(72.79)	11.77(11.71)	6.40(6.47)
XVb	142–144	64	$C_{26}H_{26}N_5OP$	21	68.49(68.56)	15.43(15.38)	6.77(6.80)
XVIa	153	52	$C_{35}H_{32}N_5P$	24	75.87(75.93)	12.59(12.65)	5.64(5.59)

4-Anilino-3-methyl-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-4λ⁵-pyrazolo[3,4-b][1,4]azaphosphinine-4-thione (**Vc**)

This compound was prepared as described for **Va**. ^1H NMR (DMSO, D_6) δ 1.53 (s, 3H, ind-3-CH_3), δ 1.63 (s, 3H, ind-3-CH_3), 2.25 (s, 3H, pyazph-3-CH_3), 3.95 (s, 3H, ind-1-CH_3), 6.34–7.73 (m, 15 H, ind H-4,5,6,7, N-Ph H-2,3,4,5,6 P-NH-Ph H-2,3,4,5.6), 8.3 (d, $^3J_{H\text{-}6,P}$ = 3.6 Hz, 1H, N=C*H*-).

4-Chloro-3-methyl-4-morpholino-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinin-4-ium Chloride (**VIa**)

To a stirred solution of **IIa** (2 mmol) and triethylamine (2 mmol) in dichloromethane (20 mL) was added morpholine (2 mmol) under an argon atmosphere. A ^{31}P-NMR signal δ_p = −3.9 was observed in the NMR spectrum of the reaction mixture. The solvent was evaporated, and the residue was dissolved in toluene (40 mL). Hexane (1 mL) was added to the resulting solution, and the precipitate that formed was filtered off. The filtrate was treated with dry hexachloroethane (2 mmol). The pale yellow crystals were filtered off and dried.

3-Methyl-4-morpholino-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolylidene)-4,5-dihydro-1H-4λ⁵-pyrazolo[3,4-b][1,4]azaphosphinine-4-one (**VIIa**)

A solution of salt **VIa** (2 mmol) in dichloromethane (20 mL) was treated with 5% aq Na_2CO_3 (20 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and evaporated. The residue was crystallized from toluene.

^1H NMR ($CDCl_3$) δ 1.70 (s, 3H, ind-3-CH_3), 1.74 (s, 3H, ind-3-CH_3), 2.54 (s, 3H, pyazph-3-CH_3), 2.96 (m, 4H, morph H-3,5), 3.50 (m, 4H, morph H-2,6), 4.05 (s, 3H, ind-1-CH_3), 7.08 (d, 1H, ind H-7), 7.23 (t, 1H, ind H-5), 7.28 (t, 1H, Ph H-4), 7.29 (d, 1H, ind H-4), 7.36 (t, 1H, ind H-6), 7.43 (t, 2H, Ph H-3,5), 7.85 (d, 2H, Ph H-2,6), 8.39 (d, $^3J_{H\text{-}6,P}$ = 25.0 Hz, 1H, pyazph H-6). ^{13}C NMR ($CDCl_3$) δ 14.8 (pyazph-3-CH_3, ^1J = 128.0 Hz), 26.6 (ind-3-CH_3, ^1J = 130.1 Hz), 27.4 (ind-3-CH_3, ^1J = 130.1 Hz), 38.0 (ind-1-CH_3, ^1J = 141.3 Hz), 44.2 (morph C-3,5, ^1J = 136.5 Hz), 52.3 (ind C-3, $^3J_{C\text{-}3,P}$ = 5.5 Hz), 67.2 (morph C-2,6, $^3J_{C\text{-}2,P}$ = 6.9 Hz), 92.6 (pyazph C-5, $^1J_{C\text{-}5,P}$ = 126.1 Hz, $^2J_{C\text{-}5,H\text{-}6}$ = 8.3 Hz), 96.9 (pyazph C-3a, $^1J_{C\text{-}3a,P}$ = 143.9 Hz, $^3J_{C\text{-}3a,3\text{-}Me}$ = 3.0 Hz), 110.8 (ind C-7), 121.6 (ind C-4), 123.5 (Ph C-2,6), 125.4 (ind C-5), 126.4 (Ph C-4), 128.3 (ind C-6), 128.7 (Ph C-3,5), 139.0 (Ph C-1), 141.0 (ind C-3a), 143.2 (ind C-7a), 148.8 (pyazph C-3, $^2J_{C\text{-}3,P}$ = 6.7 Hz, $^2J_{C\text{-}3,3\text{-}Me}$ = 6.8 Hz), 153.4 (pyazph

