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Chlorocarbonyl rhodium(I) complexes with chiral catecholphosphitoamines

K.N. Gavrilov, A.T. Teleshev and E.E. Nifantyev

Division of Organic Chemistry, V.I. Lenin Moscow State Pedagogical University, M. Pyrogovskaya 1, Moscow, 119882 (Russian Federation)

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Abstract

The interaction of chiral catecholposphitoamines  with $[Rh(CO)_2Cl]_2$ is studied. The structures of the complexes formed are discussed on the basis of IR, ^1H, ^{13}C, ^{31}P NMR and mass spectral data.

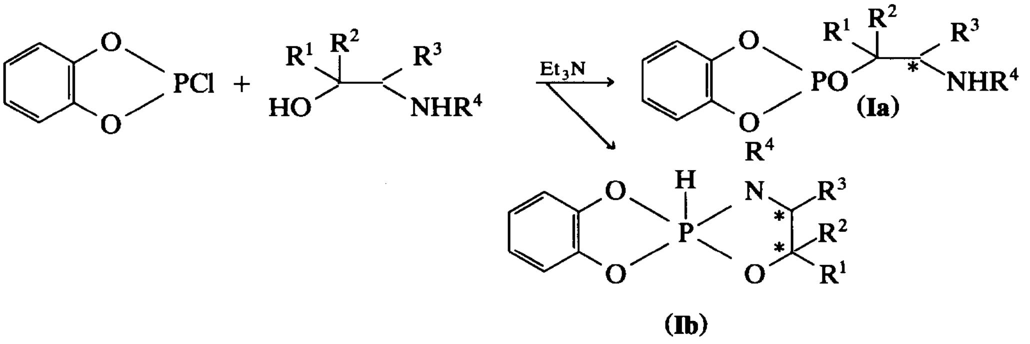
1. Introduction

Optically active P,N-bidentate ligands have found wide application in both coordination synthesis and asymmetric catalysis [1–3]. In spite of vital distinctions in the structure of chiral N-containing substituents at the phosphorus atoms, all these ligands have the same diphenyl-(sometimes dialkyl-) phosphine radicals. In this work, we propose a simple method for the preparation of new chiral phosphitoamines on the basis of benzophospholane heterocycles and discuss the complexation of rhodium(I) with these ligands. It is necessary to emphasize that these “head-footed” compounds are the most high-field systems in the spectrochemical row of phosphorus ligands and demonstrate marked electron-attracting character in accordance with the π-acceptor nature of the benzophospholane P-donor centre.

2. Results and discussion

Catecholphosphitoamines **Ia, b** were prepared through the interaction in a benzene solution of cyclic chlorophosphite with suitable amino alcohols at 0°C (Scheme 1).

Note that hydrospirophosphoran **Ib** (HSP) is the only product of the reaction. On the other hand, the



$R^1 = R^2 = H$, $R^3 = Et$, $R^4 = {}^iPr$ (**Ia**);
$R^1 = R^2 = R^3 = Ph$, $R^4 = H$ (**Ib**).

Scheme 1.

Correspondence to: Dr. E.E. Nifantyev.

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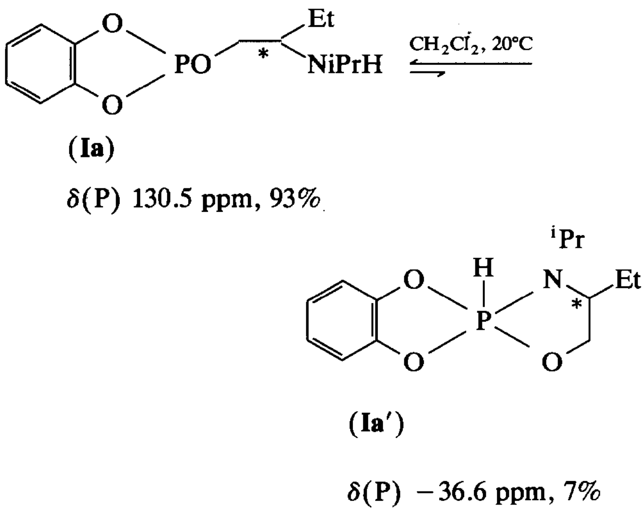
NMR ^{31}P spectrum of **Ia** shortly after dissolution in CH_2Cl_2 is given by a low-field signal, δ(P) 130.5 ppm. After a period of 3 h one can observe a certain loss of starting signal and the development of a high-field doublet, δ(P) = 36.6 ppm, ^1J(P, H) = 858.6 Hz from the tautomeric form of phosphorus(V) **Ia** (Scheme 2):



(Ia)

