Heteroatom Chemistry
Volume 21, Number 3, 2010

# 4-Phosphorylated 1,2-Disubstituted Imidazoles

A. N. Huryeva, A. P. Marchenko, G. N. Koidan, A. A. Yurchenko, E. V. Zarudnitskii, A. M. Pinchuk, and A. N. Kostyuk

*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Str. 5, Kiev-94, 02094, Ukraine*

*Received 3 December 2009; revised 1 February 2010*

ABSTRACT: *4-Selenophosphoryl-1,2-disubstituted imidazoles have been obtained by thermal decomposition of methyl 5-(diamidoselenophosphoryl)-imidazolium chlorides. The position of selenophosphoryl group in the imidazole ring was proved by $^{1}H$, $^{13}C$ NMR spectroscopy, and X-ray analysis. Previously unknown diamido- and dichloro(imidazol-4-yl)-phosphonites were synthesized, and differences in their reactivity compared to analogous 5-phosphorylated imidazoles are shown.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:103–118, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20584

## *INTRODUCTION*

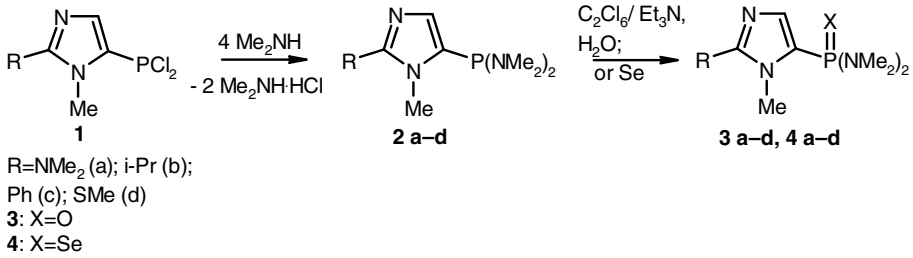
In electrophilic substitution reactions, reactivity of 1,2-disubstituted imidazoles strongly depends on the electronic nature of the substituent at the second position. For instance, 1-methyl-2-dimethylaminoimidazole reacts readily with acylating, formylating reagents, sulfenyl chlorides, adds isocyanates, enters into Mannich reaction affording exclusively 5-substituted imidazole derivatives [1]. The reactions with $PCl_3$ and AlkLi take the same course [2]. Namely, earlier we have reported that 1-methyl-2(R)-disubstituted imidazoles (R = $NMe_2$, SMe, Ph) reacted with excess of $PCl_3$ in pyridine to give 5-dihalophosphine derivatives. Also, it was found that the reaction of 2-methylthio-1-methylimidazole (2-phenyl-1-methylimidazole) with phosphorus trichloride resulted in formation of a mixture of tris(imidazolyl)phosphines. At the last stage of the phosphorylation, the substitution proceeded both at the fourth and the fifth positions of the imidazole ring.

Regioselectivity of the electrophilic substitution reactions of 1,2-disubstituted imidazoles is obviously determined by greater electronic density on the C(5) atom, preventing direct introduction of electrophilic reagents at the fourth position. From this point of view, 4-phosphorylated 1,2-disubstituted imidazoles bearing the unoccupied fifth position are of theoretical interest. There are a few compounds of such type. Among them (1-alkyl-2-aryl-5-methylthioimidazol-4-yl)triphenylphosphonium salts are known to be obtained by cyclization of the corresponding phosphonium derivatives, bearing an imidoyl chloride group in a side chain. [3]. 4-P(V)-Phosphorylated derivatives of imidazole were prepared via cross-cycloaddition between two different isocyanides, with one of them bearing a phosphonate group [4]. In the recent review on direct phosphonylation on aromatic azaheterocyles, some 4-phosphorylated imidazoles with different substitution patterns are presented [5]. Noteworthy, those corresponding trivalent phosphorus derivatives are currently unknown.

## *RESULTS AND DISCUSSION*

In the present study, we report on the synthesis of 4-phosphorylated 1,2-disubstituted imidazoles

*Correspondence to:* A. N. Kostyuk; e-mail: kostyuk@enamine.net.



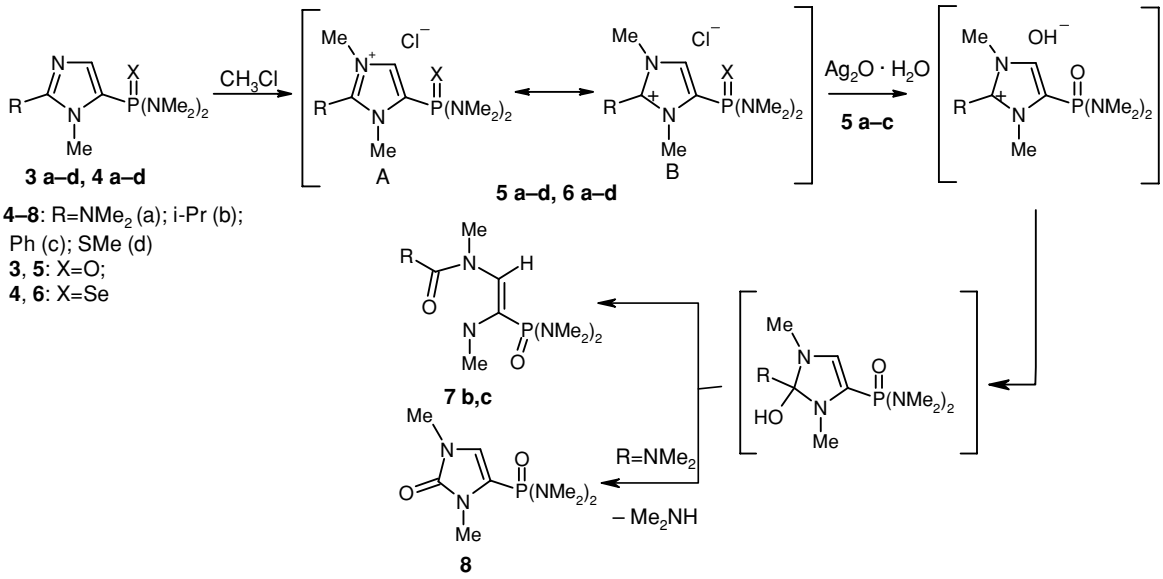

SCHEME 1

starting from available 5-phosphorylated derivatives [2]. A synthetic method was developed based on peculiarities of imidazolium salts' thermal decomposition. For instance, 4(5)-nitro-1,2,3-trimethylimidazolium iodide on heating above melting point decomposes, affording 4-nitro-1,2-dimethylimidazole in 67% yield and evolving methyl iodide [6].

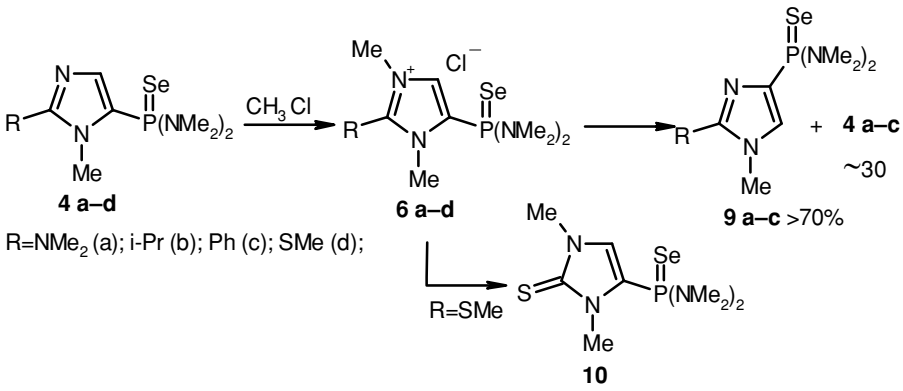
We suggested that thermal decomposition of 1,3-dimethyl-2-R-5-phosphorylimidazolium salts would also mainly lead to 4-phosphorylated imidazoles because like the $NO_2$-group, an electron-accepting phosphoryl group should have a greater effect on the lone electron pair of N(1). Toward this end, (imidazol-5-yl)diamidophosphonites **2a–d** were synthesized [2] and then by standard oxidative procedures were transformed into the corresponding 5-phosphorylated derivatives **3a–d, 4a–d** (Scheme 1).

It was found that diamidophosphonates **3a–d, 4a–d** are alkylated with methyl chloride at 75°C to give imidazolium chlorides **5, 6** (Scheme 2) as colorless high-melting crystalline compounds, soluble in water, and relatively stable in air. Their structures are consistent with $^{31}P$, $^{1}H$, and $^{13}C$ NMR spectral data. Methyl groups at nitrogen atoms of the imidazole ring are not equivalent and exhibit two singlets in $^{1}H$ and $^{13}C$ NMR spectra.

The resonance form "B" probably contributes markedly to the structure of imidazolium salts **5a–d, 6a–d**, so that the carbon atom at the second position should be prone to nucleophilic attack [7]. Indeed, compounds **5b,c** reacted with moist silver oxide to afford C-phosphorylated ethylene-1,2-diamines **7b,c**, whereas in the case of imidazolium chloride **5a** imidazolone **8** was obtained (Scheme 2). The structure of compounds **7b,c** and **8** was confirmed by $^{31}P$, $^{1}H$, and $^{13}C$ NMR spectroscopy, elemental analysis, and mass-spectrum. Analogous transformations on the reaction with hydroxide ions are known for imidazolium salts in heterocyclic series. For instance, substituted ortho-phenylenediamines were obtained by alkaline hydrolysis of benzimidazolium salts




SCHEME 2




SCHEME 3

[8], whereas κακ 1,3-dialkyl-2-benzthioimidazolium salts on treatment with aqueous $K_2CO_3$ solution transformed into 1,3-dialkyl-1,3-dihydroimidazolones [9]. Tetraalkylimidazolium-2-amidinate reacted with water via a ring opening to give ketoamidine [10].

We found that imidazolium chlorides **6a–c** on heating above melting point (200–220°C) in vacuo (12 Torr) decompose, evolving methyl chloride to afford a mixture of (imidazolyl)selenophosphonates **9a–c** ($\delta$ $^{31}$P 68 ppm) and **4a–c** ($\delta$ $^{31}$P 62 ppm) in a ratio ≈ 2: 1 as evidenced by $^{31}$P NMR (Scheme 3). As expected, 4-phosphorylated imidazoles **9a–c** exhibiting chemical shifts in $^{31}$P NMR downfield formed predominantly. Thermal decomposition of compound **6d** was under kinetic control and resulted in imidazol-2-thione **10** [11].

In the above-mentioned transformations, attack of chloride anion on the C(2) atom is unlikely due to low stability of forming α-chloralkyl amine.

5-, 4-Isomers **4a–c** and **9a–c** were separated by chromatography on silica gel (for **4a** and **9a**), crystallization from pentane (for **4b, c** and **9b, c)**, and by the so-called "salt" method (for **4a** and **9a**). The salt method is based on disparity in basicity of 4- and 5-phosphorylated 1,2-disubstituted imidazoles. So, if the amount of picric acid calculated according to integral ratio of **4a** and **9a** in a $^{31}$P NMR spectrum is added, picrate of (imidazol-5-yl)phosphonate **4a** which has higher basicity will precipitate first. Such salts are not soluble in organic solvents (diethyl ether, benzene, pentane, hexane) and could be easily separated from (imidazol-4-yl)phosphonate **9a**, which in the base state remains in solution. The salt method is general in nature and, for example, compound **9a** was retrieved from mixture with 90% yield.

The structure of selenophosphonates **9a–c** was confirmed by $^1$H and $^{13}$C NMR spectroscopy. In $^1$H NMR spectrum, the C(5)-H proton signals are observed at $\delta$ 7.40–7.65 ppm. The signals of N(1)-Me are observed at $\delta$ 2.50–2.90 ppm and in comparison to those of selenophosphonates **4a–c** shifted upfield probably due to greater remoteness of $(Me_2N)_2P(Se)$-group. In $^{13}$C NMR spectrum of compounds **9a–c**, the C(4)-P atom exhibits a doublet at $\delta$ 131.3–135.7 ppm (with coupling constant $J_{C\text{-}P}$ 157 Hz). Whereas, it is typical of compound **4a–c** that the C(5)-P atom exhibits a doublet at $\delta$ 120.0–124.2 ppm (with $J_{C\text{-}P}$ 143 Hz). Thus, the values of chemical shifts of C(4) and C(5) atoms could be considered for the determination of the position of phosphorous atom in the imidazole ring which has been already reported earlier [2].

