

Diphosphites Derived from 1,3:1',3'-Di-*O*-benzylidenedipentaerythritol—Key Synthons for New Types of Phosphorus-Containing Compounds

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Abstract—A number of cyclic diphosphites were synthesized on the basis of an accessible diol, 1,3:1',3'-di-*O*-benzylidenedipentaerythritol. The resulting diphosphites were converted into complex covalent and coordination organophosphorus compounds.

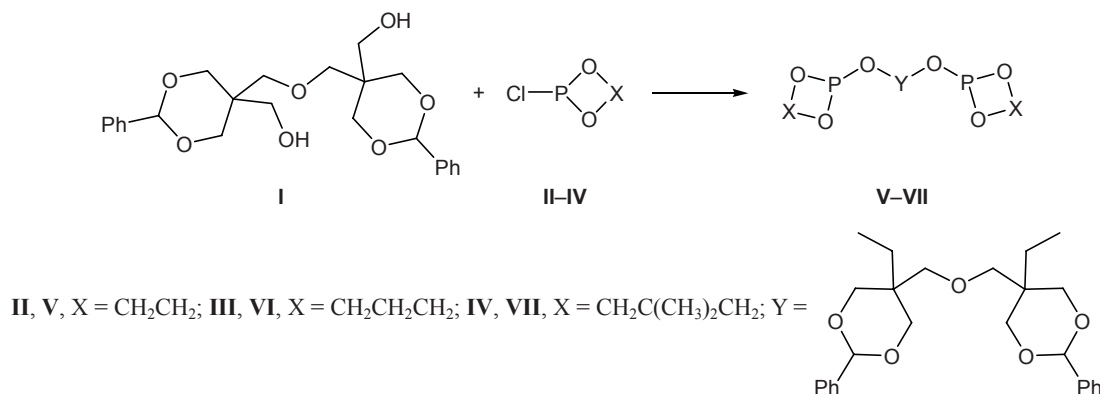
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We recently synthesized first representatives of complete esters derived from dipentaerythritol and phosphorous acid and estimated prospects in their application as ligands for the preparation of coordination compounds of platinum subgroup metals [1]. While developing studies in this line, we made an attempt to build up structurally related systems containing only two phosphite moieties located symmetrically with respect to the central ether oxygen atom. For this purpose we examined phosphorylation of 1,3:1',3'-di-*O*-benzylidenedipentaerythritol (**I**) as a mixture of configurational isomers. A procedure for the synthesis of compound **I** was developed by us previously [2]. As phosphorylating agents we used accessible di- and trimethylene phosphorochloridites **II–IV** which are highly reactive at 0°C in the system dioxane–pyridine. The yield of target phosphites **V–VII** ranged from 59

to 80% (Scheme 1). The progress of the reactions was monitored by ³¹P NMR spectroscopy (δ_P 122–133 ppm). Diphosphites **V–VII** were purified by passing solutions of the crude products through a layer of silica gel. All trivalent phosphorus compounds **V–VII** were stable on storage at room temperature in an inert atmosphere. Among these, compounds **VI** and **VII** were the most stable.

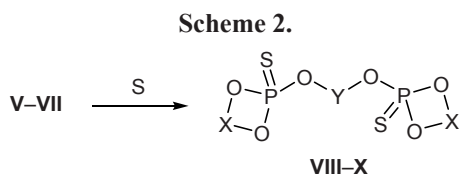
The ¹H NMR spectra of phosphites **V–VII** contained signals from all protons present in the assumed structures. Compounds **V–VII** displayed in the spectra signals from methylene protons at δ 3.30–3.39 ppm, a broadened singlet from the CHC₆H₅ protons at δ 5.45 ppm, aromatic proton signals in the region δ 7.36–7.47 ppm, and doublets from the CH₂OP protons at δ 4.11–4.15 ppm with a characteristic ¹H–³¹P coupling constant. In addition, the spectrum of bis-

Scheme 1.



