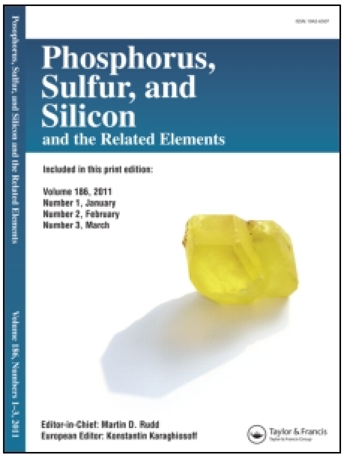

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Polyamidophosphite Complexes of Metals as Catalysts

Vera Yu. Mishina[a]; Irina V. Abrashina[a]; Andrei T. Teleshev[a]; Larisa K. Vasyanina[a]; Eduard E. Nifant'ev[a]
[a] Moscow Pedagogical State University, Moscow, Russia

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POLYAMIDOPHOSPHITE COMPLEXES OF METALS AS CATALYSTS

*Vera Yu. Mishina, Irina V. Abrashina, Andrei T. Teleshev,
Larisa K. Vasyanina, and Eduard E. Nifant'ev
Moscow Pedagogical State University, Moscow, Russia*

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Interaction between the equimolecular amounts of glycols (diatomic phenols) and phosphorous acid triamides in diglyme or without solvent gives phosphorus-bearing polyamidophosphites. The structure of these compounds was studied by NMR spectroscopy, and it was shown that a partial disproportionation of amidophosphite fragments into phosphite ones can occur in the course of their synthesis. The chemical properties of the obtained compounds are being studied. First rhodium complexes with polyamidophosphite ligands were obtained. These complexes are shown to be more active hydrogenation catalysts than the corresponding low-molecular complexes.[1]

Keywords: Complexation of polyamidophosphites on Rh(I); phosphorous acid triamides; phosphorylation; polyamidophosphites; polycondensation; subcatalysts of styrene hydrogenation

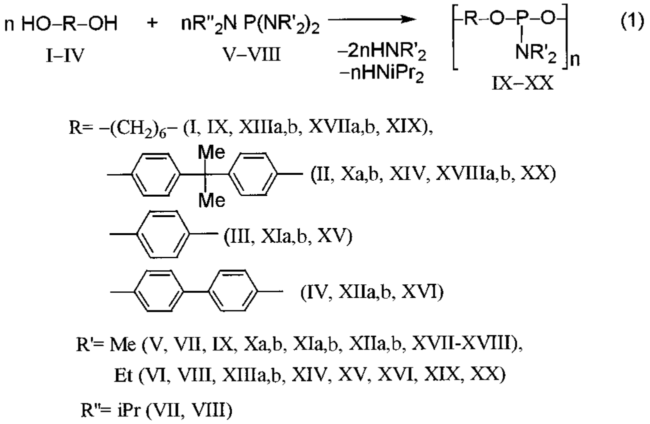
INTRODUCTION

Metallocomplexes with P(III)-derivatives of cellulose[2,3] or silica gel[4] as ligands have been described recently as hydrogenation catalysts. Unfortunately, these works were not extended, which was probably associated with experimental problems in the synthesis of ligands. In this context, we set ourselves the task of studying the design of metal complexes with arylene phosphites. First complexes were obtained in our laboratory by the interaction between the equimolecular amounts of phosphorous acid amides and different diols.[5] Their synthesis was analyzed,[6] but no structural studies were performed.

Address correspondence to Eduard E. Nifant'ev, Moscow Pedagogical State University, Moscow, 119021, Russia. E-mail: chemdept@mtu-net.ru

RESULTS AND DISCUSSION

In the present work polyalkylene and arylene amidophosphites were synthesized from diols: 1,6-hexanediol (**I**), 2,2′-bis(4-hydroxyphenyl) propane (**II**), hydroquinone (**III**), 4,4′-dihydroxydiphenyl (**IV**) and hexamethyl- and hexaethyltriamides as well as phosphorous acid tetramethyl- and tetraethyldiisopropylamides (**V–VIII**). Unsymmetrical triamides (**VII** and **VIII**) were selected on the supposition that the different reactivity of substituents in these compounds will result in the formation of polymers with diisopropylphosphamide groups in the main chain. Diols were selected because of the different spatial arrangement of their hydroxyl groups.



