Heteroatom Chemistry
Volume 11, Number 2, 2000

Penta- and Hexa-*m*-Phenylcyclophosphites and Their Derivatives

Eduard E. Nifantyev, Elena N. Rasadkina, Inna V. Yankovich, Vitaly K. Belsky, and Adam I. Stash

Lenin Pedagogical State University, per. Nesvizhskii 3, Moscow, 119021 Russia

Received 15 June 1999; revised 14 October 1999

ABSTRACT: *New representatives of an original class of crown ethers—cyclopenta- and cyclohexaresorcinolamidophosphites—were synthesized using the molecular assemblage technique. Their thio and oxo derivatives were obtained, as well as the rhodium (I) complexes. A macrocycle containing both tri- and pentavalent phosphorus atoms was synthesized.* ^{1}H *and* ^{31}P *NMR spectroscopy data suggested the higher conformational flexibility of phosphite macrocycles as compared to phosphate ones.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:129–137, 2000

INTRODUCTION

We recently obtained the first representatives of an original class of crown ethers with regularly alternating phosphorus acid residues and aromatic nuclei [1–3]. The compounds synthesized are relatively simple in composition: their cycles include only 2–4 resorcinol residues and phosphorus functional groups. Accordingly, the diameters of the systems obtained should be low. Thus, phosphite and thiophosphate derivatives of the simplest crown ethers are differing in conformation [2,3].

In this context, we sought ourselves the task of synthesizing higher crown ethers with larger cavities and some of their derivatives and investigating the effect of substitution of P^{+5} for P^{+3} in the macrocycles obtained on their conformational flexibility. In this article, we report the synthesis of penta- and hexaresorcinolamidophosphites using the molecular assemblage technique. Resorcinol (**1**) and complete amides of phosphorus acid (**2a,b**) were used as starting compounds. Macrocycles containing five resorcinol residues and phosphoryl groups were synthesized according to Scheme 1.

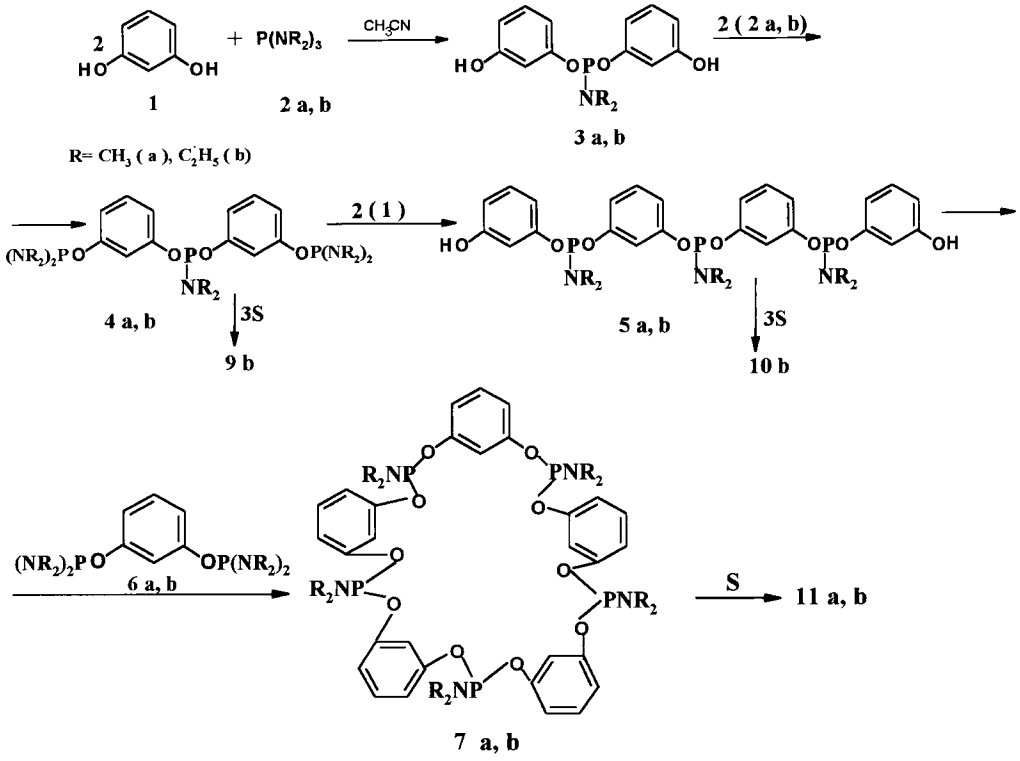
The syntheses are performed step by step, starting from the phosphorylation of resorcinol, without removal of dialkylamine formed or isolation of intermediates. Reactions proceed readily at room temperature. It should be noted that compounds **4a,b** and **5a,b** were synthesized in this work for the first time and isolated as thio derivatives **9b** and **10b.** It is notable that the substitution of the second amide group in phosphorous hexaalkyltriamide by an aryloxy group is more rapid when linear oligomers form than in the course of cyclization. The obtained macrocycles **7a,b** were dense viscous oils, regardless of the radical at the nitrogen atom; their ^{31}P NMR spectra presented singlets in the range characteristic of amidophosphites. They were transformed into thio derivatives (**11a,b**) for more complete identification. After chromatographic purification, the thiophosphates differed in physicochemical and spectral characteristics. Compound **11a** was a solid; its ^{31}P NMR spectrum exhibited two singlets with different integral intensities, which attested to the nonequivalent nature of phosphorus atoms in the molecule due to steric factors. The molecular mass of the com-

Correspondence to: Eduard E. Nifantyev.
Contract Grant Sponsor: Russian Universities: Basic Research.
Contract Grant Number: 221.
Contract Grant Sponsor: Fundamental Natural Sciences.
Contract Grant Sponsor: Russian Foundation for Basic Research.
Contract Grant Number: 97-03-38776.

