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SYNTHESIS AND PROPERTIES OF 2-(DIORGANYLPHOSPHORYL-HYDROXYMETHYL)-1-ORGANYLIMIDAZOLES*

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1-Organyl-2-formylimidazoles and -benzimidazoles react with diorganylphosphine oxides under mild conditions (room temperature, dioxane, 1 h) to give in practically quantitative yields 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles – highly reactive synthons and polydentate ligands for the design of metal complex catalysts.

Keywords: diorganylphosphine oxides, 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles, 1-organyl-2-formylbenzimidazoles, 1-organyl-2-formylimidazoles, camphorsulfonic acid, phosphorylation, sulfonates, complexes.

Aldehydes of the azole series, available recently [1] are highly reactive intermediates for the preparation of synthetic analogs of natural materials, and also potential ligands in the synthesis of metal complexes [2]. One real route for the further broadening of the synthetic potential of these aldehydes may be their reactions with secondary phosphine oxides. The latter react with formaldehyde [3], aliphatic [4] and aromatic aldehydes [4-7], chloral [5, 6], cyclohexane and cyclohexene aldehydes [6] in the presence of bases (EtONa–ethanol [3, 4], KOH–DMSO [3], NaOH–dioxane [6] systems) and also in the absence of catalysts [5-7].

The object of the present study was to synthesize new functionally substituted chiral azoles containing hydroxyl and phosphoryl groups, from 1-organyl-2-formylimidazoles and -benzimidazoles and to study the properties of these reactive compounds as potential materials for the solution of fundamental questions of coordination chemistry.

It was found that 1-organyl-2-formylimidazoles and -benzimidazoles readily react with diorganylphosphine oxides under mild conditions (room temperature, dioxane, 1 h) to give, in practically quantitative yield, 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles **1a-j**, the structures of which were studied by ^{1}H NMR spectroscopy.

* Presented to Academician of the Russian Academy of Sciences M. G. Voronkov on his 80th birthday.

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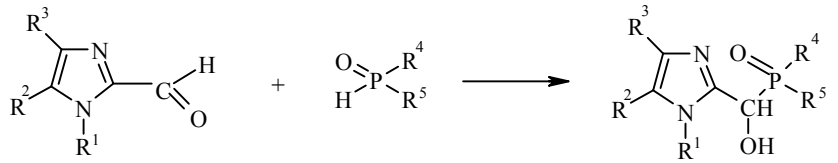
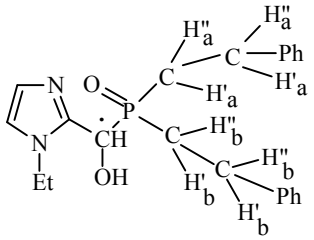


1a–j

1 a R^1 = Me, R^2 = R^3 = H, R^4 = R^5 = Ph; **b** R^1 = Et, R^2 = R^3 = H, R^4 = R^5 = Ph; **c** R^1 = Vin, R^2 = R^3 = H, R^4 = R^5 = Ph; **d** R^1 = Et, R^2 = R^3 = H, R^4 = R^5 = $PhCH_2CH_2$; **e** R^1 = Me, R^2 = R^3 = H, R^4 = Et, R^5 = Ph; **f** R^1 = Et, R^2 = R^3 = H, R^4 = Et, R^5 = Ph; **g** R^1 = Vin, R^2 = R^3 = H, R^4 = Et, R^5 = Ph; **h** R^1 = Et, R^2+R^3 = $(CH)_4$, R^4 = R^5 = Ph; **i** R^1 = Vin, R^2+R^3 = $(CH)_4$, R^4 = R^5 = Ph; **j** R^1 = Et, R^2+R^3 = $(CH)_4$, R^4 = Et, R^5 = Ph

All the compounds synthesized contain an asymmetric carbon atom and some (**1e-g, j**) also have an asymmetric phosphorus atom. The presence of a chiral carbon atom and a prochiral phosphorus atom in the phosphine oxide **1d** led to non-equivalence of all the methylene protons of two phenylethyl units [8] which appear in the ^{1}H NMR spectrum in the 2.03-2.98 ppm region as five complex multiplets with intensity ratio 1:2:2:1:2.