C-7a, $^2J_{C\text{-}7a,P}$ = 14.5 Hz, $^3J_{C\text{-}7a,H\text{-}6}$ = 17.6 Hz), 157.7 (pyazph C-6, ^1J = 174.8 Hz, $^2J_{C\text{-}6,P}$ = 5.4 Hz), 184.1 (ind C-2, $^2J_{C\text{-}2,P}$ = 3.8 Hz).

4-Amino-3-methyl-4-morpholino-1-phenyl-5-(1,3,3-trimethyl-2,3-dihydro-1H-2-indolinylidene) 4,5-dihydro-1H-pyrazolo[3,4-b][1,4]azaphosphinin-4-ium Chloride (**VIIIa**)

Ammonia was bubbled for 30 minutes into a solution of salt **VIa** (2 mmol) in dichloromethane (20 mL). The reaction mixture was washed with 5% aq Na_2CO_3 (20 mL). The organic phase was separated, dried (Na_2SO_4), filtered, and evaporated. The residue was crystallized from toluene.

^{1}H NMR ($CDCl_3$) δ 1.57 (s, 3H, ind-3-CH_3), 1.80 (s, 3H, ind-3-CH_3), 2.60 (s, 3H, pyrazph-3-CH_3), 3.18 (m, 4H, morph H-3,5), 3.67 (m, 4H, morph H-2,6), 4.11 (s, 3H, ind-1-CH_3), 6.61 (s, 2H, Ph H-2,6), 7.45 (m, 6H, ind H-4,5,6 Ph H-3,4,5), 7.89 (d, 1H, ind H-7), 8.07 (d, $^3J_{H\text{-}6,P}$ = 27.0 Hz, 1H, pyazph H-6).

4,5-Dihydro-3-methyl-4-methoxy-4-thioxo-1-phenyl-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**Xa**)

To a stirred solution of **IIa** (2 mmol) and triethylamine (2 mmol) in dichloromethane (20 mL) was added absolute methanol (2 mmol) under an argon atmosphere. A ^{31}P-NMR signal δ_p = 30.1 was observed in the spectrum of the reaction mixture. Finely divided sulfur (2 mmol) was added, and the suspension was stirred until the sulfur had completely dissolved. The resulting solution was washed with water, dried over Na_2SO_4, filtered, and evaporated. The residue was crystallized from 2-propanol (15 mL).

