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Phosphacyclophanes Derived from Hydroquinone and 4,4'-Dihydroxybiphenyl

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Abstract — The first representatives of linear phosphocyclophanes were prepared starting from hydroquinone or 4,4'-dihydroxybiphenyl and phosphorous triamides. The reaction course is influenced by the structures of the aromatic diol and alkyl substituents in the phosphamide moiety. The phosphorus atom readily enters redox reactions and complexation. The complexing power of the aromatic fragments of the synthesized molecules is lower than that of classical p-cyclophanes.

We have shown previously that 1,5- and 2,7-dihydroxynaphthalenes readily react with equimolar amounts of phosphorous triamides to give in high yields the first representatives of double-deck systems, *p*-cyclophanes [1].

Proceeding with this study, we have examined in this work the reactions of phosphamides with hydroquinone and 4,4'-dihydroxybiphenyl. The goal of this study was to prepare maximally symmetrical three-dimensional molecular structures of the amidophosphite type. Two approaches were used: (*a*) molecular assembling by bisphosphorylation of diols followed by cyclization of the resulting products with diols and (*b*) direct synthesis consisting in reaction of phosphamides with equimolar amounts of diols. It should be noted that all phosphorylations were performed at room temperature in anhydrous acetonitrile without special removal of dialkylamine released in the reaction. The reactions were performed under argon to prevent oxidation.

In the synthesis of cyclic phosphites from hydroquinone **I** and phosphorous triamides **IIa** and **IIb** by pathway a (similarly to the reaction with resorcinol [2]), along with the bisphosphorylated products **IIIa** and **IIIb** we obtained monophosphorylated compounds **IVa** and **IVb**. These compounds exhibit different chromatographic mobility and different chemical shifts in the ^{31}P NMR spectra. Compounds **IIIb** and **IVb** were characterized in the form of phosphorodiamidothioates **V** and **VI**. On keeping the reaction mixture for 1 day, the bisphosphorylation goes to completion, but in the ^{31}P NMR spectra a weak signal of phosphoromonoamidite is observed (δ_P 140.0 ppm), which, as will be shown below, is due to formation of the cyclic product. To suppress the side process and ensure faster and more complete phosphorylation, we used a molar excess of hexaalkylphosphorous triamide, which after reaction completion (1 mm) was removed in a vacuum; after that, the residue was distilled (180–200°C, 10^{-4} mm). The final stage was cyclization with an equivalent amount of hydroquinone. In the course of the reaction, an oily product precipitated, which was identified by spectroscopic methods as cyclic bis(dialkylphosphoramidite) VIIa or VIIb [scheme (1)].

Note that the products behave differently depending on the substituent at phosphorus. Freshly prepared sample with the NMe_2 substituent (**VIIa**) dissolves in methylene chloride, benzene, and dioxane. However, after washing with acetonitrile and vacuum drying this sample transforms into the form insoluble in the same solvents. In methylene chloride the sample swells to form a gel and dissolves only in DMF. Contrastingly, compound **VIIb** with the NEt_2 substituent is readily soluble in all the above-mentioned solvents even after reprecipitation and removal of solvents in a vacuum. Both products are very unstable in air and change color from light yellow to red. The ^{31}P NMR spectra of both cyclic compounds contain two singlets in the characteristic phosphoramidite range with different ratio of the integral intensities, which is probably due to stereoisomerism. The ^{1}H NMR spectra were measured only for **VIIb** and were consistent with the proposed structure.

Compounds **VIIa** and **VIIb** were prepared by method *b* at equimolar ratio of the reactants. In this case the physicochemical characteristics of the products agreed with those of the compounds prepared by method *a*. However, method *b* is preferable because of shorter reaction time.