δ(P) 130.5 ppm, 93%

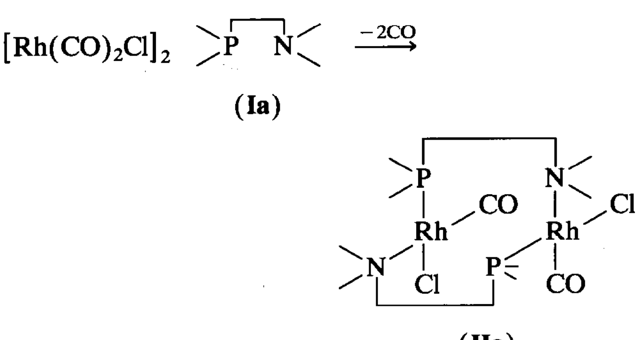
(Ia′)

δ(P) −36.6 ppm, 7%

Scheme 2.

This is in agreement with the well-known tautomeric transition $P^{III} \rightleftharpoons P^V$ for the phosphito (amidophosphito) amines with secondary outlying amino group [4].

According to Scheme 3, we began to study the interaction of **Ia, b** with such well-known coordination reagents as square-planar d_8 rhodium(I)complex[Rh-$(CO)_2Cl]_2$. The reaction of this starting compound and **Ia** is performed in CH_2Cl_2 at a molar ratio L/Rh = 1 at 20°C:



(Ia)

(IIa)

Scheme 3.

This direction of complexation agrees with ^{31}P NMR (δ(P) 142.3 ppm, ^1J(P, Ph) = 287.6 Hz), ^{13}C NMR (δ(C) 185.9 ppm, ^1J(C, Rh) = 69.7 Hz, ^2J(C, P) = 20.7 Hz) and IR (ν(CO) 2034 cm^{-1}) spectral parameters of the resulting solution. A mass spectroscopy investigation of this solution using the field desorption technique revealed the presence of molecular ions M^+ of dinuclear form **IIa**, m/z 871, as well as products of its disintegration $M^+ - Cl$ 835 and $M^+ - Cl - L$ 566. We also observed the presence of a narrow ν(N–H) 3228 cm^{-1} IR band in the solution of **IIa** in CH_2Cl_2 that may be connected with the existence of intramolecular hydrogen bonds [OCH$_2$CH(Et)N(ⁱPr)H ··· ClRh] [5]. Conformation stability of phosphitoamine in the composition of complex **IIa** follows from the analysis of the ^{1}H NMR spectrum of a solution of **IIa** in CD_2Cl_2 (δ(H) CH_{ar} 7.15 (m) and 7.07 (m); $POCH_2$ 4.28 (m); CHN 3.29 (m); NH 2.78 (broad m); CH_2 1.84 (m); CH_3 1.64 (d) and 1.31 (d), 1.03 (t) ppm. It is interesting to note the rigid fixation of the Et-group located at the chiral carbon atom relative to the twelve-membered metal cycle.

The ^{13}C NMR spectra of the free and fixed ligand **Ia** (Table 1) show the change in conformation of the phosphitoamine molecule as a result of its complexation with rhodium(I).

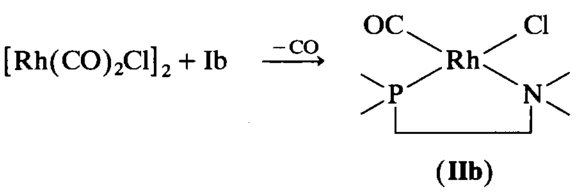
The tertiary carbon atom in the ⁱPr radical of the outlying amino group has the largest coordination shift (Δδ(C) 7.5 ppm, Table 1), which confirms the presence of a direct Rh–N bond in complex **IIa**.

The isolated compound **IIa** is a fine light-brown air-stable powder. The IR spectrum of **IIa** has two strong ν(Rh–Cl) bands at 308 and 278 cm^{-1}, characteristic of non-equivalent terminal Rh–Cl bonds.

The interaction of HSP **Ib** and $[Rh(CO)_2Cl]_2$ was run in CH_2Cl_2 at a molar ratio L/Rh = 1 at 20°C (Scheme 4).

This process was followed by IR and ^{31}P NMR spectroscopy. The IR spectrum of the reaction solution is characterized by the disappearance of the characteristic bands from free HSP at 3445 cm^{-1} (ν(N–H) and 2400 cm^{-1} (ν(P–H) and the appearance of a doublet of adsorption bands at 3296, 3240 cm^{-1}, ascribed to a species coordinated with the rhodium primary amino group. The availability of this doublet of narrow IR bands testifies to the presence of an intramolecular hydrogen bond [OC(Ph)$_2$CH(Ph)NH$_2$ ··· ClRh] in **IIb** as in **IIa**. In our previous paper [6], we described only broad ν(NH$_2$) bands by the analysis of the IR spectra of polynuclear rhodium complexes.