The structure of selenophosphonates **9a–c** was finally proved by X-ray analysis for **9a** (Fig. 1).

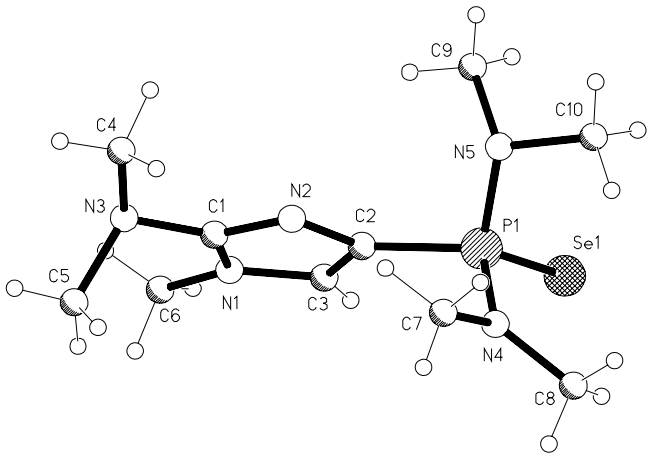
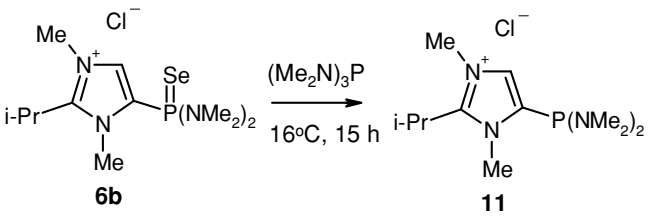



**FIGURE 1** X-ray crystal structure of compound **9a**. Selected bond lengths and angles for **9a** P1 Se1 2.1026(5), C2 P1 1.7790(19) N4 P1 1.6466(16), N5 P1 1.6791(17), C1 N3 1.394(3), C6 N1 1.462(3) Å; N4 P1 N5 105.10(8) N4 P1 C2 107.87(9) N5 P1 C2 103.62(9) N4 P1 Se1 112.72(6) N5 P1 Se1 115.40(6) C2 P1 Se1 111.43(6)°.




**SCHEME 4**

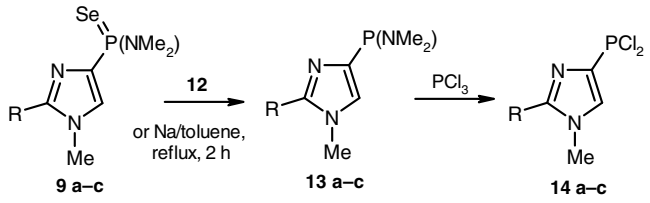
It is of special synthetic interest to prepare 1,2-disubstituted (imidazol-4-yl)phosphines, including such key compounds in organophosphorus chemistry as dihalophosphines.

(Hexalkyl)triamidophosphites are commonly used for reduction of the selenophosphoryl group [12,13]. It was shown that on treatment with (hexamethyl)triamidophosphite imidazolium salt **6b** could be readily reduced, giving salt **11** (Scheme 4).

Unfortunately, triamidophosphites are unsuitable for the reduction of compounds **9a–c** owing to reaction equilibrium. For this purpose, highly nucleophilic bis(hexalkyltriamidophosphazo)dimethylamidophosphite **12** was used successfully [14]. The reduction with metallic sodium in boiling toluene appeared to be even more convenient and simple method [15] (Scheme 5).

Amidophosphonites **13a–c** are colorless crystalline compounds sensitive to air moisture and oxygen, easily distillable in vacuo without decomposition. In $^{31}$P NMR spectrum, they exhibit a singlet at $\delta$ 86.0–88.0 ppm. In $^{1}$H NMR spectrum, the C(5)-H proton signals are observed at $\delta$ 6.55–6.76 ppm. In $^{13}$C NMR spectrum, doublets at $\delta$ 137.4–141.4 ppm ($J_{C\text{-}P}$ 22 Hz) and $\delta$ 123.1–127.4 ppm ($J_{C\text{-}P}$ 31 Hz) were assigned to the C(4)-P and the C(5)-H atoms, respectively.

Amidophosphonites **13a–c** reacted with phosphorus trichloride to give (imidazol-4-yl)dichlorophosphines **14a–c** that structure




R=NMe$_2$ (a); i-Pr (b); Ph (c)

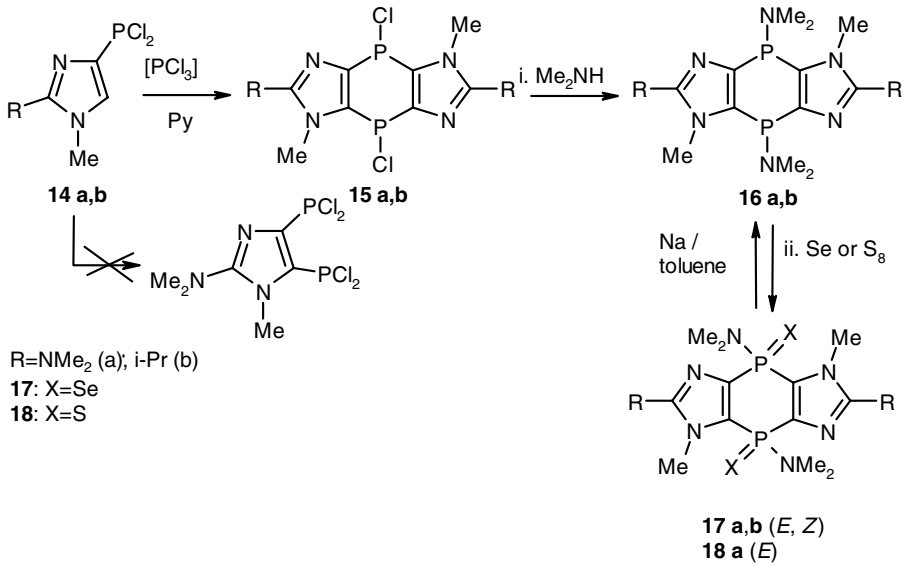
**12**- [(Et$_2$N)$_3$P=N]$_2$PNMe$_2$

**SCHEME 5**

was confirmed by $^{31}$P, $^{1}$H, and $^{13}$C NMR spectroscopy (Scheme 5). In addition, treatment of **14a** with dimethylamine followed by oxidation with selenium afforded the starting selenophosphonate **9a**. It should be noted that in $^{31}$P NMR spectrum signals of compounds **14a–c** are downfield ($\delta$ 146–147 ppm) compared with signals of (imidazol-5-yl)dichlorophosphines observed at $\delta$ 121–127 ppm [2]. Dichlorophosphines **14b,c** are viscous liquids distillable in vacuo with slight decomposition. Dichlorophosphine **14a** decomposed during distillation by 60–70% unlike isomeric (imidazol-5-yl)dichlorophosphine [2]. Obviously, low thermal stability of compound **14a** is caused by reactivity of the unoccupied fifth position of the imidazole ring activated by the dimethylaminogroup at the second position.

We have found that heating (45°C) of dichlorophosphine **14a** in pyridine in the presence of triethylamine and $PCl_3$ resulted in compound **15a**, exhibiting a broad singlet at $\delta$ $^{31}$P-{$^{1}$H} 25.1 ppm (Scheme 6). Without $PCl_3$ tar formation is observed. The presence of doublet of doublets at $\delta$ 115.0 and 135.6 ppm with coupling constant $^{3}J_{P\text{-}P}$ 317 Hz might be attributed to formation of a trace amount of 4,5-bis(dichlorophosphino)-1-methyl-2-dimethylaminoimidazole. Heating (125°C) of **14b** in pyridine for 9 days or in benzene solution in the presence of pyridine for 20 days resulted in analogous compound **15b** ($\delta$ $^{31}$P NMR 23.4 ppm).

1,4-Dichloro-1,4-diphosphinine **15a** is a yellow high-melting solid, which is sensitive to air moisture and oxygen. Its structure was confirmed by $^{1}$H and $^{13}$C NMR spectroscopy as well as by chemical transformations. Thus, compound **15a** reacted with dimethylamine to give amide **16a**, which was oxidized with selenium, sulfur under mild conditions to give [1,4]diphosphinino-4,8-diselenide **17a** or sulfide **18**, respectively. Diphosphinino-4,8-diselenide **17b** was prepared similarly without isolation of compounds **15b** and **16b**. Diphosphinino-4,8-diamines **16a,b** were obtained in analytically pure state by reduction of selenides **17a,b** with metallic sodium in benzene. In $^{31}$P NMR spectrum, compounds **16a,b** exhibited two signals of different intensity at $\delta$ 15.0 and 17.0 ppm, whereas their selenides **17a,b** exhibited a singlet at $\delta$ $^{31}$P-{$^{1}$H} 25.4 ppm. In $^{1}$H NMR spectrum, the absence of imidazolium ring proton signals corroborate the proposed structure of 1,4-dihydro-1,4-diphosphinine-1,4-diamine-1,4-diselenide for compounds **17a,b**. Doubling of the alkyl group matched with these compounds existing as the mixture of two isomers (**E** and **Z**) in 3:1 ratio that was also detected by HPLC-MS, both isomers gave molecular ion. For compound **17a**, both



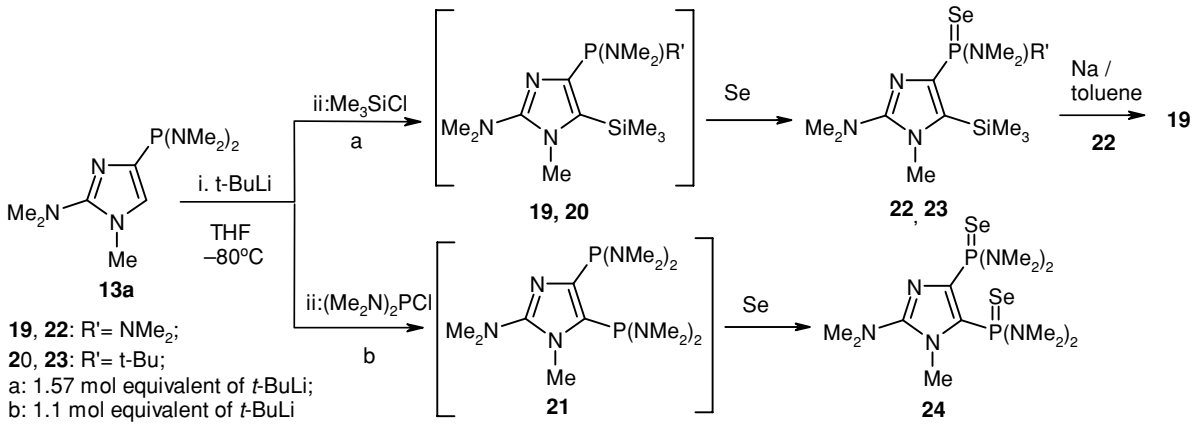

SCHEME 6

isomers were separated by chromatography on silica gel and characterized by $^{1}H$ and $^{13}C$ NMR spectroscopy. We also managed to isolate the major isomer **(E)** partially by crystallization from acetonitrile.

As we failed to carry out X-ray analysis of (*E*)-**17a** crystal, we analyzed sulfide (*E*)-**18a** the closest analogue of (*E*)-**17a**. The X-ray data of compound (*E*)-**18a** indicated (Fig. 2) that sulfur atoms are in trans-orientation. Thus, oxidizing reaction **16** → **17, 18** resulted in the mixture (3:1) of two isomers (*E* and *Z*) which are different in sulfur (selenium) atoms location toward the plane of 1,4-dihydro-1,4-diphosphinine circle.

(Imidazol-4-yl)amidophosphonites **13a–c** unlike 5-phosphorylated analogous **2a–c** undergo lithiation with t-BuLi, but the reaction proceeds very slowly (Scheme 7). Thus, after 8 h stirring with t-BuLi at −80°C, an electrophile was added affording a mixture containing, as evidenced by $^{31}P$ NMR, the starting phosphonite **13a** (62%), compound **19** (a) or **21** (b). In case (a), P—N bond cleavage furnished phosphonite **20** as well. It should be noted that use of 2 equiv of *t*-BuLi resulted in total consumption of the starting phosphonite **13a**. At the same time, yield of compound **19** decreased at expense of formation of **20**, reaching 1:1 ratio.

