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Acid-Base and Complexing Properties of Some δ-Hydroxyalkenylphosphine Oxides

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Abstract—Four new compounds, asymmetrical phosphine oxides containing 2-hydroxyphenylethenyl fragment in *cis*-orientation with respect to the phosphine oxide: dibutyl-, diphenyl-, dibenzyl-, and dinaphthyl-2-(2-hydroxy-5-chlorophenyl)-2-phenyl-ethenylphospnine oxides, have been studied in aqueous ethanol (80 vol % of EtOH) by means of potentiometry and spectrophotometry at 25±0.1°C, and their acid-base and complexing properties estimated.

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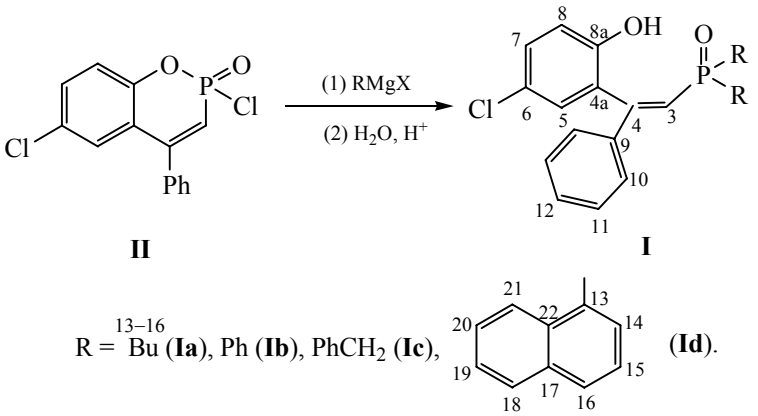
The interest to organophosphorus compounds originates from their structural diversity and unique combination of properties important for applied as well as fundamental studies. Among derivatives of four-coordinated phosphorus, phosphine oxides are of particular importance. They possess perfect extraction (complexing) properties towards rare, rare-earth, and other nonferrous metal ions; and they are precursors of phosphines that are applied as ligands in metal complex catalysis.

Commonly known organometalic chemistry methods for preparation of phosphorus-containing complex ligands are not selective and often require the use of hard-to-get chemicals [1, 2]. Furthermore, these methods are not applicable to substrates containing other active functional groups. It is noteworthy that almost all these methods start with phosphinic halides or alkali metal dialkylphosphides as precursors; as these compounds are very reactive, inert atmosphere is required. Recently, we have developed a new approach to the preparation of substituted alkenylphosphine oxides [3] based on reaction of readily available cyclic phosphorus esters with organomagnesium compounds.

In this work, four new compounds were studied. For preparation of diphenyl- (**Ib**) and dibenzyl-2-(2-hydroxy-5-chlorophenyl)-2-phenylethenylphosphine oxide (**Ic**), the method described and patented in [3] was used. The corresponding dibutyl **Ia** and dinaphthyl **Id** derivatives were prepared by the same approach for the first time. All four compounds are hydroxy-phosphine oxides. Their protolytic properties and behavior of some of them in the presence of iron(III), copper(II), and nickel(II) were studied.

Phosphine oxides **Ia–Id** were synthesized starting from 2,6-dichloro-4-phenylbenzo[*e*][1,2]oxaphos-phorine 2-oxide (**II**), phosphorus-containing hetero-cycle containing a P–C bond, which was in turn prepared via reaction of 2,2,2-trichloro-2-benzo-1,3,2-dioxaphosphole with phenylacethylene [4]. Reactions of oxaphosphorine oxide (**II**) with twofold excess of the corresponding organomagnesium compounds in ether under mild conditions lead selectively and with high yield (>90%) to target compounds (**I**). Structures of the compounds thus obtained were proved by mass spectrometry, NMR spectroscopy (^{31}P, ^{1}H, ^{13}C), and IR spectroscopy.

Phosphoryl and hydroxy groups in phosphine oxides are in *cis*-orientation, which is determined by the structure of oxaphosphorine cycle of the precursor (oxaphosphorine double bond is not affected in the reaction with Grignard reagents).



Aqueous ethanol (80 vol % EtOH) turned out to be a suitable solvent for studies of protolytic and complexing properties of compounds **Ia, Ib**. In cases of **Ic, Id**, due to their poor solubility ($<2\times10^{-3}$ M), it was not possible to achieve the concentration desired for potentiometric measurements. Compound **Ia**, as well as **Ib**, was not titrated by acid. The shape of the titration curves with no leap in alkaline pH range leads to the assumption that the studed compounds were neutral (neither basic nor acidic).

