Rhodium(I) carbonyl complexes based on naphthophosphacyclophanes

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Naphthphosphacyclophanes based on symmetrical dihydroxynaphthalenes linked by diethylamidophospite groups were used to synthesize rhodium(I) complexes containing carbonyl and acetylacetonato fragments. The physicochemical and spectral characteristics of the synthesized coordination systems were studied.

Key words: naphthophosphacyclophanes, amidophosphites, (acetylacetonato)dicarbonyl rhodium(I), complexation.

Increasing interest in the development of supramolecular systems and catalysts based on transition metal complexes has been observed since the beginning of the XXI century.[1] The mass use of phosphine ligands of various structure for the synthesis of complexes with such a metal as rhodium(I) started from the moment of discovery of the Wilkinson catalyst.[2] The formed coordination systems are applied as efficient homogeneous[3,4] and heterogeneous[5,6] catalysts for diverse processes. High efficiency of the rhodium complexes with amidophosphite ligands as catalysts for asymmetrical catalysis has been shown in the recent years.[7,8]

The purpose of the present work is the synthesis and study of some physicochemical characteristics of the carbonyl rhodium(I) complexes with naphthophosphacyclophanes of various structure. The latter are bidentate ligands containing two amidophosphite centers.

The reactions of (acetylacetonato)dicarbonyl rhodium(I) ($Rh(acac)(CO)_2$) (2 mol) with naphthophosphacyclophanes **1**—**3** (see Refs 9 and 10) afforded binuclear complexes **4**—**6** (Scheme 1).

The reactions occurred at room temperature in a dichloromethane solution within 4 h. Complexes **4**—**6** were isolated by reprecipitation in ~70—80% yields (Table 1).

Isolated compounds **4**—**6** were yellow or light brown substances highly soluble in dichloromethane, chloroform, acetone, and 1,4-dioxane. Attempts to grow single crystals of the synthesized systems **4**—**6** suitable for X-ray diffraction analysis were unsuccessful.

The ^{31}P NMR spectra of products **4**—**6** contain standard doublet signals at 134 ppm with $^1J_{P,Rh} = 260$—264 Hz (see Table 1) characteristic of the square-planar Rh(I) complexes. In the ^1H NMR spectra, the signals of all groups of protons (especially of the aromatic moiety) were broadened, which is due, most probable, to the formation of many hindered conformers of the macrocyclic ligand when the binuclear complex is formed. The ^1H NMR spectra of complexes **4**—**6** also exhibited the downfield

Scheme 1

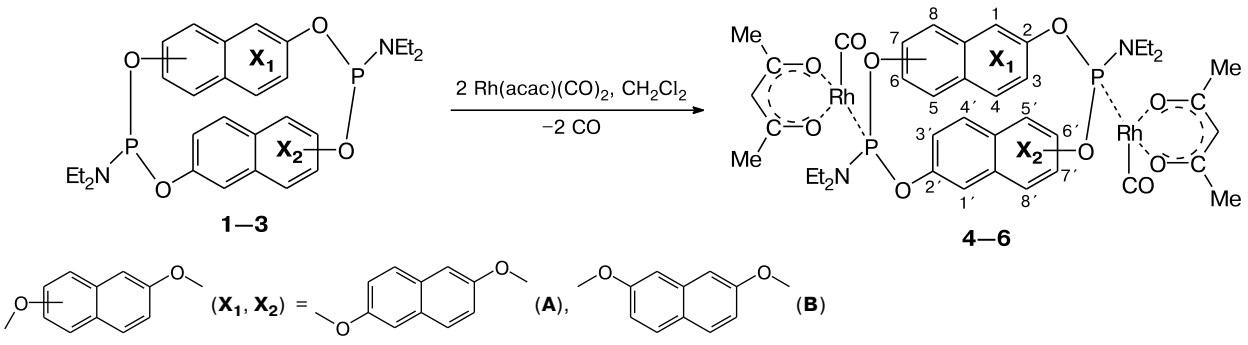

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Table 1. Physical characteristics of binuclear complexes **4—6**

Product	Fragment		Yield (%)	Decomp. point/°C	R_f*	^{31}P NMR ($CDCl_3$)	
	X_1	X_2				δ_P	$^1J_{P,Rh}$/Hz
4	**A**	**A**	71	219—221	0.63	134.1	259.6
5	**B**	**B**	85	202—204	0.59	134.7	260.9
6	**A**	**B**	65	168—170	0.55	134.1	259.7

* Eluent C_6H_6—dioxane, 5 : 1.

shift of the signals compared to the starting ligands.[9,10] The maximum shift was observed for the methylene protons of the amidophosphite fragment ($\Delta\delta_H$: 0.35 (**4**), 0.26 (**5**), and 0.33 (**6**)) and protons H_X of the ABX system of the naphthalene moiety ($\Delta\delta_H \approx 0.5$). The spin-spin coupling constants $^3J_{P,H}$ increased by ~1.5 Hz compared to those of the starting ligands **1—3**.

The IR spectra of complexes **4—6** exhibited three strong characteristic absorption bands of carbonyl groups with frequencies of 1990 cm^{-1} (Rh—CO) and 1510, 1570 cm^{-1} (Rh—acac), as well as the absorption bands corresponding to the naphthphosphacyclophane ligand.

The synthesized binuclear rhodium complexes turned out to be unstable on storage in solutions, especially in chlorine-containing solvents, with the formation of viscous homogeneous substances of oligomeric nature that cannot be dissolved.