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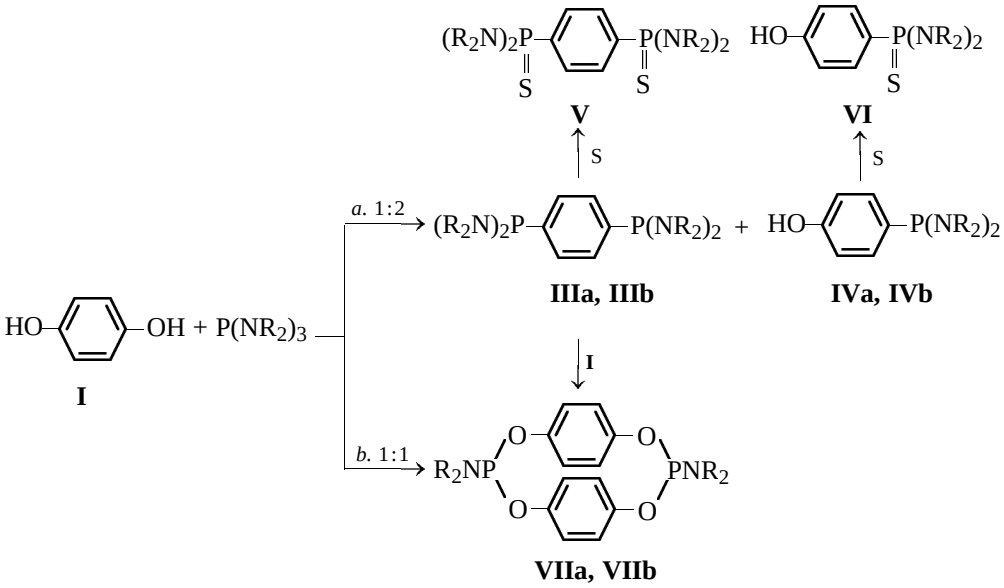
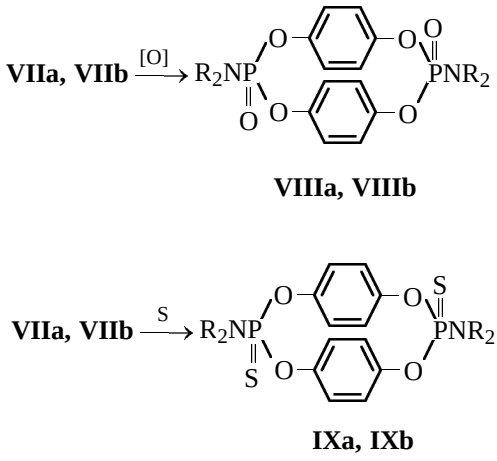
Scheme 1.



R = Me (**a**), Et (**b**).

Cyclic bis(dialkylphosphoramidites) **VIIa** and **VIIb** readily add oxygen and sulfur [Scheme (2)]:

Scheme 2.



R = Me (**a**), Et (**b**).

The resulting cyclic bis(phosphoroamidates) **VIIIa** and **VIIIb** and -amidothioates **IXa** and **IXb** are powdered substances; similar to [3, 4], their melting point decreases and the solubility increases in going from the NMe_2 to NEt_2 derivatives. Phosphorothioates **IXa** and **IXb** were isolated by column chromatography, and phosphates **VIIIa** and **VIIIb**, by chromatography and recrystallization from acetonitrile. The ^{31}P NMR spectra of all these compounds contain two singlets each, with their chemical shifts differing by 0.2–0.5 ppm, which suggests preservation of stereoisomerism.

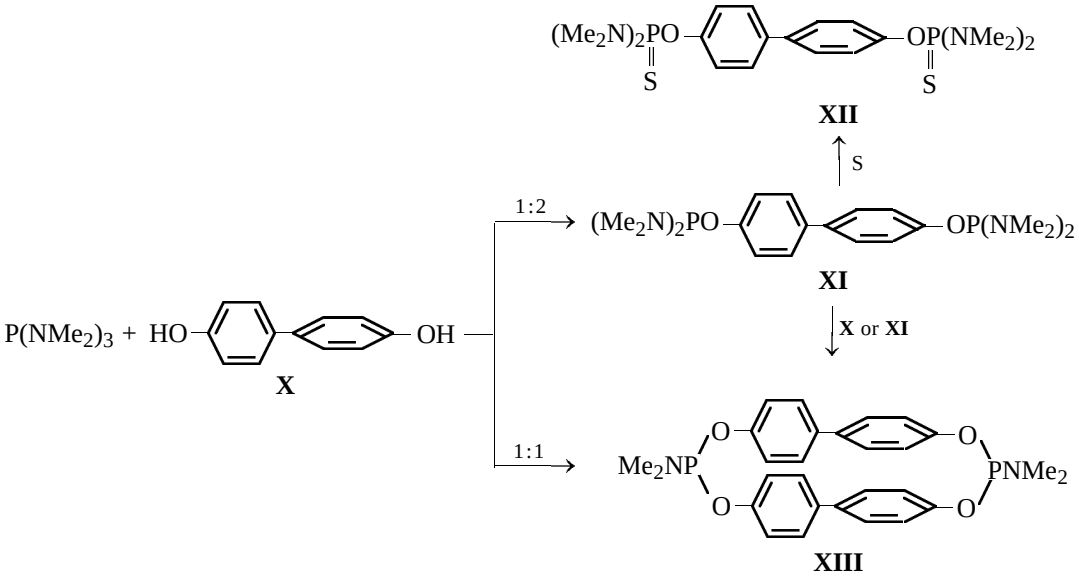
Replacement of one hydroxy group in hydroquinone by the *p*-phenoxy group affects both the course of phosphorylation and the properties of the resulting products.