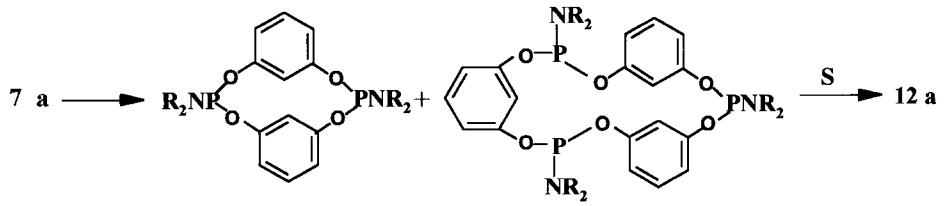
pound as determined by cryoscopy confirmed the presence of five main fragments in its molecule. Thiophosphate **11b** was isolated as a viscous oil, whose ^{31}P NMR spectrum exhibited only a singlet in the thiophosphate range. The ^{1}H NMR spectra displayed broadened signals from all proton groups with the sought ratio between the integral intensities.

It is noteworthy that the chromatographic purification of thiophosphate **11a** made it possible to isolate a compound (with a yield of 10%) that crystallized in another form than the majority of thiophosphates. X-ray diffraction analysis showed that this compound was cyclotristhioresorcinolamidophosphate **12a** (Figure 1, Tables 1, 2).

It is essential that its structure differed from that of the compound of similar composition that we obtained previously by the direct synthesis [2]. From Figure 1, it is seen that all phosphorus and sulfur atoms in the molecule of the new isomer are arranged on the same side of the macrocycle, the compound exists in the *cis* form, in distinction from the *cis, cis, trans*form that we described previously [2]. The aromatic rings are arranged at some angles relative to each other: $(C^1–C^6)$-$(C^7–C^{12})$ 20.9°; $(C^7–C^{12})$–$(C^{13}–C^{18})$ 12.3°; $(C^1–C^6)$–$(C^{13}–C^{18})$ 8.6°. The angles between the central plane passing through all benzene rings and the planes passing through atoms O–P–O were the following: $O^1–P^1–O^2$ 59°; $O^3–P^2–O^4$ 73.7°; $O^5–P^3–O^6$ 68.4°. The distances between the nearest hydrogen atoms of the inward aromatic rings $H^2–H^8–H^{14}$ were determined (3.08, 3.062, and 3.117 Å, respectively) in order to find the size of the cavity (4.102 $Å^2$) (Figure 2). This confirmed our supposition



SCHEME 1



SCHEME 2

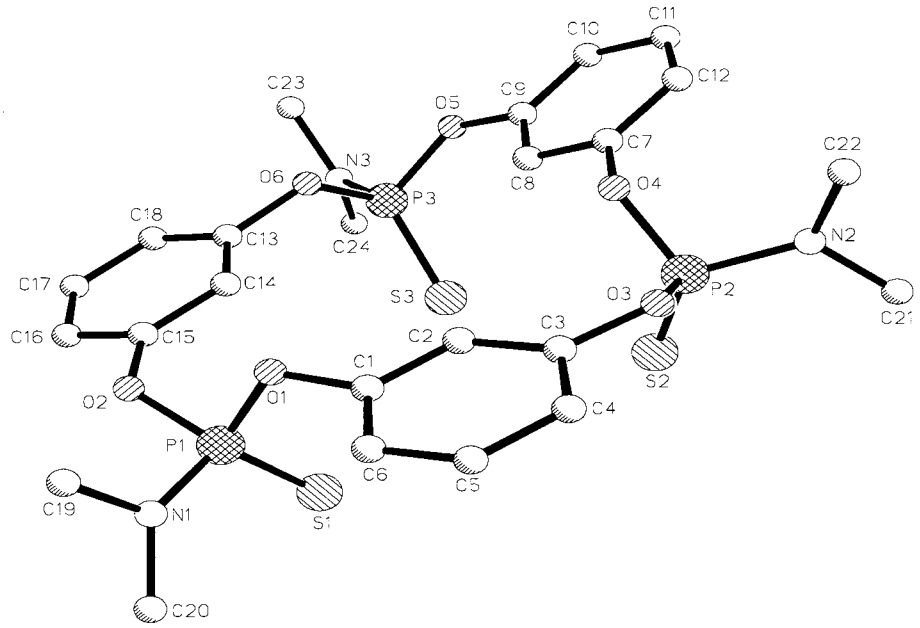


FIGURE 1 Crystal structure of 12a.

about the small size of the cycle. The analysis of the crystalline structure of this compound showed that the molecules are packed in layers so that a benzene ring from a molecule completely coincides with a benzene ring from another molecule and two neighboring molecules are arranged in the trans position relative to each other (Figure 3). Thus, it was demonstrated that the structural characteristics of the cyclic trimer changed depending on the formation conditions.

Macrocycles **15a,b** containing six resorcinol moieties were synthesized, as shown in Scheme 3. Note that we isolated and characterized phosphites **6a,b** and **13a,b** as thio derivatives previously [1,2].