(ethylene phosphite) **V** contained a multiplet at δ 3.76–4.09 ppm from methylene protons in the dioxaphospholane rings, and in the spectrum of bis(trimethylene phosphite) **VI** axial and equatorial protons in the dioxaphosphinane rings resonated as multiplets at δ 1.75, 2.33, and 4.41 ppm. The corresponding proton signals in the ^1H NMR spectrum of diphosphite **VII** were located at δ 3.97 and 4.54 ppm, and two singlets at δ 0.92 and 1.20 ppm were assigned to protons in the methyl groups.

Bis-phosphites **V–VII** were readily converted into the corresponding phosphorothioates **VIII–X** by treatment with elemental sulfur in dioxane at 30–60°C (reaction time 1–3 h; Scheme 2). Bis(*O,O*-ethylene phosphorothioate) **VIII** was isolated as an unstable oily substance, while six-membered cyclic thiophosphates **IX** and **X** were crystalline products which can be stored for several months in an inert atmosphere without appreciable decomposition. The observed difference in the stabilities of five- and six-membered cyclic thiophosphates is not surprising taking account geometric parameters of these systems.



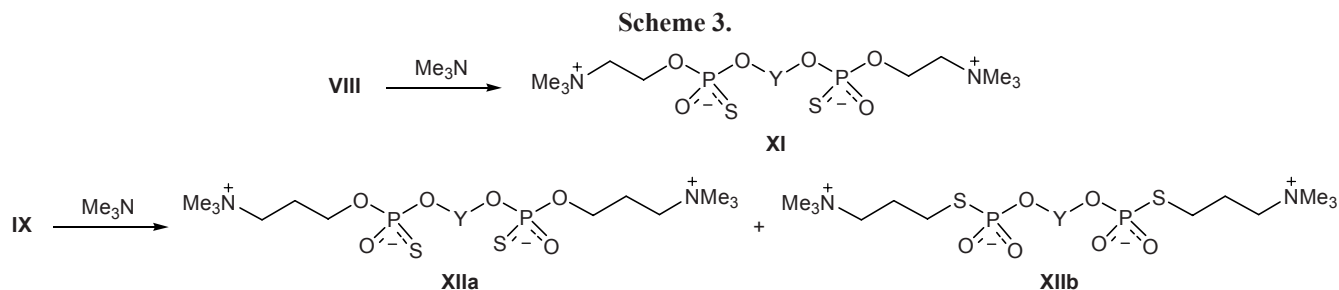
The structure and purity of thiophosphates **VIII–X** were proved by ^{31}P and ^1H NMR spectroscopy and TLC data. The ^{31}P NMR spectra of **VIII–X** contained broadened singlets at δ_{P} 84.48, 62.10, and 62.11 ppm, respectively. Their ^1H NMR spectra (see Experimental) were similar to those of phosphites **V–VII** considered above and were fully consistent with the assumed structures.

Thiophosphates **VIII** and **IX** were used to synthesize novel phosphorus-containing choline amphiphiles **XI**, **XIIa**, and **XIIb**. Previously, structurally related phosphorus-free ammonium derivatives of dipenta-

erythritol were extensively studied with a view to obtain surface-active dendrimers [3]. Multiionic compounds **XI**, **XIIa**, and **XIIb** were synthesized by alkylation of trimethylamine with thiophosphates **VIII** and **IX** (Scheme 3). The reaction of **VIII** with trimethylamine was carried out at 50°C (reaction time 2–3 h). As might be expected, the alkylation of trimethylamine with dithiophosphate **IX** occurred at 110°C [4]. The yields of **XI** and **XIIa/XIIb** were 60 and 75%, respectively. The ^{31}P NMR spectrum of the reaction mixture formed in the reaction with bis(*O,O*-ethylene phosphorothioate) **VIII** contained a singlet at δ_{P} 59.32 ppm, which is typical of acyclic *O,O*-dialkyl phosphorothioates. In the ^{31}P NMR spectrum of the reaction mixture obtained from thiophosphate **IX**, apart from the signal at δ_{P} 56.37 ppm belonging to *O*-(3-trimethylammoniopropyl) phosphorothioate **XIIa**, we observed a signal at δ 18.36 ppm, typical of *S*-(3-trimethylammoniopropyl) derivative **XIIb**, the signal intensity ratio being 2:1. The formation of *S*-alkyl phosphorothioate **XIIb** indicates that the reaction of trimethylamine with compound **IX** is accompanied by thione-thiol isomerization [5]. We failed to isolate compounds **XIIa** and **XIIb** as individual substances.