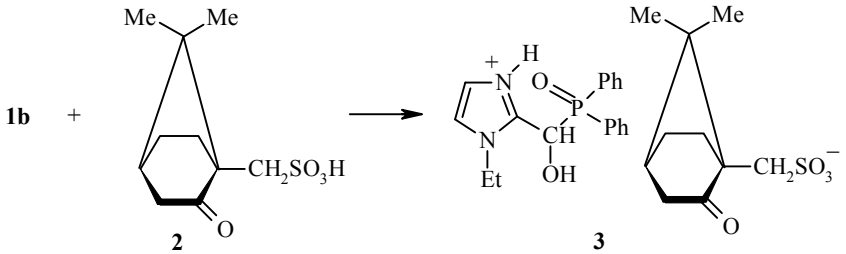


1d

Use of the 2M COSY method, ^{31}P decoupling, and analysis of the 1M 2M cross section (^{1}H, ^{13}C) of the HSQC spectrum [9] permitted the identification of each of the signals of the mentioned methylene protons in phosphine oxide **1d** (δ, ppm): O=PCH_a' 2.03; O=PCHa" 2.21; $PhCH_a$' 2.40; $PhCH_a$" 2.75; O=PCH_b' 2.21; O=PCH_b" 2.40, $PhCH_b$' 2.98; $PhCH_b$" 2.98.

Phosphine oxides **1e-g,j**, which have two chiral centers, are formed as two diastereomers. Most of the signals are splitted in both the ^{1}H and ^{31}P NMR spectra of these compounds. The differences in the integrated intensities of the signals of the two diastereomers of molecules **1e-g,j** indicate a considerable preponderance of one of them, i.e., the reaction of the aldehydes studied with unsymmetrical secondary phosphine oxides has a diastereodirecting character. In these diastereomers the difference in the chemical shifts of the protons of the O=PCH_2 unit is 0.15-0.25 ppm, while the signal of the methyne proton (OCHP=O) of the predominant diastereomer lies to weaker field. In the ^{31}P NMR spectrum the signal of this diastereomer is also to weaker field.

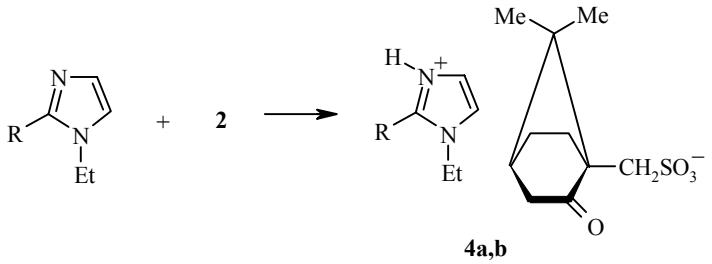
Compounds **1a-d,h,i** can serve as predecessors for optically active ligands. The reaction of 2-(diphenylphosphorylhydroxymethyl)-1-ethylimidazole (**1b**) with optically active (+)-camphorsulfonic acid (**2**), which occurs at room temperature to give a practically quantitative yield of the corresponding sulfonate **3** (as a pair of diastereomers), is the first step in realistic route to the separation of the racemate into enantiomers [10].



2 **3**

Only one signal is present in the ^{31}P NMR spectrum of the diastereomeric mixture of compound **3** and the ^{1}H NMR spectrum does not show doubling of many of the characteristic signals (e.g., the OCHP=O proton and the protons of the CH_2SO_3 group). However doubling of the proton signals of the imidazole ring in the ^{1}H NMR spectrum of compound **3** indicates the presence of two isomers, while the presence of two independent (spin independent) pairs of these protons was demonstrated by the ^{1}H–^{1}H NMR COSY method.