Cyclic amidophosphites **15a,b** were isolated as viscous oils; their ^{31}P NMR spectra exhibited two singlets at 139.5 and 139.86 (**15a**) and a singlet at 141.06 (**15b**). The cyclophosphites obtained, without additional purification, were transformed into thio derivatives **16a,b.** The ^{31}P NMR spectra of both thiophosphates isolated by chromatography exhibited four singlets in the characteristic range of thiophosphates containing aromatic substituents, and their ^{1}H NMR spectra showed broadened signals for all proton groups. We believe that the changes in spectral characteristics observed in going from the P^{3+} macrocycles to their P^{5+} derivatives are associated with the decrease in the degree of freedom for the phosphorus atoms and the formation of conformers with maximally nonequivalent phosphorus and hydrogen atoms. The presence of different radicals at the nitrogen atom also affects the conformational flexibility of the molecule, which increases from the N-methyl to the N-ethyl substituent.

In this work, we performed the synthesis of macrocycle **17b** containing both trivalent and pentavalent phosphorus atoms. For this purpose, trisamidophosphite **10b** was subjected to photocyclization with diamidophosphite **6b** (Scheme 4).

Two broadened signals are observed in the ^{31}P NMR spectrum of this compound at 140.5 and 66.1 ppm, with the integral intensity ratio of 2:3. These signals are probably resonant and correspond to the diastereomer mixture. We believed that the migration of sulfur atoms between all phosphorus atoms was possible in the molecule of regular structure at elevated temperature. However, no variations were observed in the ^{31}P NMR spectrum between 34 and 110°C.

Along with sulfurization, the obtained cycloamidophosphites **7a,b** and **15a,b** were oxidized by the complex of urea with hydrogen peroxide, which gave macrocyclic phosphates **18a,b** and **19a,b**, respectively, readily and with good yields. Their structures were proved by spectral methods; no multiple signals were found in the ^{31}P NMR spectra, as for analogous thiophosphates. We believe that this is associated with the lower volume of the oxygen atom relative to the sulfur atom, which increases the mobility of the molecule as a whole.

In addition, we performed the oxidative imination of the obtained cycloamidophosphites **7a,b** and

TABLE 1 Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^{-3}$) for **12a** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	*U*(*eq*)
S^1	8213(1)	5215(2)	3401(1)	58(1)
S^2	5513(1)	1894(2)	3453(1)	73(1)
S^3	7828(1)	1429(3)	4829(1)	71(1)
P^1	8026(1)	7434(2)	3601(1)	38(1)
P^2	4466(1)	3118(2)	3524(1)	51(1)
P^3	7718(1)	2416(2)	5507(1)	54(1)
O^1	7020(2)	7822(5)	3692(1)	40(1)
O^2	8594(2)	8036(5)	4194(1)	44(1)
O^3	4227(3)	4739(5)	3149(2)	57(1)
O^4	4520(2)	3997(5)	4106(2)	43(1)
O^5	6779(3)	2137(6)	5698(2)	63(1)
O^6	7688(3)	4392(5)	5507(2)	46(1)
N^1	8242(3)	8844(6)	3193(2)	44(1)
N^2	3496(4)	2143(8)	3393(2)	67(2)
N^3	8478(4)	1874(8)	6051(2)	70(2)
C^1	6230(4)	7423(7)	3287(2)	36(1)
C^2	5663(4)	6277(8)	3421(3)	40(2)
C^3	4850(4)	5903(7)	3050(2)	41(2)
C^4	4618(4)	6719(9)	2550(3)	48(2)
C^5	5200(5)	7881(9)	2424(3)	53(2)
C^6	6009(5)	8237(9)	2790(3)	49(2)
C^7	4749(4)	3105(7)	4605(2)	42(2)
C^8	5655(4)	3091(8)	4885(3)	46(2)
C^9	5880(4)	2258(8)	5382(3)	46(2)
C^{10}	5222(5)	1516(8)	5603(3)	49(2)
C^{11}	4321(5)	1568(9)	5311(3)	59(2)
C^{12}	4081(5)	2386(9)	4813(3)	52(2)
C^{13}	8369(4)	5335(7)	5341(2)	41(2)
C^{14}	8133(4)	6143(8)	4838(2)	40(2)
C^{15}	8765(4)	7137(7)	4683(2)	39(2)
C^{16}	9626(4)	7334(8)	5018(3)	46(2)
C^{17}	9847(5)	6518(9)	5517(3)	56(2)
C^{18}	9225(5)	5515(9)	5680(3)	50(2)
C^{19}	8126(7)	10565(11)	3314(4)	68(2)
C^{20}	8716(6)	8540(13)	2754(3)	61(2)
C^{21}	3355(9)	641(13)	3056(4)	96(3)
C^{22}	2662(6)	3001(17)	3458(5)	80(3)
C^{23}	8456(9)	2638(16)	6586(4)	73(3)
C^{24}	9117(8)	483(16)	6035(6)	102(4)

TABLE 2 Bond Lengths and Angles for **12a**

Bond	*d* (Å)	*Angle* (*deg*)	ω
S^1–P^1	1.908(2)	$O^2P^1O^1$	97.6(2)
P^1–O^2	1.602(4)	$O^2P^1N^1$	102.7(2)
P^1–O^1	1.604(4)	$O^1P^1N^1$	106.2(2)
P^1–N^1	1.610(5)	$O^2P^1S^1$	116.66(18)
O^1–C^1	1.407(6)	$O^1P^1S^1$	114.87(17)
O_2–C^{15}	1.391(6)	$N^1P^1S^1$	116.5(2)
N^1–C^{19}	1.448(10)	$O^4P^2O^3$	96.7(2)
N^1–C^{20}	1.452(8)	$O^4P^2N^2$	105.1(3)
		$O^3P^2N^2$	102.2(3)
		$O^4P^2S^2$	116.37(18)
		$O^3P^2S^2$	117.11(19)
		$N^2P^2S^2$	116.6(3)
		$C^1O^1P^1$	121.3(3)
		$C^{15}O^2P^1$	126.6(4)
		$C^3O^3P^2$	126.1(4)
		$C^7O^4P^2$	121.3(4)
		$C^9O^5P^3$	128.5(4)
		$C^{13}O^6P^2$	121.4(4)

