Synthesis and acid-base properties of phosphorylated diazacycloalkanes and their cyclic analogs

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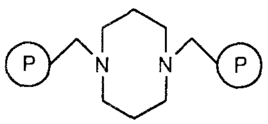
Novel cyclopendant organophosphorus complexing agents, *viz.* 1,5-bis(2-diphenylphosphorylmethyl(or ethyl))-1,5-diazacyclooctane (**1**, **2**) and 1-methyl-4-(2-diphenylphosphorylethyl)piperazine (**3**), were synthesized on the basis of 1,5-diazacyclooctane and piperazine. The protonation constants of the compounds synthesized and some of their analogs were determined by potentiometric titration in 70 % aqueous ethanol and in nitromethane. The nitrogen atoms of the ring are the protonation sites in all of the systems studied. The regularities of the variation of protonation constants have been explained by the formation of intramolecular hydrogen bonds. The conformational possibilities of the formation of H-bonds in the cations of the ligands have been examined by molecular mechanics.

Key words: cyclopendant ligands, phosphorylated diazacycloalkanes, protonation constants, potentiometric titration, intramolecular hydrogen bonds, conformational analysis.

Organophosphorus cyclopendant structures based on polyaza rings containing diphenylphosphoryl groups in pendants proved to be interesting complexing agents.[1] The effects of the size of the ring and the length of the pendant chain on the composition and structure of the complexes was examined using tetraazacyclic ligands as an example.[1,2] It was of interest to verify the observations made in the series of lower-dentate cyclopendant compounds. Novel organophosphorus complexing reagents based on 1,5-diazacyclooctane with methylene (**1**) and ethylene (**2**) pendant chains were prepared.



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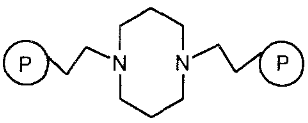
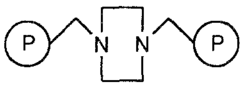
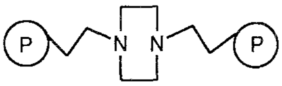


2

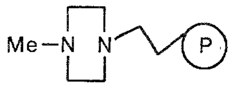
Ⓟ = Ph$_2$P(O)

In the present work we intended to study and compare the acid-base properties of phosphorylated diazacyclooctanes **1**, **2**, and their previously synthesized[3] analogs derived from piperazine:



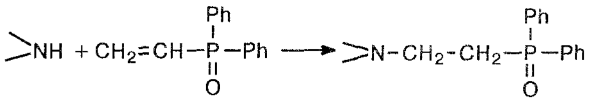


However, it turned out that diphosphorylated piperazines are very poorly soluble ($<10^{-5}$ mol L^{-1}) in aprotic dipolar solvents (nitromethane, dimethylformamide, acetonitrile), and therefore, we synthesized monophosphorylated 1-methyl-4-(2-diphenylphosphorylethyl)piperazine (**3**) for the comparison.



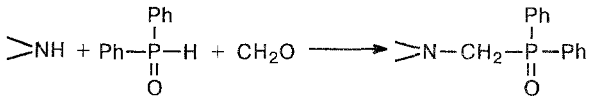
3

Diazacycloalkanes **2** and **3** containing ethylene pendant chains were prepared according to the general scheme by the reaction of the corresponding diazacycloalkane with diphenylvinylphosphine oxide



$$>\!NH + CH_2{=}CH{-}\underset{\underset{O}{\|}}{\overset{\overset{Ph}{|}}{P}}{-}Ph \longrightarrow >\!N{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{Ph}{|}}{P}}{-}Ph$$

Ligand **1** with the methylene pendant chain was prepared by the Mannich condensation of 1,5-diazacyclooctane with diphenylphosphine oxide and paraform:



$$>\!NH + Ph{-}\underset{\underset{O}{\|}}{\overset{\overset{Ph}{|}}{P}}{-}H + CH_2O \longrightarrow >\!N{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{Ph}{|}}{P}}{-}Ph$$

The structures of the resulting compounds were confirmed by the data of elemental analysis and IR and ^{31}P NMR spectra.

