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The First Representatives of Dipentaerythrite Perphosphites

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Abstract—The first representatives of dipentaerythrite perphosphites were prepared by phosphorylation of aliphatic hexaol dipentaerythrite with 1,3-alkylenchloro- and 1,3- alkylenamidophosphites. The processes of oxidation, sulfurization, hydrolysis, and complex formation of the prepared compounds were investigated.

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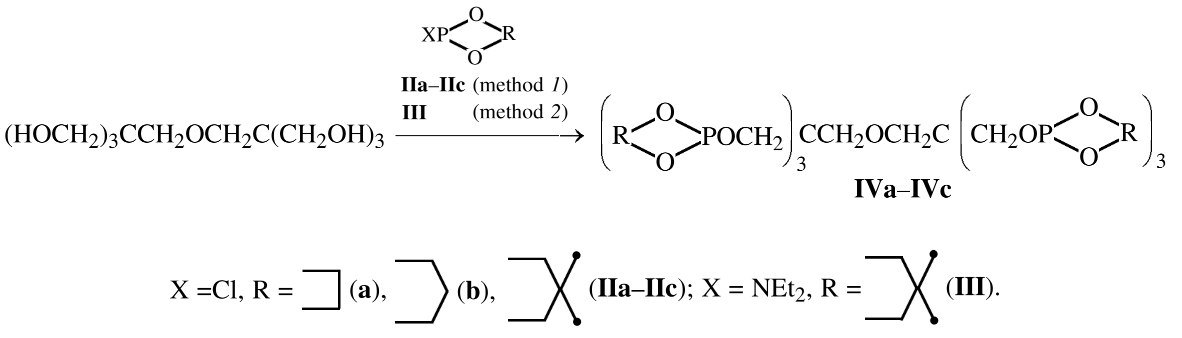
To the present time complete phosphorylation of aliphatic compounds containing from two to four nonprotected hydroxyl groups with phosphoric acid derivatives has been carefully studied [1–6]. Developing this study we decided to expand it over phosphorylation of more complicated systems which are interesting for nano-chemistry. The particular object of the study was the process of phosphorylation of accessible symmetrical hexaol dipentaerythrite and chemical behavior of the obtained hexaphosphites for revealing perspectives for their synthetic application.

We found that dipentaerythrite **I** is prone to effective phosphorylation by sixfold molar quantity of monophosphorylating reagents in a dioxane–pyridine solutions. The reagents used were 1,3-alkylene chlorophosphites **IIa**–**IIc** (method *1*), and neopentylene diethylamidophosphite **III** (method *2*). Alkylene chlorophosphites were: ethylene- **IIa**, propylene- **IIb**, and neopentylenechlorophosphites **IIc**. Phosphorylation with chlorides **IIa**–**IIc** was carried out at 0°C, and phosphorylation with amidophosphite **III** at 100°C with distilling the eliminating diethylamine off.

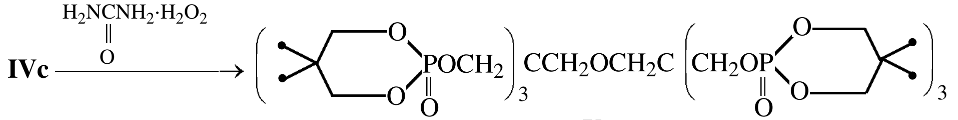


(1)

The target peralkylene phosphites **IVa**–**IVc** were purified by filtration of solutions of the crude compounds through a silica gel layer. The yields were 60–85%. We did not find a significant difference in the efficiency of the syntheses proceeded by method *1* or method *2*. All prepared phosphites **IVa**–**IVc** are stable at storage in an inert atmosphere at room temperature for a long time. Note that ethylenephosphite **IVa** and propylenephosphite **IVb** show hygroscopic property and unlike neopentylenphosphite **IVc** were readily hydrolyzed being exposed to air.