^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3H, ind-3-CH_3), 1.83 (s, 3H, ind-3-CH_3), 2.66 (s, 3H, pyazph-3-CH_3), 3.45 (d, $^3J_{OMe,P}$ = 14.8 Hz, 3H, OCH_3), 4.06 (s, 3H, ind-1-CH_3), 7.18 (d, 1H, ind H-7), 7.28 (t, 1H, ind H-5), 7.30 (d, 1H, ind H-4), 7.30 (t, 1H, Ph H-4), 7.39 (t, 1H, ind H-6), 7.47 (t, 2H, Ph H-3,5), 7.86 (d, 2H, Ph H-2,6), 8.55 (d, $^3J_{H\text{-}6,P}$ = 25.5 Hz, 1H, pyazph H-6). ^{13}C NMR ($CDCl_3$) δ 14.5 (pyazph-3-CH_3, ^1J = 128.3 Hz), 26.6 (ind-3-CH_3, ^1J = 130.1 Hz), 27.0 (ind-3-CH_3, ^1J = 130.1 Hz), 38.0 (ind-1-CH_3, ^1J = 141.6 Hz), 52.1 (OCH_3, ^1J = 146.3 Hz, $^2J_{OMe,P}$ = 8.6 Hz), 53.0 (ind C-3, $^3J_{C\text{-}3,P}$ = 7.1 Hz), 93.4 (pyazph C-5, $^1J_{C\text{-}5,P}$ = 105.9 Hz, $^2J_{C\text{-}5,H\text{-}6}$ = 9.3 Hz), 96.1 (pyazph C-3a, $^1J_{C\text{-}3a,P}$ = 129.4 Hz, $^3J_{C\text{-}3a,3\text{-}Me}$ = 3.0 Hz), 111.6 (ind C-7), 121.6 (ind C-4), 123.8 (Ph C-2,6), 125.7 (ind C-5), 126.7 (Ph C-4), 128.4 (ind C-6), 128.8 (Ph C-3,5), 138.9 (Ph C-1), 141.1 (ind C-3a), 143.2 (ind C-7a), 149.8 (pyazph C-3, $^2J_{C\text{-}3,P}$ = 8.2 Hz, $^2J_{C\text{-}3,3\text{-}Me}$ = 6.8 Hz), 151.1 (pyazph C-7a, $^2J_{C\text{-}7a,P}$ = 12.8 Hz, $^3J_{C\text{-}7a,H\text{-}6}$ = 16.8 Hz), 156.8 (pyazph C-6, ^1J = 175.6 Hz, $^2J_{C\text{-}6,P}$ = 2.8 Hz), 183.2 (ind C-2, $^2J_{C\text{-}2,P}$ = 3.3 Hz).

4,5-Dihydro-3-methyl-4-oxo-1-phenyl-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XIa**)

Water (4 mmol) was added to a stirred solution of **IIa** (2 mmol) and triethylamine (2 mmol) in dichloromethane (20 mL). A ^{31}P-NMR signal δ_p = −17,2 (J_{PH} = 532 Hz) was observed. The resulting solution was washed with water, dried over Na_2SO_4, filtered, and evaporated. The residue was crystallized from 2-propanol (15 mL).

^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3H, ind-3-CH_3), 1.87 (s, 3H, ind-3-CH_3), 2.50 (s, 3H, pyazph-3-CH_3), 4.03 (s, 3H, ind-1-CH_3), 7.4–8.1 (m, 8H, ind H-4,5,6,7, Ph H-2,3,4,5,6, 1H, -CH=N-), 8.9 (d, 1H, J_{PH} = 532 Hz, P-H).

1-(2-Cyanoethyl)-4,5-dihydro-3-methyl-4-oxo-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XIb**)

This compound was prepared as described for **XIa**. ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6H, ind-3-CH_3), 2.36 (s, 3H, pyazph-3-CH_3), 3.05 (t, 2H, -CH_2-CN), 3.90 (s, 3H, ind-1-CH_3), 4.45 (t, 2H, -CH_2-N-), 7.09 (d, 1H, ind H-7), 7.31–7.50 (m, 2H, ind H-5,6), 7.60 (d, 1H, ind H-4), 8.25 (d, $^3J_{H\text{-}6,P}$ = 11.16 Hz, 1H, pyazph H-6), 8.8 (d, J_{PH} = 484 Hz, 1 H, P-H).

4,5-Dihydro-4-hydroxy-3-methyl-4-oxo-1-phenyl-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XIIa**)

Carbon tetrachloride (20 mmol), triethylamine (2 mmol), and water (10 mmol) were added to a solution of **XIa** (2 mmol) in dichloromethane (20 mL). The mixture was stirred for 12 hours at room temperature, then washed with water, dried for 2 hours over Na_2SO_4, filtered, and evaporated. The residue was crystallized from toluene (20 mL).