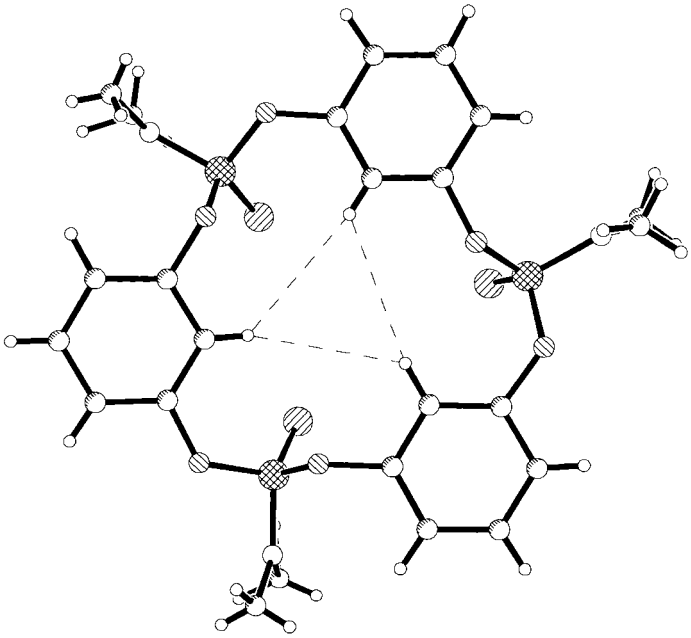


FIGURE 2 Size of macrocycle cavity of 12a.

15a,b in benzene at room temperature. A signal at −8 typical for similar imino derivatives appeared in the ^{31}P NMR spectrum of the reaction mixture. Viscous oils were obtained after removal of the solvent. During the chromatographic purification of the products formed, a new signal in the range of 6 to 7 was observed in the ^{31}P NMR spectrum of the fractions separated, along with the signal at $\delta = -8$. In addition, high-melting crystalline products were isolated that exhibited the only singlet at 6–7 ppm. Similar products were precipitated from the benzene solutions of reaction mixtures under long-term keeping (for 30 days and more). We believe that phosphimines **20a** and **21a,b** are readily hydrolyzed compounds formed in the hydrolysis of resorcinoloxydiamidophosphates like **22a,b.**

Complexation of synthesized cycloamidophosphites **7a,b** and **15a,b** was studied in reactions with equimolecular amounts of acetylacetonatodicarbonylrhodium (I). The reaction proceeded in benzene at room temperature for 2 to 4 hours. The ^{31}P NMR spectra of the complexes (**23,24a,b**) formed exhibited doublets with equal chemical and coordination shifts; the P–Rh coupling constants were typical for