In the ^{31}P NMR spectra of phosphites **IVa**–**IVc** there are the singlet signals in the fields characteristic of cyclic phosphites, and in their ^1H NMR spectra the signals of the all protons confirming the structure of the obtained compounds were obsered (see Experimental). Thus, the resonance of methylene protons of the molecule carcass was observed as singlet signals at δ 3.47 to 3.69 ppm, and the signal of CH_2OP groups protons appeared as a doublet at δ 4.17 ppm and had characteristic coupling constant with phosphorus nuclei. In the ^1H NMR spectrum of ethylenephosphite **IVa** a multiplet of methylene protons involved into phospholane ring was found at δ 4.48 ppm, and in the ^{1}H NMR spectrum of propylenephosphite **IVb** the axial and equatorial protons of phosphorinane rings were registered as characteristic multiplets at δ 1.85, 2.30 ppm, and δ 4.40, 4.60 ppm. In the spectrum of neopentylenphosphite **IVc** the axial and equatorial protons of phosphorinane rings were fixed at δ 3.92 and 4.28 ppm, and two singlet signals at δ 0.93 and 1.23 ppm corresponding to the methyl groups protons were observed.

In the present work we began studying chemical behavior of the prepared phosphites, specifically the oxidizing processes with their participation. We used adduct of carbamide with hydrogen peroxide as an oxidizer. In the case of ethylenephosphite **IVa** and propylenephosphite **IVb** under the considered conditions (20°C, 5 h) the corresponding alkylene phosphates formed as traces only. This fact probably is due to low hydrolytic stability of the starting phosphites. At the same time oxidation of neopentylenphosphite **IVc** afforded the goal phosphate **V** in 60% yield.



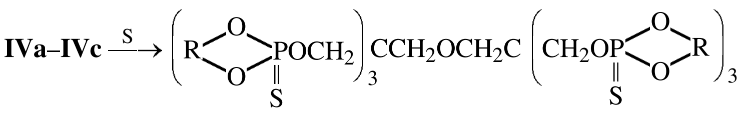
V

(2)

The process of alkylenphosphites **IVa**–**IVc** oxidizing was monitored by means of ^{31}P NMR spectroscopy through observation of disappearance of the phosphite signals and growing the signals characteristic of alkylene phosphates.

Alkylenphosphate **V** is a very hygroscopic oily substance. It should be stored at –5°C in an inert atmosphere.

The sulfurization of alkylenphosphites **IVa**–**IVc** was carried out at 40–80°C in dioxane for 3–5 h. The yields of chromatographically pure products **VIa**–**VIc** attained 80%.



VIa–**VIc**

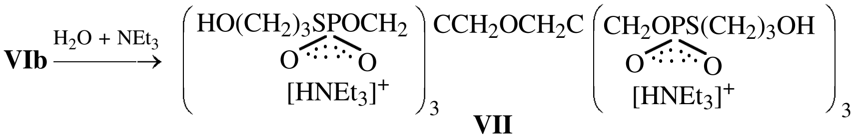
(3)

For R, see sheme (1).

Alkylene thionophosphates **VIa**–**VIc** are crystals with high melting points, stable at storage in an inert atmosphere for several months.

Individuality and structure of alkylene phosphate **V** and alkylene thionophosphates **VIa**–**VIc** were proven by the means of TLC together with ^{31}P and ^{1}H NMR spectroscopy. In the ^{31}P NMR spectra of compounds **V** and **VIa**–**VIc** occurred singlets at δ_P –7.17, and 83.46, 62.09, 61.53 ppm, respectively. The ^{1}H NMR spectra were similar to the spectra of alkylenphosphites **IVa**–**IVc** described above and they perfectly confirmed the considered structures (see Experimental).

We studied hydrolysis of alkylenthionphosphate **VIb**. The reaction was carried out in dioxane medium in the presence of triethylamine 10-fold excess at 120°C. In the ^{31}P NMR spectrum of hexaphosphoammonium salt **VII** we observed a signal at δ_P 16.31 ppm characteristic for thiolophosphates indicating that thion-thiol isomerization took place during the process [7, 8]:



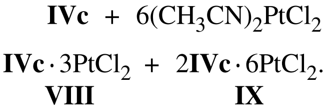
VII

(4)

In the ^1H NMR spectrum of compound **VII** remained the signals of the protons at the molecular carcass and appeared the signals of the corresponding protons of ethylammonium groups. A specific feature of this spectrum is differentiation of the signals of α-, β-, and γ-methylene protons of $SCH_2CH_2CH_2OH$ group.