The NMe_2 derivative IIa readily (within 5 min) phosphorylates 4,4'-dihydroxybiphenyl [Scheme (3)]. However, isolation of product **XI** is difficult, because it immediately starts to disproportionate to form cyclic bis(phoshoramidite) **XIII**. Addition of sulfur to the reaction solution allows isolation of bis(phosphorodiamidothioate) **XII**, which precipitates as a colorless powder readily soluble in methylene chloride. If a solution of 1 mol of **X** is added 5 min after the start of the reaction, a white powder precipitates, which is limitedly soluble in acetonitrile and methylene chloride (the solubility is sufficient to record the ^{31}P NMR spectrum) and insoluble even in such polar solvents as DMF and DMSO. According to the spectra (δ_P 140 ppm) and taking into account our previous results, the reaction product can be identified as cyclic bis(phosphoramidite) **XIII**.

This compound is also formed at equimolar ratio of reactants in one stage. The reaction starts very actively but is complete only in 1 day, as indicated by the ^{31}P NMR spectrum.

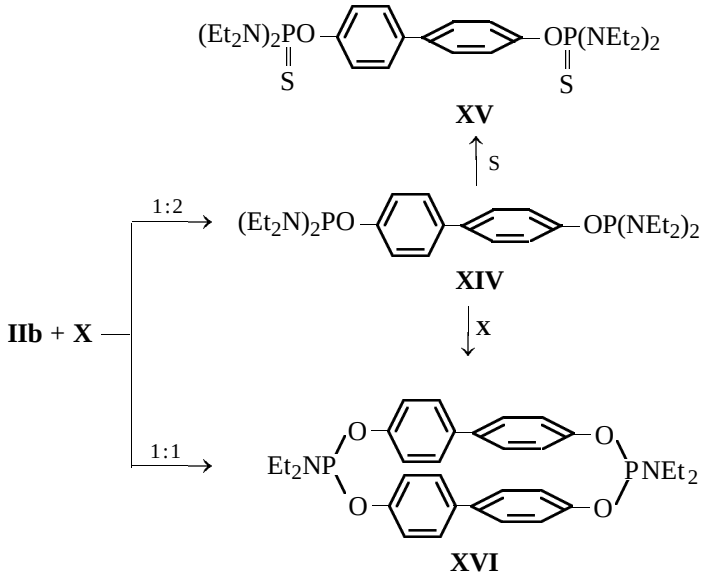
Bisphosphorylation of diol **X** with amide **IIb** is complete in 1.5 h. Phosphorodiamidite **XIV** is fairly

Scheme 3.



stable and disproportionates to form cyclic bis(phosphoramidite) **XVI** only on heating (e.g., at attempted high-vacuum distillation); it was fully characterized in the form of phosphorodiamidothioate **XV**. Both product **XIV** containing P^{3+} and phosphorothioate **XV** are oily substances readily soluble in organic solvents.

Scheme 4.

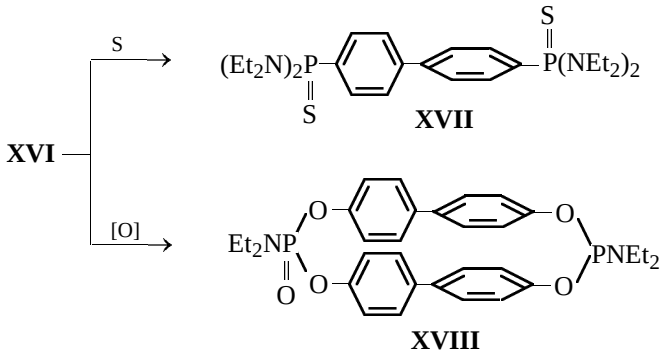


Addition of 1 mol of diol to **XIV** or single-stage synthesis at the molar ratio **IIb** : **X** = 1 : 1 yields a colorless powder of **XVI**, which precipitates from the reaction solution. In contrast to **XIII**, it is readily soluble in methylene chloride and less soluble in benzene and dioxane. Its ^{31}P NMR spectrum contains a singlet in the range typical of phosphoramidites, and the ^{1}H NMR spectrum contains two doublets in the

range of aromatic protons and signals from the NEt_2 protons. We believe that the different physicochemical properties of **XIII** and **XVI** are due to their structural features.