The complexing ability towards iron(III) in aqueous ethanol (80 vol % EtOH) was most clearly revealed in compounds **Ia, Ib**, especially, in the case of **Ia**. Upon addition of iron(III) to the **Ia** solution, it turned intensively violet (pH ≈ 2). In the absorption spectrum

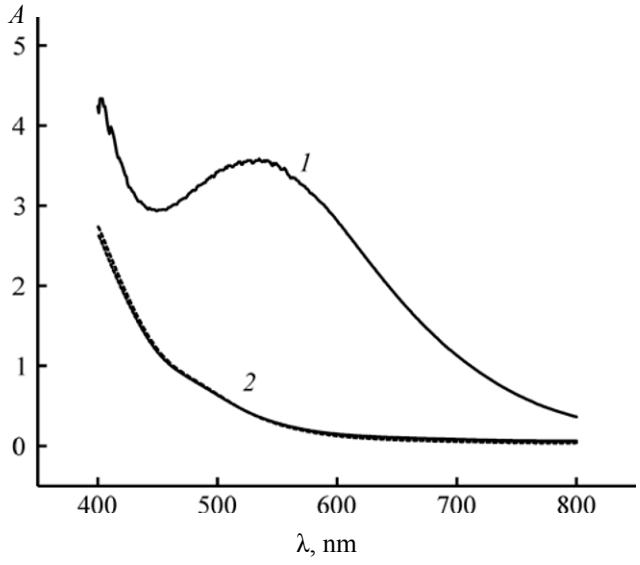


Fig. 1. Absorption spectra of aqueous ethanol solutions of (*1*) **Ia** and (*2*) **Ic** in the presence of iron(III). $c_{Fe(III)}$, M: (*1*) 5.94×10^{-3}, (*2*) 4.24×10^{-3}; $c_{\mathbf{Ia,Ic}}$, M: 1.2×10^{-2} (**Ia**), $<2\times10^{-3}$ (**Ic**); pH 2.0; ε_{525}, l mol^{-1} cm^{-1}: (*1*) 592, (*2*) 110.

(Fig. 1, curve *1*) there was a well defined maximum at the wavelength λ = 525 nm, ε_{525} = 590 l mol^{-1} cm^{-1}. This fact clearly proved the interaction of **Ia** with iron(III).

The solution of **Ib** in the presence of iron(III) under the same conditions (pH = 2.18) was also violet. However, the absorption maximum was shifted to the higher wavelength (λ_{max} = 565 nm), and the absorption intensity was somewhat smaller, ε_{565} = 420 l mol^{-1} cm^{-1} (Fig. 2, curve *3*).

Solutions of compounds **Ic, Id** in the presence of iron(III) were yellow, as well as iron(III) solution itself. Visible absorption spectra of all these solutions were identical. As an example, there was no absorption maximum at 525 nm in the spectrum of **Ic** solution in the presence of iron(III) (Fig. 1, curve *2*). The molar absorption coefficient of the **Ic**/iron(III) mixture ε_{525} = 110 l mol^{-1} cm^{-1} was higher than that of the solvated iron(III), 24 l mol^{-1} cm^{-1} (Fig. 2, curves *1*, *2*).

The quantitative analysis of the spectroscopic data was performed for the iron(III)–compound **Ia** system. The optical density at wavelength λ = 525 nm was measured for two series of samples prepared at constant concentration of the complexing agent (8.48×10^{-4} or 1.696×10^{-3} M) and variable concentration of ligand (**Ia**), its highest concentration being limited by its solubility. The desired acidity of the medium (pH ≈ 2.0) was adjusted by nitric acid. Experimental data are collected in Fig. 3.

Compounds **Ia–Id** studied in this work contained the *p*-chlorophenyl substituent. It was assumed that the HL compound **Ia** was coordinated in the phenolate form L, similar Fe(III) interaction with *p*-chlorophenol [10, 11].

The combined analysis of the data for both series revealed that equilibria defined by Eq. (1) were

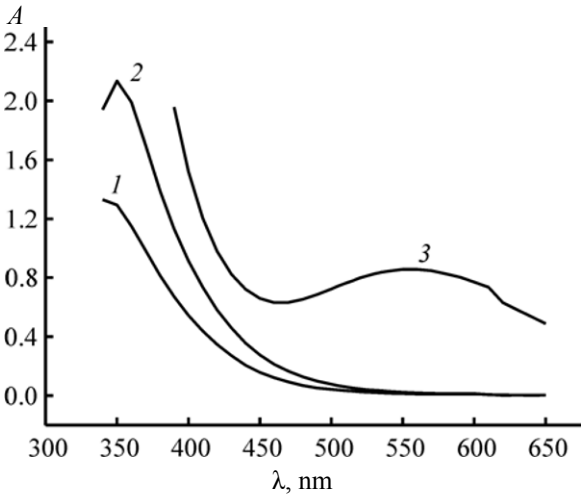


Fig. 2. Absorption spectra of aqueous ethanol solutions of (*1, 2*) iron(III) and of **Ib** in the presence of (*3*) iron(III). $c_{Fe(III)}$, M: (*1*) 8.48×10^{-4}, (*2*) 1.696×10^{-3}, (*3*) 2.0352×10^{-3}; $c_{\mathbf{Ib}}$ 3.99×10^{-3} M; pH: (*1*) 2.16, (*2*) 2.14, (*3*) 2.18; ε_{525}, l mol^{-1} cm^{-1}: (*1*) 24.8, (*2*) 23.6, (*3*) ε_{565} 420.