The next stage of our work we devoted to investigation of possible application of dipentaerythrite peralkylenphosphites as ligands at the synthesis of coordination compounds with the transition metals (*d*-elements) derivatives. Here the best results we gained with hexaneopentylenphosphite **IVc** used as a ligand and platinum and with palladium as complexing agents.

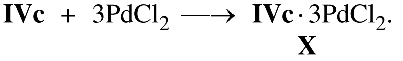
We found that hexaphosphite **IVc** reacts with platinum(II) dichlorodiacetonitrilate at room temperature in various solvents: chloroform (method *a*), benzene (method *b*), at the molar ratio of the reagents 1 : 6. Regardless from the applied solvent the complex formation led to a mixture of substances, of which two products were isolated: a monomeric compound **VIII**, with participation of six phosphorus atoms, and a dimeric product **IX** with participation of twelve phosphorus atoms, as was evidenced by MALDI–TOF spectroscopy [9].



$$\mathbf{IVc} + 6(CH_3CN)_2PtCl_2$$
$$\underset{\mathbf{VIII}}{\mathbf{IVc}\cdot 3PtCl_2} + \underset{\mathbf{IX}}{2\mathbf{IVc}\cdot 6PtCl_2}. \qquad (5)$$

The platinum complexes **VIII** and **IX** were isolated from a solution in chloroform by precipitation into hexane, and in the case of the reaction proceeding in benzene the products spontaneously precipitated from the solution. The complexes are powders stable at storage. In the ^1H NMR spectra of the prepared complexes there are all signals characteristic of the ligand **IVc**. This fact evidences that in the process of the complex formation the hexaphosphite structure remains intact. At the same time planar square constructions **VIII** and **IX** prepared in chloroform or benzene are significantly differ by their steric structures. In the chloroform medium, a mixture of the complexes was obtained showing in the ^{31}P NMR spectrum a singlet signal at δ_P 67.83 ppm and the constant of coupling with platinum J_{PPt} 5821.6 Hz. This constant evidences cisarrangement of the phosphorus atoms [10–12]. In benzene as a solvent, the complexes **VII** and **IX** were formed as mixtures of *cis*- and *trans*-configurations. This fact was elucidated proceeding from the value of the chemical shift of phosphorus nucleus and coupling constant with platinum in the ^{31}P NMR spectrum, δ_P 65.41 ppm (J_{PPt} 5751.8 Hz), and δ_P 83.33 ppm (J_{PPt} 3455.67 Hz).

Moreover, we conducted the reaction of hexaphosphite **IVc** with palladium chloride. Here we obtained complex **X**:



$$\mathbf{IVc} + 3PdCl_2 \longrightarrow \underset{\mathbf{X}}{\mathbf{IVc}\cdot 3PdCl_2}. \qquad (6)$$

The reaction was carried out at room temperature in methylene chloride for 1.5 h. Compound **X** was purified by precipitation into hexane from methylene chloride. The product is powder stable at storage. According to the MALDI–TOF spectra the complex is formed with participation of six phosphorus atoms only. This fact distinguishes this Pd-complex from the considered above Pt-complexes where either six or twelve phosphorus atoms were involved to the complex. In the ^1H NMR spectrum of complex **X** occurred all signals of the starting ligand, and in the ^{31}P NMR spectra there was a broad singlet at the field δ_P 90 ppm.

Summarizing the results of this work it may be concluded that we succeed to create an effective method of synthesis of dipentaerythrite peralkylenephosphites. Moreover we showed that dipentaerythrite hexaneopentylene phosphite **IVc** can be used as a ligand for preparation of stable complex platinum and palladium compounds which may be regarded to the original nanoformations.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz), the chemical shifts were measured against internal TMS. For assignment of the protons signals the method of double magnetic resonance was applied. The ^{31}P–$\{^1H\}$ spectra were registered on a Bruker WP-80SY instrument operating at 32.4 MHz, the chemical shifts were measured against 85% phosphoric acid.

Monoisotopic (^{12}C) molecular masses of substances were measured on a Bruker UltraFlex (Bruker Daltomics, FRG) instrument for positive ions in reflection regime with N_2 laser (λ 337 nm), accelerating voltage 25 kV.