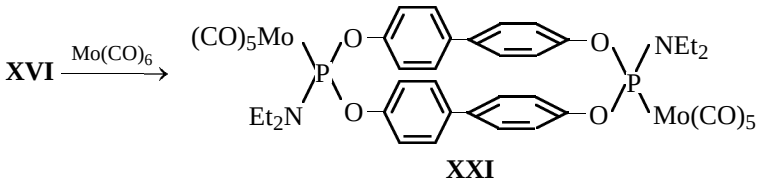
By addition of sulfur and oxidation, compound **XVI** was converted to thio and oxo derivatives **XVII** and **XVIII**, which were purified by column chromatography and reprecipitation, respectively [Scheme (5)]. These compounds are high-melting powders readily soluble in chlorinated solvents. Their ^{31}P NMR spectra contain singlets in the ranges typical of phosphoramidates and phosphoramidothioates; the retention factors of **XVII** and **XVIII** differed considerably from each other and from that of **XVI**, whereas the ^{1}H NMR spectra of all the three substances were similar.

Scheme 5.



The complexing power of the phosphorus atom was evaluated in reactions of acetylacetonatodicarbonylrhodium(I) with compounds **VIIb** and **XVI** and of $Mo(CO)_6$ with phenol derivative **X**. Rhodium complexes **XIX** and **XX** were prepared at room temperature in methylene chloride and purified by reprecipitation; their ^{31}P NMR spectra showed splitting with the direct coupling constants P–Rh typical of square planar Rh(I) complexes, and the IR spectra contained the OC–Rh absorption band at about 1990 cm^{-1}. Molybdenum complex **XXI** was prepared in dioxane (reactant concentrations 0.12 M) at 95°C:

Scheme 6.



It is interesting that in the course of the reaction even at 70°C a colorless gel started to form in the reaction solution, and at 95°C this gel occupied practically the whole reaction volume. After separation of the gel we found that the molybdenum complex was present in the solution. It was isolated in a 34% yield and fully characterized. Its ^{31}P NMR spectrum contained a singlet in the range typical of monosubstituted molybdenum phosphite complexes. The dried gel was a powdered substance insoluble in organic solvents; it could be a polymer formed in the presence of the molybdenum carbonyl complex.

We also attempted to perform complexation reactions involving the aromatic fragments. We started from cyclic phosphates **VIIIb** and **XVIII**, picric acid, and $Cr(CO)_6$. The expected complexes did not form. We believe that the phosphorus and oxygen atoms decrease the electron density in the aromatic rings, which decreases their capability to form charge-transfer complexes typical of *p*-cyclophanes [5–7].

Thus, introduction of oxygen and phosphorus atoms into *p*-cyclophane molecules strongly affects their complexing power; however, the presence of

trivalent phosphorus allows preparation of another type of complexes, which may be promising as catalysts and drug carriers.

EXPERIMENTAL

The IR spectra of **XIX** and **XX** were measured on a Specord IR-75 spectrometer in methylene chloride in the range 4000–400 cm^{-1}. The ^1H NMR spectra of **IIIa, IIIb, VIIIa, VIIIb, IXa, XII**, and **XVII**–**XXI** in $CDCl_3$ and of **VIIb** and **XVI** in C_6D_6 were measured on a Bruker WH-250 spectrometer(250 MHz) relative to TMS, and those of **V**, **VI**, **IXb**, and **XIV** in $CDCl_3$, on a Bruker AC-200 spectrometer (200 MHz). The ^{31}P NMR spectra of **VIIb, IXa, IXb, XVI, XVII**, and **XXI** in benzene, **VIIa**–**IXa, VIIb**–**IXb, XII**–**XIV**, and **XVI**–**XX** in methylene chloride, and **IIIa, IIIb, V,** and **VI** in acetonitrile were measure on a Bruker WP-80SY spectrometer at 32.4 MHz relative to 85% H_3PO_4.

The TLC analysis was performed on Silufol plates with the eluent systems benzene–dioxane, 5 : 1 (A), 10 : 1 (B), chloroform–methanol, 5 : 1 (C), and hexane–dioxane, 5 : 1 (D), 3 : 1 (E). The chromatograms were developed by exposure to iodine vapor, calcination, and treatment with 1% aqueous $AgNO_3$. Adsorption chromatography was performed in a column packed with silica gel L100/160.

1,4-Phenylene bis(tetraalkylphosphorodiamidites) IIIa and IIIb. To a solution of 67 mmol of hydroquinone in 30 ml of acetonitrile was added 21 mmol of hexaalkylphosphorous triamide, and the mixture was left for 24 h at room temperature. The solvent and excess triamide were distilled off in a vacuum, and the residue was distilled [bath temperature 140–180°C (**IIIa**), 180–200°C (**IIIb**), 10^{-4} mm].