Amidophosphonites **19, 20**, and **21** were transformed into the corresponding selenoic derivatives **22, 23**, and **24**, which were isolated in individual state by chromatography on silica gel or by




SCHEME 7

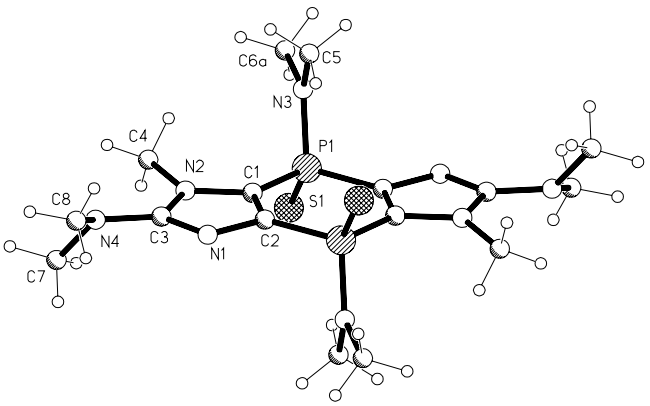



**FIGURE 2** X-ray crystal structure of compound **18a**. Selected bond lengths and angles for **18a**: P1 C1 1.781(3), P1 C2′ 1.789(3), P1 N3 1.650(3), P1 S1 1.9301(11) Å; C2 C1 P1 130.3(2), C1 P1 C2′ 100.42(12), C1 C2 P1′ 129.2(2)°. The atoms labeled with (′) are generated symmetry operation $-x+1, -y+1, -$.

crystallization (**24**). Selenide **22** was reduced to amidophosphonite **19** with metallic sodium.

## *CONCLUSION*

A facile synthetic route to 4-phosphorylated imidazoles starting from available 5-diamidoselenophosphoryl 1,2-disubstituted imidazoles has been developed. Previously unknown (imidazol-4-yl)diamido- and dihalogen phosphines have been obtained. The higher reactivity of 4-phosphorylated imidazoles compared with 5-phosphorylated imidazoles was observed.

## *EXPERIMENTAL*

### *General*

All procedures with air and moisture sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus and were uncorrected. $^{1}$H spectra were recorded on a Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer. $^{13}$C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer. $^{31}$P NMR spectra were recorded on a Varian VXR-300 (121.42 MHz) spectrometer. Chemical shifts ($\delta$) are reported in ppm downfield relative to internal TMS (for $^{1}$H, $^{13}$C) and external 85% $H_3PO_4$ (for $^{31}$P). Chromatography was performed on silica gel Gerudan SI60. Elemental analyses were performed at the Microanalytical laboratory of the Institute of the Organic Chemistry National Academy of Sciences of Ukraine.

Crystallographic measurements were performed at 173(1)K on a Bruker Smart Apex II diffractometer operating in the $\omega$ and $\varphi$ scans mode. The structure was solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 [16a,b] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically.

X-ray crystal data for **9a**: crystal system, orthorhombic; space group *Fdd*2; unit cell dimensions: $a = 24.5254(8)$, $b = 24.6691(6)$, $c = 10.0515(2)$ Å, $V = 6081.4(3)$ Å$^3$, $Z = 16$, $d_c = 1.408$ g·cm$^{-3}$, $\mu = 2.564$ mm$^{-1}$; $F(000) = 2656$; crystal size ca. 0.36 × 0.44 × 0.48 mm. 22,908 reflections were collected, 3160 unique reflections (2838 reflections with $I \geq 2\sigma(I)$, $R_{merg} = 0.0357$) were used in refinement; Mo $K_\alpha$ radiation ($\lambda = 0.71078$ Å). Convergence was obtained at $R1 = 0.0264$ and $wR2 = 0.0383$, for all reflection and $R1 = 0.0206$ and $wR2 = 0.0372$, GOF = 0.979 for observed 242 parameters. In compound **9a**, P1 atom has a slightly distorted tetrahedral coordination. The distances P1–N4 and P1–N5 are unequivalent, and sum of bond angles around N4 and N5 atoms is 357.55° (18) and 339.94° (18), respectively, because of conjugation of the LP-N4 atoms with d orbitals of phosphorus atom. The sum of bond angles around N3 atom is 337.53° (20). The geometry of imidazole cycle is normal for such systems.

X-ray-crystal data for **18a**: crystal system, monoclinic, space group, $P2_1/c$; $a = 9.0851(9)$, $b = 12.0381(11)$, $c = 10.7717(10)$ Å, $\beta = 96.721°(4)$, $V = 1169.98(19)$ Å$^3$, $Z = 2$, $d_c = 1.307$ g·cm$^{-3}$, $\mu = 0.384$ mm$^{-1}$, $F(000) = 488$, crystal size ca. 0.1 × 0.14 × 0.3 mm. 8195 reflections were collected, 2316 unique reflections, (1452 reflections with $I \geq 2\sigma(I)$, $R_{merg} = 0.0494$) were used in the refinement; Mo $K_\alpha$ radiation ($\lambda = 0.71078$ Å). Convergence was obtained at $R1 = 0.0941$ and $wR2 = 0.1144$, for all reflection and $R1 = 0.0482$ and $wR2 = 0.0953$, GOF = 1.022 for observed 175 parameters. The six-membered P2C4 central cycle in **18a** is planar due to centrosymmetric arrangement. The bond lengths (Å) in this heterocyclic system are close to corresponding ones the related system [16c], both P—C bonds in the cycle practically equivalent within standard error.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 748955 (**9a**), and CCDC 748956 (**18a**) and can be obtained free of charge on application to CCDC, 12,

Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk.

### *2-Isopropyl-1-methyl-1H-imidazol-5-yl-phosphonous Dichloride (***1b***)*

Phosphorus trichloride (7.0 g, 50 mmol) was cooled at −10 to −30°C and a solution of 2-isopropyl-1-methyl-1(*H*)-imidazole (2.5 g, 20 mmol) in pyridine (10 mL) was added. The reaction mixture was heated at 100°C for 15 h. Pyridine was removed in vacuo, the residue was treated with warm $Et_2O$ (2 × 30 mL), insoluble precipitate was filtered, and washed with $Et_2O$ (30 mL). The filtrate was concentrated in vacuo; and the oily residue was distilled (bp 110–115°C/5 × $10^{-2}$ Torr) to give **1b** (3.9 g, 70%) pale yellow solid; mp 41–44°C.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta = 1.11$ (d, $J$ = 6.5 Hz, 6H, $CH(CH_3)_2$), 2.62–2.70 (m, 1H, CH), 3.41 (s, 3H, $NCH_3$), 7.39 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 20.9$, 21.0, 26.1, 31.5 (d, $^3J_{CP} = 2.5$ Hz), 127.1 (d, $^1J_{CP} = 77.0$ Hz), 140.7 (d, $^2J_{CP} = 56.6$ Hz), 162.3 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta = 125.6$. Anal. Calcd for $C_7H_{11}Cl_2N_2P$: C, 37.36; N, 12.45; P, 13.76. Found: C, 37.10; N, 12.72; P, 13.11.

Compounds **1a,c,d** were prepared as described in [2].

### *Typical Procedure for* **2a–d** *by the Example of* **2a**

*P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N,N′,N′-tetramethyl-phosphonous diamide (***2a***).* To a solution of compound **1a** (19.6 g, 0.087 mol) in $Et_2O$ (100 mL) at −30°C to −10°C dimethylamine (17.0 g, 0.4 mol) in $Et_2O$ (20 mL) was added dropwise over 20 min. The reaction mixture was allowed to warm to r. t., and stirring was continued for further 30 min at 20°C. The precipitate was filtered and washed with $Et_2O$ (2 × 30 mL), the filtrate was concentrated in vacuo, and the oily residue was distilled (bp 137–143°C/5 × $10^{-2}$ Torr) to give **2a** (20.1 g, 96%) as pale yellow liquid.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta = 2.68$ (s, 6H, $NCH_3$), 2.70 (d, $J$ = 2.0 Hz, 12H, $NCH_3$), 3.24 (s, 3H, $NCH_3$), 7.23 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 30.4$ (d, $^3J_{CP} = 6.0$ Hz), 40.8 (d, $^2J_{CP}$ = 16.3 Hz), 42.8, 126.6 (d, $^1J_{CP} = 10.0$ Hz), 132.0 (d, $^2J_{CP} = 6.3$ Hz), 156.6 (d, $^3J_{CP} = 6.3$ Hz). $^{31}$P NMR (91 MHz, $C_6D_6$): $\delta = 83.2$. Anal. Calcd for $C_{10}H_{22}N_5P$: C, 49.37; H, 9.11; N, 28.79; P, 12.73. Found: C, 49.05; N 28.47; P, 12.33.

*P-(2-Isopropyl-1-methyl-1H-imidazol-5-yl)-N,N,N′,N′-tetramethylphosphonous Diamide (***2b***).* Following the typical procedure for **2a** using **1b**; yield: 2.6 g (87%), colorless liquid; bp 123–128°C/5 × $10^{-2}$ Torr. $^1$H NMR (500 MHz, $C_6D_6$): $\delta = 1.27$ (d, $J = 7.0$ Hz, 6H, $CH(CH_3)_2$), 2.57 (d, $J = 9.0$ Hz, 12H, $NCH_3$), 2.70 (m, 1H, CH), 3.10 (s, 3H, $NCH_3$), 7.23 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 21.5$, 26.3, 30.1 (d, $^3J_{CP} = 6.3$ Hz), 40.8 (d, $^2J_{CP} = 16.3$ Hz), 128.8 (d, $^1J_{CP} = 7.5$ Hz), 133.9 (d, $^2J_{CP} = 6.3$ Hz), 155.9 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta = 83.4$. Anal. Calcd for $C_{11}H_{23}N_4P$: C, 54.53; N, 23.12; P, 12.78. Found: C, 54.65; N, 23.03; P, 12.50.

*N,N,N′,N′-Tetramethyl-P-(1-methyl-2-phenyl-1H-imidazol-5-yl)-phosphonous Diamide (***2c***).* Following the typical procedure for **2a** using **1c**; yield: 6.9 g (93%), pale yellow liquid; bp 180–184°C/5 × $10^{-2}$ Torr. $^1$H NMR (500 MHz, $C_6D_6$): $\delta = 2.55$ (d, 12H, $J = 9.5$ Hz, $NCH_3$), 3.20 (s, 3H, $NCH_3$), 7.09–7.11 (m, 2H, 3,5-H-Ph), 7.17 (t, 1H, $J = 7.5$ Hz, 4-H-Ph), 7.41 (d, 1H, $J = 2.5$ Hz, 4-H pyr), 7.63 (d, 2H, $J = 7.5$ Hz, 2,6-H-Ph). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 33.60$ (d, $^3J_{CP} = 7.5$ Hz), 41.8 (d, $^2J_{CP} = 2.5$ Hz), 129.0, 129.2, 130.0, 132.3 (d, $^1J_{CP} = 5.0$ Hz), 132.4, 136.2 (d, $^2J_{CP} = 6.3$ Hz), 151.9 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta = 81.9$. Anal. Calcd for $C_{14}H_{21}N_4P$: C, 60.85; N, 20.28; P, 11.21. Found; C, 60.62; N, 19.95; P, 11.07.

*N,N,N′,N′-Tetramethyl-P-[1-methyl-2-(methylthio)-1H-imidazol-5-yl]-phosphonous Diamide (***2d***).* Following the typical procedure for **2a** using **1d**; yield: 8.9 g (96%), yellow liquid; bp 133–136°C/5 × $10^{-2}$ Torr. $^1$H NMR (500 MHz, $C_6D_6$): $\delta = 2.50$ (s, 3H, $SCH_3$), 2.54 (d, 12H, $J = 9.6$ Hz, $NCH_3$), 3.18 (s, 3H, $NCH_3$), 7.33 (d, 1H, $J = 2.4$ Hz, 4-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 15.34$, 30.9 (d, $^3J_{CP} = 5.0$ Hz), 40.75 (d, $^2J_{CP} = 16.3$ Hz), 131.3 (d, $^1J_{CP} = 5.0$ Hz), 135.5 (d, $^2J_{CP} = 7.5$ Hz [4]), 146.3 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta = 82.2$. Anal. Calcd for $C_9H_{19}N_4PS$: C, 43.89; N, 22.75; P, 12.57. Found: C, 43.57; N, 22.61; P, 12.35.