The acid-base properties of phosphorylated diazacycloalkanes (PDAC) and some model compounds were

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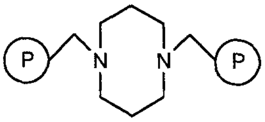
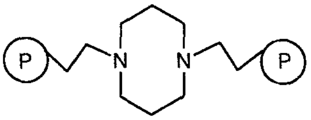
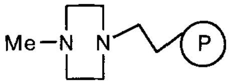
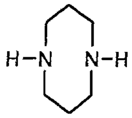
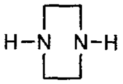
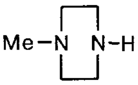
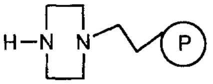
Table 1. The protonation constants (pK_1 and pK_2) of diazacycloalkanes and PDAC in 70 % w/w aqueous ethanol and in nitromethane at 298 K

Compound*		pK_1, pK_2				ΔpK_{1-2}	
		70 % ethanol		$MeNO_2$		70 % ethanol	$MeNO_2$
	**1**	—	—	13.9	3.2	—	10.7
	**2**	8.44**	3.28**	18.2	4.7	5.16	13.5
	**3**	6.71	2.20	13.7	7.1	4.51	6.6
	**4**	7.16	4.77	17.4	8.1	2.39	9.3
	**5**	(9.731)***	(5.333)***	14.6	9.0	(4.398)***	5.6
	**6**	7.56	3.07	14.4	8.2	4.49	6.2
	**7**	—	—	14.1	8.1	—	6.0

* Ⓟ = $Ph_2P(O)$

** Measurements without ionic strength (compound **2** forms a poorly soluble complex with $LiNO_3$).

*** The data for aqueous solutions.[6]

studied by potentiometric titration with a glass electrode in aqueous ethanol (70 % w/w) and nitromethane at 298 K using perchloric acid as the titrant. Notice that in spite of the extensive studies being carried out on aminophosphine oxide compounds,[4] the data concerning their p*K* values are scanty or are tentative estimates.[5]

The compounds under study are diatomic bases in both solvents. The constants of the first and second steps of their protonation and $\Delta pK = pK_1 - pK_2$ values for both solvents are listed in Table 1.

$$B + H^+ \xrightleftharpoons{K_1} BH^+ \tag{1}$$

$$BH^+ + H^+ \xrightleftharpoons{K_2} BH_2^{2+}, \tag{2}$$

From a comparison of the protonation constants for phosphorylated and nonphosphorylated compounds (Table 1), it follows that the nitrogen atoms of the ring act as the protonation sites in all cases (the basicity of phosphine oxides is approximately 10 orders of magnitude lower than that of amines). This is also confirmed by an examination of the IR spectra of mono- and diprotonated salts of PDAC.[7]

The introduction of the electron-withdrawing[8] diphenylphosphorylalkyl group to the nitrogen atom decreases the basicity of the compound. The shorter is the alkylene chain between the P and N atoms, the greater is this effect. This can be clearly seen by comparing the basicities of aliphatic amines (**8—12**) in nitromethane (Table 2). On going from amine **8** (p*K* = 15.2) to amine **11** (p*K* = 10.8) the basicity decreases by 4.4 p*K* units, while going from **8** to **12** (p*K* 13.8) results in a decrease by only 1.4 p*K* units. In addition, the basicity of compound **12** in nitromethane is increased somewhat due to the formation of the $N^+—H...O=P$ intramolecular hydrogen bond (IMHB) in the protonated cation.[7] Similar regularities of the effect of an introduced phosphoryl group on the basicity have been observed in the study of phosphorylated picolines.[12]

Similar effects are found when PDAC are compared with nonphosphorylated diazacycloalkanes. In fact, in

Table 2. The values of the protonation constants of some acyclic amines in water and nitromethane at 298 K