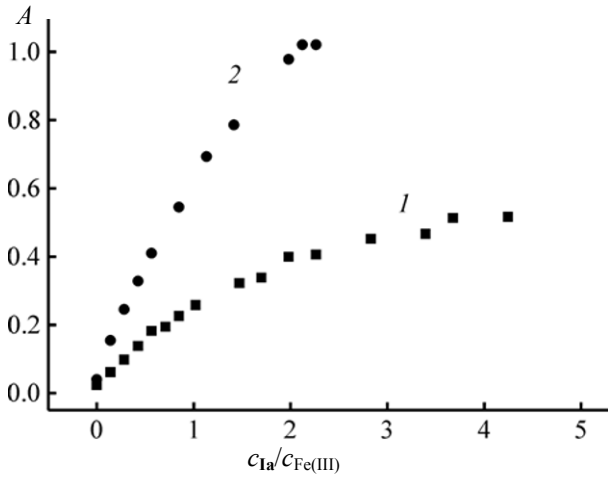


Fig. 3. Dependence of optical density A on $c_{\mathbf{Ia}}/c_{Fe(III)}$. c_{EtOH} = 80 vol % ; $c_{Fe(III)}$, M: (*1*) 8.48×10^{-4}, (*2*) 1.696×10^{-3}; pH 2.08–2.14; $A_{1\,lim}$ 0.516, $A_{2\,lim}$ 1.021; λ = 525 nm.

established in aqueous ethanol solution of **Ia** in the presence of iron(III).

$$Fe^{3+} + n\mathrm{HL} \rightleftarrows [FeL_n]^{3-n} + n\mathrm{H}^+. \quad (1)$$

Here n = 1, 2. In solution, complexes of 1:1 and 1:2 compositions, $[FeL]^{2+}$ and $[FeL_2]^+$, coexisted. The highest fractions for both of them were relatively small (Fig. 4). For the first complex, α_{max} = 0.55 in both series, for the second complex α_{max} = 0.34 at highest possible ligand concentration (3.6×10^{-3} M under conditions of the experiment). Quantitative characteristics of the complex formation process are collected in the table that contains equilibrium constants, highest complex fractions (α_{max}), and the corresponding molar absorption coefficients (ε) for both complexes.

Additionally, potentiometric titration of **Ia** and **Ib** solutions containing iron(III) was performed, at the complexing agent to ligand ratio of 2:1 (Fig. 5). The solutions, initially violet, in the course of titration changed to brown, and then became turbid, likely due to the formation of iron(III) basic salts or hydroxide. At the end of titration, the samples contained a plenty of iron(III) hydroxide precipitate. Thus, violet complexes existed in acidic medium (pH ≈ 2.0) but were readily decomposed by alkali {solubility product is 3.8×10^{-38} for $[Fe(OH)_3]$ in aqueous solution [12]}.

It is well known that for a colored complex with iron(III) to exist, it is essential that there is at least one phenol hydroxy group in the organic compound. According to [13], the sensitivity of the reaction of iron(III) with phenol increases (accompanied by the decrease in the selectivity) upon introduction in the *o*-position of donor groups, like C(O)R, OH, and some others. The presence of a carbonyl group in the *o*-position with respect to the hydroxy group stipulates the violet color of complexes formed in the presence of iron(III), for instance, of salicylate ones [14]. The complex formation is favored by reduced hydrolysis of