For elemental analysis a Perkin-Elmer 2400 instrument was used. All synthesis with participation of trivalent phosphorus compounds were carried out in the atmosphere of dry argon.

The adsorption chromatography was performed on a column of 15 mm diameter with a silica gel L 100–

250 μm; values R_f were determined by TLC method on the Silufol UV-254 plates eluting by benzene–dioxane, 3 : 1 (A), hexane–dioxane, 3 : 1 (B), chloroform–methanol, 3 : 1 (C), and chloroform–methanol–water, 65 : 25 : 4 (D) solutions.

Melting points were measured into a sealed capillary at heating with the rate of 1 deg per min.

2-Chloro-1,3,2-dioxaphospholane **IIa** was prepared by the method described earlier [13], 2-chloro-1,3,2-dioxaphosphorinane **IIb** was synthesized by the procedure [14], 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **IIc** was obtained by the method [15], 2-diethylamido-5,5-dimethyl-1,3,2-dioxaphosphrinane **III** was prepared by the method [16], and platinum(II) dichlorodiacetonitrilate was produced alongside the method [17]. The prepared compounds had the same coupling constants as had described.

Dipentaerythrite hexaethylene phosphite (IVa). To a solution of 0.75 g of 2-chlorodioxaphospholane **IIa** in 5 ml of anhydrous dioxane, 0.25 g of dipentaerythrite **I** in 5 ml of absolute pyridine was added dropwise at cooling to 0°C and stirring. The reaction mixture was kept at this temperature for 0.5 h and then the temperature was increased to room for 0.5 h. The formation of ethylene phosphite **IVa** was monitored by ^{31}P NMR spectroscopy. ^{31}P NMR spectrum, (dioxane), δ_P, ppm: 134.40 br.s. Pyridine hydrochloride was filtered off, and the filtrate was filtered through the silica gel layer (1 g). Then solvents were removed in a vacuum, and the residue was kept for 2 h at 40C (1 mm Hg) yielding 0.48 g (60%) of compound **IVa**, 1.5890, R_f 0.80 (A). ^1H NMR spectrum (C_6D_6), δ, ppm: 3.47 br.s (4H, CH_2OCH_2), 4.17 d (12H, CH_2OP, $^3J_{HP}$ 10.9 Hz), 4.48 m (24H, OCH_2CH_2O). ^{31}P NMR spectrum (benzene), δ_P, ppm: 134.61 br.s. Found, %: C 33.05; H 4.98; P 23.11. $C_{22}H_{40}O_{19}P_6$. Calculated, %: C 33.26; H 5.08; P 23.39. *M* 794.412.

Dipentaerythrite hexa-1,3-propylene phosphite (IVb) was prepared similarly to compound **IVa** from 1.7 g of 2-chloro-1,3,2-dioxaphosphorinane **IIb** and 0.5 g of dipentaerythrite **I** in 7 ml of anhydrous dioxane and 7 ml of absolute pyridine respectively. The formation of propylenephosphite **IVb** was monitored by ^{31}P NMR spectroscopy. ^{31}P NMR spectrum (dioxane), δ_P, ppm: 129.90 br.s. Yield of compound **IVb** was 1.50 g (85%), mp 127–128°C, R_f 0.85 (A). ^1H NMR spectrum (C_6D_6), δ, ppm: 1.85 d.d ($6H_e$) and 2.30 m ($6H_a$) [$OCH_2CH_2CH_2O$, $^2J(H_aH_e)$ 6.60 Hz, $^3J(H_aH_e)$ 14.99 Hz], 3.64 br.s (4H, CH_2OCH_2), 4.16 d (12H, CH_2OP, $^3J_{HP}$ 5.11 Hz), 4.40 m ($12H_e$) and 4.60 m ($12H_a$) ($OCH_2CH_2CH_2O$, $^2J(H_aH_e)$ 10.96 Hz, $^3J_{HP}$ 11.70 Hz). ^{31}P NMR spectrum (benzene), δ_P, ppm: 129.84 br.s. Found, %: C 38.35; H 5.91; P 20.98. $C_{28}H_{52}O_{19}P_6$. Calculated, %: C 38.28; H 5.97; P 21.15. *M* 878.578.