1,4-Phenylene bis(tetramethylphosphorodiamidite) IIIa. Yield 40%, R_f 0.3 (A). ^1H NMR spectrum, δ, ppm: 1.08 d (24H, Me), 7.01 s (4H, CH). ^{31}P NMR spectrum: δ_P 136.7 ppm. Found, %: C 48.46; H 8.39; N 16.03; P 17.53. $C_{14}H_{28}N_4O_2P_2$. Calculated, %: C 48.54; H 8.15; N 16.17; P 17.92.

1,4-Phenylene bis(tetraethylphosphorodiamidite) IIIb. Yield 52%, R_f 0.8 (A). ^1H NMR spectrum, δ, ppm: 1.08 t (24H, Me), 3.12 m (16H, CH_2), 6.91 s (4H, CH). ^{31}P NMR spectrum: δ_P 133 ppm. Found P, %: 13.50. $C_{22}H_{44}N_4O_2P_2$. Calculated P, %: 13.54.

1,4-Phenylene bis(tetraethylphosphorodiamidothioate-*O*) V and 4-hydroxyphenyl tetraethylphosphorodiamidothioate-*O* VI. A solution of a mixture of 1 g of hydroquinone and 5.6 g of hexaethylphosphorous triamide in 20 ml of acetonitrile was stirred for 2 h, 0.6 g of sulfur was added, and the mixture was stirred for an additional 2 h at room temperature. The solution was filtered, the solvent was vacuum-evaporated, and the residue was purified by column chromatography (eluent benzene).

1,4-Phenylene bis(tetraethylphosphorodiamidothioate-*O*) V. Yield 1.25 g (34%), mp 111–112°C, R_f 0.87 (E). ^1H NMR spectrum, δ, ppm: 1.17 t (12H, Me), 3.22 m (8H, CH_2), 7.1 (4H, CH). ^{31}P NMR spectrum: δ_P 76.8 ppm. Found, %: C 49.42; H 5.69; N 10.81; P 12.54. $C_{22}H_{44}N_4O_2P_2S_2$. Calculated, %: C 50.57; H 8.43; N 10.72; P 11.88.

4-Hydroxyphenyl tetraethylphosphorodiamidothioate-*O* VI. Yield 0.978 g (40%), mp 110–111°C, R_f 0.76 (E). ^1H NMR spectrum, δ, ppm: 1.13 t (12H, Me), 3.2 m (8H, CH_2), 6.2 s (1H, OH), 6.71 d (2H, CH), 6.91 d (2H, CH). ^{31}P NMR spectrum: δ_P 76.7 ppm. Found, %: C 53.21; H 7.74; N 8.92; P 9.62. $C_{14}H_{25}N_2O_2PS$. Calculated, %: C 53.15; H 7.97; N 8.86; P 9.79.

Cyclobis(1,4-phenylene dialkylphosphoramidites) VIIa and VIIb. To a solution of 1.4 mmol of **IIIa** or **IIIb** in 10 ml of acetonitrile was added 1.4 mmol of hydroquinone. The mixture was stirred for 4 h at room temperature. The next day the solution was decanted from the oily product formed on the bottom, and the residue was washed with acetonitrile and vacuumdried (3 h, 50°C, 1 mm).

Cyclobis(1,4-phenylene dimethylphosphoramidite) VIIa. Yield 42%, R_f 0.8 (A). ^{31}P NMR spectrum: δ_P 140.03, 140.21 ppm. Found, %: C 52.51; H 5.68; N 7.42; P 16.68. $C_{16}H_{20}N_2O_4P_2$. Calculated, %: C 52.46; H 5.50; N 7.65; P 16.94.

Cyclobis(1,4-phenylene diethylphosphoramidite) VIIb. Yield 60%, R_f 0.78 (A), 0.62 (B). ^1H NMR spectrum, δ, ppm: 0.91 t (12H, Me, $^3J_{HH}$ 6.4 Hz), 3.1 m (8H, CH_2, $^3J_{PH}$ 9.82 Hz), 7.16 s (8H, CH). ^{31}P NMR spectrum: δ_P 142.46, 142.55 ppm (CH_2Cl_2), 141.8, 142.04 ppm (C_6H_6). Found P, %: 14.21. $C_{20}H_{28}N_2O_4P_2$. Calculated P, %: 14.69.

Cyclobis(1,4-phenylene dialkylphosphoramidates) VIIIa and VIIIb. To a solution of 0.45 mmol of cyclic phosphoramidite **VIIa** or **VIIb** in 15 ml of methylene chloride was added 0.9 mmol of the complex $H_2O_2(NH_2)_2CO$. The mixture was stirred for 2 h at room temperature. The solution was filtered, the solvent was vacuum-distilled, and the residue was recrystallized from acetonitrile (**VIIIa**) or purified by column chromatography, elution with chloroform–methanol, 10 : 1 (**VIIIb**). The phosphates were vacuum-dried for 2.5 h (70°C, 1 mm).

