## Synthesis and coordination properties of new preorganized ligand on the triphenylphosphine oxide platform\*

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Tris(2-cyanomethoxyphenyl)phosphine oxide was synthesized by the reaction of tris-(2-hydroxyphenyl)phosphine oxide with chloroacetonitrile. Its coordination properties were studied for the complexation with neodymium(III) and copper(II) nitrates using vibrational spectroscopy, NMR, and quantum chemical calculations.

**Key words:** tris(2-cyanomethoxyphenyl)phosphine oxide, neodymium(III) complexes, copper(II) complexes, Raman spectroscopy, IR spectroscopy, NMR spectroscopy, quantum chemical calculations.

A promising approach to the development of new ligands and extractants for hydrometallurgy is based on the increase in denticity of ligands, that makes it possible to obtain more stable complexes. At the same time, more rigid molecular framework increases selectivity of complexation. The use of tripodal structures based on the conformationally rigid platform makes it possible to develop ligands combining both the efficiency and the selectivity of complexation. In this connection, in the last decades tripodal ligands of different structure have attracted a growing attention, in particular, those on the triarylmethane platform<sup>1,2</sup> containing the central triphenylmethane core with the chains bearing donor atoms attached to the phenyl rings.

Triarylphosphine oxides are the structural analogs of triarylmethanes and are an attractive platform for the construction of tripodal ligands, since they contain an additional coordination center, the phosphoryl group. It is known that triarylphosphine oxide molecules, including those of tris(2-methylphenyl)phosphine oxide<sup>3</sup> and tris-(2-hydroxyphenyl) phosphine oxide (1),<sup>4</sup> have a propeller conformation, with the substituents in ortho-position being directed to the same side as the phosphoryl group. The present work is devoted to the synthesis and coordination properties of the structurally related potentially tetradentate ligand tris(2-cyanomethoxyphenyl)phosphine oxide (2), which is derived from phosphine oxide 1. It could have been suggested that the propeller conformation of ligand 2 would secure the orientation of the three nitrile and the phosphoryl groups to the same side. A com-

I. P. Beletskaya on the occasion of her anniversary.

bination of conformational rigidity of the triphenylphosphine oxide core of the ligand molecule and the presence of several additional donor atoms in the side chains create conditions for the formation of a preorganized ligand environment that provides a concerted coordination of all the donating groups to the metal cation.

Tris(2-cyanomethoxy)phosphine oxide **2** was obtained in accordance with Scheme 1.



Precursor 1 was synthesized by the reaction discovered in 1981 by L. Melvin,<sup>5</sup> which included a rearrangement of aryl phosphates to 2-hydroxyarylphosphonates on treatment with metallating agents. This approach was further developed by other researchers<sup>6</sup> and used for the preparation of hydroxyarylenebis(phosphonates),<sup>7</sup> bis(2-hydroxyaryl)phosphinates,<sup>8</sup> as well as tris(2-hydroxyaryl)phosphine oxides<sup>8,9</sup> of the type 1.

Phosphine oxide 1 was synthesized by treatment of triphenyl phosphate with lithium diisopropylamide at from

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Compound	IR					RS,
	ν(P=O)	$v_5(NO_3)$	$v_1(NO_3)$	$v_2(NO_3)$	ν(OH)	ν(C≡N)
$(2-HOC_6H_4)_3P=O(1)$	1090	_	_	_	2600—3600 (br.s)	_
$(2-NCCH_2OC_6H_4)_3P=O$ (L) (2)	1184	_	_	_	_	2262, 2242
$Nd(NO)_{3} \cdot 2L \cdot 2H_{2}O(3)$ $Cu(NO_{3})_{2} \cdot 2L \cdot 3H_{2}O(4)$	1146 1146, 1123	1490 1380	1316 1380	1033 1380	3430 3390, 3070	2261, 2247 2261, 2247

**Table 1.** IR and Raman spectroscopic data for compounds 1-4 (v/cm<sup>-1</sup>)

-80 to -90 °C.\* The process included the metallation of the benzene ring at *ortho*-position with subsequent migration of phosphorus to carbon. The structure of compound 1 was confirmed by the elemental analysis data, IR and NMR spectroscopy (Tables 1 and 2), and X-ray diffraction studies.<sup>4</sup>