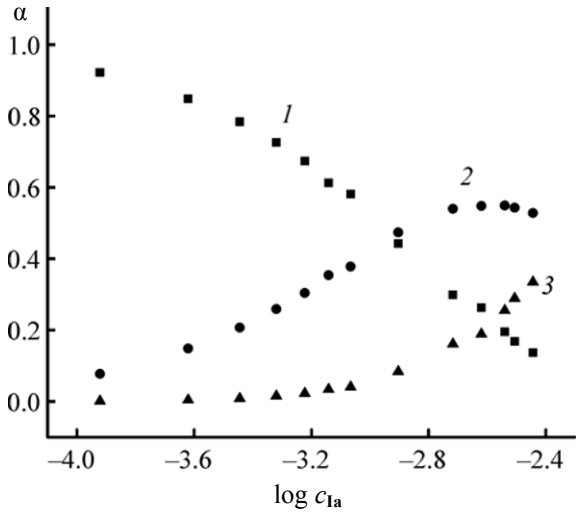


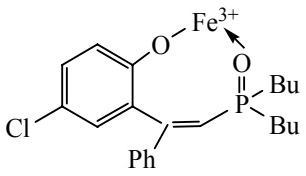
Fig. 4. Fractional distribution of complex forms in the system iron(III)–**Ia**. $c_{Fe(III)}$ 8.48×10^{-4} M; (*1*) Fe(III), (*2*) $[FeL]^{2+}$, (*3*) $[FeL_2]^+$.

Equilibrium constants in complexing reactions between iron(III) and **Ia** in aqueous ethanol solution (80 vol % EtOH). R = 3.0%

Equilibrium	log K	ε, l mol^{-1} cm^{-1} (λ 525 nm)	α_{max}
1, n = 1	1.07±0.03	643	0.55
1, n = 2	1.36±0.12	872	0.34

the cation in strongly acidic medium or in nonaqueous solvent [15].

The appearance of violet coloring (ε_{525} = 590 l mol^{-1} cm^{-1}) upon addition of iron(III) to aqueous ethanol (80 vol % EtOH) solution of dibutyl-2-(2-hydroxy-5-chlorophenyl)-2-phenylethenylphosphine oxide (**Ia**) presumed that a complex with bidentate coordination and eight-membered ring was formed. Phenolate and phosphoryl groups participated in the coordination. For the 1:1 complex, the following scheme corresponds to the assumed coordination type.



Vacant sites in the complexing agent coordination sphere are occupied by the solvent molecules.

If monodentate ligand coordination was realized (like with *p*-chlorophenol and other common phenols), the intensity of the formed complex absorption could not be that high. Indeed, for the complex of iron(III) and *p*-chlorophenol violet coloring is observed (λ_{max} = 562 nm, ε_{max} = 27.2 l mol^{-1} cm^{-1}). The coloring is stable within one hour, but disappears at high ethanol concentration [10].

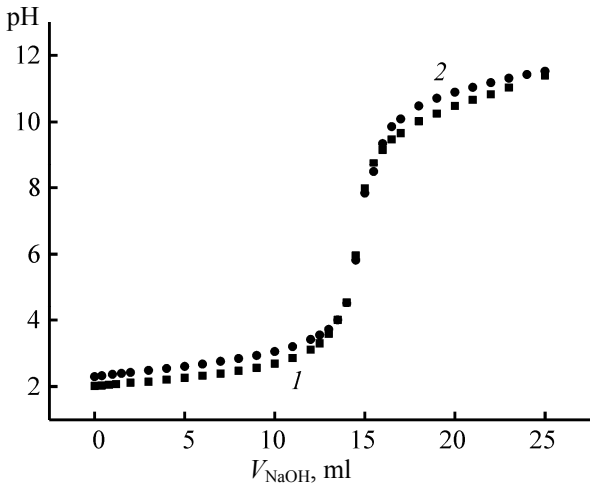
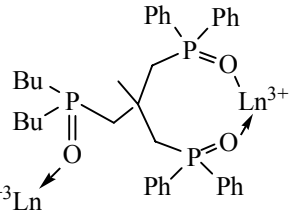


Fig. 5. Potentiometric titration curves of aqueous ethanol solutions of (*1*) **Ia** and (*2*) **Ib** in the presence of iron(III). c_{EtOH} = 80 vol %, $c_{\mathbf{Ia}}$ = 1.2×10^{-2} M, $c_{\mathbf{Ib}}$ = 3.99×10^{-3} M; $c_{Fe(III)}$, M: (*1*) 5.94×10^{-3}, (*2*) 2.04×10^{-3}; c_{NaOH}, M: (*1*) 2.385×10^{-2}, (*2*) 7.95×10^{-3}.

It is known that isolated chelate cycles with more than six atoms in the cycle are unstable. However, when accompanied with simultaneous formation of 5- or 6-membered chelate cycles, the chelate cycles of any size may be stabilized [13]. Such complementary chelate cycles are absent in the structure of the studied complex. The large cycle may have been stabilized by the rigidity of the aromatic structural fragments. Note that the formation of an eight-membered ring in the polymeric lantanide(III) complexes [Ln(NO$_3$)$_3$Z]ROH with phosphine oxide Z {CH$_3$C[CH$_2$P(O)Ph$_2$]$_3$}, ROH being methanol or ethanol, was described in [16].