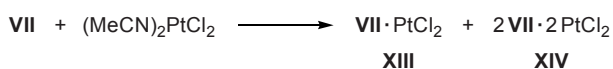
The structure of phosphocholines **XI**, **XIIa**, and **XIIb** was proved by ^{31}P and ^1H NMR spectroscopy. The ^1H NMR spectra of these compounds retained signals from protons in the dipentaerythritol skeleton, and signals from methyl protons in the ammonium fragments were present at δ 2.97 (**XI**) and 3.30 ppm (**XIIa/XIIb**). The chemical shift of the SCH_2 protons in compound **XIIb** was characteristic (δ 2.72 ppm).

At the next stage of our study, we made an attempt to use phosphites **V–VII** as ligands in the synthesis of coordination compounds with transition metals (*d* elements). The best results were obtained with bis-phosphite **VII** as ligand and platinum and palladium salts. Bis-phosphite **VII** reacted with an equimolar amount of (diacetonitrile)dichloroplatinum(II) in chloroform at room temperature to give a mixture of two complexes. According to the MALDI-TOF data, one of these com-



plexes was monomeric (**XIII**; it contained two phosphorus atoms), while the other (**XIV**) contained four phosphorus atoms (Scheme 4); the ratio of complexes **XIII** and **XIV** was 9:1. Mixture **XIII/XIV** was isolated by precipitation from chloroform with hexane; it was a powder stable on storage on exposure to air. The ^1H NMR spectrum of **XIII/XIV** contained signals typical of initial ligand **VII**. Like analogous complexes obtained from complete esters of unsubstituted dipentaerythritol [1], the coordination entities in complexes **XIII** and **XIV** have square-planar configuration characterized by a broadened phosphorus signal at δ_{P} 70.59 ppm ($J_{\text{P,Pt}} = 5843.37$ Hz) in the ^{31}P NMR spectrum. The value of $J_{\text{P,Pt}}$ indicates *cis* arrangement of the phosphorus atoms [6, 7].

Scheme 4.



Likewise, the reaction of **VII** with palladium(II) chloride gave (according to the MALDI-TOF data) a mixture of monomeric and dimeric complexes **XV** and **XVI** involving one or two substituted dipentaerythritol molecules and two or four phosphorus atoms, respectively (Scheme 5). The reaction was carried out in methylene chloride at room temperature. Precipitation from methylene chloride with hexane gave powder-like mixture **XV/XVI** (ratio 6:1) which is stable on storage. The ^1H NMR spectrum of that mixture contained signals typical of initial ligand **VII**, and in the ^{31}P NMR spectrum we observed a broadened singlet at δ 94.38 ppm.

Scheme 5.



To conclude, we have proposed an efficient procedure for the synthesis of novel bis(*O,O*-di- and trimethylene phosphites) which are promising as synthons for new covalently bonded organophosphorus compounds and their complexes with transition metals.

EXPERIMENTAL

The ^1H NMR spectra were measured on a Bruker WM-250 spectrometer (250 MHz) relative to tetramethylsilane as internal reference; proton signals were assigned using two-dimensional NMR techniques. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra were obtained on a Bruker WP-80SY instrument at 32.4 MHz using 85% phos-

phoric acid as external reference. Single-isotope (^{12}C) molecular weights were determined by mass spectrometry on a Bruker UltraFlex instrument (Bruker Daltonics, Germany; positive ion detection in the reflector mode; nitrogen laser, $\lambda = 337$ nm; accelerating voltage 25 kV). The elemental compositions were determined on a Perkin-Elmer 2400 analyzer. Column chromatography was performed using a 10-mm (i.d.) column packed with silica gel L (100–250 μm); R_f values were determined by TLC on Silufol UV-254 plates using benzene–dioxane (3:1, A), hexane–dioxane (3:1, B), chloroform–methanol (3:1, C), or chloroform–methanol–water (65:25:4, D) as eluent. The melting points were measured in sealed capillaries by heating at a rate of 1 deg/min. All syntheses with trivalent phosphorus compounds were carried out under dry argon.