The main feature of the structure of phosphine oxide 1 in solutions and in crystal is the formation of intra- and intermolecular hydrogen bonds between the phenolic hydroxy groups and the oxygen atom of the phosphoryl group. Thus, the IR spectrum of compound 1 in the solid state exhibits a broad absorption band related to the stretching vibrations of the OH groups involved in the hydrogen bonding ( $3600-2600 \text{ cm}^{-1}$ ). The absorption band of the P=O group is shifted to the low-frequency region as compared to that of triphenylphosphine oxide  $(1200 \text{ cm}^{-1})$  by more than  $100 \text{ cm}^{-1}$  (1090 cm<sup>-1</sup>), that is explained by the trifurcate hydrogen bond formed by the phosphoryl oxygen atom with three hydroxy groups. From the IR spectra of compound 1 in solutions, it follows that the intramolecular hydrogen bond still exists in chloroform and is destroyed in DMSO, while different species are in the equilibrium in acetonitrile.

The  ${}^{31}P{}^{1}H{}$  NMR spectra exhibit singlets, whose chemical shift strongly depends on the nature of the solvent and is upfield shifted by 10–15 ppm on going to the solvents capable of destroying hydrogen bonds.

Tris(2-hydroxyphenyl)phosphine oxide **1** reacted with chloroacetonitrile in the presence of  $K_2CO_3$  and KI in DMF upon heating to 50 °C. Cyanomethoxy derivative **2** was isolated as colorless crystals well soluble in ethyl alcohol, DMF, chloroform, and acetone. The structure of compound **2** was confirmed by the elemental analysis, vibrational spectroscopy (IR, Raman), and NMR spectroscopy (<sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C) (see Tables 1 and 2). To study the coordination potentialities of ligand **2**, as well as to correctly interpret vibrational spectra, we carried out quantum chemical calculations for the molecular conformations and the normal vibrational modes. In the global minimum, molecule 2 has a propeller conformation, in which the blades of the phenyl rings are turned along the C-P bonds so that the torsional angles O-P-C-C are  $46-50^{\circ}$  (Fig. 1). The oxygen atoms of the cyanomethoxy groups are above the plane formed by the carbon atoms of three C-P bonds and on the same side with the P=O group. Two  $-C-C\equiv N$  groups are virtually parallel to each other and symbatic to the P=O bond, the third group is directed to the opposite side.

The theoretical analysis of vibrations of molecule 2 in this conformation showed, in particular, that the frequency 1193 cm<sup>-1</sup> corresponded to the vibration of the P=O bond. However, this vibration, overlapping with vibrations of the P-C bonds and close in frequency vibrations of phenyl rings, also contribute to several frequencies in the region 1125-1260 cm<sup>-1</sup>. Characteristic vibrations of the nitrile bonds have the frequencies 2266, 2268, and 2287  $\text{cm}^{-1}$ , with the virtually overlapped first two bands being related to the vibrations of the oppositely directed bonds, while the band of higher frequency being associated with one of the parallel bonds. This bond structurally differs from two other ("the oppositely directed") bonds by its parallel orientation with respect to its phenyl ring, whereas two other bonds are oriented at the angle of  $\sim 60^{\circ}$ to the plane of "their own" phenyl rings.

The IR spectrum of phosphine oxide 2 exhibits an absorption band of the phosphoryl group at 1184 cm<sup>-1</sup>. No



**Fig. 1.** Conformation of tris(2-cyanomethoxyphenyl)phosphine oxide molecule **2** in the region of the global minimum according to quantum chemical calculations.

<sup>\*</sup> The published procedure<sup>9</sup> was slightly modified: the metallation was carried out at lower temperature, the work-up of the reaction mixture and the isolation of the product were simplified.