^{1}H NMR (DMSO, D_6) δ 1.46 (s, 3H, ind-3-CH_3), δ 1.73 (s, 3H, ind-3-CH_3), 2.28 (s, 3H, pyazph-3-CH_3), 3.96 (s, 3H, ind-1-CH_3), 7.15–7.75 (m, 9H, ind H-4,5,6,7, N-Ph H-2,3,4,5,6), 8.1 (d, $^3J_{H\text{-}6,P}$ = 11.8 Hz, 1H, N=C*H*-).

4,5-Dihydro-4-hydroxy-3-methyl-4-thioxo-1-phenyl-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XIIIa**)

Finely divided sulfur (2 mmol) was added to a solution of **XIa** (2 mmol) in dichloromethane (20 mL),

and the suspension was stirred until the sulfur had completely dissolved and evaporated. The residue was crystallized from 2-propanol (15 mL).

^{1}H NMR (DMSO, D_6) δ 1.44 (s, 3H, ind-3-CH_3), δ 1.72 (s, 3H, ind-3-CH_3), 2.27 (s, 3H, pyazph-3-CH_3), 3.88 (s, 3H, ind-1-CH_3), 7.23–7.96 (m, 9H, ind H-4,5,6,7, N-Ph H-2,3,4,5,6), 8.21 (d, $^3J_{H\text{-}6,P}$ = 19 Hz, 1H, N=C*H*-).

1,4-Diphenyl-4,5-dihydro-3-methyl-4-thioxo-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XIVa**)

Sulfur (2 mmol) was added to a solution of **IIIa** (2 mmol) in dichloromethane (20 mL), and the reaction mixture was stirred until the sulfur had completely dissolved. After evaporation of the solvent, the residue was crystallized from toluene.

^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3H, ind-3-CH_3), 1.74 (s, 3H, ind-3-CH_3), 2.15 (s, 3H, pyazph-3-CH_3), 3.85 (s, 3H, ind-1-CH_3), 6.90 (d, 1H, ind H-7), 7.10–7.5 (m, 9H, ind H-4,5,6, N-Ph H-3,4,5 P-Ph H-3,4,5), 7.72 (m, 2H, P-Ph H-2,6), 7.82 (d, 2H, N-Ph H-2,6), 8.58 (d, $^3J_{H\text{-}6,P}$ = 22 Hz, 1H, pyazph H-6).

1,4-Diphenyl-4,5-dihydro-3-methyl-4-oxo-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XVa**)

To a stirred solution of **IIIa** (2 mmol) in dichloromethane (20 mL) was added 50% hydrogen peroxide (4 mmol). The reaction mixture was stirred for 6 hours at room temperature and then washed with 5% aq Na_2CO_3 (20 mL). The organic layer was separated, dried (Na_2SO_4), filtered, and evaporated. The residue was crystallized from toluene.