SCHEME 1

Phosphorylation was performed at the triamide:diol molar ratio of 1:1 without solvent (method A) and in diglyme (method B) with the distillation of the resulting amine (Scheme 1). Polyamidophosphites were obtained as gummy or glassy substances with a yield of 96–99%; they melt in a wide characteristic range (the difference between the beginning and end of melting reaches 16°C). Their molecular masses vary between 5000 and 15,000.

The obtained polyamidophosphites (**IX–XX**) swell in organic solvents such as chloroform, diglyme, and dioxane (Figures 1 and 2), which allowed us to record their signals in the ^{31}P (δ_P139–146 ppm) and ^{1}H NMR spectra (see Experimental) and to carry out some reactions with trivalent phosphorus compounds. It should be noted that a signal with δ_P 128 ppm, which corresponds to neutral phosphites, was observed in some ^{31}P MNR spectra along with signals at δ_P 139 ppm

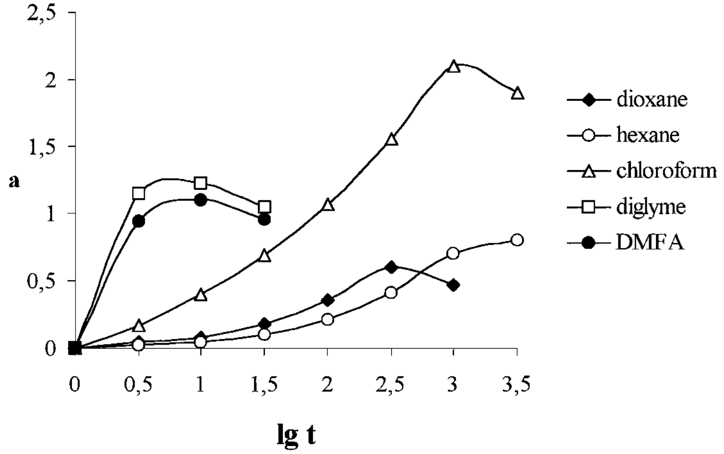


FIGURE 1 The swelling index of polymer **Xa** as a function of the organic solvent nature (25°C; $\boldsymbol{a} = (\boldsymbol{m}-\boldsymbol{m}_0)/\boldsymbol{m}_0$, where $\boldsymbol{m}_0$ is the mass of the initial polymer, $\boldsymbol{m}$ is the mass of the swollen polymer, and $\boldsymbol{t}$ is the time of swelling, s).

attributed to the diphosphamide fragment. These data indicate that the obtained polyamidophosphites can participate in exchange processes of substituents at the phosphorus atom. The ^{1}H and ^{31}P NMR data, as well as the determination of reaction mixture masses, allowed us to draw the final conclusion about the nature of substituents at the phosphorus atom in the elementary unit of the main chain of polyphosphites

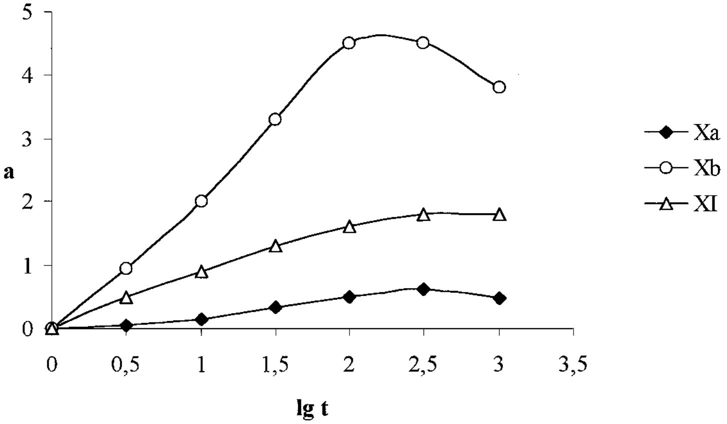
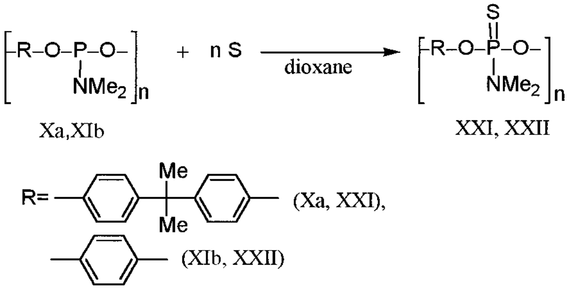