Com- pound 1	Solvent	$\delta$ , J/Hz, $\Delta_{1/2}$ /Hz						
		<sup>1</sup> H	${}^{1}H{}^{31}P{}$	$^{13}C{^{1}H}$	$^{31}P{^{1}H}$ (s)			
	DMSO-d <sub>6</sub>	6.85 (dd, 3 H, H(3), ${}^{3}J_{3,4} = 8.2, {}^{4}J_{H,P} = 5.4$ ); 6.89 (tdd, 3 H, H(5), ${}^{3}J_{5,4} = {}^{3}J_{5,6} = 7.5,$ ${}^{4}J_{5,3} = 2.3, {}^{4}J_{H,P} = 1.0$ ); 7.41 (br.t, 3 H, H(4), ${}^{3}J_{4,3} = {}^{3}J_{4,5} = 7.7$ ); 7.44 (ddd, 3 H, H(6), ${}^{3}J_{6,5} = 7.7, {}^{4}J_{6,4} = 1.7,$ ${}^{3}J_{H,P} = 14.3$ ); 10.77 (s, 3 H, OH)	6.86 (d, 3 H, H(3), ${}^{3}J_{3,4} = 8.2$ ); 6.90 (t, 3 H, H(5), ${}^{3}J_{5,4} =$ $= {}^{3}J_{5,6} = 7.5$ ); 7.42 (td, 3 H, H(4), ${}^{3}J_{4,3} = {}^{3}J_{4,5} = 7.8$ , ${}^{4}J_{4,6} = 1.7$ ); 7.46 (d, 3 H, H(6), ${}^{3}J_{6,5} = 7.7$ ); 10.77 (s, 3 H, OH)		35.95			
	CD <sub>3</sub> CN	_	—	—	38.27			
	DMF	_	_	_	40.46			
	CDCl <sub>3</sub>	6.90 (td, 3 H, H(5), ${}^{3}J_{5,4} =$ = ${}^{3}J_{5,6} = 7.5$ , ${}^{4}J_{H-P} = 2.7$ ); 6.95-7.06 (m, 6 H, H(3), H(6)); 7.46 (t, 3 H, H(4), ${}^{3}J_{4,3} =$ = ${}^{3}J_{4,5} = 7.8$ ); 9.42 (s, 3 H, OH)	6.90 (t, 3 H, H(5), ${}^{3}J_{5,4} =$ = ${}^{3}J_{5,6} = 7.5$ ); 6.95–7.05 (m, 6 H, H(3), H(6)); 7.46 (t, 3 H, H(4), ${}^{3}J_{4,3} = {}^{3}J_{4,5} =$ = 7.8); 9.42 (s, 3 H, OH)	_	51.60			
2	CD3CN	4.68 (s, 6 H, CH <sub>2</sub> O); 7.14 (dd, 3 H, H(3), ${}^{3}J_{3,4} = 7.9$ , ${}^{4}J_{H,P} =$ = 4.9); 7.21 (tdd, 3 H, H(5), ${}^{3}J_{5,4} = 7.5$ , ${}^{3}J_{5,6} = 7.6$ , ${}^{4}J_{5,3} =$ = 0.8, ${}^{4}J_{H,P} = 2.2$ ); 7.54 (ddd, 3 H, H(6), ${}^{3}J_{6,5} = 7.6$ , ${}^{4}J_{6,4} =$ = 1.7, ${}^{3}J_{H,P} = 14.8$ ); 7.64 (dddd, 3 H, H(4), ${}^{3}J_{4,3} = 8.4$ , ${}^{3}J_{4,5} = 7.5$ , ${}^{4}J_{4,6} = 1.7$ , ${}^{5}J_{4,5} = 7.1$ ,	4.68 (s, 6 H, CH <sub>2</sub> O); 7.14 (d, 3 H, H(3), ${}^{3}J_{3,4} = 8.4$ ); 7.22 (t, 3 H, H(5), ${}^{3}J_{5,4} =$ = 7.5, ${}^{3}J_{5,6} = 7.6$ ); 7.54 (dd, 3 H, H(6), ${}^{3}J_{6,5} = 7.6$ , ${}^{4}J_{6,4} = 1.7$ ); 7.64 (ddd, 3 H, H(4), ${}^{3}J_{4,3} = 8.4$ , ${}^{3}J_{4,5} = 7.5$ , ${}^{4}J_{4,6} = 1.7$ )	55.04 (s, CH <sub>2</sub> O); 114.61 (d, C(3), ${}^{1}J_{CH}$ 6.53); 116.28 (s, C=N); 123.22 (d, C(1), ${}^{1}J_{CP}$ = 109.62); 124.05 (d, C(5), ${}^{1}J_{CH}$ = 12.03); 135.02 (d, C(4), ${}^{1}J_{CH}$ = = 2.06); 135.27 (d, C(6), ${}^{1}J_{CH}$ = 8.25); 159.09 (d, C(2), ${}^{1}J_{CP}$ = 2.06)	21.46 3 $(\Delta_{1/2} = 3)$			
3	CD <sub>3</sub> CN	4.25 (s, 6 H, OCH <sub>2</sub> ); 7.25–7.40 (m, 3 H, H(3)); 7.46 (br.s, 3 H, H(5)); 7.89 (t, 3 H, H(4), ${}^{3}J_{4,5} = {}^{3}J_{4,3} = 7.9$ ); 9.47 (br.s, 3 H, H(6))	_	_	143.65 ( $\Delta_{1/2} = 50$ )			
4	CD <sub>3</sub> CN	5.30 (br.s, 6 H, OCH <sub>2</sub> ); 6.75–8.20 (m, 12 H, Ar)	_	_	_			