### *Typical Procedure for* **3a–d** *by Oxidation of* **2d**

*N,N,N′,N′-Tetramethyl-P-[1-methyl-2-(methylthio)-1H-imidazol-5-yl]-phosphonic diamide (***3d***).* A solution of **2d** (3.44 g, 14 mmol) in $CH_2Cl_2$ (20 mL) was cooled to 0–5°C, and a solution of hexachloroethane (3.22 g, 14 mmol) in $CH_2Cl_2$ (15 mL) was added. After stirring for 30 min, a solution of $Et_3N$ (2.83 g, 28 mmol) in $CH_2Cl_2$ (15 mL) was added. The reaction mixture was recooled to 0–5°C, and degassed water (0.2 mL) was added. In 10–15 min, $CH_2Cl_2$ was removed in vacuo. The residue was treated with warm $Et_2O$ (50 mL), insoluble precipitate was filtered and washed with $Et_2O$

(2 × 20 mL), and the filtrate was concentrated to 20 mL. The solid precipitating on cooling was filtered and washed with $Et_2O$ (10 mL) to give **3d** (3.10 g, 85%) colorless solid; mp 90–91°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.66$ (s, 3H, $SCH_3$), 2.85 (d, 12H, $J = 10.0$ Hz, $NCH_3$), 3.73 (s, 3H, $NCH_3$), 7.25 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 15.1$, 32.2, 36.2 (d, $^3J_{CP} = 4.0$ Hz), 123.4 (d, $^1J_{CP} = 185.0$ Hz), 137.6 (d, $^2J_{CP} = 16.3$ Hz), 149.4 (d, $^3J_{CP} = 12.8$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 18.7$. Anal. Calcd for $C_9H_{19}N_4OPS$: C, 41.21; N, 21.36; P, 11.81. Found: C, 41.03; N, 21.65; P, 11.57.

*P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N,N′,N′-tetramethylphosphonic Diamide (***3a***).* Following the typical procedure for **3d** using **2a**; yield: 3.6 g (68%), colorless solid; mp 72–74°C ($Et_2O$).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.85$ (d, 12H, $J = 9.5$ Hz, $NCH_3$), 2.70 (s, 6H, $NCH_3$), 3.53 (s, 3H, $NCH_3$), 6.92 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 31.9$, 36.3 (d, $^3J_{CP} = 3.8$ Hz), 42.4, 119.0 (d, $^1J_{CP} = 188.6$ Hz), 134.9 (d, $^2J_{CP} = 15.1$ Hz), 157.7 (d, $^3J_{CP} = 13.8$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 20.3$. Anal. Calcd for $C_{10}H_{22}N_5OP$: C 46.32; N, 27.01; P, 11.95. Found: C 46.18; N, 26.85; P, 11.77.

*P-(2-Isopropyl-1-methyl-1H-imidazol-5-yl)-N,N,N′,N′-tetramethylphosphonic Diamide (***3b***).* Following the typical procedure for **3d** using **2b**; yield: 5.9 g (91%), colorless solid; mp 77–79°C ($Et_2O$). $^1$H NMR (500 MHz, $CDCl_3$); $\delta = 1.34$ (d, 6H, $J = 6.6$ Hz, $CH(CH_3)_2$), 2.69 (d, 12H, $J = 9.6$ Hz, $NCH_3$), 3.00–3.10 (m, 1H, CH), 3.78 (s, 3H, $NCH_3$), 7.19 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 20.9$, 25.9, 31.4, 36.1 (d, $^3J_{CP} = 3.8$ Hz), 121.1 (d, $^1J_{CP} = 186.1$ Hz), 136.3 (d, $^2J_{CP} = 17.6$ Hz), 158.0 (d, $^3J_{CP} = 12.8$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 23.6$. Anal. Calcd for $C_{11}H_{23}N_4OP$: C, 51.15; N, 21.69; P, 11.99. Found: C, 50.93; N, 21.56; P, 11.85.

*N,N,N′,N′-Tetramethyl-P-(1-methyl-2-phenyl-1H-imidazol-5-yl)-phosphonic Diamide (***3c***).* Following the typical procedure for **3d** using **2c**, the crude product was distilled (bp 120–130°C/5 × $10^{-2}$ Torr) and crystallized from $Et_2O$; yield: 3.0 g (92%), colorless solid; mp 82–84°C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.74$ (d, 12H, $J = 10.0$ Hz, $NCH_3$); 3.89 (s, 3H, $NCH_3$); 7.36 (s, 1H, 4-H), 7.45–7.50 (m, 3H, 2′,4′,6′-H), 7.60–7.63 (m, 2H, 3′,5′-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 33.8$, 36.3 (d, $^3J_{CP} = 5.0$ Hz), 123.2 (d, $^1J_{CP} = 183.6$ Hz), 128.5, 129.0, 129.2, 129.9, 137.5 (d, $^2J_{CP} = 16.3$ Hz), 152.7 (d, $^3J_{CP} = 12.8$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 23.5$. Anal. Calcd for $C_{14}H_{21}N_4OP$: C, 57.52; N, 19.17; P, 10.60. Found: C, 57.37; N, 19.05; P, 10.45.

### *Typical Procedure for* **4a–d** *by Selenoxidation of* **2a**

*P-[2-(Dimethylamino)-1-methyl-1H-imidazol-5-yl]-N,N,N′,N′-tetramethylphosphonoselenoic diamide (***4a***).* To a solution of **2a** (5.35 g, 22 mmol) in benzene (20 mL), selenium (1.86 g, 24 mmol) was added portionwise. The reaction mixture was stirred at 20°C for 1 h. Selenium excess was filtered and washed with benzene (2 × 5 mL). The filtrate was concentrated in vacuo; the residue recrystallized from pentane (60 mL) to give **4a** (6.45 g, 91%) yellow solid; mp 57–58°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (d, 12H, $J = 12.0$ Hz, $NCH_3$), 2.82 (s, 6H, $NCH_3$), 3.65 (s, 3H, $NCH_3$), 7.06 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 32.5$, 37.5 (d, $^3J_{CP} = 2.5$ Hz), 42.4, 119.6 (d, $^1J_{CP} = 142.4$ Hz), 134.8 (d, $^2J_{CP} = 12.5$ Hz), 158.2 (d, $^3J_{CP} = 13.8$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 61.4$. Anal. Calcd for $C_{10}H_{22}N_5PSe$: C, 37.27; N, 21.73; P, 9.61. Found: C, 37.11; N, 21.48; P, 9.36.

*P-(2-Isopropyl-1-Methyl-1H-Imidazol-5-yl)-N,N,N′,N′-Tetramethylphosphonoselenoic Diamide (***4b***).* Following the typical procedure for **4a** using **2b**, the crude product was distilled (bp 165°C/5 × $10^{-2}$ Torr) and crystallized from $Et_2O$; yield: 8.8 g (85%), yellow solid; mp 82–83°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (d, 6H, $J = 7.0$ Hz, $CH(CH_3)_2$), 2.69 (d, 12H, $J = 12.0$ Hz, $NCH_3$), 2.98–3.08 (m, 1H, CH), 3.79 (s, 3H, $NCH_3$), 7.18 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 21.0$, 26.81, 31.9, 37.5 (d, $^3J_{CP} = 3.8$ Hz), 122.0 (d, $^1J_{CP} = 145.0$ Hz), 136.2 (d, $^2J_{CP} = 13.0$ Hz), 158.8 (d, $^3J_{CP} = 10.0$ Hz, C-2). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 62.0$. Anal. Calcd for $C_{11}H_{23}N_4PSe$: C, 41.13; N, 17.44; P, 9.64. Found: C, 41.06; N, 17.65; P, 9.80.

*N,N,N′,N′-Tetramethyl-P-[1-methyl-2-phenyl-1H-imidazol-5-yl]-phosphonoselenoic Diamide (***4c***).* Following the typical procedure for **4a** using **2c**; yield: 8.0 g (90%), yellow solid; mp 110–111°C ($Et_2O$).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.62$ (d, 12H, $J = 12.5$ Hz, $NCH_3$); 3.77 (s, 3H, $NCH_3$); 7.33 (m, 3H, 2′,4′,6′-H), 7.48 (dd, 2H, $J = 1.5$, 8.0 Hz, 3′,5′-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 34.3$, 37.6 (d, $^3J_{CP} = 3.8$ Hz), 123.9 (d, $^1J_{CP} = 143.0$ Hz), 128.6, 129.2, 129.4, 129.8, 137.24 (d, $^2J_{CP} = 11.0$ Hz), 153.3 (d, $^2J_{CP} = 11.0$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 61.1$. Anal. Calcd for $C_{14}H_{21}N_4PSe$: C, 47.33; N, 15.77; P, 8.72. Found: C, 47.15; N, 15.83; P, 8.56.

*N,N,N′,N′-Tetramethyl-P-[1-methyl-2-(methylthio)-1H-imidazol-5-yl]-phosphonoselenoic Diamide*

*(**4d**)*. Following the typical procedure for **4a** using **2d**; yield: 6.9 g (96%), yellow solid; mp 95–96°C (pentane).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.67$ (s, 3H, $SCH_3$), 2.71 (d, 12H, $J = 12.5$ Hz, $NCH_3$), 3.75 (s, 3H, $NCH_3$), 7.29 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 15.2$, 32.7, 37.5 (d, $^3J_{CP} = 4.0$ Hz), 124.2 (d, $^1J_{CP} = 143.4$ Hz), 137.4 (d, $^2J_{CP} = 12.8$ Hz), 150.5 (d, $^3J_{CP} = 11.3$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 60.2$. Anal. Calcd for $C_9H_{19}N_4PSSe$: C, 33.23; N, 17.22; P, 9.52. Found: C, 33.12; N, 17.30; P, 9.35.

### *Typical Procedure for* **5a–d, 6a–d** *by Alkylation of* **4b**

*4(5)-[Bis(dimethylamino)phosphoroselenoyl]-2-isopropyl-1,3-dimethyl-1H-imidazolium chloride (**6b**)*. A solution of compound **4b** (8.0 g, 25 mmol) in MeCl (7.7 g, 150 mmol) was heated at 70–75°C for 6 days in a sealed tube. MeCl excess was removed, the solid residue was treated with $Et_2O$ and filtered and dried in vacuo to give **6b** (9.0 g, 91%) colorless solid; mp 214–215°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.46$ (d, 6H, $J = 7.5$ Hz, $CH(CH_3)_2$), 2.58 (d, 12H, $J = 12.0$ Hz, $NCH_3$), 3.53–3.56 (m, 1H, CH), 3.84 (s, 3H, $NCH_3$), 3.98 (s, 3H, $NCH_3$), 8.50 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 18.5$, 25.4, 36.9, 34.6, 37.6 (d, $^3J_{CP} = 3.8$ Hz), 126.5 (d, $^1J_{CP} = 136.0$ Hz), 130.6 (d, $^2J_{CP} = 16.3$ Hz), 153.6. $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 55.0$. Anal. Calcd for $C_{12}H_{26}N_4PSeCl$: C, 38.77; N, 15.07; P, 8.33. Found: C, 38.43; N, 14.77; P, 8.18.

*4(5)-[Bis(dimethylamino)phosphinyl]-2-(dimethylamino)-1,3-dimethyl-1H-imidazolium Chloride (**5a**)*. Following the typical procedure for **6b** using **3a**; yield: 1.2 g (86%), colorless solid; mp 162–165°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (d, 12H, $J = 10.2$ Hz, $NCH_3$), 3.13 (s, 6H, $NCH_3$), 3.75 (s, 3H, $NCH_3$), 3.96 (s, 3H, $NCH_3$), 8.19 (d, $J = 2.7$ Hz, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 33.8$, 35.5, 35.9 (d, $^3J_{CP} = 5.0$ Hz), 40.9, 121.1 (d, $^1J_{CP} = 135.0$ Hz), 128.3 (d, $^2J_{CP} = 18.0$ Hz), 149.6 (d, $^3J_{CP} = 9.0$ Hz, C-2). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 15.7$. Anal. Calcd for $C_{11}H_{25}N_5OPCl$: C, 42.65; N, 22.61; P, 10.00. Found: C, 42.46; N, 22.34; P, 9.85.