5,5'-Oxydimethylenebis(2-phenyl-1,3-dioxan-5-ylmethanol) (**I**, a mixture of three conformers) was synthesized as described in [2]; 2-chloro-1,3,2-dioxaphospholane (**II**) [8], 2-chloro-1,3,2-dioxaphosphinane (**III**) [9], and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane (**IV**) [10] were prepared by known methods. Their physical constants coincided with those reported in the literature.

5,5'-Oxydimethylenebis[5-(1,3,2-dioxaphospholan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (**V**). A solution of 0.5 g (1.16 mmol) of bis-acetal **I** in 5 ml of anhydrous pyridine was added dropwise to a solution of 0.29 g (2.32 mmol) of 2-chloro-1,3,2-dioxaphospholane (**II**) in 5 ml of anhydrous dioxane under stirring at 0°C. The mixture was kept for 0.5 h at that temperature and was allowed to warm up to room temperature over a period of 0.5 h. The formation of bis-phosphite **V** was monitored by ^{31}P NMR spectroscopy (dioxane; δ_{P} 132.98 ppm, br.s). Pyridine hydrochloride was filtered off, the filtrate was passed through 1.5 g of silica gel, the solvent was removed under reduced pressure, and the residue was evacuated at a residual pressure of 1 mm for 1 h at 40°C. Yield 0.4 g (59%), $n_{\text{D}}^{20} = 1.5930$, R_f 0.79 (A). ^1H NMR spectrum (C_6D_6), δ , ppm: 3.26 s and 3.36 s (4H, CH_2OCH_2), 3.76 m and 4.09 m (6H, CH_2OP , $^3J_{\text{HP}} = 9.97$ Hz), 4.38 m (4H, H_{ax}) and 4.55 m (4H, H_{eq}) (CH_2OCH_2 , $^2J = 7.93$ Hz), 5.44 br.s (2H, CHC_6H_5), 7.36 br.s (6H, *m*-H, *p*-H), 7.48 br.s (4H, *o*-H). ^{31}P NMR spectrum (benzene): δ_{P} 132.96 ppm, br.s. Found, %: C 55.13; H 6.04; P 10.23. $\text{C}_{28}\text{H}_{36}\text{O}_{11}\text{P}_2$. Calculated, %: C 55.08; H 5.94; P 10.15. *M* 610.52.

5,5'-Oxydimethylenebis[5-(1,3,2-dioxaphosphinan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (**VI**) was

synthesized in a similar way from 0.4 g (2.84 mmol) of 2-chloro-1,3,2-dioxaphosphinane (**III**) and 0.6 g (1.42 mmol) of compound **I** using 8 ml of anhydrous dioxane and 8 ml of anhydrous pyridine. The formation of bis-phosphite **VI** was monitored by ^{31}P NMR spectroscopy (dioxane; δ_{P} 129.82 ppm, br.s). Yield 0.47 g (80%), mp 104–106°C, R_{f} 0.90 (A). ^1H NMR spectrum (C_6D_6), δ , ppm: 1.75 m (2H, H_{eq}) and 2.23 m (2H, H_{ax}) ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.31 s and 3.41 s (4H, CH_2OCH_2), 3.93 m (8H, H_{ax}) and 4.41 m (8 H_{eq}) ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$, CH_2OCH , $^2J = 9.35$, $^3J_{\text{HP}} = 11.60$ Hz), 4.15 d (4H, CH_2OP , $^3J_{\text{HP}} = 12.10$ Hz), 5.45 br.s (2H, CHC_6H_5), 7.36 br.s (6H, *m*-H, *p*-H), 7.46 br.s (4H, *o*-H). ^{31}P NMR spectrum (benzene): δ_{P} 129.80 ppm, br.s. Found, %: C 56.37; H 6.29; P 9.64. $\text{C}_{30}\text{H}_{40}\text{O}_{11}\text{P}_2$. Calculated, %: C 56.42; H 6.31; P 9.70. *M* 638.57.