Cyclobis(1,4-phenylene dimethylphosphoramidate) VIIIa. Yield 86%, mp 80–82°C, R_f 0.56 (C). ^{1}H NMR spectrum, δ, ppm: 2.68 d (12H, Me, $^3J_{HH}$ 7.26 Hz), 7.26 s (8H, CH). ^{31}P NMR spectrum: δ_P 1.81, 2.2 ppm. Found, %: C 48.32; H 4.95; N 7.12; P 15.64. $C_{16}H_{20}N_2O_6P_2$. Calculated, %: C 48.25; H 5.06; N 7.04; P 15.55.

Cyclobis(1,4-phenylene diethylphosphoramidate) VIIIb. Yield 91%, mp 70–72°C, R_f 0.60 (C). ^{1}H NMR spectrum, δ, ppm: 1.02 t (12H, Me, $^3J_{HH}$ 6.83 Hz), 3.18 m (8H, CH_2, $^3J_{PH}$ 11.95 Hz), 7.18 s (8H, CH). ^{31}P NMR spectrum: δ_P 1.21, 1.34 ppm (CH_2Cl_2). Found P, %: 13.71. $C_{20}H_{28}N_2O_6P_2$. Calculated P, %: 13.63.

Cyclobis(1,4-phenylene dialkylphosphoramidothioates-*O,O'*) IXa and IXb. To a solution of 1.2 mmol of cyclic phosphoramidite **VIIa** or **VIIb** in 10 ml of methylene chloride was added 2.4 mmol of sulfur, and the mixture was stirred for 2.5 h at room temperature. The solution was filtered and vacuum-evaporated, and the residue was purified by column chromatography, eluent benzene–dioxane, 10 : 1. Products **IXa** and **IXb** were vacuum-dried (2.5 h, 60°C, 1 mm).

Cyclobis(1,4-phenylene dimethylphosphoramidothioate-*O,O'*) IXa. Yield 49%, mp 72–73°C, R_f 0.37 (A). ^{1}H NMR spectrum, δ, ppm: 2.95 d (12H, Me), 7.16 s (8H, CH). ^{31}P NMR spectrum: δ_P 68.80, 69.45 ppm (CH_2Cl_2), 68.28, 68.89 ppm (C_6H_6). Found, %: C 44.76; H 4.59; N 6.46; P 14.26. $C_{16}H_{20}N_2O_4P_2S_2$. Calculated, %: C 44.64; H 4.68; N 6.51; P 14.39.

Cyclobis(1,4-phenylene diethylphosphoramidothioate-*O,O'*) IXb. Yield 49%, mp 62–63°C, R_f 0.72 (A), 0.52 (B). ^{1}H NMR spectrum, δ, ppm: 1.12 t (12H, Me), 3.39 m (8H, CH_2), 7.15 s (8H, CH). ^{31}P NMR spectrum: δ_P 68.1, 68.63 ppm (CH_2Cl_2), 67.73, 68.36 ppm (C_6H_6). Found P, %: 12.54. $C_{20}H_{28}N_2O_4P_2S_2$. Calculated P, %: P 12.76.

Biphenyl-4,4'-diyl bis(tetramethylphosphorodiamidothioate-*O*) XII. To a solution of 0.121 g of 4,4'-dihydroxybiphenyl in 10 ml of acetonitrile was added 0.212 g of hexamethylphosphorus triamide. The solution was stirred for 5 min at room temperature, after which 0.041 g of sulfur was added, and the mixture was stirred for an additional 2 h at room temperature. The resulting precipitate was filtered off, washed with acetonitrile, and vacuum-dried (2.5 h, 60°C, 1 mm Hg). Yield of the colorless crystalline compound 0.188 g (62%), mp 216–218°C, R_f 0.60 (B), 0.32 (D). ^{1}H NMR spectrum, δ, ppm: 2.66 d (24H, Me, $^3J_{PH}$ 12.37 Hz), 7.05 d (4H, CH, $^3J_{HH}$ 8.96, $^4J_{HH}$ 1.71 Hz), 7.47 d (4H, CH, $^3J_{HH}$ 8.11 Hz). ^{31}P NMR spectrum: δ_P 81.2 ppm. Found, %: C 49.41; H 6.39; N 11.43; P 12.89. $C_{20}H_{32}N_4O_2P_2S_2$. Calculated, %: C 49.37; H 6.63; N 11.52; P 12.73.