Table 2. <sup>1</sup>H, <sup>1</sup>H $\{^{31}P\}$ , <sup>13</sup>C $\{^{1}H\}$ , and <sup>31</sup>P $\{^{1}H\}$  NMR spectra of compounds 1–4

vibration of the nitrile bond was detected, that is not uncommon, since the intensity of absorption for this band depends on the bond environment.<sup>10</sup> It the Raman spectrum, the vibration of the C=N bonds is observed as two weak lines at 2242 and 2262 cm<sup>-1</sup>, with the band of higher frequency being stronger, that agrees with the calculations.

The  ${}^{31}P{}^{1}H$  NMR spectrum exhibits a singlet in the region characteristic of triarylphosphine oxides; the  ${}^{1}H$  and  ${}^{13}C$  NMR spectra correspond to the structure of compound **2**.

Coordination properties of the preorganized tripodal ligand 2 on the triphenylphosphine oxide platform were studied for the complexation with neodymium(III) and copper(II) nitrates. The complexes obtained were characterized by IR, Raman, and NMR spectroscopy (see Tables 1 and 2). Unfortunately, the low solubility of these com-

plexes in low polarity solvents considerably limits the possibilities of their studies in solutions.

The reaction of tris(2-cyanomethoxyphenyl)phosphine oxide **2** with neodymium nitrate leads to complex (**3**), which according to the elemental analysis data has the composition  $Nd(NO_3)_3 \cdot 2L \cdot 2H_2O$ .

The IR spectrum of complex 3 exhibited no absorption band for the free P=O group ( $1184 \text{ cm}^{-1}$ ), while new bands appeared at 1146 and 1123 cm<sup>-1</sup>. The former is characteristic<sup>11</sup> of the vibration of coordinated P=O group. The emergence of the latter can be explained by the fact that, as was shown by quantum chemical calculations, the vibration of the P=O group contributes to the frequencies of the mixed vibrations in this region.

As to the cyano group, determination of its involvement in the coordination by spectroscopic methods is more complicated problem. It is known that coordination at the nitrogen atom leads to the increase in the vibrational frequency of the C=N bond by 30–50 cm<sup>-1</sup>, with the value of the shift being dependent on the nature of the metal, coordination number, and other factors. Coordination at the triple bond is also possible, leading in this case to a considerable decrease in the frequency of the CN vibration, sometimes by more than 100 cm<sup>-1</sup>.<sup>12</sup> The Raman spectrum of complex **3**, like the spectrum of the free ligand, exhibits two lines related to the vibrations of the C=N bonds (at 2247 and 2261 cm<sup>-1</sup>) with redistributed intensity, *i.e.*, the frequency difference is only 5 cm<sup>-1</sup>. In our opinion, such a change in the spectrum cannot indicate coordination of the cyano group and is apparently caused by the spatial rearrangement.