Dipentaerythrite hexa-2,2-dimethyl-1,3-propylene phosphite (IVc). *Method 1.* The procedure is similar to the described above for preparation of compound **IVa**, from 1.2 g of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **IIc** in 5 ml of anhydrous dioxane and 0.3 g of dipentaerythrite **I** in 5 ml of absolute pyridine. The formation of neopentylenephosphite **IVc** was monitored by ^{31}P NMR spectroscopy. ^{31}P NMR spectrum, (dioxane), δ_P, ppm: 122.09 br.s. Yield of compound **IVc** is 1.02 g (80%), mp 138–139°C, R_f 0.90 (A). ^1H NMR spectrum (C_6D_6), δ, ppm: 0.93 s and 1.23 s [36H, $OCH_2C(CH_3)_2CH_2O$], 3.59 s and 3.69 s (4H, CH_2OCH_2), 3.92 m ($12H_e$) and 4.28 m ($12H_a$), [$OCH_2C(CH_3)_2CH_2O$, $^2J(H_aH_e)$ 10.68 Hz], 4.17 d (12H, CH_2OP, $^3J_{HP}$ 6.41 Hz). ^{31}P NMR spectrum (benzene), δ_P, ppm: 122.34 br.s. Found, %: C 45.71; H 7.29; P 17.54. $C_{40}H_{76}O_{19}P_6$. Calculated, %: C 45.89; H 7.32; P 17.75. *M* 1046.90.

Method 2. A mixture of 0.2 g of dipentaerythrite **I** and 1 g of amidophosphite **III** in 5 ml of mixture containing from dioxane and pyridine, 2 : 1, was heated at 90–100°C for 2 h distilling off the liberated diethylamine and solvents. ^{31}P NMR spectrum, δ_P, ppm: 122.15 br.s. Yield of compound **IVc** is 0.74 g (87%), mp 138–140°C. The chromatographic mobility and the ^1H and ^{31}P NMR spectroscopic data are the same as for compound prepared by method *1*.

Dipentaerythrite hexa-2,2-dimethyl-1,3-propylene phosphate (V). To a solution of 0.5 g of neopentylene phosphite **IVc** in 10 ml of anhydrous benzene, 0.28 g of adduct of carbamide with hydrogen peroxide (molar ratio 1 : 6.2) was added at room temperature, and the reaction mixture was kept at the same temperature for 5 h. Then not reacted adduct was filtered off, and benzene was removed in a vacuum. The residue was dissolved in 5 ml of chloroform and reprecipitated into hexane (2 × 3 ml). The oily product was kept for 2 h at 40°C in a vacuum (1 mm Hg) yielding 0.33 g (60%) of compound **V**, 1.5980, R_f 0.41 (A). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 br.s and 1.24 br.s [36H, $OCH_2C(CH_3)_2 \cdot CH_2O$], 3.40 m ($12H_e$) and 4.36 m ($12H_a$), [$OCH_2 \cdot C(CH_3)_2CH_2O$, $^2J(H_aH_e)$ 8.79 Hz], 3.50 s (4H, CH_2OCH_2), 4.10 d (12H, CH_2OP, $^3J_{HP}$ 11.55 Hz). ^{31}P NMR spectrum (chloroform), δ_P, ppm: –7.17 br.s. Found, %: C 42.18; H 6.64; P 16.03. $C_{40}H_{76}O_{25}P_6$. Calculated, %: C 42.03; H 6.70; P 16.26. *M* 1142.86.

Dipentaerythrite hexaethylene thionophosphate

(VIa). To a solution of 0.24 g of ethylene phosphite **IVa** in 5 ml of anhydrous dioxane at room temperature, 0.06 g of finely crushed sulfur was added, and the temperature was increased to 40°C, then the reaction mixture was kept at the temperature for 5 h. Excess of sulfur was filtered off, and dioxane was removed in a vacuum. For purification from sulfur excess the product was dissolved in acetone (2 × 5 ml) followed by filtration and distilling the solvent off. Additional purification of ethylenethionphosphonate **VIa** was performed on a chromatographic column with silica gel (10 g) filled with benzene. Compound **VIa** was eluted by 30 ml of mixture benzene–dioxane, 10 : 1. Solvents were removed in a vacuum, and the residue was kept at 40°C for 2 h (1 mm Hg) obtaining 0.18 g (59%) of compound **VIa**, mp 103–105°C, R_f 0.65 (A), 0.28 (B). ^{1}H NMR spectrum in $CDCl_3$ of compound **VIa** is the same to the spectrum of ethylenephosphite **IVa**. ^{31}P NMR spectrum (chloroform), δ_P, ppm: 83.46 br.s. Found, %: C 26.61; H 3.99; P 18.98. $C_{22}H_{40}O_{19}P_6S_6$. Calculated, %: C 26.78; H 4.08; P 18.83. *M* 986.79.