Compound*		pK(H$_2$O)[9]	pK(MeNO$_2$)
Et$_2$NH	**8**	11.04	15.2**
Pr$_2$NH	**9**	11.00	15.0**
Et$_3$N	**10**	10.78	15.6**; 15.7[11]
	**11**	—	10.8
	**12**	—	13.8

* Ⓟ = Ph$_2$P(O)

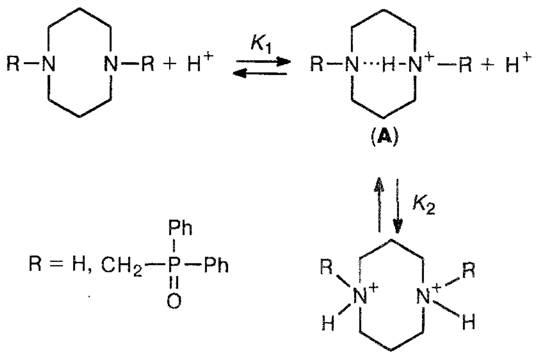
** The pK values reported in the literature[10] were converted to the nitromethane pH scale[11] used in the present work.

the efficiently solvating aqueous alcohol, the pK_1 and pK_2 values of monophosphorylated piperazine **3** are 0.8 log. units lower than those of prototype **6** (see Table 1). Unfortunately, for the pair of diazacyclooctanes **2** and **4**, such a comparison cannot be carried out, due to dissimilarity of the conditions for the experimental determination of pK (see Note to Table 1). Notice as well that the ΔpK_{1-2} values of piperazine bases in water and in aqueous alcohol are almost identical, which is typical of homologs with the same mechanism of protonation in efficiently solvating solvents. However, in nitromethane, which weakly solvates cations, the picture is somewhat more intricate.

Actually, the basicity of 1,5-diazacyclooctane **4** at the first protonation step (pK_1) in nitromethane is higher than basicity of alkylamines (*cf.* compound **4**, Table 1 and compounds **8—10**, Table 2). An additional stabilization of the proton in the monoprotonated cation **4** may be provided *inter alia* by the formation of the N$^+$—H...N IMHB, which closes a six-membered chelate ring (structure **A**, Eq. (3)), in a manner similar to that proposed for 1,3-diaminopropane and 1,4-diaminobutane in acetonitrile.[13]

The molecular mechanics (MM) method (the MMX 88 program, PC Model, Serena Software, Bloomington IN) was used for calculating the conformational energies of monoprotonated forms of **4** in which interactions of the proton of the N$^+$—H...N type are possible. The "crown"-shaped conformer with a distance between the nitrogen atoms of 2.77 Å, in which the directions of the electron pair of the nitrogen atom and of the N$^+$—H bond allow the formation of the H-bond, is the most stable. One more conformer with the required direction of the functional groups also exists. Its energy is higher by 2.8 kcal mol^{-1} (a local minimum) and the distance between the nitrogen atoms is 2.71 Å. The typical distance between nitrogen atoms in the N$^+$—H...N bonds is known[14] to be 2.98 Å. Thus, the formation of an N$^+$—H...N bond in monoprotonated **4** is quite possible.

When two diphenylphosphoryl groups are attached to the nitrogen atoms *via* the methylene pendant chain (compound **1**, Table 1), the basicity of PDAC decreases, and the ΔpK_{1-2} magnitudes for phosphorylated (**1**) and mononphosphorylated (**4**) amines differ only by 1.4 log units (Table 1). In nitromethane, these bases are probably protonated *via* identical mechanisms, and the phosphoryl groups only decrease the pK value due to their electron-withdrawing effect. The scheme of the protonation of both bases may be represented by the following equation:



(3)

A similar stabilization of the proton in monoprotonated cations of compounds with a piperazine ring is unfavorable. The MM calculations for the monoprotonated cation of piperazine gave three conformers: a chair, a twist, and a twist-boat conformer. The chair is the most stable conformer for both the cation and the piperazine molecule,[15] however, it does not allow the formation of the IMHB, since the electron pair of nitrogen and the N$^+$—H bond are oppositely directed. In the less stable conformers, the directions of the functional groups are also not optimal: they are either parallel to one another or are arranged at a diverging angle. In fact, the variation of the basicities of compounds **3**, **5—7** (Table 1) following a change in the solvent (the ΔpK_{1-2} values) and the relative pK_1 and pK_2 values follow the expected tendencies.