FIGURE 2 The swelling index of polyamidophosphites in dioxane as a function of the polymer nature (25°C; $\boldsymbol{a} = (\boldsymbol{m}-\boldsymbol{m}_0)/\boldsymbol{m}_0$, where $\boldsymbol{m}_0$ is the mass of the initial polymer, $\boldsymbol{m}$ is the mass of the swollen polymer, and $\boldsymbol{t}$ is the time of swelling, s).

XVII–XX. The substitution of the diisopropylamide group at the phosphorus atom in triamide (**VII** or **VIII**) occurred in this case, which refuted our supposition about the N(i-Pr)$_2$-substituents at the phosphorus atom in the main chain of the polyphosphites obtained.

Polyamidophosphites **Xa** and **XIb** swollen in dioxane react with elementary sulphur at 100°C to form the corresponding polythionamidophosphates **XXI** and **XXII** (Scheme 2):

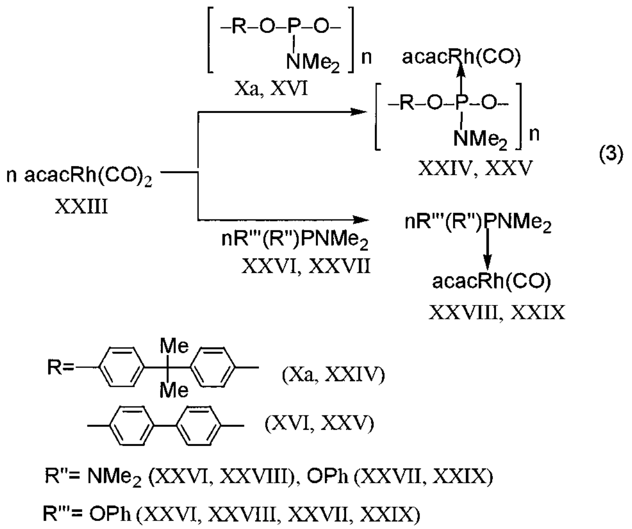


SCHEME 2

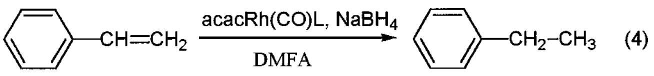
Signals at 69 and 53 ppm corresponding to the thionamidophosphate fragments were observed in the ^{31}P NMR spectra of **XXI** and **XXII**. In the ^{1}H NMR spectra, signals from all protons of elementary units were observed (see Experimental). Polythionamidophosphate **XXI** is a yellowish glassy substance with m.p. 230–240°C; polythionamidophosphate **XXII** is a yellowish elastic compound with m.p. 170–175°C. The resistance of these compounds to the air moisture is noteworthy.

It is interesting that the stability of initial polyamidophosphites is similar to that of polythionamidophosphites: no signals from the pentavalent phosphorus nuclei were found in their ^{31}P NMR spectra even after the storage in the air for three months. This property of polyamidophosphites is noteworthy and can be useful for their practical use.