In the ^{31}P NMR spectrum of the reaction solution, we discover the disappearance of the doublet signals of



(IIb)

Scheme 4.

TABLE 1. ^{13}C NMR spectral data for the solution of **Ia** and **IIa** in CD_2Cl_2

Substance	δ(C) ppm (J(C, P) Hz)						
	C_{ar}	$POCH_2$	CHN	CH<	$CH(CH_3)_2$	CH_2	CH_3
Ia	145.0–112.2	66.1	55.9	45.6	23.5, 23.1	25.0	10.3
IIa	145.3–112.8	67.5 (4.2)	57.3 (4.8)	53.1	25.9, 25.5	22.9	10.2 (7.9)

Ib (two isomers) (δ(P) -37.6 ppm, ^1J(P, H) = 834.3 Hz and δ(P) -38.5 ppm, ^1J(P, H) = 832.1 Hz) and the appearance of a doublet from **IIb** (δ(P) 134.1 ppm, ^1J(P, Rh) = 289.2 Hz).

Both spectral methods indicate that complexation of rhodium(I) with HSP **Ib** involves opening of the amidophosphite ring to give a P,N-bidentate ligand.

The IR and ^{13}C NMR (Fig. 1) investigations of the solution **IIb** in CH_2Cl_2 indicate the *trans*-position of the amino and carbonylgroups in the coordination sphere of rhodium [7] (ν(CO) 2088 and 2038 cm^{-1}; δ(C) 184.0 ppm, ^1J(C, Rh) = 69.8 Hz, ^2J(C, P) = 22.3 Hz, δ(C) 179.9 ppm, ^1J(C, Rh) = 74.7 Hz, ^2J(C, P) $\approx$ 0 Hz. The ν(CO) band at 2088 cm^{-1} and the ^{13}C NMR doublet δ(C) 179.9 ppm probably arise from deflection of the carbonyl ligand from the plane of rhodium's coordination sphere. We can voice a supposition about the existence of a conformer of **IIb** with tetrahedral distortion of rhodium's square, as in the case of some palladium species [8].

Exposure of solution **IIb** in CH_2Cl_2 for several hours led to a ν(CO) band at 2015 cm^{-1}, which is typical for *cis*-positioned carbonyl and amino groups [9] and may be connected with isomerization of the **IIb** moiety with *cis*-orientation CO and $-NH_2$.

Isolated **IIb** is a bright-yellow, air-stable powder. Its mass spectroscopy investigation showed the presence of a molecular ion M^+ m/z 594 of mononuclear form **IIb**. The IR spectrum of solid complex, in addition to the $\nu(NH_2)$ bands at 3300 and 3240 cm^{-1} (which correspond to the coordinated primary amino group), contain two strong ν(CO) bands at 2082 and 2030