The basicity of PDAC **2** with ethylene pendant chains at the first protonation step in nitromethane is surprisingly higher than that of the nonphosphorylated prototype **4** (Table 1) and is even higher than that of alkylamines **8—10** (Table 2). Thus, the protonation of PDAC **2** occurs by a different mechanism than its analogs **1** and **4**. A study of the IR spectra of solutions of mono- or diprotonated salts **2** in acetonitrile showed that an additional stabilization of the proton in the monoprotonated **2** is achieved by the formation of an IMHB involving one phosphoryl group.[7] The monoprotonated cation of **2** can have various structures.

By the MM calculations of the conformational energy of the monoprotonated cation of **2**, the global minimum corresponding to the stable conformation has been determined. This conformation is shown in Fig. 1. As can be seen from Fig. 1, in this conformation, the

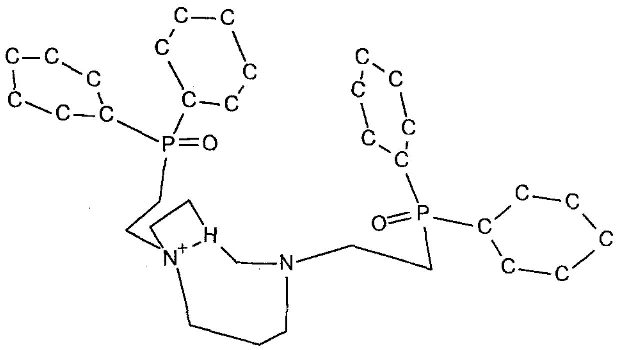


Fig. 1. The conformation of the monoprotonated cation derived from PDAC **2** in the global minimum region. The distances between the N$^+$ atom and the O atoms of the two phosphoryl groups are 3.20 and 3.75 Å, and that between the nitrogen atoms of the ring is 2.92 Å.

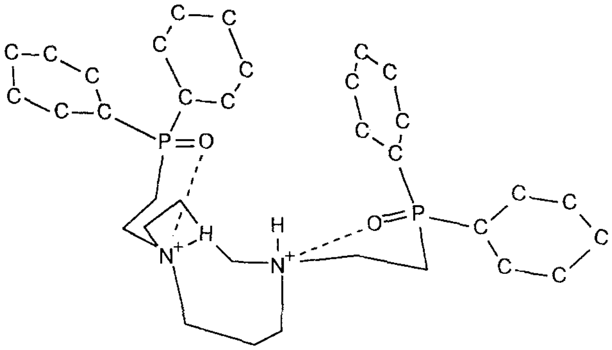
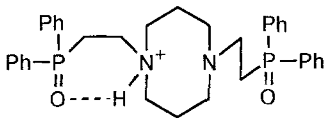
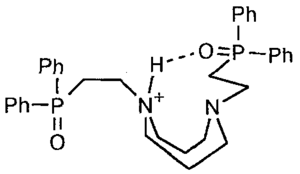


Fig. 2. The conformation of the diprotonated cation derived from PDAC **2** in the global minimum region. The distances between the N$^+$ atom and the O atoms of the phosphoryl groups denoted by the dashed lines are 3.11 and 3.16 Å, and that between the nitrogen atoms of the ring is 3.13 Å.