*4(5)-[Bis(dimethylamino)phosphoryl]-2-isopropyl-1,3-dimethyl-1H-imidazolium Chloride (**5b**)*. Following the typical procedure for **6b** using **3b**; yield: 6.4 g (96%), colorless solid; mp 118–122°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.46$ (d, 6H, $J = 7.5$ Hz, $CH(CH_3)_2$), 2.69 (d, 12H, $J = 12.0$ Hz, $NCH_3$), 3.66–3.80 (m, 1H, CH), 3.99 (s, 3H, $NCH_3$), 4.17 (s, 3H, $NCH_3$), 8.91 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 18.3$, 25.1, 34.5, 35.9, 36.5, 124.8 (d, $^1J_{CP} = 177.3$ Hz), 131.6 (d, $^2J_{CP} = 19.0$ Hz), 153.0 (d, $^3J_{CP} = 6.3$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 14.4$. Anal. Calcd for $C_{12}H_{26}N_4OPCl$: C, 46.68; N, 18.14, P, 10.03. Found: C, 46.50; N, 18.35, P, 10.22.

*4(5)-[Bis(dimethylamino)phosphinyl]-1,3-dimethyl-2-phenyl-1H-imidazolium Chloride (**5c**)*. Following the typical procedure for **6b** using **3c**; yield: 2.5 g, (90%), colorless solid; mp 185–187°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.52$ (d, 12H, $J = 10.0$ Hz, $NCH_3$); 3.59 (s, 3H, $NCH_3$); 3.71 (s, 3H, $NCH_3$), 7.38–7.48 (m, 5H, Ph-H), 8.68 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 35.2$, 36.1 (d, $^3J_{CP} = 4.0$ Hz), 36.4, 120.3, 125.5 (d, $^1J_{CP} = 177.3$ Hz), 129.8, 130.2, 131.2 (d, $^2J_{CP} = 10.0$ Hz), 132.9, 148.2 (d, $^3J_{CP} = 6.3$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 15.2$. Anal. Calcd for $C_{15}H_{24}N_4OPCl$: C, 52.56; N, 16.34; P, 9.04. Found: C, 52.37; N, 16.22; P, 9.25.

*4(5)-[Bis(dimethylamino)phosphinyl]-1,3-dimethyl-2-(methylthio)-1H-imidazolium Chloride (**5d**)*. Following the typical procedure for **6b** using **3d**; yield: 2.7 g (76%), colorless solid; mp 174–175°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.66$ (s, 3H, $SCH_3$), 2.73 (d, 12H, $J = 10.0$ Hz, $NCH_3$), 4.10 (s, 3H, $NCH_3$), 4.24 (s, 3H, $NCH_3$), 8.99 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 17.9$, 35.8, 36.2 (d, $^3J_{CP} = 5.0$ Hz), 37.2, 127.8 (d, $^1J_{CP} = 175.0$ Hz), 132.9 (d, $^2J_{CP} = 19.0$ Hz), 145.1 (d, $^3J_{CP} = 7.5$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 14.6$. Anal. Calcd for $C_{10}H_{22}N_4OPSCl$: C, 38.40; N, 17.91; P, 9.90. Found: C, 38.23; N, 17.70; P, 9.76.

*4(5)-[Bis(dimethylamino)phosphinoselenoyl]-2-(dimethylamino)-1,3-dimethyl-1H-imidazolium Chloride (**6a**)*. Following the typical procedure for **6b** using **4a**; yield: 5.8 g (86%), colorless solid; mp 218–220°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (d, 12H, $J = 10.2$ Hz, $NCH_3$), 3.13 (s, 6H, $NCH_3$), 3.75 (s, 3H, $NCH_3$), 3.96 (s, 3H, $NCH_3$), 8.19 (d, $J = 2.7$ Hz, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 33.8$, 35.5, 35.9 (d, $^3J_{CP} = 5.0$ Hz), 40.9, 121.1 (d, $^1J_{CP} = 135.0$ Hz), 128.3 (d, $^2J_{CP} = 18.0$ Hz), 149.6 (d, $^3J_{CP} = 9.0$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 57.0$. Anal. Calcd for $C_{11}H_{25}N_5PSeCl$: C, 35.45; N, 18.79; P, 8.31. Found: C, 35.62; N, 18.95; P, 8.16.

*4(5)-[Bis(dimethylamino)phosphoroselenoyl]-1,3-dimethyl-2-phenyl-1H-imidazolium Chloride (**6c**)*. Following the typical procedure for **6b** using **4c**;

yield: 2.3 g (95%), colorless solid; mp 193–194°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.86$ (d, 12H, $J = 12.0$ Hz, $NCH_3$); 3.80 (s, 3H, $NCH_3$); 3.93 (s, 3H, $NCH_3$), 7.59–7.67 (m, 3H, 2′,4′,6′-H), 7.76–7.79 (m, 2H, 3′,5′-H), 8.43 (d, $J = 2.4$ Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 35.0$, 36.8, 37.8 (d, $^3J_{CP} = 4.0$ Hz), 120.3, 127.2 (d, $^1J_{CP} = 136.0$ Hz), 129.9, 130.2 (d, $^2J_{CP} = 16.3$ Hz), 130.4, 133.0, 148.8 (d, $^3J_{CP} = 7.5$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 56.0$. Anal. Calcd for $C_{15}H_{24}N_4PSeCl$: C, 44.40; N, 13.81; P, 7.63. Found: C, 44.72; N, 13.55; P, 7.34.

*4(5)-[Bis(dimethylamino)phosphinoselenoyl]-1,3-dimethyl-2-(methylthio)-1H-imidazolium Chloride (***6d***).* Following the typical procedure for **6b** using **4d**; yield: 1.2 g (95%), colorless solid; mp 182–183°C (dec.).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.76$ (s, 3H, $SCH_3$), 2.88 (d, 12H, $J = 12.6$ Hz, $NCH_3$), 4.13 (s, 3H, $NCH_3$), 7.29 (s, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 16.8$, 33.3, 34.7, 37.0 (d, $^3J_{CP} = 4.0$ Hz), 120.3 (d, $^1J_{CP} = 145.0$ Hz), 126.6 (d, $^2J_{CP} = 19.0$ Hz), 166.2 (d, $^3J_{CP} = 6.3$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 55.6$. Anal. Calcd for $C_{10}H_{22}N_4PSSeCl$: C, 31.96; N, 14.91; P, 8.24. Found: C, 31.63; N, 14.65; P, 8.06.

## *Typical Procedure for* **7b,c** *by an Example of* **7b**

*P-[2-(dimethylamino)-1-isobutyrylvinyl]-N,N,N′,N′-tetramethylphosphonic diamide (***7b***).* A solution of compound **5b** (2.6 g, 8.3 mmol) in MeOH (20 mL) was added to moist AgOH (1.1 g, 8.8 mmol) in MeOH (20 mL). The suspension was stirred at 20°C for 60 min. MeOH was removed in vacuo at 20°C. The solid residue was recrystallized from benzene to give **7b** (1.8 g, 75%) pale brown solid; mp 176–178°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 0.89$ (d, 3H, $J = 6.5$ Hz, $CHMe_2$), 0.96 (d, 3H, $J = 7.0$ Hz, $CHMe_2$), 2.48 (d, 6H, $J = 7.0$ Hz, PNMe), 2.50 (d, 6H, $J = 9.0$ Hz, PNMe), 2.81 (d, 3H, $J = 4.5$ Hz, NHMe), 2.87 (s, 3H, NMe), 2.88 (m, 1H, CHMe), 4.43 (br s, 1H, NH), 6.58 (dd, 1H, $J_1 = 6.0$ Hz, $J_2 = 13.5$ Hz, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 19.6$, 20.6, 36.1 (d, $^2J_{CP} = 4.0$ Hz), 36.2 (d, $^2J_{CP} = 4.0$ Hz), 30.5, 33.6, 34.1, 100.1 (d, $^1J_{CP} = 83.0$ Hz), 148.0 (d, $^2J_{CP} = 34.0$ Hz), 180.0. $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 28.5$; $^{31}$P (121 MHz, $CH_3OH$): $\delta = 32.7$. HPLC-MS: 290 (95%). Anal. Calcd for $C_{12}H_{27}N_4O_2P$: C, 49.64; N, 19.30; P, 10.67. Found: C, 49.75; N, 19.08; P, 10.86.

*N-[2-[Bis(dimethylamino)phosphoryl]-2-(methylamino)vinyl]-N-methylbenzamide (***7c***).* Following the typical procedure for **7b** using **5d**; yield: 2.5 g (95%), yellow solid; mp 195–196°C (benzene).

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.31$ (d, 6H, $J = 12.6$ Hz, NMe), 2.35 (d, 6H, $J = 9.0$ Hz, NMe), 2.97 (s, 3H, $J = 4.5$ Hz, NHMe), 3.13 (s, 3H, NMe), 4.95–5.10 (m, 1H, NH), 6.40–6.46 (dd, 1H, $J_1 = 6.0$; $J_2 = 13.5$ Hz, CH), 7.26–7.29 (m, 3H, H-Ph), 7.58 (d, 2H, $J = 6.6$ Hz, H-Ph). $^1$H NMR (500 MHz, $CD_3OD$): $\delta = 2.06$ (d, 6H, $J = 10.0$ Hz, NMe), 2.49 (d, 6H, $J = 10.0$ Hz, NMe), 2.99 (s, 3H, NMe), 3.11 (s, 3H, NMe), 6.44 (d, 1H, $J = 6.0$ Hz, CH), 7.31–7.38 (m, 3H, H-Ph), 7.50–7.53 (m, 2H, H-Ph). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 34.4$, 35.3, 35.6 (d, $^2J_{CP} = 4.0$ Hz), 35.8 (d, $^2J_{CP} = 4.0$ Hz), 99.9 (d, $^1J_{CP} = 205.0$ Hz), 127.4, 129.5, 136.7, 148.1 (d, $^2J_{CP} = 31.4$ Hz), 173.0. $^{13}$C NMR (125 MHz, $CD_3OD$): $\delta = 34.5$, 35.8 (d, $^2J_{CP} = 4.0$ Hz), 36.1, 36.2 (d, $^2J_{CP} = 4.0$ Hz), 97.9 (d, $^1J_{CP} = 211.3$ Hz), 127.9, 128.5, 130.5, 138.5, 150.0 (d, $^2J_{CP} = 34.0$ Hz), 175.8. $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 28.20$; $^{31}$P (121 MHz, $CD_3OD$): $\delta = 32.0$. MS (EI, 70eV): $m/z$ (%) = 280 (94) $[M + H]^+$. Anal. Calcd for $C_{15}H_{25}N_4O_2P$: C, 55.54; N, 17.27; P, 9.55. Found: C, 55.27; N, 17.05; P, 9.33.

*P-(2,3-Dihydro-1,3-dimethyl-2-oxo-1H-imidazol-4-yl)-N,N,N′,N′-tetramethyl-phosphonic Diamide (***8***)*

A solution of compound **5a** (2.50 g, 6.2 mmol) in MeOH (10 mL) was added to moist AgOH (1.55 g, 12.4 mmol) in MeOH (20 mL). The suspension was stirred at 16°C for 15 h. The precipitate was filtered and washed with MeOH (2 × 10 mL), the filtrate was concentrated in vacuo at 60°C. The residue was treated with warm $Et_2O$ (40 mL), impurities were filtered, the filtrate was concentrated in vacuo to 10 mL, and the solid precipitated on cooling was filtered to give **8** (1.50 g, 98%) colorless solid; mp 134–136°C.

$^1$H NMR (500 MHz, $CDCl_3$); $\delta = 2.45$ (d, 12H, $J = 12.6$ Hz, $NCH_3$), 3.10 (s, 3H, $NCH_3$), 3.17 (s, 3H, $NCH_3$), 6.39 (s, 1H, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 29.3$, 30.6, 36.2 (d, $^3J_{CP} = 3.8$ Hz), 112.8 (d, $^1J_{CP} = 194.0$ Hz), 121.0 (d, $^2J_{CP} = 19.0$ Hz, C-4), 154.4 (d, $^3J_{CP} = 9.0$ Hz, C-2). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 18.2$. MS (EI, 70eV): $m/z$ (%) = 247 (91) $[M + H]^+$. Anal. Calcd for $C_9H_{19}N_4O_2P$: C, 43.90; N, 22.75; P, 12.58. Found: C, 43.63; N, 22.46; P, 12.35.