Cyclobis(biphenyl-4,4'-diyl dimethylphosphoramidite) XIII. To a solution of 0.321 g of 4,4'-dihydroxybiphenyl in 10 ml of acetonitrile was added 0.282 g of hexamethylphosphorous triamide, and the mixture was stirred at room temperature for 4 h. The resulting colorless precipitate was filtered off, washed with acetonitrile, and vacuum-dried (3 h, 50°C, 1 mm Hg). Yield 0.351 g (78%), mp 153–155°C, R_f 0.86 (B). ^{31}P NMR spectrum: δ_P 140.3 ppm. Found, %: C 66.78; H 6.25; N 4.98; P 10.64. $C_{28}H_{28}N_2O_4P_2$. Calculated, %: C 66.89; H 6.32; N 4.88; P 10.78.

Biphenyl-4,4'-diyl bis(tetraethylphosphorodiamidothioate-*O*) XIV. To a solution of 0.161 g of 4,4'-dihydroxybiphenyl in 10 ml of acetonitrile was added 0.43 g of hexaethylphosphorous triamide. The mixture was stirred for 100 min at room temperature, after which 0.06 g of sulfur was added, and the mixture was stirred for an additional 2 h at room temperature. The solution was filtered to remove excess sulfur and vacuum-evaporated; the residue was purified by column chromatography, elution with benzene. Compound **XV** (yellow oil) was vacuum-dried (2.5 h, 60°C, 1 mm). Yield 0.41 g (69%), R_f 0.61 (B). ^{1}H NMR spectrum, δ, ppm: 1.16 t (24H, Me), 3.25 m (16H, CH_2), 7.18 d (4H, CH), 7.48 d (4H, CH). ^{31}P NMR spectrum: δ_P 76.1 ppm. Found P, %: 10.44. $C_{28}H_{48}N_4O_2P_2S_2$. Calculated P, %: 10.35.

Cyclobis(biphenyl-4,4'-diyl diethylphosphoramidite) XVI. To a solution of 0.18 g of 4,4'-dihydroxybiphenyl in 10 ml of acetonitrile was added 0.24 g of hexaethylphosphorous triamide. The mixture was stirred for 4 h at room temperature. After 20 h the solution was partially evaporated, and the colorless precipitate that formed was filtered off, washed with acetonitrile, and vacuum-dried (3 h, 50°C, 1 mm). Yield 0.149 g (84%), mp 89–90°C, R_f 0.76 (B). ^{1}H NMR spectrum, δ, ppm: 0.92 t (12H, Me), 3.14 m (8H, CH_2), 7.19 d (8H, CH, $^3J_{HH}$ 8.11 Hz), 7.29 d (8H, CH, $^3J_{HH}$ 8.53 Hz). ^{31}P NMR spectrum: δ_P 141.5 ppm. Found P, %: 10.65. $C_{32}H_{36}N_2O_4P_2$. Calculated P, %: P 10.78.

Cyclobis(biphenyl-4,4'-diyl diethylphosphoramidothioate-*O,O'*) XVII. To a solution of 0.196 g of **XVI** in 5 ml of methylene chloride was added 0.022 g of sulfur. The mixture was stirred for 1.5 h at room temperature. The solution was filtered, the solvent was removed in a vacuum, and the residue was puri-

fied by column chromatography, eluent benzene–dioxane, 10 : 1. The product **XVII** was vacuum-dried (2.5 h, 60°C, 1 mm). Yield 0.15 g (69%), mp 208–209°C, R_f 0.51 (B). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 1.11 t (12H, Me), 3.41 m (8H, CH_2), 7.27 d (8H, CH, $^3J_{HH}$ 7.24 Hz), 7.50 d (8H, CH, $^3J_{HH}$ 8.54 Hz). ^{31}P NMR spectrum: δ_P 67.44 ppm (CH_2Cl_2), 66.93 ppm (C_6H_6). Found, %: C 6.03; H 5.64; N 4.23. $C_{32}H_{36}N_2O_4P_2S_2$. Calculated, %: C 60.17; H 5.68; N 4.39.