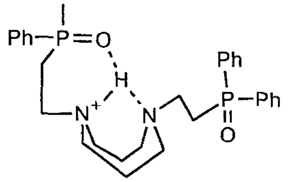
N$^+$ atom and the O atoms of the two phosphoryl groups are rather closely spaced (3.20 and 3.75 Å), and the distance between the nitrogen atoms of the ring is 2.92 Å. With certain expenditures of energy, various interactions of the proton of the N$^+$—H group can occur in this conformer, namely, an H-bond with its own phosphoryl group (structure **B**), that with the other phosphoryl group (structure **C**), and a three-center H-bond (structure **D**).



(B)



(C)



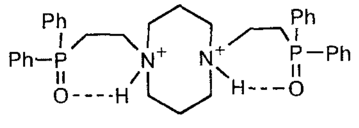
(D)

Structures **B**—**C** were optimized at a specified N$^+$...O distance of 2.98 Å; for structure **D**, the N$^+$...N distance equal to 2.98 Å was also specified (these are typical distances for this type of H-bonds[14]). These calculations yielded strain energies for forms **B**, C, and **D** equal to 0.5, 4.2, and 5.4 kcal mol^{-1}, respectively.

The data of IR and ^{31}P NMR spectra of solutions of salts do not allow one to decide unambiguously between these structures.[7] However, though structure **B** has the lowest strain energy, we believe that in nonaqueous solutions, the cation of PDAC **2** exists as structure **D**. First, one should take into account that, although the strain energy of structure **D** is the highest, it is nevertheless substantially lower than the total energy of the two H-bonds formed. Second, a comparison of the pK values of aminophosphoryl compounds indicates that the formation of an IMHB with closure of the six-membered chelate ring (as in structure **B**) does not increase pK as much as in the case of PDAC **2**. In fact, despite the formation of H-bonds of this type,[7] the pK_2 value of compound **3** and pK of compound **12** are lower than the corresponding values for the nonphosphorylated prototypes by 1.1 and 1.4 log units (see Tables 1 and 2).

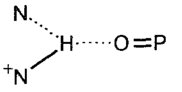
Notice that structures with bi- and trifurcate intramolecular H-bonds have been found in the study of protonation of tridentate phosphoryl ligands[16] and in complexones of aminopolycarboxylic acids.[17,18]

According to the data of IR spectra, the addition of the second proton to PDAC **2** results in the formation of the cation with two identical IMHB.[7] The MM calculation of the conformational energy of this cation showed that the preferred conformation is that shown in Fig. 2 with the N$^+$...O distances equal to 3.11 и 3.16 Å and the N$^+$...N distance equal to 3.13 Å. The strain energy of the optimized structure with a specified N$^+$...O distance of 2.98 Å is as low as 0.5 kcal mol^{-1}. It is likely that the second step of the protonation of compound 2 yields the structure **E** cation.



E

Thus, we believe that the first step of protonation of PDAC **2** in nitromethane affords the cation stabilized by a three-center hydrogen bond

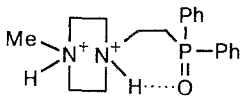


(structure **D**), or an equilibrium between three forms of the cation, **B**, **C**, and **D**, and the addition of the second fragment gives the cation with two type N$^+$—H...O=P IMHB (structure **E**).

In monophosphorylated piperazines **3** and **7** (Table 1), the formation of the IMHB would be expected. However, the order in which the two nitrogen atoms in these compounds are protonated remains unclear, since their basicities in a poorly solvating medium may be close to one another, due to the possibility of the formation of the IMHB. A spectroscopic study of mono- and diprotonated salts **3** showed[7] that the nitrogen atom bearing the methyl substituent is the first to be protonated, and the phosphoryl group attached to the second nitrogen atom of the piperazine ring remains unbound (free). The addition of the second proton produces a diprotonated cation with an N$^+$—H..O=P IMHB.