As far as copper(II) is concerned, a considerable acidification of copper(II) solution in the presence of **Ia** (pH 4.41 and 3.61, correspondingly), as well as the changes in the absorption spectra as compared with that of solvated copper, show the interaction of the studied system components, accompanied with protons release. In the solvated copper(II) spectrum, no new bands appeared upon addition of **Ia**, whereas the intensity of the present band only slightly increased. In this case, the formation of chelate complex is also possible, like in the case of iron(III).

Spectra of copper-containing solutions of compounds **Ia** (curve *1*) and **Ib** (curve *4*) are shown in Fig. 6 [ligand:copper(II) = 2:1].

Higher concentration of **Ib** could not be achieved due to its poor solubility. Visible light absorption of both systems was similar (ε_{800} = 23.2 l mol^{-1} cm^{-1} and 24.2 l mol^{-1} cm^{-1}, correspondingly). However, the limited solubility of **Ib** impedes the studies of its complexing with copper(II) in solution, as the desired ligand concentration could not be attained.

Molar absorption of both compounds solutions in the presence of nickel(II) were even lower than in case of copper(II). Their values were close to those of nickel(II) solvates. Note that absorption bands of

nickel(II) aqua complex are of low intensity: λ_1 = 395 nm, ε = 5 l mol^{-1} cm^{-1}; λ_2 = 658 nm, ε = 2 l mol^{-1} cm^{-1}; λ_3 = 724 nm, ε = 2 l mol^{-1} cm^{-1} [17].

EXPERIMENTAL

Electron absorption spectra were recorded using spectrophotometers Lambda 35 101N6112101 (Perkin–Elmer UV WinLab) and SPEKOL 11, in quartz cell (optical path length = 1 cm), with pure solvent as a reference. ^{1}H, ^{31}P, and ^{31}P–{^{1}H} NMR spectra were collected using Bruker MSL-400 (^{1}H 400.0 MHz; ^{31}P 162.0 MHz) and Avance 600 (^{1}H 600.0 MHz) instruments in DMSO-d_6 (30°C) and $CDCl_3$ (25°C), reference Me_4Si or H_3PO_4. Residual solvent proton signals were also used as internal reference (^{1}H). IR spectra of suspensions in mineral oil were recorded using UR-20 and Bruker Vector-22 instruments. Electron impact mass spectra were detected using TRACE MS Finnigan MAT or MKh-1310 with high-precision *m/z* determination, coupled with the CM-4 computer. The ionizing electrons energy was 70 eV, electrons source temperature was up to 250°C. The system of direct substance injection into the ion source was used. Mass spectra were analyzed with Xcalibur program.

Electron absorption spectra were analyzed with CPESSP program [7]. Reliability of the selected models was characterized with F and R factors [8, 9].

$$F = \Sigma_{k+1}^{N} [(Q_{Kexp} - Q_{Ktheor})W_K]^2,$$

$$F = F_{min}/(N - 2n).$$

In these equations, Q_{Kexp} is a property of the solution measured in the k experiment, Q_{Ktheor} is its theoretical analog, N is the number of experimental points, W_K is a normalizing factor, or statistical weight, n is the number of varied parameters. For spectrophotometric experiment, $F = F_{min}/(N - 2n)$ (varied parameters are equilibrium constants and molar absorptivities). Average deviation of theoretical data from experimental ones, R [9] was less than 0.05 (5%).

Protolytic and complexing properties of the compounds under study in aqueous ethanol (80 vol % EtOH) were estimated from potentiometric and spectrophotometric data. Measurements were performed in a temperature-controlled chamber at 298 K. The pH of solutions was measured with a MV88 PRAZISIONS-LABOR-pH-MESSGERAT instrument. Glass electrode (ELS-63-07) was used as a working electrode, and saturated silver chloride electrode was used as a reference one. Glass electrode was calibrated towards HCl solutions of known concentration [5], after incubation for at least one day in the corresponding solvent. Solutions of **Ia–Id** were prepared from precisely weighed specimens. Anhydrous ethanol was prepared according to [6]. Solutions of carbonate-free sodium hydroxide, hydrochloric acid, nitrates of nickel(II), copper(II), and iron(III) were prepared from the corresponding chemicals of the chemically pure grade. The solutions concentration was determined by volumetric analysis. The same concentration of organic solvent was maintained in titrants as well as in titrates. Ionic strength of the solutions was solely due to their components, as base electrolyte addition could reduce studied compounds solubility, or influence association in solution. The titration was performed under argon stream. Titrated solutions were stirred using a magnetic stirrer. In the solutions prepared for titration, reproducible values of glass electrode potential were established within 15–20 min; in the course of the titration, this period was reduced to 3–5 min.