Since phosphine oxides are also capable of forming salts with acids [11, 12], while the values of the relative basicities (shift of the phenol bands on forming the associates) for tertiary phosphine oxides [13] and 1-organylimidazoles [14] are similar ($\Delta\nu_{OH}$ in the 430-530 cm^{-1} region), we synthesized the model compounds **4a,b** to confirm the structure of sulfonate **3**.



4a,b

4a R = H, **b** R = $HOCH_2$

Comparative analysis of the IR spectra of sulfonates **3** and **4a,b** shows that the center of protonation in the reaction of compound **1b** with the acid **2** is the "pyridine" nitrogen atom . Thus the expected intense band at ~3000 cm^{-1} with a complex structure, characteristic of the ν_{NH}+ vibrations, is present in the spectra of the salts **4a,b** and sulfonate **3**. The spectra of the salts **4a,b** contain the band corresponding to stretching vibrations of the imidazole ring at 1545 and 1527 cm^{-1}, shifted (by 35 and 23 cm^{-1} respectively) to higher frequencies in comparison with the analogous vibrations in 1-ethyl- and 1-ethyl-2-hydroxymethylimidazole starting materials. The band of stretching vibrations of the imidazole ring in sulfonate **3** is found at 1520 cm^{-1}, whereas it appears at 1509 cm^{-1} in the initial heterocycle **1b**, i.e., in this case protonation of the imidazole ring has led to an increase in the frequency of the stretching vibrations of the ring.

In the spectrum of the initial solid imidazole **1b** a broad band at 2600 cm^{-1}corresponds to the stretching vibrations of the OH group, which is involved in intermolecular OH···N bonds. The phosphoryl group remains free and has $\nu_{P=O}$ at 1195 cm^{-1}, which is characteristic of tertiary phosphine oxides containing aryl substituent [13]. In compound **3** this band appears at 1204 cm^{-1} which shows that it also is free.

Using imidazoles **1c,e** as examples, it was shown that compounds **1a-j** may be used in the synthesis of metal complexes. Imidazoles **1c,e** react readily with zinc and cadmium dichlorides in ethanol to give 1:1 complexes (from elemental analysis data) in high yield. The structures of these complexes are being investigated.

Thus reactions of aldehydes of the azole series with available diorganylphosphine oxides [15] is a valuable method for the synthesis of new functionally substituted derivatives of imidazole which have promise for the synthesis of amphiphilic ligands (including optically active ones), extractants for precious and rare metals, antipyrenes, and intermediates for the synthesis of biologically active materials.

EXPERIMENTAL

^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX (400 MHz) spectrometer in $CDCl_3$ solution with HMDS as internal standard and 85% H_3PO_4 as external standard. IR spectra were recorded with a Bruker IFS 25 apparatus as KBr disks or microlayers.

General Method for the Preparation of 2-(Diorganylphosporylhydroxymethyl)-1-organylimidazoles (1a-j). Mixture of 1-organyl-2-formylimidazole (3 mmol), and diorganylphosphine oxide (3 mmol) in dioxane (2 ml) was stirred at room temperature for 1 h, here the crystalline product was formed. The solvent was removed in vacuum, and the residue was washed with ether and dried.

2-(Diphenylphosphorylhydroxymethyl)-1-methylimidazole (1a). Yield 99%; mp 156-158°C (hexane). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 3.71 (3H, s, CH_3); 5.64 (1H, d, $^2J_{HP}$ = 5.2, CHP); 6.81 (1H, s); 6.83 (1H, s, H-4 and H-5); 7.43-7.82 (10H, m, Ph). ^{31}P NMR spectrum: 31.8. IR spectrum, ν, cm^{-1}: 2600 (OH); 3175, 3066 (CH of phenyl and imidazole ring); 2957, 2889 (C–H); 1589, 1520, 1486 (C=C, C=N of phenyl and imidazole rings); 1178 (P=O); 1055 ($\delta_{C–O–H}$). Found, %: C 65.48; H 5.53; N 8.79; P 9.65. $C_{17}H_{17}N_2O_2P$. Calculated, %: C 65.38; H 5.49; N 8.97; P 9.92.