The IR spectrum of complex **3** also exhibits broad absorption bands of the nitrate groups coordinated in bidentate mode: at 1490 ( $v_5$ ), 1316 ( $v_1$ ), and 1033 ( $v_2$ ) cm<sup>-1</sup>.<sup>12</sup> The complex contains the outer-sphere water, which is indicated by the broad band of stretching OH vibrations with the maximum at 3430 cm<sup>-1</sup> and the band of bending OH vibrations at 1650 cm<sup>-1</sup>.

The <sup>31</sup>P NMR spectrum of neodymium complex **3** exhibits a broad signal, which is downfield shifted by ~122 ppm as compared to the spectrum of the starting ligand, that indicates the coordination of the Nd<sup>III</sup> cation at the oxygen atom of the phosphoryl group. In the <sup>1</sup>H NMR spectrum of complex **3**, all the proton signals are also broadened, and the signal for the protons of the methylene group is upfield shifted by ~0.4 ppm. The signals for protons H(3), H(4), and H(5) are shifted downfield by ~0.2 ppm, whereas the signal for proton H(6) is shifted by ~2 ppm, that confirms the coordination of the Nd<sup>III</sup> cation at the P=O group.

To sum up, the elemental analysis data, vibrational spectroscopy, and NMR spectroscopy show that the complexation of ligand **2** with  $Nd(NO_3)_3 \cdot 6H_2O$  leads to the complex  $[NdL_2(NO_3)_3] \cdot 2H_2O$  due to the coordination of neodymium at the oxygen atom of the phosphoryl group.

It should be noted that ligand 2 is potentially tetradentate, *i.e.*, the coordination to the cyano group is in principle possible. However, such a coordination does not apparently take place in the neodymium complex. In this connection, a divalent copper having an affinity to nitrogen atoms was chosen as the complexing metal.

The reaction of a solution of tris(2-cyanomethoxyphenyl)phosphine oxide **2** with copper nitrate leads to the complex, which according to the elemental analysis data has the composition  $Cu(NO_3)_2 \cdot 2L \cdot 3H_2O$  (**4**).

The IR spectrum of complex **4** in the region of the P=O bond vibrations virtually does not differ from the spectrum of complex **3**: the absorption band of the free P=O group is absent, a new band is observed at  $1145 \text{ cm}^{-1}$  and the absorption at  $1124 \text{ cm}^{-1}$  becomes stronger .Therefore, like in the neodymium complex **3**, the phosphoryl group is coordinated in the copper complex **4**.

In the Raman spectrum of complex 4, the lines of the CN vibration is observed at the same frequencies as that in the case of complex 3: at 2247 and 2261 cm<sup>-1</sup>. However, their intensities are low with the high-frequency line is the strongest. Thus, the vibrational spectra show that the bisligand copper complex, like the neodymium one, is formed due to the coordination of the phosphoryl groups.

The copper complex **4** also includes the nitrate groups and water. The coordination of these groups in complexes **3** and **4** differ from each other. Thus, if in complex **3** the stretching vibration maximum for water is observed at  $3430 \text{ cm}^{-1}$  and corresponds to the absorption of the crystal (outer-sphere) water, the IR spectrum of complex **4** exhibits two absorption maxima at lower frequencies: 3390 and 3070 cm<sup>-1</sup>; a weak maximum at ~1680 cm<sup>-1</sup> belongs apparently to the bending vibration of water. Such a spectrum can correspond to the inner-sphere coordination of water.

The band at 1380 cm<sup>-1</sup>, which corresponds to the  $D_{3h}$  symmetry of the "free" NO<sub>3</sub> anion, can be assigned to the vibrations of the nitrate groups in complex 4. A similar band characterizes copper nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O.<sup>13</sup> It can be suggested that the nitrate groups are either in the axial position of the stretched coordination octahedron of the copper cation or in the outer coordination sphere.

The <sup>31</sup>P NMR spectrum of copper complex **4** failed to be recorded because of the line broadening. In the <sup>1</sup>H NMR spectrum, the broadening of all the proton signals is observed, including the methylene one, which is shifted downfield by ~0.6 ppm. The protons of the aromatic rings in the spectrum of complex **4** are found as a broad multiplet in the region  $\delta$  6.75–8.20, that does not allow us to assign the signals.