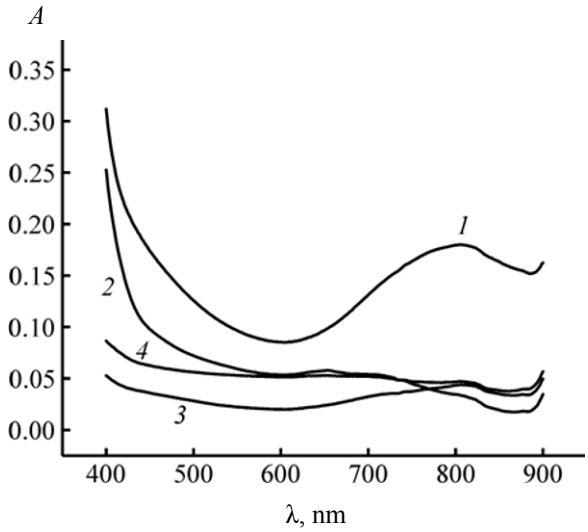


Fig. 6. Absorption spectra of aqueous ethanol solutions of **Ia**, **Ib** in the presence of (*1*, *4*) copper(II) and (*2*, *3*) nickel(II). c_{Ia} 1.6×10^{-2}, c_{Ib} 4×10^{-3}; $c_{Cu(II)}$, M: (*1*) 7.75×10^{-3}, (*4*) 1.94×10^{-3}; $c_{Ni(II)}$, M: (*2*) 8.78×10^{-3}, (*3*) 2.20×10^{-3}; pH: (*1*) 3.20, (*2*) 3.61, (*3*) 5.36, (*4*) 4.14; ε_{800}, l mol^{-1} cm^{-1}: (*1*) 23.2, (*4*) 24.2, ε_{655}, l mol^{-1} cm^{-1}: (*2*) 6.6, (*3*) 11.2.

Dibutyl-2-(2-hydroxy-5-chlorophenyl)-2-phenylethenylphosphine oxide (**Ia**). Grignard reagent was obtained via a standard procedure from 3.7 g (0.15417 mol) of magnesium and 16.6 ml (21.15 g, 0.1542 mol) of bromobutane in 15 ml of diethyl ether. The solution containing 20 g (0.0643 mol) of oxaphosphorine oxide (**II**) in 20 ml of benzene was added dropwise to the Grignard reagent, and the mixture was

heated to boiling for 0.5 h. Then the solution was cooled and hydrolyzed with distilled water and 28.4 ml of hydrochloric acid. The organic and aqueous layers were separated. The organic phase was washed with distilled water; then the solvents were distilled off under a reduced pressure. 20.4 g (89.5%) of (**Ia**) was obtained in the form of yellowish viscous oil-like substance. IR, ν, cm^{-1}: 766 (P–C), 1128 (P=O), 1572 (C=C_{Ar}), 1588 (C=C_{Ar}), 3363 (OH). ^{1}H NMR (600 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.9 t (6H, CH_3, $^3J_{HCCH}$ 7.3), 1.38 m (4H, CH_2), 1.49 m (4H, CH_2), 1.55–1.8 m (4H, PCH_2, AB of $ABMX_2$), 6.4 d (1H, PCH, $^2J_{PH}$ 19.1), 6.91 d (1H, H^5, $^4J_{HH}$ 2.6), 7.1 d (1H, H^8, $^3J_{HH}$ 8.4), 7.27 br.d.d (1H, H^7, $^3J_{HH}$ 8.4, $^4J_{HH}$ 2.6), 7.3–7.4 (5H, H^{10}, H^{11}, H^{12}). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C), δ_C, ppm (*J*, Hz) (hereinafter view of the signal in the ^{13}C–{^{1}H} NMR spectrum is given in parentheses): 119.30 br.d.d (d) (C^3, $^1J_{PC}$ 90.4, $^1J_{HC}$ 150.8), 154.92 m (d) (C^4, $^2J_{PC}$ 2.5), 127.28 m (br.d) (C^{4a}, $^3J_{PC}$ 5.6, $^3J_{HC}$ 6.9), 129.26 d.d (s) (C^5, $^1J_{HC}$ 165.3, $^3J_{HC}$ 5.8), 123.15 d.d.d (s) (C^6, $^3J_{HC}$ 11.3, $^2J_{HC}$ 3.8, $^2J_{HC}$ 3.8), 129.49 d.d (s) (C^7, $^3J_{HC}$ 5.8, $^1J_{HC}$ 160.5), 118.48 d (s) (C^8, $^1J_{HC}$ 162.8), 153.78 d.d.d (s), (C^{8a}, $^3J_{HC}$ 9.3, $^3J_{HC}$ 8.5, $^2J_{HC}$ 1.7), 139.95 m (d) (C^9, $^3J_{PC}$ 15.5, $^3J_{HC}$ 7.2–8.1, $^3J_{HC}$ 6.6), 126.76 br.d.m (s) (C^{10}, $^1J_{HC}$ 158.9, $^3J_{HC}$ 6.2–6.9), 127.98 br.d.d (s) (C^{11}, $^1J_{HC}$ 160.5, $^3J_{HC}$ 7.3–7.5), 129.01 d.t (s) (C^{12}, $^1J_{HC}$ 161.4, $^3J_{HC}$ 7.4), 28.30 t.d.m (d) (PCH_2^{13}, $^1J_{PC}$ 69.5, $^1J_{HC}$ 129.6), 23.15 t.m (br.s) (CH_2^{14}, $^1J_{HC}$ 128.6), 23.65 t.d.m (d) (CH_2^{15}, $^1J_{HC}$ 123.8, $^3J_{PC}$ 15.0), 13.58 comp. m (s) (CH_3^{16}, $^1J_{HC}$ 125.0, $^3J_{HC}$ 4.0–4.2). ^{31}P–{^{1}H} NMR (DMSO-d_6): δ_P 41.3 ppm. EI MS, *m*/*z*: 390 $[M]^{+\bullet}$ ($C_{22}H_{28}Cl^{35}O_2P$), 373 [*M* – OH], 355 [*M* – Cl], 333 [*M* – C_4H_9], 317 [*M* – C_4H_9 – OH], 290 [*M* – C_4H_9 – C_3H_7], 258 [*M* – $2C_4H_9$ – OH], 230 [$C_{14}H_{11}ClO$], 228 [$C_{14}H_9ClO$], 214, 176, 162 [$C_8H_{19}OP$], 132, 119, 91, 106, 77, 63, 29. Found, %: C 67.63; H 7.16; P 8.37. $C_{22}H_{28}ClO_2P$. Calculated, %: C 67.60; H 7.22; P 7.92.