^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, ind-3-CH_3), 1.73 (s, 3H, ind-3-CH_3), 2.14 (s, 3H, pyazph-3-CH_3), 3.83 (s, 3H, ind-1-CH_3), 6.88 (d, 1H, ind H-7), 7.19 (t, 1H, ind H-5), 7.26 (d, 1H, ind H-4), 7.28 (t, 1H, ind H-6), 7.29 (t, 1H, N-Ph H-4), 7.38 (m, 3H, P-Ph H-3,4,5), 7.45 (t, 2H, N-Ph H-3,5), 7.72 (m, 2H, P-Ph H-2,6), 7.85 (d, 2H, N-Ph H-2,6), 8.54 (d, $^3J_{H\text{-}6,P}$ = 21.4 Hz, 1H, pyazph H-6). ^{13}C NMR ($CDCl_3$) δ 13.8 (pyazph-3-CH_3, ^1J = 128.2 Hz), 25.9 (ind-3-CH_3, ^1J = 130.1 Hz), 27.9 (ind-3-CH_3, ^1J = 130.1 Hz), 37.9 (ind-1-CH_3, ^1J = 141.4 Hz), 52.3 (ind C-3, $^3J_{C\text{-}3,P}$ = 5.5 Hz), 93.9 (pyazph C-5, $^1J_{C\text{-}5,P}$ = 103.0 Hz, $^2J_{C\text{-}5,H\text{-}6}$ = 9.0 Hz), 97.3 (pyazph C-3a, $^1J_{C\text{-}3a,P}$ = 129.7 Hz, $^3J_{C\text{-}3a,3\text{-}Me}$ = 3.0 Hz), 110.7 (ind C-7), 121.6 (ind C-4), 123.8 (N-Ph C-2,6), 125.3 (ind C-5), 126.6 (N-Ph C-4), 128.2 (ind C-6), 128.4 (P-Ph C-3,5, $^3J_{C\text{-}3,P}$ = 12.6 Hz), 128.8 (N-Ph C-3,5), 130.9 (P-Ph C-4, $^4J_{C\text{-}4,P}$ = 2.7 Hz), 131.5 (P-Ph C-2,6, $^2J_{C\text{-}2,P}$ = 10.2 Hz), 137.7 (P-Ph C-1, $^1J_{C\text{-}1,P}$ = 117.3 Hz), 138.9 (N-Ph C-1), 141.0 (ind C-3a), 143.1 (ind C-7a), 149.7 (pyazph C-3, $^2J_{C\text{-}3,P}$ = 8.0 Hz, $^2J_{C\text{-}3,3\text{-}Me}$ = 6.8 Hz), 151.4 (pyazph C-7a, $^2J_{C\text{-}7a,P}$ = 12.5 Hz, $^3J_{C\text{-}7a,H\text{-}6}$ = 16.7 Hz), 157.1 (pyazph C-6, ^1J = 175.5 Hz, $^2J_{C\text{-}6,P}$ = 3.3 Hz), 184.4 (ind C-2, $^2J_{C\text{-}2,P}$ = 5.5 Hz).

1-(2-Cyanoethyl)-4-phenyl-4,5-dihydro-3-methyl-4-oxo-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XVb**)

This compound was prepared as described for **XVIa**. ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 6H, ind-3-CH_3), 1.87 (s, 3H, pyazph-3-CH_3), 3.08 (t, 2H, -CH_2-CN), 3.94 (s, 3H, ind-1-CH_3), 4.5(t, 2H, -CH_2-N), 6.98 (d, 1H, ind H-7), 7.15–7.75 (m, 6H, ind H-4,5,6, P-Ph H-3,4,5), 7.84 (m, 2H, P-Ph H-2,6), 8.46 (d, $^3J_{H\text{-}6,P}$ = 24 Hz, 1H, pyazph H-6).

1,4-Diphenyl-4,5-dihydro-3-methyl-4-phenylimino-5-(1,3,3-trimethyl-2-indolinylidene)-1H-pyrazolo-[3,4-b][1,4]azaphosphinine (**XVIa**)

Phenyl azide (2 mmol) was added to a solution of **IIIa** (2 mmol) in dichloromethane (20 mL), and the reaction mixture was stirred for 24 hours evaporated. The residue was crystallized from toluene.

^{1}H NMR ($CDCl_3$) δ 1.71 (s, 6H, ind-3-CH_3), 2.23 (s, 3H, pyazph-3-CH_3), 3.94 (s, 3H, ind-1-CH_3), 6.15 (d, 1H, ind H-7), 7.09–7.83 (m, 18 H, ind H-4,5,6, N-Ph H-2,3,4,5,6 P-Ph H-2,3,4,5,6 P=N-Ph H-2,3,4,5,6), 8.23 (d, $^3J_{H\text{-}6,P}$ = 21 Hz, 1H, pyazph H-6).

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