2-(Diphenylphosphorylhydroxymethyl)-1-ethylimidazole (1b). Yield 99%; mp 138-140°C (hexane). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.31 (3H, t, ^3J = 7.3, CH_3); 4.11 (2H, m , CH_2); 5.70 (1H, d, $^2J_{HP}$ = 4.9, CHP); 6.70 (1H, s); 6.83 (1H, s) (2H, H-4, H-5); 7.32-7.85 (10H, m. Ph). ^{31}P NMR spectrum: 34.2. IR spectrum, ν, cm^{-1}: 2620 (OH); 3100, 3050, 3010 (CH of phenyl and imidazole ring); 2970, 2940 (C–H); 1590, 1490 (C=C, C=N of phenyl and imidazole rings); 1195 (P=O); 1050 ($\delta_{C–O–H}$). Found, %: C 66.07; H 6.01; N 8.56; P 9.25. $C_{18}H_{19}N_2O_2P$. Calculated, %: C 66.25; H 5.87; N 8.58; P 9.49.

2-(Diphenylphosphorylhydroxymethyl)-1-vinylimidazole (1c). Yield 96%; mp 146-148°C. ^{1}H NMR spectrum, δ, pp, *J* (Hz): 4.85 (1H, dd, ^2J = 1.3, ^3J = 8.8, $=CH_2$-*cis*); 5.16 (1H, dd, ^2J = 1.3, ^3J = 15.6, =CH-*trans*); 5.70 (1H, d, $^2J_{HP}$ = 6.0, CHP); 6.84 (1H, d, ^3J = 0.8, H-5); 7.17 (1H, s, H-4); 7.42 (1H, dd, =CH); 7.36-7.90 (10H, m, Ph). ^{31}P NMR spectrum: 30.2. IR spectrum, ν, cm^{-1}: 2620 (OH); 3100, 3052, 3010, 2970 ($=CH_2$, CH of phenyl and imidazole ring); 1645 (C=C, vinyl); 1589, 1528, 1486 (C=C, C=N of phenyl and imidazole ring); 1202 (P=O); 1035 ($\delta_{C–O–H}$). Found, %: C 66.49; H 5.32; N 5.89; P 9.42. $C_{18}H_{17}N_2O_2P$. Calculated, %: C 66.66; H 5.28; N 8.54; P 9.55.

2-[Bis(2-phenylethyl)phosphorylhydroxymethyl]-1-ethylpyrimidine (1d). Yield 98%, (oil). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.42 (1H, t, ^3J = 7.3, CH_3); 2.03 (1H, m), 2.21 (2H, m), 2.40 (2H, m), 2.75 (1H, m), 2.98 (2H, m) ($(CH_2CH_2Ph)_2$); 4.13 (2H, m, CH_2N); 5.08 (1H, d, $^2J_{HP}$ = 7.7, CHP); 6.94 (1H, d, $^3J_{54}$ = 1.4, H-5); 6.98 (1H, d, $^3J_{45}$ = 1.4, H-4); 7.07-7.28 (10 H, m, Ph). ^{31}P NMR spectrum: 54.7. IR spectrum, ν, cm^{-1}: 3100 (OH); 3080, 3065, 3020 (C–H of phenyl and imidazole ring); 2960, 2920, 2840 (C–H); 1600, 1580, 1498 (C=C, C=N, of phenyl and imidazole ring); 1157 (P=O); 1045 ($\delta_{C–O–H}$). Found, %: C 68.96; H 6.95; N 7.80; P 7.21. $C_{22}H_{27}N_2O_2P$. Calculated, %: C 69.09; H 7.12; N 8.10; P 7.32.