In conclusion, the reaction of ligand **2** with Nd<sup>III</sup> and Cu<sup>II</sup> nitrates leads to the complexes only due to the coordination to the P=O group. We further plan to modify precursor **1** with other substituents.

## Experimental

<sup>1</sup>H, <sup>1</sup>H{<sup>31</sup>P}, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13 (<sup>1</sup>H), 161.98 (<sup>31</sup>P{<sup>1</sup>H}), and 100.61 MHz (<sup>13</sup>C{<sup>1</sup>H})). The signals of residual protons of deuterated solvents were used as internal references in the <sup>1</sup>H and <sup>1</sup>H{<sup>31</sup>P} NMR spectra, in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the signal for the carbon atom of the deuterated solvent was the internal reference, 85% aqueous H<sub>3</sub>PO<sub>4</sub> was used as an external standard for <sup>31</sup>P{<sup>1</sup>H} NMR spectra.

IR spectra of compounds **1**–**4** in Nujol and KBr pellets in the region 400–4000 cm<sup>-1</sup> and solutions of phosphine oxide **1** in CDCl<sub>3</sub>, CD<sub>3</sub>CN, and DMSO-d<sub>6</sub> in the region 700–4000 cm<sup>-1</sup> with the concentrations of 0.1, 0.01, and 0.001 mol L<sup>-1</sup> in 0.02-, 0.23-, and 0.54-cm pathlength cuvettes were obtained on a Nikolet Magna IR-750 Fourier-transform spectrometer. Raman spectra of solid samples in the region 200–4000 cm<sup>-1</sup> were recorded on a Jobin–Yvon LabRAM Raman laser spectrometer (Ge–Ne-laser, 632.8 nm).

Quantum chemical calculations at the density functional theory (DFT) level with the PBE functional for tris(2-cyano-

methoxyphenyl)phosphine oxide 2 were performed using the Priroda 6 (2006.08.20) software<sup>14,15</sup> (see Ref. 16). The optimization of geometric parameters and calculations of frequencies, shapes, and IR intensities of normal vibrations were carried out on the L2 relativistic basis set level.<sup>17</sup>

Deuterated solvents (CDCl<sub>3</sub>, CD<sub>3</sub>CN, DMSO-d<sub>6</sub>) for recording NMR spectra (the Russian Scientific Center of Applied Chemistry, Saint-Petersburg) were used without additional purification. Other organic solvents were purified according to the standard procedures.<sup>18</sup>

A 1.6 *M* solution of butyllithium in hexane (Aldrich) was used in the work, diisopropylamine (Acros) was distilled over Na.

Elemental analysis was performed in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

**Tris(2-hydroxyphenyl)phosphine oxide (1).** <u>Step 1</u>. A mixture of phenol (28.2 g, 0.3 mol), phosphorus oxychloride (15.3 g, 0.1 mol), and magnesium (0.048 g, 2 mmol) was heated at 160 °C for 3 h (until the evolution of hydrogen chloride ceased). The volatile products were evaporated *in vacuo*. The residue was purified by flash chromatography on Al<sub>2</sub>O<sub>3</sub> to obtain triphenyl phosphate (29.0 g, 89%), m.p. 49–50 °C (hexane). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 7.23–7.48 (m, 5 H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>),  $\delta$ : -17.52 s.

Step 2. A solution of triphenyl phosphate (19.6 g, 0.06 mol) in anhydrous THF (110 mL) was added over 40 min to a cooled to -80 °C solution of lithium diisopropylamide prepared from diisopropylamine (19.4 g, 0.192 mol) in anhydrous THF (60 mL) and a 1.6 M solution of butyllithium in hexane (120 mL), keeping the temperature in the range from -80 to -90 °C. The reaction mixture was stirred for 1 h at this temperature and was allowed to warm up to ~20 °C. Then, water (50 mL) and concentrated hydrochloric acid (58 mL) were added dropwise to the reaction mixture with stirring and cooling with cold water. The organic layer was separated, the aqueous layer was extracted with dichloromethane (4×20 mL). The combined organic extracts were washed with water (4×10 mL) and dried with anhydrous sodium sulfate. The drying agent was filtered off, the filtrate was concentrated. The crystals formed were washed with diethyl ether to obtain product 1 (16.7 g, 87%), m.p. 216-217 °C (EtOH) (cf. Ref. 8: m.p. 215-217 °C). Found (%): C, 66.27; H, 4.57; P, 9.41. C<sub>18</sub>H<sub>15</sub>O<sub>4</sub>P. Calculated (%): C, 66.26; H, 4.63; P, 9.49.