5,5'-Oxydimethylenebis[5-(5,5-dimethyl-1,3,2-dioxaphosphinan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (VII) was synthesized in a similar way from 0.23 g (1.39 mmol) of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane (**IV**) and 0.3 g (0.7 mmol) of compound **I** using 5 ml of anhydrous dioxane and 5 ml of anhydrous pyridine. The formation of bis-phosphite **VII** was monitored by ^{31}P NMR spectroscopy (dioxane; δ_{P} 121.88 ppm, br.s). Yield 0.38 g (79%), mp 148–150°C, R_{f} 0.95 (A). ^1H NMR spectrum (C_6D_6), δ , ppm: 0.92 br.s and 1.20 br.s (12H, CH_3), 3.30 s and 3.39 s (4H, CH_2OCH_2), 3.92 m (4H, H_{ax}) and 4.49 m (4H, H_{eq}) (CH_2OCH), 3.97 m (4H, H_{ax}) and 4.54 m (4H, H_{eq}) [$\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O}$, $^2J = 11.33$ Hz], 4.11 d (4H, CH_2OP , $^3J_{\text{HP}} = 6.81$ Hz), 5.45 br.s (2H, CHC_6H_5), 7.37 br.s (6H, *m*-H, *p*-H), 7.47 br.s (4H, *o*-H). ^{31}P NMR spectrum (benzene): δ_{P} 122.88 ppm, br.s. Found, %: C 58.69; H 6.89; P 8.87. $\text{C}_{34}\text{H}_{48}\text{O}_{11}\text{P}_2$. Calculated, %: C 58.78; H 6.96; P 8.92. *M* 694.67.

5,5'-Oxydimethylenebis[5-(2-thioxo-1,3,2 λ^5 -dioxaphospholan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (VIII). Finely powdered sulfur, 0.02 g (0.69 mmol), was added at room temperature to a solution of 0.2 g (0.33 mmol) of bis-phosphite **V** in 3 ml of anhydrous dioxane, and the mixture was heated to 30°C and kept for 0.5 h at that temperature. Excess sulfur was filtered off, and the solvent was removed under reduced pressure. To remove traces of sulfur, the residue was dissolved in 3 ml of acetone, the solution was filtered, and the solvent was distilled off. This procedure was repeated once more. The product was additionally purified by chromatography on a column charged with 8 g of silica gel and filled with benzene.

Compound **VIII** was eluted using 20 ml of benzene–dioxane (10:1). The eluate was evaporated under reduced pressure, and the residue was evacuated at a residual pressure of 1 mm for 2 h at 40°C. Yield 0.12 g (55%); $n_{\text{D}}^{20} = 1.5995$; R_{f} 0.70 (A), 0.30 (B). The ^1H NMR spectrum of **VIII** (CDCl_3) was similar to the spectrum of bis-phosphite **V**. ^{31}P NMR spectrum (chloroform): δ_{P} 84.47 ppm, br.s. Found, %: C 49.92; H 5.41; P 9.25. $\text{C}_{28}\text{H}_{36}\text{O}_{11}\text{P}_2\text{S}_2$. Calculated, %: C 49.85; H 5.38; P 9.18. *M* 674.65.

5,5'-Oxydimethylenebis[5-(2-thioxo-1,3,2 λ^5 -dioxaphosphinan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (IX) was synthesized in a similar way from 0.4 g (0.62 mmol) of compound **VI** and 0.05 g (1.4 mmol) of sulfur in 10 ml of anhydrous dioxane (40°C, 1 h). The product was purified by chromatography on a column charged with 15 g of silica gel and filled with benzene using 35 ml of benzene–dioxane (5:1) as eluent. The eluate was evaporated under reduced pressure, and the residue was evacuated at a residual pressure of 1 mm for 2 h at 40°C. Yield 0.37 g (83%); mp 124–125°C; R_{f} 0.8 (A), 0.35 (B). The ^1H NMR spectrum of **IX** (CDCl_3) was similar to that of bis-phosphite **VI**. ^{31}P NMR spectrum (chloroform): δ_{P} 62.10 ppm, br.s. Found, %: C 51.35; H 5.80; P 8.89. $\text{C}_{30}\text{H}_{40}\text{O}_{11}\text{P}_2\text{S}_2$. Calculated, %: C 51.27; H 5.74; P 8.82. *M* 702.70.