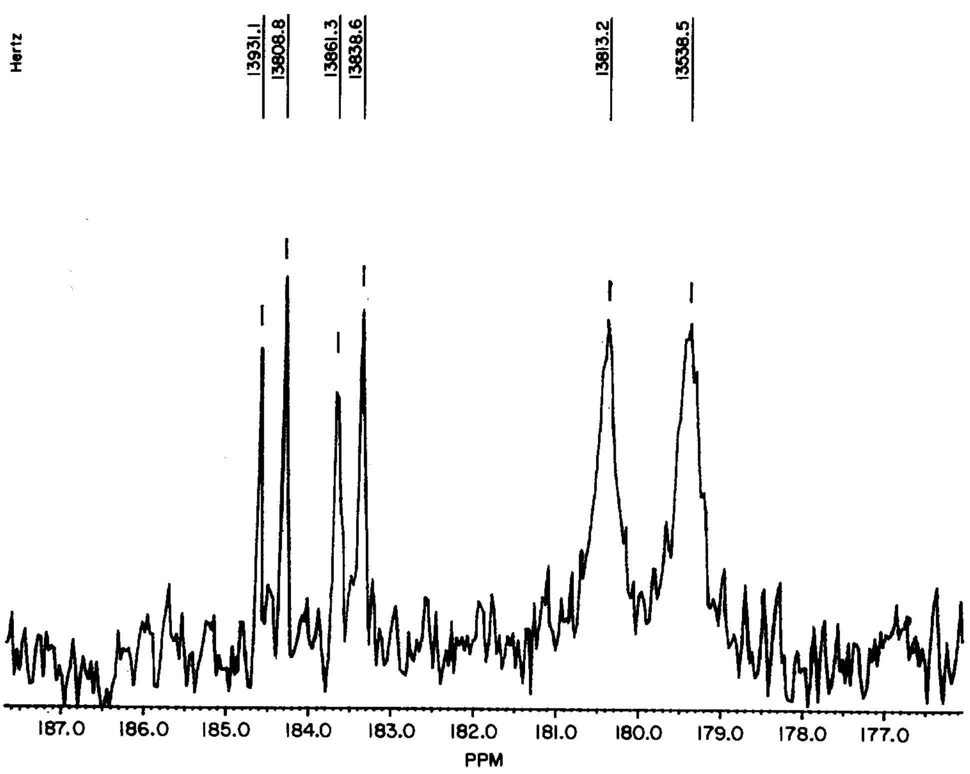


Fig. 1.

cm^{-1} and two ν(Rh–Cl) bands at 304 and 292 cm^{-1}, which, as stated above, belong to pseudo-tetrahedral and square-planar conformers of **IIb**.

3. Experimental details

3.1. General

All manipulations were carried out under an atmosphere of dry argon. Organic solvents were dried and degassed directly before use.

^1H (400.14), ^{13}C (75.50), ^{31}P (81.02 MHz) NMR spectra were recorded with Bruker AM 400, Bruker AM 300 and Bruker AC 200 spectrometers (internal standard HMDS, TMS and external standard 85% H_3PO_4 in D_2O, respectively). IR spectra were taken on a Specord M 80 instrument in KBr disks or in Nujol and CH_2Cl_2 between CsJ plates. Mass spectra using the field-desorption technique were obtained on a Varian-MAT 731. Optical rotation was measured on a Jasco Dip-360 polarimeter.

3.2. Synthesis of catecholphosphitoamines

Compounds **Ia, b** were prepared through interaction in benzene solution of cyclic catecholchlorophosphite with amino alcohols (Scheme 1). The liberated hydrogen chloride was bound by an amine and in the form of a salt isolated from the reaction product. After heating the benzene solution for 60 min, the solvent had been evaporated off and the liquid residuals were cleaned by means of extraction of boiling hexane.

2-(β-N-Isopropilamino)-ethoxy-4,5-benzo-1,3,2-dioxaphospholane (**Ia**). Viscous 1 oil. Yield 86%, n_D^{18} 1.5130, $[\alpha]_0^{20}$ −0.15 (C 1.0 $CHCl_3$). IR: ν(N–H) assoc. 3340, $\nu(PO–C_{ar})$ 1238, $\nu(PO–C_{al})$ 1010 (CH_2Cl_2) cm^{-1}.

5-Hydro-2,3-benzo-7-diphenil-8-1,4,6-threeoxa-9-aza-5-phosphaspiro-[4.4]nonane (**Ib**)

White crystals. Yield 89%m m.p. 93–96°C, $[\alpha]_0^{20}$ +2.18 (C 1.0 CH_2Cl_2). ^{13}C NMR: δ(C) 138.7–109.8 (C_{ar}); 78.9 and 78.0 (C–O); 58.0 (^2J(C, P) = 9.8 Hz); 57.4 (^2J(C, P) = 11.3 Hz, CHN, CD_2Cl_2, both isomers). IR: ν(N–H) 3432, ν(P–H) 2400, $\nu(PO–C_{ar})$ 1250, $\nu(PO–C_{al})$ 1012 (disk KBr) cm^{-1}.

3.3. Synthesis of chlorocarbonyl complexes

Compounds **IIa, b** were obtained by treating $[Rh(CO)_2Cl]_2$ with the appropriate catecholhposhitoamine in CH_2Cl_2, molar ratio P/Rh = 1. After stirring for 40 min at room temperature, the solution was concentrated by evaporation under reduced pressure and hexane was added. The solid was separated by centrifugation, washed with hexane and ether and dried. In the case of **IIb**, this substance in addition was refined by column chromatography on silufol UV-254, eluent CH_2Cl_2.

μ-[di-{2-(β-N-Isopropilamino)-ethoxy-4,5-benzo-1,3,2-dioxaphospholane}] bis(carbonylchlororhodium) **(IIa)**

Brown crystalline powder. Yield 97%, m.p. 240–241°C with dec. IR: ν(N–H) 3236, ν(CO) 2022, $\nu(PO–C_{ar})$ 1226, $\nu(PO–C_{al})$ 1032 (disk KBr) cm^{-1}.

[2-β-Aminoethoxy-α-diphenil-β-phenil-4,5-benzo-1,3,2-dioxaphospholane] carbonylchlororhodium **(IIb)**

Yellow crystalline powder. Yield 91%, m.p. 134–135°C with dec. IR: $\nu(PO–C_{ar})$ 1230, $\nu(PO–C_{al})$ 1015.

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