Thus, the binuclear carbonyl rhodium(I) complexes, where naphthophosphacyclophanes of various structure act as ligands, were synthesized for the first time. It is assumed to test the synthesized coordination compounds to catalytic activity.

Experimental

All syntheses were carried out in anhydrous dichloromethane under dry nitrogen atmosphere.

The ^{1}H and ^{31}P NMR spectra of compounds **4—6** in $CDCl_3$ were recorded on a Bruker AC-200 instrument at a frequency of 200 and 162 MHz, respectively. The chemical shifts (δ) are presented relative to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P). The mass spectrum was obtained on a Reflex III instrument (Bruker) (solvent $CHCl_3$, template 2,4,6-trihydroxyacetophenone). IR spectra were recorded in a range of 4000—550 cm^{-1} on a NEXUS FT-IR spectrometer (Nicolet) using the attenuated total reflectance method. The TLC analysis was conducted on the Silufol UV-254 plates. The substances were developed with iodine vapor and burning-through. (Acetylacetonato)dicarbonyl rhodium(I) was obtained using a known method.[11]

Synthesis of μ-[3,7-bis(diethylamino)-1,5-dinaphthalene-2,4,6,8-tetraoxa-3,7-diphosphacyclooctaphane]-bis[acetylacetonatocarbonylrhodium(I)] 4—6 (general procedure). A solution of cycloamidophosphites **1—3** (0.1 g, 0.2 mmol) in anhydrous dichloromethane (8 mL) was added with $Rh(acac)(CO)_2$ (0.1 g, 0.42 mmol) at room temperature with continuous stirring. In 4 h the solution was filtered, the solvent was removed *in vacuo*, and the residue was doubly precipitated with hexane from dichloromethane. The obtained complexes **4—6** were dried *in vacuo* for 2 h (50 °C, 1 Torr).

μ-[3,7-Bis(diethylamino)-1,5(2,6)-dinaphthalene-2,4,6,8-tetraoxa-3,7-diphosphacyclooctaphane]-bis[acetylacetonatocarbonylrhodium(I)] (4). ^{1}H NMR (δ): 1.15 (t, 12 H, CH_3, ^3J = 7.0 Hz); 1.44 (s, 6 H, Me_{acac}); 1.99 (s, 6 H, Me_{acac}); 3.65 (m, 8 H, CH_2, $^3J_{P,H}$ = 11.6 Hz); 5.34 (s, 2 H, CH_{acac}); 7.47 (br.d, 4 H, H(3), H(3′), H(7), H(7′)); 7.71 (br.m, 8 H, H(1), H(1′), H(4), H(4′), H(5), H(5′), H(8), H(8′)). IR, ν/cm^{-1}: 1988 (Rh—CO); 1508; 1566 (CO_{acac}). Found: P, 6.36. *m/z* 985.56 $[M + H]^+$. $C_{40}H_{48}N_2O_{10}P_2Rh_2$. Calculated: P, 6.29. M = 984.61.

μ-[3,7-Bis(diethylamino)-1,5(2,7)-dinaphthalene-2,4,6,8-tetraoxa-3,7-diphosphacyclooctaphane]-bis[acetylacetonatocarbonylrhodium(I)] (5). ^{1}H NMR (δ): 0.97 (t, 12 H, Me, ^3J = 6.4 Hz); 1.46 (s, 6 H, Me_{acac}); 1.78 (s, 6 H, Me_{acac}); 3.54 (m, 8 H, CH_2, $^3J_{P,H}$ = 12.0 Hz); 5.18 (s, 2 H, CH_{acac}); 7.47 (d, 4 H, H(3), H(3′), H(6), H(6′), $^3J_{H(3),H(4)} = {}^3J_{H(3'),H(4')} = {}^3J_{H(5),H(6)} = {}^3J_{H(5'),H(6')}$ = 9.4 Hz); 7.60 (d, 4 H, H(4), H(4′), H(5), H(5′), $^3J_{H(3),H(4)} = {}^3J_{H(3'),H(4')} = {}^3J_{H(5),H(6)} = {}^3J_{H(5'),H(6')}$ = 9.4 Hz); 7.92 (s, 4 H, H(1), H(1′), H(8), H(8′)). IR, ν/cm^{-1}: 1990 (Rh—CO); 1511; 1570 (CO_{acac}). Found (%): C, 48.72; H, 4.99; N, 2.82; P, 6.30. $C_{40}H_{48}N_2O_{10}P_2Rh_2$. Calculated (%): C, 48.80; H, 4.91; N, 2.85; P, 6.29.

μ-[3,7-Bis(diethylamino)-1(2,6),5(2,7)-dinaphthalene-2,4,6,8-tetraoxa-3,7-diphosphacyclooctaphane]-bis[acetylacetonatocarbonylrhodium(I)] (6). ^{1}H NMR (δ): 1.10 (t, 12 H, Me, ^3J = 6.9 Hz); 1.42 (s, 6 H, Me_{acac}); 1.96 (s, 6 H, Me_{acac}); 3.62 (m, 8 H, CH_2, $^3J_{P,H}$ = 11.6 Hz); 5.28 (s, 2 H, CH_{acac}); 7.41 (m, 4 H, H(3), H(3′), H(6′), H(7)); 7.69 (br.m, 8 H, H(1), H(4), H(5), H(8), H(1′), H(4′), H(5′), H(8′)). IR, ν/cm^{-1}: 1995 (Rh—CO); 1518; 1577 (CO_{acac}). Found (%): C, 48.74; H, 4.98; N, 2.88. $C_{40}H_{48}N_2O_{10}P_2Rh_2$. Calculated (%): C, 48.80; H, 4.93; N, 2.82.

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