Complexation of polyamidophosphites on Rh(I) was performed with rhodium(I) dicarbonyl acetylacetonate **XXIII** (Scheme 3). The reaction proceeded in diglyme at 20°C for 1 h. In accordance with the IR-spectral data, only one carbonyl group in complex **XXIII** was substituted in this case (Table I). The disappearance of the signal from the initial polyamidophosphate and the appearance of a new doublet with characteristic coupling constants $^{1}J_{PRh}$ were observed in the ^{31}P NMR spectrum (Table I). The comparison of the spectral parameters of rhodium polyamidophosphite complexes with the data for model complexes, which were obtained in the reaction of low-molecular phosphorous acid amides **XXVI** and **XXVII** with rhodium(I) dicarbonyl acetylacetonate



SCHEME 3



SCHEME 4

(Scheme 3, Table I), confirmed that the elementary unit of the polymers obtained includes the [$O_2P(NR_2)$] function.

The catalytic activity of polyamidophosphite complexes **XXIV** and **XXV** was studied in the reaction of styrene hydrogenation (Scheme 4). The reaction was performed at 50°C and atmospheric pressure of hydrogen.

TABLE I Spectral Parameters of Rhodium Complexes with Poly- and Monoamidophosphites

AcacRh(CO)L, where L is	^{31}P NMR spectrum (diglyme) δ_P, ppm	$^{1}J_{PRh}$, Hz	IR spectrum, ν, cm^{-1}
XXIV	134	262	1985
XXV	134	261	1985
XXVIII	124	220	1960
XXIX	135	265	1985

It was found that the hydrogenation rate of styrene with subcatalysts **XXIV** and **XXV** is doubled in comparison with the known catalysts of this kind.[1] The relatively high stability of rhodium polamidophosphite catalysts, which remain active after the hydrogenation of 1600 mol of substrate per 1 mol of metal, is also noteworthy. Therefore, it can be suggested that the new polymeric catalysts are more promising than the known catalyst types.[1]

EXPERIMENTAL

The synthesis of polyphosphites was performed in diglyme (method A) and without solvent (method B). ^{1}H NMR spectra in $CDCl_3$ were recorded with Bruker AC-200 and Bruker AM-400 instruments using TMS as an internal standard. ^{31}P NMR spectra in dioxane or diglyme were recorded with a Bruker WP-80 instrument (at 32.4 MHz, 85% H_3PO_4 as an external standard). The molecular mass of compounds was determined by gel-permeation chromatography with a Waters instrument and Styragel columns (10^3Å, 10^5Å, linear). A Waters-410 refractometer/diffusiometer was used as a detector. A Data-Modul-730 integrator was used for calculation. An HPLC pump (Waters Model 590) was used. Calibration was performed with polystyrene standards (Waters). IR spectra were recorded with a Specord 75 IR spectrometer.

Polyphosphite IX. Triamide **V** (0.82 g, 5.1 mmol) was added to 0.59 g (5.1 mmol) of diol **I** in 2 ml of diglyme, and the reaction mixture was stirred at 80–90°C for 4 h. The solvent was removed at 80°C (1 mm Hg); the residues was dried in vacuum. Yield 0.96 g (97%); m.p. 260–275°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.38 s (4H, $C\underline{H}_2$), 2.6 d (6H, $N(C\underline{H}_3)_2$, $^3J_{HP}$ 8.47 Hz), 1.6 s (4H, $C\underline{H}_2$), 3.6 m (4H, $C\underline{H}_2$, $^3J_{HH}$ 1.6 Hz). ^{31}P NMR (dioxane, δ, ppm): 145, 139 (5:1). Mr 5500.

Polyphosphite Xa. It was obtained analogously to **IX** from 2.67 g (11.7 mmol) of phenol **II** in 3 ml of diglyme and 1.90 g (11.7 mmol) of triamide **V** at 80°C (5 h). Yield 3.53 g (99%); m.p. 290–300°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.62 s (6H, $C(C\underline{H}_3)_2$), 2.77 d (6H, $N(C\underline{H}_3)_2$, $^3J_{HP}$ 9.35 Hz), 6.92 d (4H, $C\underline{H}$ arom., $^3J_{HH}$ 8.29 Hz), 7.11 d (4H, $C\underline{H}$ arom., $^3J_{HH}$ 8.25 Hz). ^{31}P NMR (diglyme, δ, ppm): 139. Mr 15 000.