2-[Ethyl(phenyl)phosphorylhydroxymethyl]-1-methylimidazole (1e). Mixture of two diastereomers (ratio 2:1). Yield 99%; mp 157-159°C (hexane). *First diastereomer,* ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.00 (3H, dt, ^3J = 7.6, $^3J_{HP}$ = 17.0, $\underline{CH_3}CH_2P$); 2.28 (2H, m, CH_2P); 3.32 (1H, s, CH_3N); 5.42 (1H, d, $^2J_{HP}$ = 7.2, CHP); 6.94 (1H, d, $^3J_{54}$ = 1.4, H-5); 7.11 (1H, d, $^3J_{45}$ = 1.4, H-4); 7.48-7.51 (5H, m, Ph); ^{31}P NMR spectrum: 48.3. *Second diastereomer*, ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.01 (3H, dt, ^3J = 7.6, $^3J_{HP}$ = 17.2, $\underline{CH_3}CH_2P$); 2.15 (2H, m, CH_2P); 3.33 (1H, s, CH_3N); 5.33 (1H, d, $^3J_{HP}$ = 7.8, CHP); 6.88 (1H, d, $^3J_{54}$ = 1.3, H-5); 7.09 (1H, d, $^3J_{45}$ = 1.3, H-4); 7.48-7.51 (5H, m, Ph). ^{31}P NMR spectrum: 48.2. IR spectrum, ν, cm^{-1}: 2600 (OH); 3100, 3030 (C–H of phenyl and imidazole ring); 2970, 2930, 2870 (C–H); 1580, 1480 (C=C, C=N of phenyl and imidazole ring); 1435 ($\delta_{CH3,\ P–Ph}$, ν imidazole ring); 1275 ($\delta_{C–H}$); 1180 (P=O); 1160, 1105 ($\delta_{C–H}$); 1050 ($\delta_{C–O–H}$). 1070, 930, 780, 755, 735, 700, 550, 490 ($\delta_{C–H}$). Found, %: C 58.94; H 6.46; N 10.12; P 11.83. $C_{13}H_{17}N_2O_2P$. Calculated, %: C 59.09; H 6.48; N 10.62; P 11.72.

2-[Ethyl(phenyl)phosphorylhydroxymethyl]-1-ethylimidazole (1f). Mixture of two diastereomers (ratio 2.3:1). Yield 97%; mp 194-195°C (hexane). *First diastereomer:* ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.03 (3H, dt, ^3J = 7.7, $^3J_{HP}$ = 17.3, $\underline{CH_3}CH_2P$); 1.40 (3H, t, ^3J = 7.3, $\underline{CH_3}CH_2N$); 2.13 (2H, m, CH_2P); 4.12 (2H, m, CH_2N); 5.29 (1H, d, $^2J_{HP}$ = 5.8, CHP); 6.87 (1H, d, ^3J = 1.3, H-5); 6.93 (1H, d, H-4); 7.41-7.95 (5H, m, Ph); ^{31}P NMR spectrum: 47.9. *Second diastereomer:* ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.01 (3H, dt, ^3J = 7.7, $^3J_{HP}$ = 17.1, $\underline{CH_3}CH_2P$); 1.40 (3H, t, ^3J = 7.3, $\underline{CH_3}CH_2N$); 2.40 (2H, m, $\underline{CH_2}P$); 4.11 (2H, m, CH_2N); 5.25 (1H, d,

$^2J_{HP}$ = 6.5, CHP); 6.99 (1H, d, $^3J_{54}$ = 1.3, H-5); 7.08 (1H, d, $^3J_{45}$ = 1.3, H-4); 7.41-7.95 (5H, m, Ph); ^{31}P NMR spectrum: 47.7. IR spectrum, ν, cm^{-1}: 2630 (OH); 3120, 3095 (C–H of phenyl and imidazole ring); 2970, 2940, 2870 (C–H); 1580, 1490 (C=C, C=N of phenyl, imidazole ring); 1180 (P=O); 1045 (δ_{C-O-H}). Found, %: C 60.53; H 7.11; N 10.07; P 11.30. $C_{14}H_{19}N_2O_2P$. Calculated, %: C 60.42; H 6.88; N 10.07; P 11.13.