5,5'-Oxydimethylenebis[5-(5,5-dimethyl-2-thioxo-1,3,2 λ^5 -dioxaphosphinan-2-yloxymethyl)-2-phenyl-1,3-dioxane] (X) was synthesized in a similar way from 0.3 g (0.43 mmol) of compound **VII** and 0.03 g (0.91 mmol) of sulfur in 6 ml of anhydrous dioxane (60°C, 3 h). The product was purified by chromatography on a column charged with 10 g of silica gel and filled with benzene using 25 ml of benzene–dioxane (3:1) as eluent. The eluate was evaporated under reduced pressure, and the residue was evacuated at a residual pressure of 1 mm for 2 h at 40°C. Yield 0.25 g (80%); mp 232–233°C; R_{f} 0.85 (A), 0.40 (B). The ^1H NMR spectrum of **X** (CDCl_3) was similar to the spectrum of bis-phosphite **VII**. ^{31}P NMR spectrum (chloroform): δ_{P} 62.11 ppm, br.s. Found, %: C 56.24; H 6.71; P 8.64. $\text{C}_{34}\text{H}_{48}\text{O}_{11}\text{P}_2\text{S}_2$. Calculated, %: C 56.19; H 6.66; P 8.52. *M* 726.74.

O,O'-5,5'-Oxydimethylenebis(2-phenyl-1,3-dioxan-5-ylmethylene) bis[O-(2-trimethylammonioethyl) phosphorothioate] (XI). An ampule was charged with a solution of 0.1 g (0.15 mmol) of thiophosphate **VIII** and 0.09 g (1.4 mmol) of trimethylamine in 5 ml of anhydrous benzene. The ampule was sealed and heated for 2 h at 50°C. The solvent was

removed under reduced pressure, and the oily residue was washed with benzene (2×5 ml) and hexane (2×5 ml) and dried for 2 h at 40°C under reduced pressure (1 mm). Yield 0.07 g (60%); mp 215–217°C (becomes wet at 120°C); R_f 0.00 (A), 0.65 (C), 0.45 (D). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.77 br.s (18H, NCH_3), 2.97 br.m (4H, NCH_2), 3.30 br.m (4H, CH_2OCH_2), 3.76 m (4H, H_{ax}) and 4.27 m (4H, H_{eq}) (CH_2OCH), 3.87 m (4H, $\text{POCH}_2\text{CH}_2\text{N}$), 4.13 m (4H, CH_2OP), 5.42 br.s (2H, CHC_6H_5), 7.34 br.s (6H, *m*-H, *p*-H), 7.45 br.s (4H, *o*-H). ^{31}P NMR spectrum (chloroform): δ_p 59.32 ppm, br.s. Found, %: C 51.56; H 6.84; P 7.78. $\text{C}_{34}\text{H}_{54}\text{N}_2\text{O}_{11}\text{P}_2\text{S}_2$. Calculated, %: C 51.50; H 6.86; P 7.81. M 792.87.

***O,O'*-5,5'-Oxydimethylenebis(2-phenyl-1,3-dioxan-5-ylmethylene) bis[*O*-(3-trimethylammonio-propyl) phosphorothioate] (XIIa) and *O,O'*-5,5'-oxydimethylenebis(2-phenyl-1,3-dioxan-5-ylmethylene) bis[*S*-(3-trimethylammonio-propyl) phosphorothioate] (XIIb) (mixture of isomers)** were synthesized in a similar way from 0.2 g (0.28 mmol) of thiophosphate IX and 0.17 g (2.79 mmol) of trimethylamine in 5 ml of anhydrous benzene (100–110°C, 3 h). Yield 0.18 g (75%); mp 270–273°C (becomes wet at 200°C); R_f 0.00 (A), 0.58 (C), 0.20 (D). ^1H NMR spectrum (CDCl_3 – CD_3OD , 99:1), δ , ppm: 1.94 br.m (4H, $\text{POCH}_2\text{CH}_2\text{CH}_2$); 2.72 br.m (4H, $\text{PSCH}_2\text{CH}_2\text{CH}_2$); 2.85 s, 2.98 s, and 3.08 s (4H, CH_2OCH_2); 3.08 m (4H, H_{ax}) and 4.15 m (4H, H_{eq}) (CH_2OCH); 3.30 br.s (18H, NCH_3); 3.45 br.m (4H, CH_2N); 3.68 br.m (4H, POCH_2CH_2); 3.88 br.m (4H, CH_2OP); 5.37 br.s (2H, CHC_6H_5); 7.29 br.s (6H, *m*-H, *p*-H); 7.39 br.s (4H, *o*-H). ^{31}P NMR spectrum (chloroform–methanol, 99:1), δ_p , ppm: 18.36 br.s (XIIb), 56.37 br.s (XIIa); intensity ratio 2:1. Found, %: C 52.62; H 7.09; P 7.60. $\text{C}_{36}\text{H}_{58}\text{N}_2\text{O}_{11}\text{P}_2\text{S}_2$. Calculated, %: C 52.67; H 7.12; P 7.55. M 820.92.