Polyphosphite Xb was obtained analogously to **IX** from 3.35 g (14.7 mmol) of phenol **II** in 3 ml of diglyme and 2.39 g (14.7 mmol) of triamide **V** at 70–80°C (4 h). Yield 4.09 g (98%); m.p. 252–260°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.62 s (6H, $C(C\underline{H}_3)_2$), 2.75 d (6H, $N(C\underline{H}_3)_2$, $^3J_{HP}$ 9.39 Hz), 6.92 d (4H, $C\underline{H}$ arom., $^3J_{HH}$ 8.53 Hz), 7.12 d (4H, $C\underline{H}$ arom., $^3J_{HH}$ 8.11 Hz). ^{31}P NMR (diglyme, δ, ppm): 139. Mr 9500.

Polyphosphite XIa. Triamide **V** (1.07 g, 6.59 mmol) was added to 0.72 g (6.59 mmol) of phenol **III**. The reaction mixture was stirred at 70–80°C for 3 h and then kept in the vacuum at 80°C (1 mm Hg) for 2 h. Yield 1.19 g (98%); m.p. 290–297°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.38 s (4H, C$\underline{H}_2$), 2.75 d (6H, N(C$\underline{H}_3$)$_2$, $^3J_{HP}$ 9.39 Hz), 6.87 s (4H, C$\underline{H}$ arom., $^3J_{HH}$ 8.09 Hz). ^{31}P NMR (diglyme, δ, ppm): 140.

Polyphosphite XIb was obtained analogously to **IX** from 3.32 g (2.92 mmol) of phenol **III** in 1.5 ml of diglyme and 0.47 g (2.92 mmol) of triamide **V** at 100–110°C (9 h). Yield 0.86 g (97%); m.p. 284–290°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.75 d (6H, N(C$\underline{H}_3$)$_2$), 6.87 s (2H, C$\underline{H}$ arom.), 7.08 s (2H, C$\underline{H}$ arom.). ^{31}P NMR (diglyme, δ, ppm): 139.

Polyphosphite XIIa was obtained analogously to **IX** from 0.60 g (3.2 mmol) of phenol **IV** in 1.5 ml of diglyme and 0.52 g (3.2 mmol) of triamide **V** at 100°C (8 h). Yield 1.21 g (99%); m.p. 185–190°C. ^{31}P NMR (dioxane, δ, ppm): 140.

Polyphosphite XIIb was obtained analogously to **XIa** from 0.87 g (4.6 mmol) of phenol **IV** and 0.76 g (4.6 mmol) of triamide **V** at 100°C (14 h). Yield 1.16 g (95%); m.p. 264–280°C. ^{31}P NMR (dioxane, δ, ppm): 140, 139 (4:1).

Polyphosphite XIIIa was obtained analogously to **IX** from 0.23 g (1.98 mmol) of diol **I** in 2 ml of diglyme and 0.49 g (1.98 mmol) of triamide **VI** at 100–110°C (25 h). Yield 0.39 g (98%); m.p. 248–258°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.13 m (6H, N(CH$_2$—C$\underline{H}_3$)$_2$, 1.38 s (4H, C$\underline{H}_2$), 1.6 s (4H, C$\underline{H}_2$), 2.6 d (4H, N(C$\underline{H}_2$ CH$_3$)$_2$, $^3J_{HP}$ 8.47 Hz), 3.6 m (4H, CH$_2$, $^3J_{HH}$ 1.6 Hz). ^{31}P NMR (dioxane, δ, ppm): 146, 139 (10:1).

Polyphosphite XIIIb was obtained analogously to **XIa** from 0.37 g (3.17 mmol) of diol **I** and 0.81 g (3.17 mmol) of triamide **VI** at 80–90°C (3 h). Yield 0.72 g (98%); m.p. 274–280°C. ^{31}P NMR (dioxane, δ, ppm): 146, 139 (4:1).