Dinaphthyl-2-(2-hydroxy-5-chlorophenyl)-2-phenylethenylphosphine oxide (**Id**) was obtained via a similar procedure. Yield 86.7%, mp 225–228°C. IR, ν, cm^{-1}: 764 (P–C), 1146 (P=O), 1537 (C=C_{Ar}), 1568 (C=C_{Ar}), 1590 (C=C_{Ar}), 3391 (OH). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 5.28 br.d (1H, H^5, X of ABX, $^4J_{HCH}$ 2.6), 6.90 d.d (1H, H^7, A of ABX, $^4J_{AX}$ 2.6, $^3J_{AB}$ 8.67), 7.01 d (1H, H^8, B of ABX, $^3J_{AB}$ 8.67), 7.18 m (2H, H^{18}), 7.25 m (2H, H^{15}), 7.29–7.38 m (6H, H^{14}, H^{20}, H^{19}), 7.36 (1H, H^3, $^3J_{PH}$ 19.1), 7.59 and 7.78 two m (5H, H^9, H^{10}, H^{11}, H^{12}), 7.98 m (2H, H^{16}), 8.04 br.d (2H, H^{21}, $^3J_{HH}$ 8.1), 8.05 br.s (1H, OH). ^{13}C NMR (100.6 MHz, DMSO-d_6, 45°C), δ_C, ppm (*J*, Hz): 122.32 d.d (d) (PC^3, $^1J_{PC}$ 103.6, $^1J_{HC}$ 153.0), 155.35 m.d (d) (C^4, $^2J_{PC}$ 1.2), 126.85 m (d) (C^{4a}, $^3J_{PC}$ 7.0–8.0, partially overlap with C^{20} signal), 129.93 d.d (s) (C^5, $^1J_{HC}$ 170.8, $^3J_{HC}$ 5.7–6.0), 121.47 d.d.d (s) (C^6, $^2J_{HC}$ 3.9–4.0, $^2J_{HC}$ 3.9–4.0, $^3J_{HC}$ 12.4), 128.80 br.d.d (s) (C^7, $^1J_{HC}$ 218.8, $^3J_{HC}$ 5.3–5.6), 116.82 d (s) (C^8, $^1J_{HC}$ 161.1), 153.70 br.d.d (s) (C^{8a}, $^3J_{HC}$ 8.3, $^3J_{HC}$ 8.3), 140.21 m (d) (C^9, $^3J_{PC}$ 17.1), 129.03 d.m (s) (C^{10}, $^1J_{HC}$ 160.6), 128.47 br.d.d (s) (C^{11}, $^1J_{HC}$ 161.3, $^2J_{HC}$ 5.48–5.74), 129.19 d.d (d) (C^{12}, $^1J_{HC}$ 161.3), 129.98 d.m (d) (PC^{13}, $^1J_{PC}$ 103.2), 132.58 br.d.m (d) (C^{14}, $^1J_{HC}$ 162.2, $^2J_{PC}$ 10.3, $^3J_{HC}$ 9.5), 124.84 br.d.d (d) (C^{15}, $^3J_{PC}$ 13.7, $^1J_{HC}$ 162.9), 132.72 br.d.d.d (s) (C^{16}, $^1J_{HC}$ 164.7, $^3J_{HC}$ 5.8–6.0, $^3J_{HC}$ 5.0–5.2), 132.70 d.m (d) (C^{17}, $^3J_{PC}$ 8.6), 126.82 br.d.d.d (C^{18}, $^1J_{HC}$ 160.1, $^3J_{HC}$ 5.8–6.0, $^3J_{HC}$ 5.0–5.2), 126.30 d.d (s) (C^{19}, $^1J_{HC}$ 161.2, $^3J_{HC}$ 8.4), 126.86 d.d (s) (C^{20}, $^1J_{HC}$ 161.9, $^3J_{HC}$ 8.9), 126.79 br.d.d.d (C^{21}, $^1J_{HC}$ 160.0, $^3J_{HC}$ 8.0–8.2, $^3J_{PC}$ 4.8), 133.49 m (d) (C^{22}, $^2J_{PC}$ 9.2). ^{31}P–{^{1}H} NMR (DMSO-d_6): δ_P 25.4 ppm. EI MS, *m*/*z*: 530 $[M]^{+\bullet}$ ($C_{34}H_{24}Cl_{35}O_2P$), 495 [*M* – Cl], 478 [*M* – Cl – OH], 453 [*M* – C_6H_5], 438, 423, 409, 395, 383, 368 [*M* – $C_{10}H_7$ – Cl], 302 [$C_{20}H_{15}OP$], 253, 215, 173, 128, 97, 83, 57, 55, 43. Found, %: C 76.85; H 4.60; P 5.83. $C_{34}H_{24}ClO_2P$. Calculated, %: C 76.91; H 4.56; 5.86.