Platinum complexes XIII/XIV. (Diacetonitrile)dichloroplatinum(II), 0.05 g (0.14 mmol), was added in one portion under stirring to a solution of 0.1 g (0.14 mmol) of bis-phosphite VII in 2 ml of anhydrous chloroform. The mixture was stirred for 1.5 h at room temperature, mixture XIII/XIV was precipitated with hexane, the liquid phase was separated by decanting, and the precipitate was repeatedly washed with benzene and hexane and dried for 1 h at 50°C under reduced pressure (1 mm). Yield 0.15 g, ratio XIII: XIV = 9:1, mp 287–289°C (decomp.), R_f 0.6 (C). ^{31}P NMR spectrum (chloroform): δ_p 70.59 ppm, br.s ($^1J_{\text{P,Pt}} = 5843.37$ Hz). Found, %: C 42.48; H 5.36; P 6.23. $\text{C}_{34}\text{H}_{48}\text{O}_{11}\text{P}_2 \cdot \text{PtCl}_2$ (XIII), $\text{C}_{68}\text{H}_{96}\text{O}_{22}\text{P}_4 \cdot \text{Pt}_2\text{Cl}_4$

(XIV). Calculated, %: C 42.51; H 5.04; P 6.45. M 960.69 (XIII), 1920.49 (XIV). Mass spectrum, m/z (^{12}C , ^{195}Pt): 925.25 [$M - \text{Cl}$] $^+$, 1884.32 [$M - \text{Cl}$] $^+$. Calculated [$M - \text{Cl}$] (^{12}C , ^{195}Pt): 924.78 (XIII), 1885.03 (XIV).

Palladium complexes XV/XVI. Bis-phosphite VII, 0.15 g (0.22 mmol), was dissolved in 5 ml of methylene chloride, 0.05 g (0.26 mmol) of PdCl_2 was added in one portion under stirring, and the mixture was stirred for 1 h at room temperature. Unreacted palladium(II) chloride was filtered off, and mixture XV/XVI was precipitated with hexane. The liquid phase was separated by decanting, and the precipitate was washed with hexane and dried for 1 h at 50°C under reduced pressure (1 mm). Yield 0.19 g, ratio XV:XVI = 6:1, mp 230–232°C (decomp.), R_f 0.65 (C). ^{31}P NMR spectrum (chloroform): δ_p 94.38 ppm, br.s. Found, %: C 46.79; H 5.41; P 7.07. $\text{C}_{34}\text{H}_{48}\text{O}_{11}\text{P}_2 \cdot \text{PdCl}_2$ (XV), $\text{C}_{68}\text{H}_{96}\text{O}_{22}\text{P}_4 \cdot \text{Pd}_2\text{Cl}_4$ (XVI). Calculated, %: C 46.83; H 5.55; P 7.10. M 872.03 (XV), 1744.09 (XVI). Mass spectrum, m/z (^{12}C , ^{106}Pd): 835.62 [$M - \text{Cl}$] $^+$, 1707.27 [$M - \text{Cl}$] $^+$. Calculated [$M - \text{Cl}$] (^{12}C , ^{106}Pd): 835.78 (XV), 1707.02 (XVI).

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