The MM calculations show that the conformer in which the piperazine ring exists as a chair form and the N$^+$...O distance is 4.27 Å is the preferred conformation of the monoprotonated cation of **3** (Fig. 3). Optimization of the structure at a specified N$^+$...O distance of 2.98 Å (the H-bond with the "foreign" phosphoryl group) produces a strain energy equal to 8.0 kcal mol^{-1}, which indicates that this bond is unfavorable. The N$^+$...O distance in the preferred conformation of the diprotonated cation is 3.04 Å. Optimization of the structure at an N$^+$...O distance of 2.98 Å results in a value for the strain energy of only 0.1 kcal mol^{-1}. To the contrary, the strain energy of the conformer, which allows the formation of the H-bond with the oxygen of the "foreign" phosphoryl group, amounts to 17.1 kcal mol^{-1}.

Thus, the second step of the protonation of piperazine **3** results in the cation stabilized with an H-bond (structure **F**):



F

Analysis of the protonation constants of compounds **3** and **7** (Table 1) is in agreement with the mechanism suggested. In compounds **3** and **7**, the first proton is added to the nonphosphorylated nitrogen atom of the ring. Hence, the pK_1 value is only slightly less than pK of the nonphosphorylated prototype (*cf.* pairs **5**—**7** and **6**—**3** in Table 1) due to the long-range influence of the electron-withdrawing diphenylphosphoryl group. The addition of the second proton is accompanied by the formation of an IMHB, which closes the six-membered chelate ring (the cation structure **F**), which should increase somewhat the basicity with respect to the second step and balance the effect of the phosphoryl group. In fact, the pK_2 values for compounds **3** and **7** are ~1 log unit less than pK of the nonphosphorylated prototypes **5** and **6**.

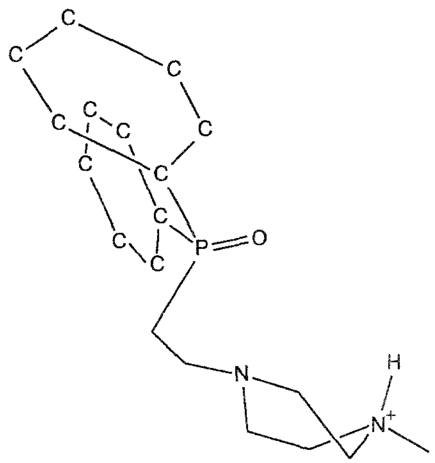


Fig. 3. The conformation of the monoprotonated cation derived from PDAC **3** in the global minimum region. The distance between the N$^+$ and O atoms is 4.27 Å.

It is of interest that the ΔpK_{1-2} values of compounds of the piperazine series (Table 1) are close to each other and vary regularly as the solvent is changed. At the same time, ΔpK_{1-2} of PDAC of the diazacyclooctane series (compounds **4** and **2**) in nitromethane are substantially greater than would be expected judging from the corresponding values in aqueous ethanol. This fact may be considered evidence that on going from water—ethanol mixtures to aprotic nitromethane, the protonation mechanism of these compounds changes (in aqueous ethanol, the cations are mostly solvated due to the formation of hydrogen bonds with the solvent molecules).

Thus, the PDAC studied are diatomic bases in both hydroxyl-containing and aprotic solvents and are protonated at the nitrogen atoms irrespective of the size of the ring and the length of the pendant chain. The mechanism of protonation in aprotic media depends on the size of the ring. In the first step of protonation, derivatives of 1,5-diazacyclooctane, unlike piperazine derivatives, produce cations with the N$^+$—H...N IMHB. In the cations derived from all of the PDAC with ethylene pendant chains, IMHB involving phosphoryl groups are formed. The increased basicity of PDAC in aprotic media is accounted for by the formation of the IMHB, which stabilize the cation.

Experimental

The ^{31}P{H} NMR were recorded on a Bruker-WP-200-SY spectrometer. 85% H_3PO_4 was used as the external standard. IR spectra were recorded on a UR-20 instrument (KBr pellets or solutions in acetonitrile and chloroform).

All solutions were prepared in anhydrous purified solvents.

Cyclic diamines **5** and **6** of the "pure" grade were dried over KOH and then distilled. The purity of the compounds was checked by their boiling points and neutralization equivalents. The boiling points coincided with the literature data to within 1—2 deg. and the neutralization equivalents were identical to the theoretical values to within the experimental error (±1 %).