## *Typical Procedure for* **9a–c** *by Thermal Decomposition of* **6b**

*P-(2-Isopropyl-1-methyl-1H-imidazol-4-yl)-N,N,N′,N′-tetramethylphosphonoselenoic Diamide (***9b***).* Compound **6b** (24 mmol) was heated at 210–220°C under water-jet pump pressure until gas stopped

to evolve. The residue was distilled (bp 160–180°C/ $5 \times 10^{-2}$ Torr). The distillate was recrystallized from pentane (30 mL) to give **9b** (3.5 g, 47%), pale brown solid; mp 80–81°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.31$ (d, 6H, $J =$ 6.6 Hz, $CH(CH_3)_2$), 2.65 (d, 12H, $J = 13.2$ Hz, $NCH_3$), 2.91–3.04 (m, 1H, CH), 3.60 (s, 3H, $NCH_3$), 7.62 (s, 1H, 5-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 21.2$, 26.3, 32.8, 37.2 (d, $^4J_{CP} = 2.5$ Hz), 133.2 (d, $^2J_{CP} =$ 40.24 Hz), 133.9 (d, $^1J_{CP} = 157.2$ Hz), 155.3 (d, $^3J_{CP} =$ 17.6 Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 67.7$. Anal. Calcd for $C_{11}H_{23}N_4PSe$: C, 41.13; N, 17.44; P, 9.64. Found: C, 40.85; N, 17.30; P, 9.44.

*P-[2-(Dimethylamino)-1-methyl-1H-imidazol-4-yl]- N,N,N′,N′-tetramethyl-phosphonoselenoic Diamide (***9a***).* The mixture of **2a** and **9a** (6.6 g, 20 mmol) prepared by thermal decomposition of **6a** (8.0 g, 21 mmol) following the typical procedure described for **9b** was dissolved in $CH_2Cl_2$ (30 mL), then cooled to −80°C and a solution of picric acid (1.5 g, 7 mmol) in $CH_2Cl_2$ (25 mL) was added dropwise. The reaction mixture was allowed to warm to 20°C and stirred for another 15–20 min. The solvent was removed in vacuo; the oily residue was treated with hot pentane (4 × 30 mL). Impurities were collected, the solution was concentrated, the residue distilled in vacuo (bp 150–155°C/5 × $10^{-2}$ Torr) to give **9a** (3.91 g, 86%) yellow solid; mp. 41–42°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.65$ (d, 12H, $J =$ 13.2 Hz, $NCH_3$), 2.77 (s, 6H, $NCH_3$), 3.50 (s, 3H, $NCH_3$), 7.51 (s, 1H, 5-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 32.5$, 37.2 (d, $^4J_{CP} = 4.0$ Hz), 42.7, 131.2 (d, $^2J_{CP} =$ 39.0 Hz), 131.4 (d, $^1J_{CP} = 157.2$ Hz), 155.2 (d, $^3J_{CP} =$ 20.1 Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 68.4$. Anal. Calcd for $C_{10}H_{22}N_5PSe$: C, 37.27; N, 21.73; P, 9.61. Found: C, 37.10; N, 21.52; P, 9.35.

*N,N,N′,N′-Tetramethyl-P-(1-methyl-2-phenyl-1H-imidazol-4-yl)phosphonoselenoic Diamide (***9c***).* Following the typical procedure for **9b** using **6c**; yield: 600 mg (61%), bp 132–140°C/5 × $10^{-2}$ Torr; pale yellow solid, mp 90–91°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (d, 12H, $J =$ 13.2 Hz, $NCH_3$); 3.73 (s, 3H, $NCH_3$); 7.43–7.50 (m, 3H, 2′,4′,6′-H), 7.58–7.63 (m, 2H, 3′,5′-H), 7.83 (br. s 1H, 5-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 34.7$, 37.3 (d, $^4J_{CP} = 3.8$ Hz), 128.6, 129.0, 129.3, 129.9, 135.0 (d, $^2J_{CP} = 36.5$ Hz), 136.7 (d, $^1J_{CP} = 156.0$ Hz), 150.0 (d, $^3J_{CP} = 18.9$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 67.3$. Anal. Calcd for $C_{14}H_{21}N_4PSe$: C, 47.33; N, 15.77; P, 8.72. Found: C, 47.05; N, 15.62; P, 8.97.

*P-(1,3-Dimethyl-2-thioxo-2,3-dihydro-1H-imidazol-4-yl)-N,N,N′,N′-tetramethylphosphonoselenoic Diamide (***10***)*

Following the typical procedure for **9b** using **6d**; yield: 6.6 g (97%), bp 200–205°C/5 × $10^{-2}$ Torr; yellow solid, mp 167–168°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.70$ (d, 12H, $J = 12.6$ Hz, $NCH_3$), 3.64 (s, 3H, $NCH_3$), 3.78 (s, 3H, $NCH_3$), 7.15 (d, $J = 3.3$ Hz, 1H, 4-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 34.4$, 35.4, 37.6 (d, $^3J_{CP} =$ 3.8 Hz), 121.8 (d, $^1J_{CP} = 140.0$ Hz), 127.0 (d, $^2J_{CP} =$ 20.1 Hz), 167.2 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 60.9$. Anal. Calcd for $C_9H_{19}N_4PSSe$: C, 33.23; N, 17.22; P, 9.52. Found: C, 33.56; N, 16.87; P, 9.90.

*4(5)-[Bis(dimethylamino)phosphino]-2-isopropyl-1,3-dimethyl-1H-imidazolium Chloride (***11***)*

To compound **6c** (3.9 g, 10 mmol) in THF (20 mL) hexamethyltriamidophosphite $(Me_2N)_3P$ (1.96 g, 12 mmol) was added. The reaction mixture was stirred at 16°C for 15 h. The precipitate was filtered and washed with THF (2 × 10 mL) and dried in vacuo to give **11** (2.85 g, 92%) colourless solid; mp 130–145°C.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta = 1.12$ (d, 6H, $J =$ 7.2 Hz, $CH(CH_3)_2$), 2.46 (d, 12H, $J = 10.0$ Hz, $NCH_3$), 3.51 (s, 3H, $NCH_3$), 3.52 (m, 1H, $CH(CH_3)_2$), 3.86 (s, 3H, $NCH_3$), 7.28 (s, 1H, 4(5)-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 18.6$, 25.1, 33.7 (d, $^3J_{CP} = 6.3$ Hz), 36.0, 36.7, 41.1 (d, $^2J_{CP} = 17.6$ Hz), 127.7 (d, $^2J_{CP} = 7.5$ Hz), 133.5 (d, $^1J_{CP} = 11.3$ Hz), 151.8. $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 76.8$. Anal. Calcd for $C_{12}H_{26}N_4PCl$: C, 49.23; N, 19.14; P, 10.58. Found: C, 49.41; N, 18.84; P, 10.75.

*N,N-Dimethyl-N′,N″-bis[tris(diethylamino)-phosphinidene]phosphorous Triamide (***12***)*

A solution of hexamethylphosphorimidic triamide $(Et_2N)_3PNH$ (37.2 g, 14.2 mmol) in benzene (15 mL) was cooled to 0–5°C and added dropwise to dichloroamidophosphite $Me_2NPCl_2$ (6.0 g, 41.1 mmol) in benzene (40 mL) at 0–5°C over 60 min. Benzene was removed in vacuo, the residue was dissolved in liquid ammonia (70 mL), and metallic sodium (1.75 g, 7.6 mmol) was added portionwise till the solution turned stable blue. Liquid ammonia excess was removed; the oily residue was treated with pentane (75 mL). Insoluble precipitate was filtered and washed with pentane (2 × 30 mL). The filtrate was concentrated in vacuo; the residue was distilled

(bp 190–200°C/5 × $10^{-2}$ Torr) to give **12** (13.8 g, 57%) colorless liquid.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 1.11 (t, 36H, $J$ = 7.2 Hz, $CH_3$); 2.86 (d, 6H, $J$ = 7.8 Hz, $CH_3$), 3.07–3.29 (m, 24H, $CH_2$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 14.0, 36.6 (d, $^2J_{CP}$ = 10.0 Hz), 39.4. $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 15.43 (d, $J_{P\text{-}N\text{-}P}$ = 75.3 Hz), 97.45 (t, $J_{P\text{-}N\text{-}P}$ = 75.3 Hz). Anal. Calcd for $C_{26}H_{66}N_9P_3$: C, 52.24; N, 21.09; P, 15.54. Found: C, 52.67; N, 21.04; P, 15.32.

## *Typical Procedure for* **13a–c** *by Reduction of* **9a**

*P-[2-(Dimethylamino)-1-methyl-1H-imidazol-4-yl]-N,N,N′,N′-tetramethyl-phosphonous Diamide (***13a***). Method A*. A solution of compound **9a** (1.6 g, 5 mmol) and **12** (3.3 g, 5.5 mmol) in benzene (5 mL) was stirred for 10–15 min. Benzene was removed in vacuo, the oily residue was distilled (112–120°C/5 × $10^{-2}$ Torr) affording **13a** (1.14 g, 94%), colorless solid; mp. 55–56°C.

*Method B*. To a sodium suspension (410 mg, 18 mmol) in toluene (30 mL) a solution of **9a** (4.2 g, 13 mmol) in toluene (10 mL) was added. The reaction mixture was heated with stirring at 120°C for 1.5 h in a sealed flask. Toluene was removed in vacuo; the residue was treated with hot pentane (30 mL). The precipitate was filtered out and washed with pentane (2 × 20 mL). The filtrate was concentrated in vacuo, and the residue was distilled (112–116°C/5 × $10^{-2}$ Torr) to give **13a** (3.06 g, 97%).

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 2.52 (s, 6H, $NCH_3$), 2.75 (s, 3H, $NCH_3$), 2.91 (d, $J$ = 9.0 Hz, 12H, $NCH_3$), 6.55 (d, $J$ = 1.5 Hz, 1H, 5-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 31.2, 41.7, 42.8, 123.1 (d, $^2J_{CP}$ = 30.2 Hz), 137.4 (d, $^1J_{CP}$ = 22.6 Hz), 154.7 (d, $^3J_{CP}$ = 10.0 Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta$ = 88.2. Anal. Calcd for $C_{10}H_{22}N_5P$: C, 49.37; N, 28.79; P, 12.73. Found: C, 49.25; N, 28.60; P, 12.43.

*P-(2-Isopropyl-1-methyl-1H-imidazol-4-yl)-N,N,N′,N′-tetramethylphosphonous Diamide (***13b***)*. Following method B for **13a** using **9b**; yield: 2.6 g (93%), colorless liquid; bp 110–115°C/5 × $10^{-2}$ Torr.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 1.22 (d, 6H, $J$ = 7.0 Hz, $CH(CH_3)_2$), 2.74 (s, 3H, $NCH_3$), 2.87 (d, 12H, $J$ = 10.0 Hz, $NCH_3$), 2.46–2.58 (m, 1H, CH), 6.62 (d, 1H, $J$ = 1.0 Hz, 5-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 21.5, 26.1, 31.3, 36.6 (d, $^4J_{CP}$ = 4.0 Hz), 41.7 (d, $^2J_{CP}$ = 15.0 Hz), 125.2 (d, $^2J_{CP}$ = 31.4 Hz), 139.6 (d, $^1J_{CP}$ = 23.0 Hz), 153.9 (d, $^3J_{CP}$ = 9.0 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 87.7. Anal. Calcd for $C_{11}H_{23}N_4P$: C, 54.53; N, 23.12; P, 12.78. Found: C, 54.23; N, 23.45; P, 12.67.

*N,N,N′,N′-Tetramethyl-P-(1-methyl-2-phenyl-1H-imidazol-4-yl)phosphonous Diamide (***13c***)*. Following **method B** for **13a** using **9c**; yield: 700 mg, (90%), pale yellow liquid; bp 165–170°C/5 × $10^{-2}$ Torr.

$^1$H NMR (500 MHz, $C_6D_6$); $\delta$ = 2.90 (d, 12H, $J$ = 9.3 Hz, $NCH_3$); 2.96 (s, 3H, $NCH_3$); 6.76 (d, 1H, $J$ = 1.8 Hz, 5-H), 7.10–7.19 (m, 3H, 2′,4′,6′-H), 7.61 (d, 2H, $J$ = 6.6 Hz, 3′,5′-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 33.7, 41.8 (d, $^2J_{CP}$ = 16.3 Hz), 127.4, 128.0, 128.3, 128.6, 131.6, 141.4 (d, $^1J_{CP}$ = 21.4 Hz), 149.0 (d, $^3J_{CP}$ = 9.0 Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta$ = 87.0. Anal. Calcd for $C_{14}H_{21}N_4P$: C, 60.85; N, 20.28; P, 11.21. Found: C, 61.08; N, 20.15; P, 10.95.