Dipentaerythrite hexa-1,3-propylene thionphosphate (VIb) was synthesized similarly to compound **VIa** from 0.5 g of propylenephosphite **IVb** and 0.11 g of sulfur in 10 ml of anhydrous dioxane at 80°C for 3 h. Purification of prepared propylene thionphosphate **VIb** was conducted on a chromatographic column with silica gel (20 g) filled with benzene. Compound **VIb** was eluted by 40 ml of mixture benzene–dioxane, 5 : 1. Solvents were distilled off in a vacuum, and the residue was kept for 2 h at 40°C (1 mm Hg). Yield of compound **VIb** is 0.49 g (80%), mp 150–152°C, R_f 0.75 (A), 0.30 (B). ^{1}H NMR spectrum in $CDCl_3$ of compound **VIb** is the same to the spectrum of propylenephosphite **IVb**. ^{31}P NMR spectrum (chloroform), δ_P, ppm: 62.09 br.s. Found, %: C 31.51; H 4.95; P 17.49. $C_{28}H_{52}O_{19}P_6S_6$. Calculated, %: C 31.40; H 4.89; P 17.35. *M* 1070.95. Mass spectrum: found, *M* (^{12}C): 1070.84 $(M + H)^+$. Calculated, *M* (^{12}C): 1071.67 $(M + H)^+$.

Dipentaerythrite hexa-2,2-dimethyl-1,3-propylene thionphosphate (VIc) was prepared by the same procedure as described for compound **VIa** from 0.4 g of neopentylenphosphite **IVc** and 0.075 g of sulfur in 6 ml of anhydrous dioxane at 80°C for 5 h. Purification of neopentylenethionphosphate **VIc** was carried out on a chromatographic column with silica gel (10 g) filled with benzene. Compound **VIc** was eluted by 30 ml of mixture benzene–dioxane, 3 : 1. Solvents were distilled off in a vacuum, and the residue was kept for 2 h at 40°C (1 mm Hg) obtaining 0.39 g (82%) of compound **VIc**, mp 169–170°C, R_f 0.85 (A), 0.35 (B). ^{1}H NMR spectrum ($CDCl_3$) of compound **VIc** is analogous to the spectrum of neopentylene phosphite **IVc**. ^{31}P NMR spectrum (chloroform), δ_P, ppm: 61.53 br.s. Found, %: C 38.89; H 6.20; P 15.09. $C_{40}H_{76}O_{19}P_6S_6$. Calculated, %: C 38.77; H 6.18; P 15.00. *M* 1239.26.

3-Hydroxypropyl thiolophosphate hexatriethylammonium salt (VII). A solution of 0.1 g of propylenethionophosphate **VIb**, 0.01 g of water, and 0.25 g of triethylamine in 2 ml of dioxane (pH > 10) into sealed ampoule was heated at 120°C for 4 h. After that dioxane and triethylamine excess was removed in a vacuum, and the remaining oily substance was dissolved in 1 ml of dioxane and twice reprecipitated with hexane, then washed with diethyl ether (2 × 5 ml) and dried for 2 h at 50°C in a vacuum (1 mm Hg). Yield of compound **VII** is 0.05 g (28%), mp 240°C (decomp.), R_f 0.00 (A), 0.41 (D). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t [54H, NCH_2CH_3, ^3J(HH) 7.31 Hz], 1.85 br.m (12H, $PSCH_2CH_2CH_2OH$), 2.70 br.m (12H, $PSCH_2CH_2CH_2OH$), 3.09 q (36H, NCH_2CH_3, ^3J(PH) 7.14 Hz), 3.64 s and 3.72 s (4H, CH_2OCH_2), 4.17-4.60 br.m (30H, $CH_2OPSCH_2CH_2 \cdot CH_2OH$). ^{31}P NMR spectrum (chloroform), δ_P, ppm: 16.31 br.s. Found, %: C 43.21; H 8.43; P 10.51. $C_{64}H_{148}N_6O_{25}P_6S_6$. Calculated, %: C 43.15; H 8.38; P 10.44. *M* 1780.12.