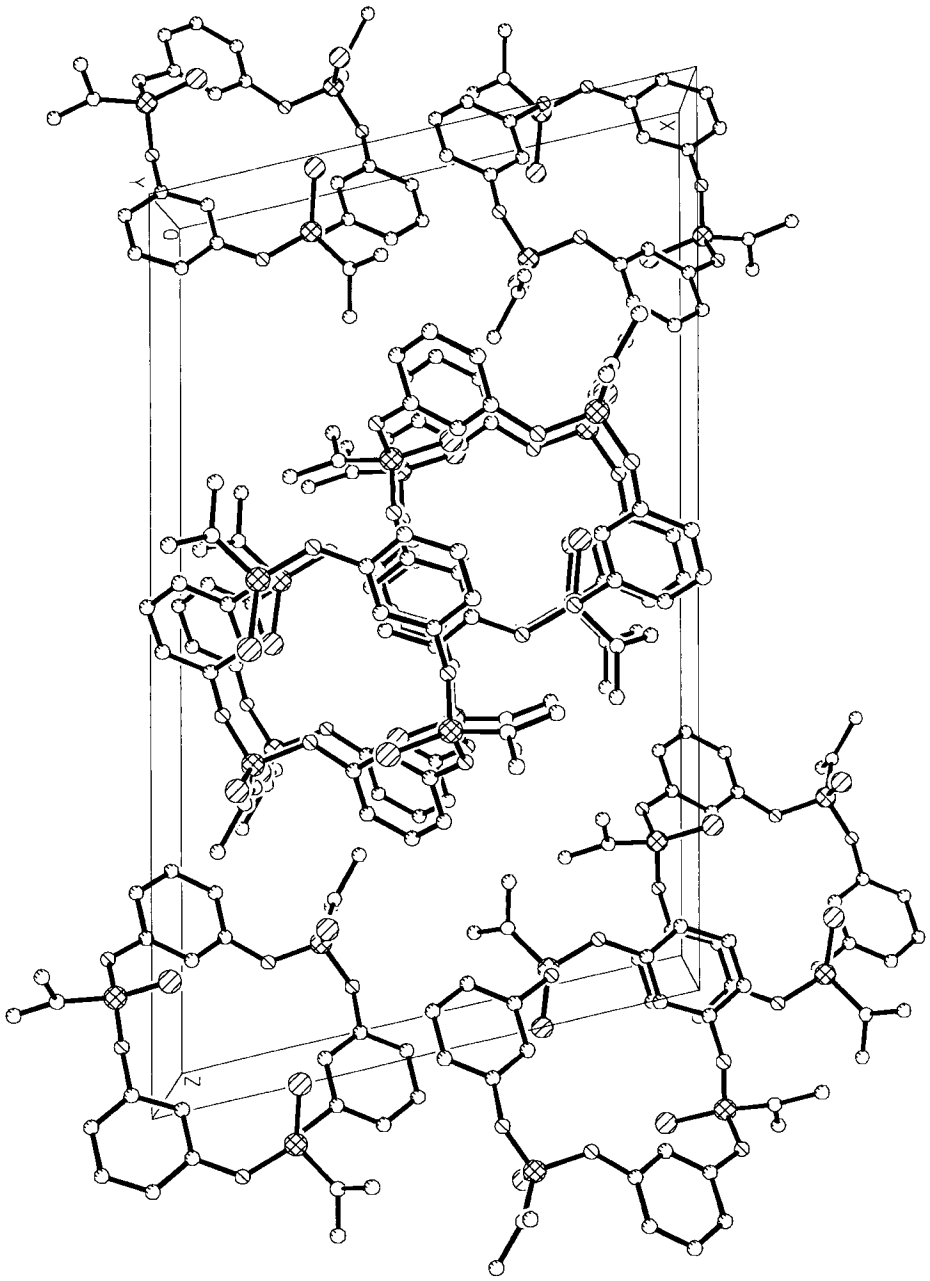


FIGURE 3 Crystal structure of 12a.

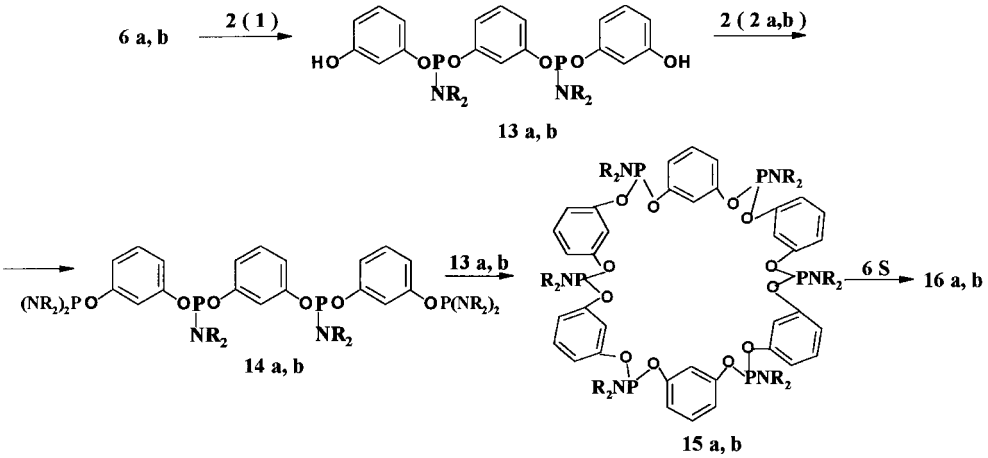
plane square complexes of rhodium (I) containing amidophosphite ligands. An absorption band at 1990 cm^{-1} typical for the CO–Rh bond was observed in their IR spectra.

EXPERIMENTAL

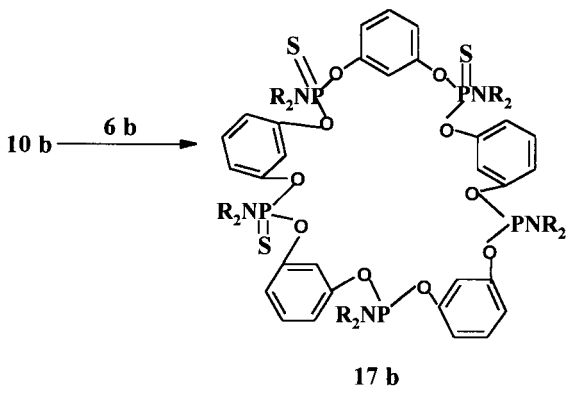
^1H NMR spectra of compounds **10b, 11b, 16a,b, 17b,** and **18b** in C_6D_6 were recorded on a Bruker WH-250 instrument at 250 MHz; those of **9a, 11a, 18a, 19a, 23a,b,** and **24a,b** in C_6D_6 were recorded on a Bruker AC-200 instrument at 200 MHz with TMS as the internal standard. ^{31}P NMR spectra of **9b, 10b, 11a,b, 16a,b, 17b, 18a,b, 23a,b, 24a,b** (in benzene) and **19a** (in methylene chloride) were recorded on a Bruker WP-80 SY at 32.4 MHz (85% H_3PO_4 being used as the external standard).

IR spectra of **24a,b** (in petroleum jelly) and **23a,b** (in methylene chloride) were recorded on a Specord IR-75 spectrometer.

The X-ray diffraction analysis was performed on a Syntex P-1 automatic diffractometer. Monoclinic



SCHEME 3



SCHEME 4

colorless crystal of **12a** (C_{24} H_{30} N_3 O_6 P_3 S_3, M = 645.60), size 0.45 × 0.17 × 0.07 mm, prism, space group P2(1)/n, a = 14.986(3), b = 8.125(2), c = 24.835(5) Å. V = 2945.5(11) Å ^{3}. Z = 4 (1.456 Mg/m^3). μ = 4.219 mm^{-1}. F(000) = 1344. $\theta/2\theta$ data collection, θ range 3.16 to 57.43° in $-15 \le h \le 16$, $-8 \le k \le 0$, $-27 \le 1 \le 0$, independent reflections: 2592/2523 (Rint = 0.0226).