## *Typical Procedure for* **14a–c** *by the Example of* **14a**

*[2-(Dimethylamino)-1-methyl-1H-imidazol-4-yl]-phosphonous dichloride (***14a***)*. A solution of compound **13a** (730 mg, 3 mmol) in phosphorus trichloride (8.0 g, 58 mmol) was stirred at 20°C for 10 min. Phosphorus trichloride excess was removed in vacuo. The residue was distilled (120–140°C/5 × $10^{-2}$ Torr) to give **14a** (260 mg, 39%), pale yellow solid; mp 42–44°C.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 2.39 (s, 6H, $NCH_3$), 2.60 (s, 3H, $NCH_3$), 6.66 (s, 1H, 5-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 31.8, 42.0, 126.1 (d, $^2J_{CP}$ = 40.2 Hz), 135.9 (d, $^1J_{CP}$ = 39.0 Hz), 155.8 (d, $^3J_{CP}$ = 12.75 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 146.7. Anal. Calcd for $C_6H_{10}Cl_2N_3P$: C, 31.88; N, 18.59; P, 13.70. Found: C, 31.65; N, 18.27; P, 13.55.

*(2-Isopropyl-1-methyl-1H-imidazol-4-yl)phosphonous Dichloride (***14b***)*. Following the typical procedure for **14a** using **13b**; yield: 820 mg (96%), colorless solid; 116–120°C/5 × $10^{-2}$ Torr, mp 24–26°C.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 1.09 (d, 6H, $J$ = 7.2 Hz, $CH(CH_3)_2$), 2.45 (m, 1H, CH), 3.76 (s, 3H, $NCH_3$), 6.97 (d, 1H, $J$ = 3.3 Hz, 5-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 21.0, 26.1, 32.0, 128.3 (d, $^2J_{CP}$ = 34.0 Hz), 138.3 (d, $^1J_{CP}$ = 36.5 Hz), 156.1 (d, $^3J_{CP}$ = 13.8 Hz). $^{31}$P (121 MHz, $C_6D_6$): $\delta$ = 147.5. Anal. Calcd for $C_7H_{11}Cl_2N_2P$: C, 37.36; N, 12.45; P, 13.76. Found: C, 37.54; N, 12.15; P, 14.00.

*(1-Methyl-2-phenyl-1H-imidazol-4-yl)phosphonous Dichloride (***14c***)*. Following the typical procedure for **14a** using **13c**; yield: 300 mg, (53%), pale yellow liquid; bp 160–165°C/5 × $10^{-2}$ Torr.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 2.76 (s, 3H, $NCH_3$); 6.92 (s, 1H, 5-H), 7.09–7.20 (m, 3H, 2′,4′,6′-H), 7.37–7.44 (m, 2H, 3′,5′-H). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 34.0, 128.5, 128.7, 129.2, 129.5

(d, $^2J_{CP}$ = 33.0 Hz), 129.8, 140.0 (d, $^1J_{CP}$ = 37.7 Hz), 150.5 (d, $^3J_{CP}$ = 13.8 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 146.2. Anal. Calcd for $C_{10}H_9Cl_2N_2P$: C, 46.36; N, 10.81; P, 11.96. Found: C, 46.70; N, 11.07; P, 11.55.

### *4,8-Dichloro-1,5,N,N,N′,N′-hexamethyl-1,4,5,8-tetrahydro-1,3,5,7-tetraaza-4,8-diphospha-s-indacene-2,6-diamine (***15a***)*

To a solution of compound **13a** (2.61 g, 11.5 mmol) in phosphorus trichloride (1.6 g, 11.6 mmol), a solution of $Et_3N$ (1.42 g, 14 mmol) in pyridine (15 mL) was added. The reaction mixture was heated at 45°C for 4 days. Pyridine and phosphorus trichloride excess were removed in vacuo, the residue was treated with hot benzene (25 mL), insoluble precipitate was filtered and the filtrate was concentrated in vacuo. The solid residue was treated with warm $Et_2O$ (30 mL), and insoluble products were removed. The solid precipitated on cooling was filtered and dried to give **15a** (1.59 g, 73%), yellow solid; mp 190–191°C (dec.).

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 2.41 (s, 12H, $NCH_3$), 3.07 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 31.2, 41.8, 129.7, 137.4, 159.0 (t, $^3J_{CP}$ = 12.8 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 25.8. Anal. Calcd for $C_{12}H_{18}Cl_2N_6P_2$: C, 38.01; N, 22.16; P, 16.34. Found: C, 37.66; N, 21.82; P, 16.57.

### *1,5,N,N,N′,N′,N″,N″,N‴,N‴-Decamethyl-1H,5H-1,3,5,7-tetraaza-4,8-diphospha-s-indacene-2,4,6,8-tetraamine (***16a***)*

*Method A*. A solution of **15a** (1.5 g, 4 mmol) in benzene (5 mL) was cooled to 0–5°C, and dimethylamine (800 mg, 18 mmol) in benzene (10 mL) was added dropwise. The reaction mixture was stirred at 0–5°C to 20°C and then heated at 60°C for 5–10 min in a sealed flask. The precipitate was filtered out and was washed with benzene (5 mL); the filtrate was concentrated in vacuo. The residue was dissolved in benzene (8 mL) on reflux. In 4 h, the solid precipitated on cooling to −7°C was filtered and dried to give **16a** (510 mg, 32%) yellow solid; mp 240–242°C.

*Method B*. To a sodium (330 mg, 14 mmol) suspension in benzene (20 mL) compound **(E) 17a** (550 mg, 1 mmol) was added. The reaction mixture was heated on stirring at 125°C for 2.5 h in a sealed tube. Insoluble precipitate was filtered and washed with benzene (2 × 10 mL). The filtrate was concentrated in vacuo to give **16a** (370 mg, 98%).

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 2.54 (br d, 12H, $J$ = 9.0 Hz, $NCH_3$), 2.57 (s, 12H, $NCH_3$), 3.56 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 31.3 (t, $J$ = 4.0 Hz), 40.2 (t, $J$ = 6.3 Hz), 42.5, 130.9 (t, $J$ = 4.0 Hz), 139.3 (t, $J$ = 7.0 Hz), 157.8 (t, $J$ = 9.0 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 15.6. Anal. Calcd for $C_{16}H_{30}N_8P_2$: C, 48.48; N, 28.27; P, 15.63. Found: C, 48.48; N, 28.27; P, 15.63.

### *2,6-Diisopropyl-1,5,N,N,N′,N′-hexamethyl-1H,5H-1,3,5,7-tetraaza-4,8-diphospha-s-indacene-4,8-diamine(***16b***)*

Following method B for **16a** using **17b**, the crude product was crystallized from $Et_2O$; yield: 130 mg (96%), yellow solid; mp 236–238°C.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 1.24 (d, 6H, $J$ = 7.0 Hz, $CH(CH_3)_2$), 1.29 (d, 6H, $J$ = 6.5 Hz, $CH(CH_3)_2$), 2.49 (d, 12H, $J$ = 9.0 Hz, $NCH_3$), 2.56–2.62 (m, 2H, CH), 3.90 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 21.5 (d, $^3J_{CP}$ = 22.6 Hz); 26.5; 31.5 (m); 40.5 (m); 133.3 (t, $^1J_{CP}$ = 4.0 Hz); 141.4 (t, $^1J_{CP}$ = 7.5 Hz); 158.0 (t, $^3J_{CP}$ = 10.0 Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta$ = 15.1. Anal. Calcd for $C_{18}H_{32}N_6P_2$: C, 54.81; N, 21.31; P, 15.71. Found: C, 54.55; N, 21.16; P, 15.43.

### *1,5,N,N,N′,N′,N″,N″,N‴,N‴-Decamethyl-4,8-diselenoxo-1,4,5,8-tetrahydro-1,3,5,7-tetraaza-4 λ$^5$,8 λ$^5$-diphospha-s-indacene-2,4,6,8-tetraamine(***17a***)*

*Method A*. To a solution of **13a** (1.13 g, 5 mmol) in phosphorus trichloride (1.86 g, 13.5 mmol), a solution of $Et_3N$ (940 mg, 9 mmol) in pyridine (0.5 mL) was added. The reaction mixture was heated at 45°C for 4 days. The excess of pyridine and phosphorus trichloride was removed in vacuo, the residue was dissolved in benzene (6 mL), the solution was cooled at −20 to −30°C, and dimethylamine (2.0 mL, 28 mmol) was added. The reaction mixture was allowed to warm to 20°C and stirred for another 30 min. Insoluble precipitate was filtered out and was washed with benzene (2 × 5 mL); the filtrate was concentrated in vacuo. The residue was treated with warm $Et_2O$ (3 × 40 mL), the solid (450 mg) precipitated on cooling was collected, and the filtrate was concentrated in vacuo. The residue was treated with hot pentane (2 × 40 mL), insoluble products were collected, the pentane was removed in vacuo, and the solid residue (260 mg) was dried. The solids were combined (710 mg) and dissolved in pyridine (6 mL). Selenium (160 mg, 2 mmol) was added, and the reaction mixture was heated at 90°C for 20 min. The pyridine was removed in vacuo, the residue was treated with warm $Et_2O$ (2 × 40 mL), insoluble products were collected, and $Et_2O$ was removed in vacuo. The residue was crystallized from acetonitrile (15 mL). The solid precipitated on cooling was collected by filtration to give **(E)-17a** (190 mg,

13.4%). The filtrate was concentrated in vacuo, and the residue was purified by chromatography on silica gel (EtOAc–hexane, 19:1) affording **(E)-17a** (340 mg, 24.0%) yellow solid; mp 280–282°C; $R_f = 0.70$ and **(Z)-17a** (150 mg, 10.6%) orange oil; $R_f = 0.26$.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.77$ (d, 12H, $J = 12.6$ Hz, $NCH_3$), 2.88 (s, 12H, $NCH_3$), 3.75 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 32.6$, 37.4, 42.4, 122.7 (dd,$J^1_{CP} = 26.4$; $J^2_{CP} = 118.2$ Hz), 136.1 (dd, $J^1_{CP} = 11.3$; $J^2_{CP} = 137.0$ Hz), 159.4 (m). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 21.1$. Anal. Calcd for $C_{16}H_{30}N_8P_2Se_2$: C, 34.67; N, 20.21; P, 11.18. Found: C, 34.93; N, 20.45; P, 10.88.

(*Z*)-**17a**. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.79$ (d, 12H, $J = 13.0$ Hz, $NCH_3$), 2.87 (s, 12H, $NCH_3$), 3.73 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 37.3$, 37.4, 42.4, 122.0 (dd, $J_{1\,CP} = 26.0$; $J_{2\,CP} = 119.5$ Hz), 136.0 (dd, $J_{1\,CP} = 12.6$; $J_{2\,CP} = 135.8$ Hz), 159.2 (m). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 21.4$. MS (EI, 70eV): *m/z* (%) = 555 (64), 555 (29.5) $[M + H]^+$.

*Method B.* A mixture of compound **(E)-16a** (430 mg, 1.1 mmol) and selenium (170 mg, 2.2 mmol) in benzene (3 mL) was refluxed for 5–10 min. Selenium excess was filtered, the filtrate was concentrated in vacuo, and the residue was recrystallized from acetonitrile (15 mL) to give **(E)-17a** (0.5 g, 90%), mp. 280–282°C.

### *2,6-Diisopropyl-1,5,N,N,N′,N′-hexamethyl-4,8-diselenoxo-1,4,5,8-tetrahydro-1,3,5,7-tetraaza-4λ$^5$,8λ$^5$-diphospha-s-indacene-4,8-diamine(***17b***)*

A solution of **14b** (1.3 g, 5.8 mmol) in a mixture of benzene (10 mL) and toluene (1 mL) was heated at 125°C for 20 days in a sealed tube. The solvents were removed in vacuo to dryness, the residue was dissolved in benzene (20 mL), the solution was cooled to −30°C, and dimethylamine (2.5 mL, 35.5 mmol) was added dropwise. The reaction mixture was allowed to warm to 20°C and stirred for another 1 h. Excess of benzene and dimethylamine was removed in vacuo, the residue was treated with $Et_2O$ (20 mL), insoluble precipitate was filtered, washed with $Et_2O$ (3 × 10 mL), and the filtrated product was concentrated in vacuo. The residue was dissolved in pyridine (3 mL), selenium (460 mg) was added, and the reaction mixture was heated at 90°C for 30 min. Pyridine was removed in vacuo, the residue was treated with $CH_2Cl_2$ (10 mL). Insoluble products were filtered and washed with $CH_2Cl_2$ (5 mL), the filtrate was concentrated in vacuo, and the residue recrystallized from benzene (5 mL). The solid (0. 64 g, 40%, a mixture of isomers) precipitated on cooling was filtered. The second crystallization from acetonitrile (4 mL) afforded **(E)-17b** (0.2 g, 20%) orange solid; mp 263–265°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 1.37$ (d, 6H, $J = 6.5$ Hz, $CH(CH_3)_2$), 1.39 (d, 6H, $J = 7.0$ Hz, $CH(CH_3)_2$), 2.63 (d, 12H, $J = 12.6$ Hz, $NCH_3$), 3.04–3.10 (m, 2H, CH), 3.90 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 21.1$, 26.7, 32.1, 37.2, 125.2 (dd, $J_{1C\text{-}P} = 28.0$; $J_{2C\text{-}P} = 117.0$ Hz), 138.0 (dd, $J_{1C\text{-}P} = 13.0$; $J_{2C\text{-}P} = 137.0$ Hz), 160.8 (m). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 22.0$. Anal. Calcd for $C_{18}H_{32}N_6P_2Se_2$: C, 39.14; N, 15.21; P, 11.22. Found: C, 38.84; N, 14.85; P, 11.00.