Mixture of platinum complex VIII and platinum complex IX. *Method a.* To a solution of 0.1 g of neopentylene phosphite **IVc** in 2 ml of anhydrous chloroform, 0.2 g of $(CH_3CN)_2PtCl_2$ (ligand to metal molar ratio 1 : 6) was at simultaneously added with stirring. The reaction mixture was stirred at room temperature for 2 h, and then mixture of compounds **VIII** and **IX** was reprecipitated into hexane, the solution was decanted, and the precipitate was some times washed first with benzene, and then with hexane, and dried for 1 h for 50°C (1 mm Hg). Yield of mixture of *cis*-complexes **VIII** and **IX** is 0.31 g, mp 332°C (decomp.), R_f 0.5 (C). ^{31}P NMR spectrum (chloroform), δ_P, ppm: 67.83 br.s, $^1J^{cis}$(P–Pt) 5821.6 Hz. Found, %: C 26.38; H 4.03; P 10.23. $C_{40}H_{76}O_{19}P_6 8$. Pt_3Cl_6 (compound **VIII**) and $C_{80}H_{152}O_{38}P_{12}Pt_6Cl_{12}$ (compound **IX**). Calculated, %: C 26.04; H 4.15; P 10.07. *M* 1844.883 (compound **VIII**) and 3689.766 (compound **IX**). Mass spectrum: found, *M* (^{12}C, ^{195}Pt): 1808.84 $(M – Cl)^+$, 3653.15 $(M – Cl)^+$. Calculated, *M* (^{12}C, ^{195}Pt): 1808.70 (compound **VIII** – Cl)$^+$, 3652.91 (compound **IX** – Cl)$^+$.

Method b. To a solution of 0.05 g of neopentylene phosphite **IVc** in 3 ml of absolute benzene, 0.1 g of $(CH_3CN)_2PtCl_2$ (molar ration of ligand and metal 1 : 6) was simultaneously added with stirring. The precipitate was formed from the reaction mixture for 2 h at room temperature. The solution was decanted, and the precipitate was washed with benzene, then it was dissolved in 5 ml of chloroform. Insoluble admixtures were filtered off, and the mixture of complexes **VIII** and **IX** was reprecipitated into hexane. The solid was dried at 50°C for 1 h (1 mm Hg). Yield of mixture of *cis*- and *trans*-complexes **VIII** and **IX** is 0.13 g, mp 328°C (decomp.), R_f 0.45 (C). ^{31}P NMR spectrum (chloroform), δ_P, ppm: 65.41 br.s, $^1J^{cis}$(P–Pt) 5751.8 Hz, 83.33 br.s, $^1J^{trans}$(P–Pt) 3455.76 Hz.

Palladium complex (X). To a solution of 0.3 g of neopentylene phosphite **IVc** in 5 ml of methylene chloride, 0.1 g of $PdCl_2$ (molar ratio of ligand and metal 1 : 3.2) was simultaneously added with stirring. The reaction mixture was stirred at room temperature for 1.5 h. Unreacted $PdCl_2$ was filtered off, and complex **X** was reprecipitated into hexane. The solution was decanted, and the solid was washed with hexane and dried at 50°C (1 mm Hg) for 1 h. Yield of complex **X** is 0.4 g, mp 275°C (decomp.), R_f 0.6 (C). ^{31}P NMR spectrum (chloroform), δ_P, ppm: 90.00 br.s. Found, %: C 30.12; H 4.81; P 11.67. $C_{40}H_{76}O_{19}P_6 \cdot Pd_3Cl_6$. Calculated, %: C 30.43 H 4.85; P 11.77. *M* 1578.90. Mass spectrum: found, *M* (^{12}C, ^{106}Pd): 1541.21 $(M - Cl)^+$. Calculated, *M* (^{12}C, ^{106}Pd): 1541.70 $(M - Cl)^+$.

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