Cyclobis(biphenyl-4,4'-diyl diethylphosphoramidate) XVIII. To a solution of 0.156 g of **XVI** in 10 ml of methylene chloride was added 0.051 g of $H_2O_2 \cdot (NH_2)_2CO$, and the mixture was stirred at room temperature for 2 h. The solution was filtered off, the solvent was distilled off in a vacuum, and the residue was recrystallized from acetonitrile and vacuum-dried (2.5 h, 70°C, 1 mm Hg), yield 0.15 g (91%), mp 206–207°C, R_f 0.60 (C). ^{1}H NMR spectrum, δ, ppm: 1.02 t (12H, Me, $^3J_{HH}$ 7.26 Hz), 3.20 m (8H, CH_2, $^3J_{PH}$ 12.1 Hz), 7.23 d (8H, CH, $^3J_{HH}$ 8.25 Hz), 7.43 d (8H, CH, $^3J_{HH}$ 8.79 Hz). ^{31}P NMR spectrum: δ_P 1.41 ppm (CH_2Cl_2). Found P, %: 10.09. $C_{32}H_{36}N_2O_6P_2$. Calculated P, %: 10.21.

μ-[Cyclobis(1,4-phenylene diethylphosphoramidite)]bis[acetylacetonatocarbonylrhodium(I)] XIX. A solution of 0.056 g of **VIIb** in 3 ml of methylene chloride was added dropwise to a solution of 0.068 g of Rh(acac)$(CO)_2$ in 3 ml of methylene chloride. The mixture was left for 24 h at room temperature. Compound XIX was reprecipitated from hexane, filtered, and vacuum-dried for 2 h (40°C, 1 mm). Yield 0.872 g (84%), decomposition point 164–167°C, R_f 0.48 (C). IR spectrum, ν, cm^{-1}: 1990 (CO–Rh), 1510, 1570 (*acac*). ^{1}H NMR spectrum, δ, ppm: 1.08 t (12H, Me, $^3J_{HH}$ 11.55 Hz), 1.66 s (3H, Me-*acac*), 2.01 s (3H, Me-*acac*), 3.51 m (8H, CH_2), 5.38 s (H, CH-*acac*) 7.19 s (8H, CH). ^{31}P NMR spectrum: δ_P 134.4 ppm (J_{PRh} 261.22 Hz). Found P, %: 7.91. $C_{32}H_{42}N_2O_{10}P_2Rh_2$. Calculated P, %: 7.88.

μ-[Cyclobis(biphenyl-4,4'-diyl diethylphosphoramidite)]bis[acetylacetonatocarbonylrhodium(I)] XX. A solution of 0.076 g of **XIIIb** in 3 ml of methylene chloride was added dropwise to a solution of 0.068 g of Rh(acac)$(CO)_2$ in 3 ml of methylene chloride. The mixture was left for 24 h at room temperature. Compound **XX** was reprecipitated from hexane, filtered, and vacuum-dried for 2 h (40°C, 1 mm). Yield 0.128 g (94%), decomposition point 175–177°C, R_f 0.62 (C). IR spectrum, ν, cm^{-1}: 1990 (CO–Rh), 1510, 1570 (*acac*). ^{1}H NMR spectrum, δ, ppm: 1.09 t (12H, Me, $^3J_{HH}$ 7.01 Hz), 1.51 s (3H, Me-*acac*), 1.96 s (3H, Me-*acac*), 3.57 m (8H, CH_2, $^3J_{PH}$ 11.95 Hz), 5.33 s (H, CH-*acac*), 7.28 d (8H, CH, $^3J_{HH}$ 8.11 Hz), 7.41 d (8H, CH, $^3J_{HH}$ 8.54 Hz). ^{31}P NMR spectrum: δ_P 133.72 ppm (J_{PRh} 260.98 Hz). Found, %: C 51.20; H 4.79; N 2.58. $C_{44}H_{50}N_2O_{10} \cdot P_2Rh_2$. Calculated, %: C 51.08; H 4.87; N 2.71.

μ-[Cyclobis(biphenyl-4,4'-diyl diethylphosphoramidite)]bis[pentacarbonylmolybdenum(0)] XXI. To a solution of 0.104 g of **XVI** in 2 ml of benzene was added 0.095 g of $Mo(CO)_6$, and the mixture was heated for 8 h in a sealed ampule at 95°C. The solution was decanted, the solvent was distilled off in a vacuum, and the residue was washed with acetonitrile and vacuum-dried (5 h, 50°C, 1 mm). Yield 0.064 g (34%), decomposition point 132–135°C, R_f 0.75 (A). ^{1}H NMR spectrum, δ, ppm: 1.2 t (12H, Me, $^3J_{HH}$ 7.15 Hz), 3.42 m (8H, CH_2), 7.26 d (8H, CH, $^3J_{HH}$ 8.25 Hz), 7.54 d (8H, CH, $^3J_{HH}$ 8.25 Hz). ^{31}P NMR spectrum: δ_P 164.6 ppm. Found, %: C 48.26; H 3.61; N 2.64. $C_{42}H_{36}Mo_2N_2O_{14}P_2$. Calculated, %: C 48.19; H 3.47; N 2.68.

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