1,5-Diazacyclooctane (4) was prepared by the reaction of 1,3-dibromopropane with hydrazine hydrate.[19] The free base was isolated by treatment with solid NaOH.

1,5-Bis(2-diphenylphosphorylethyl)-1,5-diazacyclooctane (2). A mixture of 1.05 g of 1,5-diazacyclooctane **4**, 9.65 g of diphenylvinylphosphine oxide, and 5 mL of benzene was heated in a sealed tube at 150—160 °C for 6 h. The crystalline precipitate was separated and recrystallized from benzene to give 3.5 g (67 %) of colorless crystals, m.p. 189—190 °C. Found (%): P, 10.8; N, 5.0. $C_{34}H_{40}N_2O_2P_2$. Calculated (%): P, 10.8; N, 4.9. IR (KBr pellets), ν/cm^{-1}: 2810 (N—CH$_2$), 1180 (P=O), 1595, 1490, 1440 and 1125 (Ph). ^{31}P{^{1}H} NMR (CHCl$_3$), δ: 34.8 s.

1,5-Bis(diphenylphosphorylmethyl)-1,5-diazacyclooctane (1). A mixture of 1.25 g of 1,5-diazacyclooctane **4**, 4.44 g of diphenylphosphine oxide, 0.66 g of paraform, and 5 mL of benzene was heated in a sealed tube at 150—160 °C for 6 h. The colorless crystals that precipitated on storage and cooling were separated and recrystallized from benzene to give 1.90 g (32 %) of **1**, m.p. 128—130 °C (from benzene). Found (%): P, 11.4; N, 5.3. $C_{32}H_{36}N_2O_2P_2$. Calculated (%): P, 11.4; N, 5.2. IR (KBr pellets), ν/cm^{-1}: 2810 (N-CH$_2$), 1180 (P=O), 1595, 1490, 1440 и 1125 (Ph); ^{31}P {^{1}H} NMR (CHCl$_3$), δ: 26.9 s.

1-Methyl-4-(2-diphenylphosphorylethyl)piperazine (3). A mixture of 0.53 g of *N*-methylpiperazine, 1.15 g of diphenylvinylphosphine oxide, and 2.5 mL of benzene was heated in a sealed tube at 120 °C for 2 h and at 140—145 °C for 3 h. The crystals that precipitated on storage and cooling were filtered off and recrystallized from acetonitrile to give 1.06 g (64 %) of **3**, m.p. 132—134 °C (from acetonitrile). Found (%): C, 69.7; H, 7.6; N, 8.4; P, 9.4. $C_{19}H_{25}N_2OP$. Calculated (%): C, 69.5; H, 7.6; N, 8.5; P, 9.5. IR (KBr pellets), ν/cm^{-1}: 2790 (N—CH$_3$), 2810 (N—CH$_2$), 1185 (P=O), 1595, 1490, 1440 and 1125 (Ph). ^{31}P{^{1}H} NMR spectrum (CHCl$_3$), δ: 31.4 s.

1-(2-Diphenylphosphorylethyl)piperazine (7),[3] **(diethylaminomethyl)diphenylphosphine oxide (11),**[20] and **(2-diethylaminoethyl)diphenylphosphine oxide (12)**[20] were prepared and purified by the previously reported procedures. Prior to the measurements, all compounds were dried *in vacuo* over KOH. The equivalents of neutralization of all of the bases were identical to the theoretical values to within the experimental error.

Basicities of the compounds were determined at 298±0.1 K according to the known procedure[11] using a Radelkis OP-211/1 pH meter, a Radiometer G 202C glass electrode, a Radiometer K-401 calomel electrode with the junction through porous ceramics. The basicity in 70 % w/w aqueous ethanol at 298±0.1 K was determined by potentiometry[21] using HClO$_4$ as the titrant and 0.01 *M* LiNO$_3$ as the supporting electrolyte.

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