Refinement method: full-matrix least-squares on F^2; data/restraint/parameters: 2523/0/473, GoF on F^2 = 1.100, final R indices [$I > 2\theta(I)$]: R_1 = 0.0478, wR_2 = 0.0977, largest difference peak/hole: 0.665/−0.323 e Å^{-3}.

Column chromatography was carried out on L 100/250 silica gel; TLC was conducted on Silufol plates. The detection of compounds was achieved using iodine vapor treatment, calcination, and the treatment with a 1% aqueous solution of $AgNO_3$.

We synthesized 1,3-*bis*(tetraalkyldiamidophosphitoxybenzenes) **6a,b** and amidophosphites **3a,b** previously [1], as well as amidophosphites **13a,b** [2].

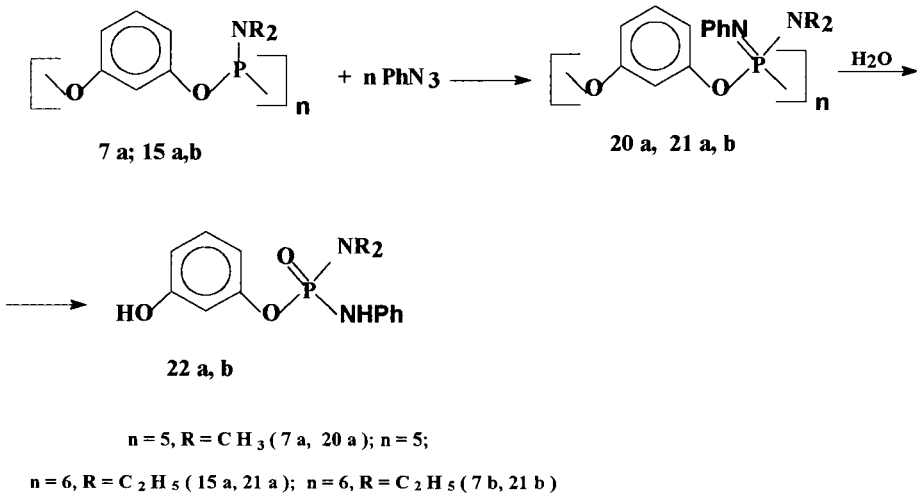
Physicochemical and spectral characteristics of the compounds synthesized are given in Tables 3, 4.

Synthesis of Cyclopenta(*m-phenylenedialkylamidothionophosphates*) (**11a,b**)

Hexaalkyltriamide of phosphorous acid **2a** or **2b** (1.7 mmol) was added to a solution of 3.4 mmol of resorcinol (**1**) in 17 mL of acetonitrile and the reaction mixture was stirred at room temperature for 1.5 hours. Then, 3.4 mmol more of **2a** or **2b** was added, and the mixture was stirred for 2 hours. An additional 3.4 mmol of **1** in 17 mL of acetonitrile was added; the mixture was stirred for 2 hours, and 1.7 mmol of 1,3-*bis*(tetraalkyldiamidophosphitoxybenzene) **4a** or **4b** was added. The reaction mixture was left to stand overnight. Acetonitrile was removed; the reaction products were dissolved in 15 mL of benzene; 4.25 mmol of dry sulfur was added to the solution, and the mixture was stirred at room temperature for 3 hours. The solvent was evaporated, and chromatography was performed on the residue on a column; compounds **11a,b** were eluted by the benzene-dioxane (10:1) system and dried for 3 hours in vacuo (1 mmHg, 60°C). Anal. Calcd. for $C_{40}H_{50}N_5O_{10}P_5S_5$ (**11a**): M, 1076. Found: M, 1045 (cryoscopy).

Bis(*m-tetraethyldiamidothiophosphatoxyphenyl*)*diethylamidothionophosphate* (**9b**)

Compound **2b** (0.37 g) was added to 0.33 g of **1** in acetonitrile; the mixture was stirred for 1.5 hours. More (0.74 g) of **2b** was added, and the mixture was