Polyphosphite XIV was obtained analogously to **IX** from 1.55 g (6.79 mmol) of phenol **II** in 2 ml of diglyme and 1.68 g (6.79 mmol) of triamide **VI** at 80°C (25 h). Yield 1.95 g (87%); m.p. 310–315°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.04 t (6H, N(CH$_2$ C$\underline{H}_3$)$_2$, $^3J_{HP}$ 6.83 Hz), 1.61 s (6H, N(C$\underline{H}_3$)$_2$), 3.21 t (4H, N(C$\underline{H}_2$ CH$_3$)$_2$), 6.92 d (4H, C$\underline{H}$ arom., $^3J_{HH}$ 8.97 Hz), 7.1 d (4H, C$\underline{H}$ arom., $^3J_{HH}$ 8.54 Hz). ^{31}P NMR (dioxane, δ, ppm): 140.

Polyphosphite XV was obtained analogously to **XIa** from 0.46 g (4.2 mmol) of phenol **III** and 1.04 g (4.2 mmol) of triamide **VI** at 100°C (6 h). Yield 0.96 g (91%); m.p. 280–287°C. ^{31}P NMR (dioxane, δ, ppm): 142, 129 (15:1).

Polyphosphite XVI was obtained analogously to **XIa** from 0.62 g (3.36 mmol) of phenol **IV** and 0.83 g (3.36 mmol) of triamide **VI** at

100°C (4 h). Yield 0.88 g (91%); m.p. 290–300°C. ^{31}P NMR (dioxane, δ, ppm): 140.

Polyphosphite XVIIa. Triamide **VII** (1.7 g, 7.8 mmol) was added to 0.91 g (7.8 mmol) of diol **I** in 2 ml of diglyme. The reaction mixture was stirred at 70–80°C for 5 h and kept at 60°C (1 mm Hg) for 2 h. Yield 1.72 g (90%); m.p. 250–258°C. ^{31}P NMR (benzene, δ, ppm): 146, 139 (1.5:1).

Polyphosphite XVIIb was obtained analogously to **XVIIa** from 0.83 g (7.03 mmol) of diol **I** in 2 ml of diglyme and 1.54 g (7.03 mmol) of triamide **VII** at 110°C (6 h). The reaction mixture was kept at 80°C (1 mm Hg) for 3 h. Yield 1.48 g (85%); m.p. 225–230°C. ^{31}P NMR (benzene, δ, ppm): 145, 138 (10:1).

Polyphosphite XVIIc was obtained analogously to **XVIIa** from 0.86 g (7.26 mmol) of diol **I** in 2 ml of diglyme and 1.59 g (7.26 mmol) of triamide **VII** at 160–170°C (2 h). The reaction mixture was kept at 80°C (1 mm Hg) for 3 h. Yield 1.68 g (94%); m.p. 250–260°C. ^{31}P NMR (benzene, δ, ppm): 145, 138 (10:1).

Polyphosphite XVIIIa was obtained analogously to **XVIIa** from 1.04 g (5.6 mmol) of phenol **II** in 2 ml of diglyme and 1.01 g (5.6 mmol) of triamide **VII** at 80°C (6 h). The reaction mixture was kept at 70°C (1 mm Hg) for 2 h. Yield 1.54 g (93%); m.p. 210–215°C. ^{31}P NMR (benzene, δ, ppm): 139.

Polyphosphite XVIIIb was obtained analogously to **XVIIa** from 2.09 g (3.19 mmol) of phenol **II** and 2.01 g (3.19 mmol) of triamide **VII** in 2 ml of diglyme at 150–160°C (3 h). The reaction mixture was kept at 80°C (1 mm Hg) for 3 h. Yield 3.03 g (92%); m.p. 305–310°C. ^{31}P NMR (benzene, δ, ppm): 139.

Polyphosphite XVIIIc obtained analogously to **XVIIa** from 1.66 g (7.6 mmol) of triamide **VII** and 1.73 g (7.6 mmol) of phenol **II** in 2 ml of diglyme at 100–110°C (5 h). The reaction mixture was kept at 80°C (1 mm Hg) for 3 h. Yield 2.24 g (85%); m.p. 270–274°C. ^{31}P NMR (benzene, δ, ppm): 139.