2-[Ethyl(phenyl)phosphorylhydroxymethyl]-1-vinylimidazole (1g). Mixture of two diastereomers (1.4:1). Yield 96%; mp 192-196°C (hexane). *First diastereomer:* ^{1}H NMR spectrum ($CDCl_3/CD_3OD$), δ, ppm, *J* (Hz): 1.03 (3H, dt, ^3J = 7.6, $^3J_{HP}$ = 17.2 , CH_3); 2.25 (2H, m, CH_2); 4.78 (1H, dd, ^2J = 1.7, ^3J = 8.8, =CH_2 *cis*); 5.28 (1H, dd, ^2J = 1.7, ^3J = 15.7, =CH_2 *trans*); 5.53 (1H d, $^2J_{HP}$ = 5.8, CHP); 7.02 (1H, d, ^3J = 1.4, H-5); 7.30 (1H, dd, =CH); 7.45-7.80 (6H m, H-4, Ph); ^{31}P NMR spectrum: 48.4. *Second diastereomer*: ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 0.99 (3H, dt, ^3J = 7.6, $^3J_{HP}$ = 17.2, CH_3); 2.10 (2H, m, CH_2); 4.85 (1H, dd, ^2J = 1.6, ^3J = 8.8, =CH_2 *cis*); 5.32 (1H, dd, ^2J = 1.6, ^3J = 15.7, =CH_2 *trans*); 5.42 (1H, d, $^2J_{HP}$ = 7.4, CHP); 6.96 (1H, d, ^3J = 1.2, H-5); 7.39 (1H, dd, =CH); 7.45-7.80 (6H, m, 4-H, Ph); ^{31}P NMR spectrum: 48.1. IR spectrum, ν, cm^{-1}: 2650 (OH); 3050, 3100 (CH_2, C–H of phenyl and imidazole ring); 2965, 2870 (C–H); 1645 (C=C vinyl); 1590, 1490 (C=C, C=N of phenyl and imidazole ring); 1185 (P=O); 1045 (δ_{C-O-H}). Found, %: C 60.76; H 6,13; N 10.30; P 11.74. $C_{14}H_{17}N_2O_2P$. Calculated, %: C 60.86; H 6.20; N 10.14; P 11.21.

2-(Diphenylphosphorylhydroxymethyl)-1-ethylbenzimidazole (1h). Yield 98%; mp 142-143°C (hexane). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.41 (3H, t, ^3J = 7.2, CH_3); 4.44 (2H, m CH_2); 5.85 (1H, d, $^3J_{HP}$ = 6.6, CHP); 7.19-7.49 (10H, m, Ph); 7.68 (2H, m, H_{arom}); 7.90 (2H, m, H_{arom}). ^{31}P NMR spectrum: 31.1. IR spectrum, ν, cm^{-1}: 3000 (OH); 3057 (C–H of phenyl, benzimidazole ring); 2936, 2861 (C–H); 1613, 1591, 1487 (C=C, C=N of phenyl, benzimidazole ring); 1202 (P=O); 1067 (δ_{C-O-H}). Found, %: C 70.56; H 5.73; N 7.44; P 8.22. $C_{22}H_{21}N_2O_2P$. Calculated, %: C 70.20; H 5.62; N 7.44; P 8.23.