SCHEME 5

TABLE 3 Physicochemical Characteristics of Compounds Obtained

				Found, %					*Calculated (%)*			
Compound	*Yield (%)*	State, m.p.	Rf[a] (*system*)	*C*	*H*	*N*	*P*	*Molecular Formula*	*C*	*H*	*N*	*P*
9b	68	oil	0.72(B)				12.08	$C_{32}H_{58}N_5O_4P_3S_3$				12.13
10b	72	oil	0.36(B)				11.10	$C_{36}H_{48}N_3O_8P_3S_3$				11.06
11a	65	189°C	0.72(A)	44.91	4.80	6.43	14.55	$C_{40}H_{50}N_5O_{10}P_5S$	44.65	4.68	6.51	14.39
11b	63	oil	0.64(A)	49.67	5.72	5.57	12.85	$C_{50}H_{70}N_5O_{10}P_5S_5$	49.37	5.80	5.76	12.73
16a	72	134°C	0.71(B)	45.02	4.93	6.87	14.50	$C_{48}H_{60}N_6O_{12}P_6S_6$	44.65	4.68	6.51	14.39
16b	67	oil	0.65(B)	49.63	5.65	5.86	12.68	$C_{60}H_{84}N_6O_{12}P_6S_6$	49.37	5.80	5.76	12.73
17b	56	oil	0.47(C)				13.56	$C_{50}H_{70}N_5O_{10}P_5S_3$				13.44
18a	73	oil	0.72(D)	48.43	5.17	7.10	15.61	$C_{40}H_{50}N_5O_{15}P_5$	48.24	5.06	7.03	15.55
18b	87	oil	0.88(D)	53.04	6.27	6.25	13.81	$C_{50}H_{70}N_5O_{15}P_5$	52.86	6.21	6.17	13.63
19a	75	oil	0.74(D)	48.20	5.02	6.95	15.42	$C_{48}H_{60}N_6O_{18}P_6$	48.24	5.06	7.03	15.55
19b	85	oil	0.86(D)	52.97	6.04	6.07	13.48	$C_{60}H_{84}N_6O_{18}P_6$	52.86	6.21	6.17	13.63
23a	78	110–111°C	0.94(E)				7.62	$C_{70}H_{85}N_5O_{25}P_5Rh_5$				7.497
23b	78	117–119°C	0.92(E)				7.14	$C_{80}H_{105}N_5O_{25}P_5Rh_5$				7.02
24a	82	122–123°C	0.93(E)				7.41	$C_{84}H_{102}N_6O_{30}P_6Rh_6$				7.497
24b	85	110°C	0.85(E)				7.53	$C_{96}H_{126}N_6O_{30}P_6Rh_6$				7.02

[a]Eluents: (A) benzene-dioxane (5:1); (B) benzene-dioxane (10:1); (C) benzene-hexane (1:3); (D) chloroform-ethanol (5:1); (E) chloroform-ethanol (10:1).

left to stand for 2 hours. Then, 0.143 g of sulfur was added to the solution obtained, and the reaction mixture was stirred for 4 hours. The solvent was removed in vacuo; chromatography was performed on the residue on a column, and of the product **10b** was eluted by the benzene-hexane (1:3) system.

Bis[(m,m'-hydroxyphenyl-diethylamidothiophosphatoxy)phenyl]-diethylamidothionophosphate (**10b**)

Compound **4b** (1.45 g) was added to a solution of 0.44 g of **1** in 20 mL of acetonitrile; the mixture was stirred for 1.5 hours at room temperature. More (0.19 g) of sulfur was added, and the mixture was stirred at room temperature. The solvent was removed; the residue was chromatographed on a column, and the product **10b** was eluted by the benzene-hexane (3:2) system.

Cyclohexa(m-phenylenedialkylamidothionophosphates) (**16a,b**)

Compound **4a** or **4b** (1.73 mmol) was added to 3.46 mmol of **1** in 17 mL of acetonitrile; the mixture was stirred at room temperature for 2 hours. Next, the

TABLE 4 Spectral Characteristics of Compounds Obtained

Compound	*^{31}P NMR (δ, ppm)*	*^{1}H NMR (δ, ppm)*	*IR spectrum (ν, cm^{-1})*
9b	66.17s, 75.90s	0.95t (30H, SH_3), 3.11 b m (20H, SH_2), 6.47 b s (2H, OH), 7.04 b m, 7.48 b d, (8H, SH-ar)	
10b	66.27s, 66.22s	0.93 t (18H, SH_3), 3.25 m (12H, SH_2, $^{3}J_{P\text{-}H}$ 12.66 Hz), 6.47 b s (2H, OH), 6.87 b m, 6.96 b m, 6.87 b s, 6.96 b s, 7.52 b s (16H, SH-ar)	
11a	66.93 s, 67.64 s	2.66 b m (30H, SH_3), 7.106 b m, 7.18 b m, 7.55 b s, 7.62 b s, 7.69 b s (20H, SH-ar,)	
11b	66.29 s	0.94 b m (30H, SH_3), 3.24 b m (20H, SH_2, $^{3}J_{P\text{-}H}$ 13.66 Hz), 6.93 b m, 7.08 b m, 7.54 b s, (20H, SH-ar)	
16a	66.21s, 67.22s, 66.54 s, 67.16s	2.61 m (36H, SH_3), 6.93, 7.02, 7.52, 7.58 b m (24H, SH-ar)	
16b	65.12s, 65.67s, 66.21s, 66.93s	0.95 m (36H, SH_3, $^{2}J_{H\text{-}H}$ 6.83 Hz), 3.24 m (24H, SH_2, $^{3}J_{P\text{-}H}$ 12.81 Hz), 7.03 m, 7.13 b d, 7.59 b s (24H, SH-ar)	
17b	140.56 b s, 66.11 b s	0.97 t (30H, SH_3), 3.37 b (20H, SH_2), 7.01 b m, 7.12 b m, 7.6 b m (20H, SH-ar)	
18a	1.04 s	2.48 m (SH_3, 0H), 6.9 m, 7.15 m, 7.30 m (20H, SH)	
18b	0.24 s	0.95 b m (36H, SH_3,), 3.241 b m (24H, SH_2), 6.97 b m, 7.12 b m, 7.54 b s, (24H, SH-ar)	
19a	1.43 s	2.77 d (36H, SH_3), 7.03 d, 7.16 s, 7.27 t (24H, SH)	
19b	0.37 s	1.009 t (36H, SH_3), 3.197 m (24H, SH_2), 7.09 d, 7.16 s, 7.256 t, (24H, SH)	
23a	133.8 d, $^{1}J_{P\text{-}Rh}$ 263.26 Hz	1.6 s (15H, SH_3 *acac*), 1.9 s (15H, SH_3 *acac*), 2.89 d (30H, SH_3), 5.29 s (5H, SH *acac*), 7.10 m, 7.25 m, 7.5 m (20H, SH)	1990 (CO), 1520, 1580 (*acac*)
23b	133.9 d, $^{1}J_{P\text{-}Rh}$ 262.94 Hz	1.10 s (30H, SH_3), 1.73 s (15H, SH_3 *acac*), 1.92 s (15H, SH_3 *acac*), 3.64 m (20H, SH_2), 5.34 s (5H, SH *acac*), 7.10 s, 7.3 m, 7.71 d (20H, SH)	1990 (CO), 1520, 1580 (*acac*)
24a	133.7 d, $^{1}J_{P\text{-}Rh}$ 262.72 Hz	1.78 s (18H, SH_3 *acac*), 1.92 s (18H, SH_3 *acac*), 2.9 d (36H, SH_3), 5.3 s (6H, SH *acac*), 7.07 t, 7.25 m, 7.72 d (24H, SH)	1990 (CO), 1520, 1580 (*acac*)
24b	133.86 d, $^{1}J_{P\text{-}Rh}$ 263.10 Hz	1.10 t (b t, CH_3, 30H), 1.72 (b s, CH_3 − *acac,* 18H), 1.93 (b s,, CH_3 − *acac,* 18H), 3.62 (b m, CH_2, 20H), 5.34 (s, CH − *acac,* 12H), 7.09, 7.45, 7.70 (b m, CH − ar, 20H)	1990 (CO), 1520, 1570 (*acac*)