Polyphosphite XVIIId. Triamide **VII** (1.49 g, 6.8 mmol) was added to 1.55 g (6.8 mmol) of phenol **II**. The reaction mixture was stirred at 100–110°C for 5 h and kept at 60°C (1 mm Hg) for 3 h. Yield 2.29 g (94%); m.p. 230–235°C. ^{31}P NMR (benzene, δ, ppm): 139.

Polyphosphite XIX was obtained analogously to **XVIIId** from 0.47 g (3.9 mmol) of diol **I** and 1.09 g (3.9 mmol) of triamide **VIII** at 100–110°C (1 h). The reaction mixture was kept at 80°C (1 mm Hg) for 1 h. Yield 1.24 g (95%); m.p. 270–274°C. ^{31}P NMR (benzene, δ, ppm): 147.

Polyphosphite XX was obtained analogously to **XVIIId** from 0.85 g (3.72 mmol) of phenol **II** and 1.03 g (3.72 mmol) of triamide **VIII** at 80°C

(1 h). The reaction mixture was kept at 80°C (30 mm Hg) for 0.5 h. Yield 1.74 g (93%); m.p. 290–295°C. ^{31}P NMR (benzene, δ, ppm): 147.

Polythionophosphate XXI. Finely ground sulphur (0.09 g, 2.8 mmol) was added to 0.85 g (2.8 mmol) of polyphosphite **Xa** in 1.5 ml of dioxane, and the reaction mixture was stirred at 60–70°C for 3 h. The solvent was removed in the vacuum. Yield 0.92 g (97%); m.p. 230–240°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.75 s (6H, $C(C\underline{H}_3)_2$), 2.6 d (6H, $N(C\underline{H}_3)_2$), 6.98 m (4H, $C\underline{H}$ arom.), 7.15 m (4H, $C\underline{H}$ arom., $^{3}J_{HH}$ 7.11 Hz). ^{31}P NMR (dioxane, δ, ppm): 67.

Polythionophosphate XXI was obtained analogously to **XXI** from 0.05 g (0.35 mmol) of polyphosphite **XIb** in 2.3 ml of dioxane and 0.01 g (0.35 mmol) of sulphur. Yield 0.06 g (96%); m.p. 170–175°C. ^{31}P NMR (dioxane, δ, ppm): 69.

Complexes XXIV, XXV, XXVIII, XXIX. A solution of 2 mmol of polyphosphite **Xa** or **XVI** or amidophosphite **XXVI** or **XXVII** in diglyme was added to a solution of 2 mmol $acacRh(CO)_2$ in 1 ml of diglyme, and the reaction mixture was kept at 20°C for 2 h. The solvent was removed in the vacuum, and the residue was dried in the vacuum at 70–80°C. Spectral parameters of products are given in the table.

Hydrogenation of styrene on subcatalysts XXIV, XXV was performed in accordance with the procedure descried.[1] A solution of the catalyst-precursor complex was prepared in the open air by the reaction of the corresponding organophosphorus compound with a solution of $4{,}3 \times 10^{-5}$ mol $acacRh(CO)_2$ in 5 ml of DMFA. The subcatalyst was activated by 10^{-3} g $NaBH_4$ for 5 min. Hydrogenation was carried out in a glass hydrogenation reactor at 50°C and 1 atm. of hydrogen. The solution of catalyst precursor was placed in the reactor and blown with the five-fold volume of hydrogen; styrene was introduced with a syringe through a silicone membrane at the styrene: rhodium molar ratio of 100. The moment when the shaker (700–800 swing/min) was switched on was taken as the beginning of the reaction. The reaction was monitored by the determination of the amount of hydrogen absorbed per unit time and by GLC on a LKhM-8MD instrument, with a thermal-conductivity detector and helium as carrier gas (40 ml/min). A column (1.5 m long and 3 mm in diameter) with 15% methysilicone SE 30 on Chromaton HMDS was used for separating the mixtures analyzed.

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