2-(Diphenylphosphorylhydroxymethyl)-1-vinylbenzimidazole (1i). Yield 97%; mp 178-180°C (hexane). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 5.25 (1H, dd, ^2J = 1.0, ^3J = 8.8, =CH_2 *cis*); 5.52 (1H, dd, ^2J = 1.3, ^3J = 15.6, =CH_2 *trans*); 5.84 (1H, d, $^2J_{HP}$ = 7.2, CHP); 7.25 (1H, dd, =CH); 7.36-7.63 (10 H, m, Ph); 7.90 (2H, m, H_{arom}). ^{31}P NMR spectrum: 31.3. IR spectrum, ν, cm^{-1}: 3180 (OH); 3086, 3053 (CH_2, CH, phenyl, benzimidazole ring); 1643 (C=C vinyl); 1607, 1590, 1518, 1457 (C=C, C=N phenyl, benzimidazole ring); 1190 (P=O); 1051 (δ_{C-O-H}). Found, %: C 70.49; H 4.99; N 7.32; P 8.23. $C_{22}H_{19}N_2O_2P$. Calculated, %: C 70.58; H 5.12; N 7.48; P 8.27.

2-[Ethyl(phenyl)phosphorylhydroxymethyl-1-ethylbenzimidazole (1j). Mixture of two diastereomers (2:1). Yield 96%; mp 129-132°C (hexane). *First diastereomer*: ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.09 (3H, dt, ^3J = 7.7, $^3J_{HP}$ = 17.4, $\underline{CH_3}CH_2P$); 1.35 (3H, t, ^3J = 7.2, $\underline{CH_3}CH_2N$); 2.35 (2H, m CH_2P); 4.35 (2H, m, CH_2N); 5.46 (1H, d, $^2J_{HP}$ = 7.0, CHP); 7.15-7.28 (9H, m, Ph, H_{arom}); ^{31}P NMR spectrum: 47.1. *Second diastereomer:* ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 0.98 (3H, dt, ^3J = 7.9, $^3J_{HP}$ = 17.2, $\underline{CH_3}CH_2P$); 1.33 (3H, t, ^3J = 7.3, $\underline{CH_3}CH_2N$); 2.16 (2H, m CH_2P); 4.28 (2H, m, CH_2N); 5.41 (1H, d, $^2J_{HP}$ = 7.9, CHP); 7.15-7.28 (9H, m, Ph, H_{arom}). ^{31}P NMR spectrum: 45.8. IR spectrum, ν, cm^{-1}: 2700 (OH); 3070, 3010 (CH_2, CH, phenyl, benzimidazole ring); 2970, 2930 (C–H); 1605, 1480 (C=C, C=N phenyl, benzimidazole ring); 1190 (P=O); 1055 (δ_{C-O-H}). Found, %: C 65.62; H 6.53; N 8.56; P 9.38. $C_{18}H_{21}N_2O_2P$. Calculated, %: C 65.84; H 6.45; N 8.53; P 9.43.

Synthesis of Sulfonate 3. Mixture of imidazole **1b** (0.29 g, 0.9 mmol) and camphorsulfonic acid **2** (0.21 g, 0.9 mmol) in THF (6 ml) was stirred at room temperature for 0.5 h. The precipitate was filtered off, washed with ether, and dried to give sulfonate **3** (0.49 g, 99%) as a mixture of diastereomers (ratio 1:1); mp 184-186°C (hexane), $[\alpha]_D$ = 15.058° (*c* = 10, CH_3OH). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 0.79 (3H, s), 1.05 (3H, s) (2 CH_3); 1.37 (t, ^3J = 7.3), 1.37 (t, ^3J = 7.3) (3H, $\underline{CH_3}CH_2$ of 2 diastereomers); 1.35 (1H, m), 1.61 (1H, m), 1.84 (1H, d, ^3J = 18.2), 1.97 (1H, m), 2.02 (1H, m), 2.29 (1H, m), 2.58 (1H, m) (cyclohexane ring); 2.69 (1H, d, ^2J = 14.7), 3.14 (1H, d) (CH_2S); 4.42 (2H, m, CH_2N); 6.52 (1H, d, $^2J_{HP}$ = 9.0, CHP); 7.01 (d, $^3J_{54}$ = 1.9), 7.02 (d, $^3J_{54}$ = 1.9) (1H, H-5 of two diastereomers); 7.28 (d, $^3J_{45}$ = 1.9), 7.31 (d, 1H, $^3J_{45}$ = 1.9) (H-4 of two diastereomers); 7.44-7.94 (10H, m, Ph). IR spectrum, ν, cm^{-1}: ~3000 (NH^+); 1737 (C=O); 1590, 1520, 1470 (C=C, C=N of imidazole and phenyl rings); 1163, 1144 ($\nu_{as\ S=O}$); 1040 ($\nu_{s\ S=O}$); 1204 (P=O). Found, %: C 59.35; H 6.53; N 4.81; P 5.57; S 5.53. $C_{28}H_{35}N_2O_6PS$. Calculated, %: C 60.20; H 6.32; N 5.01; P 5.54; S 5.74.