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REFERENCES

1. *The Chemistry of Organophosphorus Compounds*, Hartley, F.R., Ed., Chichester: John Wiley & Sons, 1992, vol. 2.
2. Korbridge, D.E.C., *Phosphorus 2000. Chemistry, Biochemistry & Technology*, Amsterdam: Elsevier, 2000.
3. Mironov, V.F., Tatarinov, D.A., and Varaksina, E.N., RF Patent 2329271, 2008; *Byull Izobret*, 2008, no. 20.
4. Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Russ. J. Gen. Chem.*, 1998, vol. 68, no. 9, pp. 1414–1442.
5. Aleksandrov, V.V., *Kislotnost' nevodnych rastvorov* (Acidity of Nonaqueous Solutions), Kharkiv: Vishcha Shkola, 1981.
6. *Preparativnaya organicheskaya khimiya* (Preparative Organic Chemistry), Vul'fson, N.S., Ed., Moscow: Khimiya, 1964.

7. Sal'nikov, Yu.I., Glebov, A.N., and Devyatov, F.V., *Poliyadernye kompleksy v rastvorah* (Polynuclear Complexes in Solutions), Kazan: Kazan. Univ., 1989.
8. Doerffel, K., *Statistik in der Analytischen Chemie,* Leipzig, 1969.
9. Hartley, F.R., Burgess, C., and Alcock, R.M., *Solution Equilibria*, Chichester: John Wiley & Sons, 1980.
10. Gore, P.H. and Newman, P.J., *Anal. Chim. Acta,* 1964, vol. 31, no. 2, pp. 111–120.
11. Desai, A.G. and Milburn, R.M., *J. Am. Chem. Soc.,* 1969, vol. 91, no. 8, pp. 1958–1961.
12. Lur'e, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook of Analytical Chemistry), Moscow: Khimiya, 1965.
13. Umland, F., Yansen, A. Tirig, D., and Vyunsch, G., *Kompleksnye soedineniya v analiticheskoi khimii* (Complex Compounds in Analytical Chemistry), Moscow: Mir, 1975.
14. Tel'zhenskaya, P.N. and Shrarts, E.M., *Koord. Khim.,* 1977, vol. 3, no. 9, p. 1279.
15. Babko, A.K. and Pilipenko, A.T., *Fotometricheskii analiz. Obshchie svedeniya i apparatura* (Photometrical Analysis. Basics and Instrumentation), Moscow: Khimiya, 1968.
16. Lees, A.M.J. and Platt, A.W.G., *Polyhedron,* 2005, vol. 24, no. 3, pp. 427–433.
17. Liver, E., *Elektronnaya spectroskopiya neorganicheskikh soedinenii* (Electronic Spectroscopy of Inorganic Compounds), Moscow: Mir, 1987, vol. 2.