solution obtained was divided into two equal parts. More (1.73 mmol) of **2a** (or **2b**) was added to the first part. The mixture was stirred for 2 hours; the second part of the solution was added, and the reaction mixture was left for a night. Acetonitrile was removed; the residue was dissolved in 15 mL of benzene. Dry sulfur (5.2 mmol) was added, and the mixture was stirred for 3 hours. The solvent was removed in vacuo; the residue was chromatographed on a column, and of the products 16a or 16b were eluted by the benzene-hexane (4:1) systems. Anal. Calcd. for $C_{48}H_{60}N_6O_{12}P_6S_6$ (**16a**): *M,* 1291. Found: *M,* 1263 (cryoscopy).

Cyclo[bis(m-phenylenediethylamidophosphite)-tris(m-phenylenediethylamidothionophosphate)] (**17b**)

Bisphosphite **4b** (1.04 g) was added to a solution of 2.5 g of **10b** in 10 mL of acetonitrile; the mixture was stirred for 48 hours. The solvent was removed to a minimum in vacuo, and hexane was added. The oil formed was separated and dried in vacuo for 3 hours (1 mmHg, 55–60°C).

Cyclopenta(m-phenylenedimethylamidophosphate) (**18a**) *and cyclohexa*s(*m-phenylenedimethylamidophosphate*) (**19a**)

The calculated amount of complex $(NH_2)_2CO{\cdot}H_2O_2$ was added to a solution of cycloamidophosphite **7a** or **15a** in benzene. The molar ratio between **7a** or **15a** and $(NH_2)_2CO{\cdot}H_2O_2$ was 1:5 for **7a** and 1:6 for **15a**. The reaction mixture was stirred at room temperature for 3 hours and left to stand for 24 hours. A dense oil was precipitated. The benzene solution was decanted; the oil residue was dissolved in CH_2Cl_2, filtered from urea, evaporated to a minimum, washed with benzene, and dried in vacuo for 3.5 hours (1 mmHg; 60–65°C).

Cyclo[penta(m-phenylenediethylamidophosphate)] (**18b**) *and cyclo[hexa*s*(m-phenylenediethylamidophosphate)]* (**19b**)

The calculated amount of complex $(NH_2)_2CO{\cdot}H_2O_2$ was added to a benzene solution of **7b** or **15b** and stirred at room temperature for 4 hours. On the next day, the solution obtained was filtered from urea and evaporated to minimum. The product was washed with hexane and dried in vacuo for 3.5 hours (1 mmHg; 60–65°C). The molar ratio between **7b** or **15b** and $(NH_2)_2CO{\cdot}H_2O_2$ was 1:5 for **7b** and 1:6 for **15b**.

Synthesis of μ-[cyclopenta(m-phenylene dialkylamidophosphite)]penta[acetylacetonatocarbonylrhodium(I)] (**23a,b**) *and μ-[cyclohexa(m-phenylenedialkylamidophosphite)] hexa[acetylacetonatocarbonylrhodium(I)]* (**24a,b**)

The calculated amount of $Rh[(acac)(CO)_2]$ was added to a benzene solution of cycloamidophosphite **7a,b** or **15a,b** under an argon atmosphere. The molar ratio between **7a,b** or **15a,b** and $Rh[(acac)(CO)_2]$ was 1:5 for **7a,b** and 1:6 for **15a,b.** The solution was kept at room temperature for 3 hours. The solvent was evaporated. The residue was washed with hexane and redissolved in benzene; more (4 mL) of hexane was added. The residue was separated and dried in vacuo for 3.5 hours (1 mmHg; 45–50°C).

REFERENCES

[1] Nifantyev, E. E.; Rasadkina, E. N.; Yankovich, I. V. Zh Obshch Khim 1997, 67, 1812.
[2] Nifantyev, E. E.; Rasadkina, E. N.; Yankovich, I. V.; Vasyanina, L. K.; Belsky, V. K.; Stash, A. I. Heteroat Chem 1998, 9, 643.
[3] Nifantyev, E. E.; Rasadkina, E. N.; Yankovich, I. V. Zh Obshch Khim 1999, 69, 36.