Synthesis of Sulfonate 4a. Mixture of 1-ethylimidazole (0.14 g, 1.5 mmol) and camphorsulfonic acid **2** (0.34 g, 1.5 mmol) in THF (6 ml) was stirred at room temperature for 0.5 h. The solvent was evaporated in vacuum, the residue was washed with ether and dried to give sulfonate **4a** (0.46 g, 95% yield); mp 50-56°C (pentane). IR spectrum, ν, cm^{-1}: ~3000 (NH^+); 1741, 1731 (C=O); 1576, 1545, 1471 (C=C, C=N of imidazole and phenyl rings); 1189, 1172 ($\nu_{as\ S=O}$); 1042 ($\nu_{s\ S=O}$). Found, %: C 54.79; H 7.34; N 8.56; S 9.68. $C_{25}H_{24}N_2O_4S$. Calculated, %: C 54.86; H 7.37; N 8.53; S 9.76.

Synthesis of Sulfonate 4b. Mixture of 1-ethyl-2-hydroxymethylimidazole (0.19 g, 1.5 mmol) and camphorsulfonic acid **2** (0.34 g, 1.5 mmol) in THF (6 ml) was stirred at room temperature for 0.5 h. The solvent was evaporated in vacuum, the residue washed with ether, and dried to give sulfonate **4b** (0.52 g, 98%); mp 94-98°C (pentane). IR spectrum, ν, cm^{-1}: 3290 (OH); ~3000 (NH^+); 1742, 1732 (C=O); 1602, 1527, 1456 (C=C, C=N of imidazole and phenyl rings); 1189, 1172 ($\nu_{as\ S=O}$); 1042 ($\nu_{s\ S=O}$). Found, %: C 53.39; H 7.28; N 7.81, S 8.96. $C_{16}H_{26}N_2O_5S$. Calculated, %: C 53.61; H 7.31; N 7.82; S 8.95.

Synthesis of Zinc Chloride Complex with Ligand 1c. Equimolar amounts of imidazole **1c** and $ZnCl_2$ in ethanol were stirred for 15 h at 60°C. The product was precipitated with ether, filtered, and dried. Yield 74%; mp 160°C (dec). IR spectrum, ν, cm^{-1}; 1483, 1442 (C=C, C=N of imidazole and phenyl ring); 1140 (P=O). Found, %: C 47.15; H 3.97, Cl 15.22; N 6.35; P 6.73. $C_{18}H_{17}Cl_2N_2O_2PZn$. Calculated, %: C 46.94; H 3.72; Cl 15.39; N 6.08; P 6.72.

Synthesis of Cadmium Complex with Ligand 1e was carried out analogously with imidazole **1e** and $CdCl_2$. Yield 59%; mp 160°C (dec). IR spectrum, ν, cm^{-1}: 1490, 1440 (C=C, C=N of imidazole and phenyl ring); 1150 (P=O). Found, %: C 35.03; H 4.17, Cl 15.76; N 6.57; P 6.85. $C_{13}H_{17}CdCl_2N_2O_2P$. Calculated, %: C 34.89; H 3.83; Cl 15.84; N 6.26; P 6.92.

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