### *1,5,N,N,N′,N′,N″,N″,N‴,N‴-Decamethyl-4,8-dithioxo-1,4,5,8-tetrahydro-1,3,5,7-tetraaza-4λ$^5$,8λ$^5$-diphospha-s-indacene-2,4,6,8-tetraamine (***18a***)*

To a solution of compound **16a** (400 mg, 1 mmol) in pyridine (3 mL) powdered sulfur (65 mg, 2 mmol) was added. The reaction mixture was stirred at 25°C for 10–15 min. Pyridine was removed in vacuo; the residue was dissolved in acetone and refined with activated charcoal. The filtrate was concentrated, and the residue recrystallized from acetonitrile (15 mL) to give **18a (**0.39 g, 85%) yellow solid; mp 280–283°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.73$ (d, 12H, $J = 12.6$ Hz, $NCH_3$), 2.87 (s, 12H, $NCH_3$), 3.73 (s, 6H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 32.5$, 36.7, 42.4, 124.4 (dd, $J_{1C\text{-}P} = 29.0$; $J_{2C\text{-}P} = 128.3$ Hz), 137.0 (dd, $J_{1C\text{-}P} = 13.0$; $J_{2C\text{-}P} = 148.0$ Hz), 159.3 (m). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 31.9$. Anal. Calcd for $C_{16}H_{30}N_8P_2S_2$: C, 41.73; N, 24.33; P, 13.45. Found: C, 42.05; N, 24.02; P, 13.64.

### *P-[2-(Dimethylamino)-1-methyl-5-(trimethylsilyl)-1H-imidazol-4-yl]-N,N,N′,N″-tetramethylphosphonous Diamide (***19***)*

Following the typical procedure for **12a** using **22**, heating at 125°C for 3h; yield: 430 mg (98%), colorless solid; bp 110–113°C /5 × $10^{-2}$ Torr.

$^1$H NMR (500 MHz, $C_6D_6$): $\delta = 0.38$ (s, 9H, $SiCH_3$), 2.54 (s, 6H, $NCH_3$), 2.95 (d, 6H, $J = 9.6$ Hz, $NCH_3$), 3.09 (s, 3H, $NCH_3$). $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta = 1.3$ (d, $J_{Si\text{-}P} = 54.0$ Hz), 32.5, 42.0 (d, $^3J_{CP} = 15.0$ Hz), 42.8, 131.7 (d, $^2J_{CP} = 54.0$ Hz), 149.6 (d, $^1J_{CP} = 2.5$ Hz), 156.4 (d, $^3J_{CP} = 5.0$ Hz). $^{31}$P NMR (121 MHz, $C_6D_6$): $\delta = 81.9$. Anal. Calcd for $C_{13}H_{30}N_5PSi$: C, 49.49; N, 22.20; P, 9.82. Found: C, 49.37; N, 22.45; P, 9.47.

*P-[2-(Dimethylamino)-1-methyl-5-(trimethylsilyl)-1H-imidazol-4-yl]-N,N,N′,N′-tetramethylphosphonoselenoic Diamide (**22**)*

To a solution of compound **12a** (2.0 g, 8.2 mmol) in THF (45 mL), t-BuLi (1.7 H solution in pentane) (8.2 mL, 14 mmol) was added dropwise at −90°C over 5 min. The reaction mixture was stirred at −80°C for 8 h and was recooled to −90°C, and $Me_3SiCl$ (1.92 g, 17.7 mmol) was added. The reaction mixture was allowed to warm to 20°C, and stirring was continued for further 12 h, at that the solution became clear. The solution was concentrated to 15 mL and was cooled to −20°C, and dimethylamine (9 mL) was added. In 10–15 min, the solvents were removed in vacuo leaving the residue that was distilled (bp 125–130°C/5 × $10^{-2}$ Torr). To a solution of the distillate (1.76 g) in pyridine (15 mL), selenium (0.65 g, 8.2 mmol) was added and the mixture was stirred at 20°C for 30 min. Selenium excess was filtered and washed with pyridine (10 mL); the filtrate concentrated in vacuo. The residue (a mixture of **22** and **23)** was refined by chromatography on silica gel (EtOAc–hexane, 1:1) to give phosphonate **22** (730 mg, 22%) pale yellow solid; $R_f = 0.51$; mp 116–117°C and phosphinate **23** (770 mg, 23%) orange solid; $R_f = 0.82$; mp 95–96°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 0.45$ (s, 9H, $SiCH_3$), 2.69 (d, 12H, $J = 12.0$ Hz, NMe), 2.74 (s, 6H, NMe), 3.50 (s, 3H, NMe). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 1.07$, 33.89, 38.20 (d, $^3J_{CP} = 4.0$ Hz), 42.7, 135.6 (d, $^2J_{CP} = 4.0$ Hz), 141.9 (d, $^1J_{CP} = 161.0$ Hz), 156.0 (d, $^3J_{CP} = 20.1$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 70.9$. Anal. Calcd for $C_{13}H_{30}N_5PSeSi$: C, 39.59; N, 17.76; P, 7.85. Found: C, 39.33; N, 17.52; P, 8.10.

*P-(Tert-butyl)-P-[2-(dimethylamino)-1-methyl-5-(trimethylsilyl)-1H-imidazol-4-yl]-N,N-dimethylphosphinoselenoic Amide (**23**)*

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 0.45$ (s, 9H, $SiCH_3$), 1.45 (d, 9H, $J = 12.6$ Hz, $C(CH_3)$), 2.73 (s, 6H, $NCH_3$), 2.81 (d, 6H, $J = 9.0$ Hz, $NCH_3$), 3.53 (s, 3H, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 1.1$, 26.8, 33.8, 39.6 (d, $^3J_{CP} = 4.0$ Hz), 43.8 (d, $^2J_{CP} = 56.6$ Hz), 44.0, 136.5 (d, $^2J_{CP} = 31.0$ Hz), 140.2 (d, $^1J_{CP} = 132.0$ Hz), 155.6 (d, $^3J_{CP} = 20.0$ Hz). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 77.6$. Anal. Calcd for $C_{15}H_{33}N_4PSeSi$: C, 44.22; N, 13.75; P, 7.60. Found: C, 43.90; N, 13.53; P, 7.45.

*4,5-[Bis(dimethylamido)selenophosphonoyl)]-2-(dimethylamino)-1-methyl-1H-Imidazole (**24**)*

To a solution of compound **12a** (2.0 g, 8.2 mmol) in THF (45 mL), t-BuLi (1.7 H solution in pentane) (5.0 mL, 8.5 mmol) was added dropwise at −90°C over 5 min. After stirring at −80°C for 8 h, the reaction mixture was recooled to −90°C and solution of bis(tetramethylamino)chlorophosphine (1.3 g, 8.2 mmol) in pentane (10 mL) was added dropwise over 10 min, at that the solution became clear. The reaction mixture was allowed to warm to 20°C, and stirring was continued for further 12 h. The mixture was recooled to −20°C, and dimethylamine (5.5 mL) was added. In 10–15 min, the solvents were removed in vacuo to dryness. The residue was treated with benzene (40 mL), insoluble products were filtered, the filtrate concentrated in vacuo, then the residue was distilled twice (bp 110–120°C/5 × $10^{-2}$ Torr). To a solution of the distillate (1.61 g, 57%) in pyridine (15 mL), selenium (0.37 g, 4.7 mmol) was added and the mixture was stirred at 20°C for 30 min. Selenium excess was filtered and washed with pyridine (10 mL); the filtrate concentrated in vacuo. The residue was recrystallized from pentane to give **24** (1.8 g, 42%) reddish-brown solid; mp 135–137°C.

$^1$H NMR (500 MHz, $CDCl_3$): $\delta = 2.73$ (br s, 6H, NMe), 3.66 (s, 3H, NMe), 2.78 (d, 24H, $J = 10.0$ Hz, $NCH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta = 33.6$, 38.7, 38.8 (d, $^3J_{CP} = 5.0$ Hz), 42.4, 126.2 (dd, $J_{1CP} = 5.0$; $J_{2CP} = 149.7$ Hz, C-5), 139.7 (dd, $J_{1CP} = 12.8$; $J_{2CP} = 149.7$ Hz, C-4), 156.7 (dd, $J_{1\ CP} = 15.0$; $J_{2CP} = 22.6$ Hz, C-2). $^{31}$P NMR (121 MHz, $CDCl_3$): $\delta = 62.7$ ($^1J_{PP} = 2.0$ Hz); 66.53 ($^1J_{PP} = 2.0$ Hz). Anal. Calcd for $C_{14}H_{33}N_7P_2Se_2$: C, 32.38; N, 18.88; P, 11.93. Found: C, 32.65; N, 19.06; P, 11.71.

## *REFERENCES*


[1] Yurchenko, A. A.; Huryeva, A. N., et al. Журнал орг. та фарм. хімії 2009, 7, 33.
[2] Yurchenko, A. A.; Huryeva, A. N.; Marchenko, A. P.; Koidan, G. N.; Zarudnitskiy, Y. V.; Pinchuk, A. M. Heteroatom Chem 2009, 5, 289.
[3] Smoliy, O. B.; Brovarets, V. S.; Pirogenko, V. V.; Drach, B. S. J Gen Chem 1988, 58, 2635.
[4] Kanazava, C.; Kamijo, S.; Yamamoto, Y. J Am Chem Soc 2006, 128, 10662.
[5] Van der Jeught, S.; Stevens, C. V. Chem Rev 2009, 109, 2672.
[6] Bhagwat, V. K.; Pyman, F. L. J Chem Soc 1925, 127, 1832.
[7] Saito, T.; Inoue, I.; Fujii, T. Chem Pharm Bull 1990, 38, 1536.
[8] Smith, et al. J Am Chem Soc 1949, 71, 1082.
[9] Seikou, N.; Naoki, T.; Masayuki, Y.; Kawasaki, I.; Yoshitaka, O. J Chem Soc, Perkin Trans 1 2001, 3, 429.
[10] Kuhn, N.; Steimann, M.; Weyers, G.; Henkel, G. Z Naturforschung, B: Chem Sci 1999, 54, 434 (in German).

[11] (a) Iwasaki, S. Heterocycles 1982, 17, 125; (b) Baker, J. J Am Chem Soc 1958, 2387.
[12] Nifantiyev, E. N.; Koroteyev, M. P.; Rumianceva, S. A.; Elinec, A. M.; Kochetkov, N. K. J Gen Chem 1990, 60, 345.
[13] Kostyuk, A. N.; Svyaschenko, Y. V.; Volochnyuk, D. M. Tetrahedron 2005, 61, 9263.
[14] Marchenko, A. P.; Koidan, G. N.; Pinchuk, A. N.; Kyrsanov, A. V. J Gen Chem 1984, 54, 1774.
[15] (a) King, R. B. et al. J Org Chem 1976, 41, 972; (b) Kagan, H. B. et al. Bull Soc Chim Belges 1979, 88, 923.
[16] (a) Sheldric, G. M. SHELXS97 Program for the Solution of Crystal Structure; University of Gottingen: Germany, 1997; (b) Sheldric, G. M. SHELXL97 Program for the Refinement of Crystal Structure; University of Gottingen: Germany, 1997; (c) Ivonin, S. P.; Tolmachev, A. A.; Chernega, A. N.; Pinchuk, A. M. Heteroatom Chem 2002, 13, 46.