Tris(2-cyanomethoxyphenyl)phosphine oxide (2). A freshly distilled chloroacetonitrile (11.5 g, 0.15 mol) was added to a mixture of freshly calcined K<sub>2</sub>CO<sub>3</sub> (27.64 g, 0.2 mol), tris-(2-hvdroxyphenyl)phosphine oxide (6.52 g, 0.02 mol). KI (24.9 g, 0.15 mol), and DMF (300 mL). The reaction mixture was stirred for 8 h at ~20 °C, and then for 3 h at 50–55 °C. The solvent was evaporated in vacuo to dryness and water (150 mL), sodium metabisulfite (13.3 g, 0.07 mol), and chloroform (100 mL) were added to the solid residue. The organic layer was separated, the aqueous layer was extracted with chloroform (5×20 mL). The organic extracts were combined, the solvent was evaporated in vacuo, the residue was purified by column chromatography on alumina (eluent acetone-chloroform (1:1)) to obtain tris(2-cyanomethoxyphenyl)phosphine oxide 2 (4.5 g, 51%), m.p. 180–182 °C (hexane). Found (%): C, 64.91; H, 3.98; N, 9.37; P, 6.90. C<sub>24</sub>H<sub>18</sub>N<sub>3</sub>O<sub>4</sub>P. Calculated (%): C, 65.01; H, 4.09; N, 9.48; P, 6.99.

Trinitratobis[tris(2-cyanomethoxyphenyl)phosphine oxide]neodymium(III) dihydrate (3). A solution of  $Nd(NO_3)_3 \cdot 6H_2O$ (0.0763 g, 0.174 mmol) in acetonitrile (5 mL) was added dropwise to a solution of tris(2-cyanomethoxyphenyl)phosphine oxide (2) (0.0770 g, 0.174 mmol) in chloroform (4 mL) with stirring. The mixture obtained was stirred for 1.5 h at ~20 °C, then most of the solvent was evaporated *in vacuo*, diethyl ether was added. A white precipitate formed was filtered off, twice washed with diethyl ether, and dried to obtain complex **3** (0.08 g, 95%) of the composition Nd(NO<sub>3</sub>)<sub>3</sub>·2L·2H<sub>2</sub>O, m.p. 124 °C (decomp.). Found (%): C, 46.02; H, 3.20; N, 9.75; P, 4.73. C<sub>48</sub>H<sub>40</sub>N<sub>9</sub>NdO<sub>19</sub>P<sub>2</sub>. Calculated (%): C, 46.01; H, 3.22; N, 10.06; P, 4.94.

**Triaquabis**[**tris**(**2**-**cyanomethoxyphenyl)phosphine oxide**)]**copper**(**n**) **nitrate (4).** A solution of  $Cu(NO_3)_2 \cdot 3H_2O$  (0.0792 g, 0.328 mmol) in acetonitrile (5 mL) was added dropwise to a solution of tris(2-cyanomethoxyphenyl)phosphine oxide (**2**) (0.1157 g, 0.261 mmol) in chloroform (4 mL) with stirring. The mixture obtained was stirred for 2 h at ~20 °C, then most of the solvent was evaporated *in vacuo*, diethyl ether was added. A light blue precipitate formed was filtered off, twice washed with diethyl ether, and dried to obtain complex **4** (0.08 g, 54%) of the composition  $Cu(NO_3)_2 \cdot 2L \cdot 3H_2O$ , m.p. 125 °C (decomp.). Found (%): C, 51.07; H, 3.55; N, 9.91; P, 4.97.  $C_{48}H_{42}CuN_8O_{17}P_2$ . Calculated (%): C, 51.09; H, 3.75; N, 9.93; P, 5.49.

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