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Complexation of rhodium(I) with hydrophosphorane derivatives of bicyclo[3.3.0]-1-phospha-2,8-dioxa-5-aza-octane

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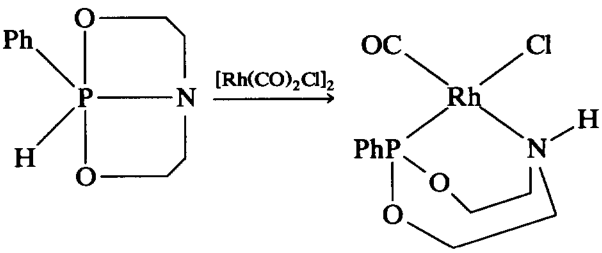
Abstract

The interaction of hydrophosphorane derivatives of bicycloamidophosphite (BAP) with square-planar d^8 rhodium(I) complex $[Rh(CO_2)Cl]_2$ is studied. The structures of the complexes formed are discussed on the basis of IR, ^{31}P and ^{13}C NMR and X-ray electron spectral data.

1. Introduction

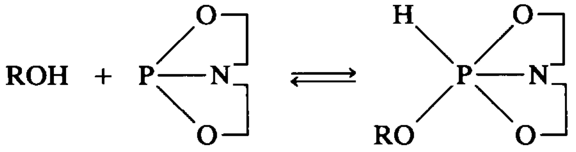
Coordination of "head-footed" P,N-bidentate ligands is an intensively developing field of metallocomplex synthesis and catalysis [1–5]. However, most systems have a tertiary outlying amino group. Therefore, the preparation of new ligands with outlying N–H groups is of very great significance [6].

There are two methods for the synthesis of P,N-bidentate systems with a secondary outlying amino group. The phosphorylation of 1,3-amino alcohols with secondary amino group is usually employed for the preparation of such compounds [7]. Another widely used procedure is based on employing derivatives of phosphorus(V)-hydrophosphoranes. Thus, Bondoux *et al.* [8] were the first to report the synthesis of the unusual mononuclear rhodium complex



Coordination of such oxaza- and tetraza hydrophosphorane ligands has been investigated in detail [9–15].

In this work, we propose a novel procedure for the preparation of rhodium complexes with P,N-bidentate ligands containing a secondary outlying amino group based on the reaction of metal species with hydrophosphorane derivatives of BAP (I). These compounds, II, were obtained *in situ* by protonation of BAP [16,17]:



I IIa, b

R = Ph, Bornil (d and b)

(1)

2. Results and discussion

According to eqn. (1), we began our studies with such well-known proton donor reagents as phenol and borneol. In this paper, we discuss the interaction of BAP with borneol for the first time. This reaction was followed by ^{31}P spectroscopy. The ^{31}P NMR spectrum of the starting solution of BAP in CH_2Cl_2 contained two low-field singlets at $\delta(P)$ 139.1 and 135.1 ppm in accordance with the nature of this substance [18]. On addition of the borneol to this solution at 20°C (molar ratio 1/1), one can observe an abrupt loss of the original signal from BAP ($\delta(P)$ 139.1 ppm), with only a small decrease in the other signal ($\delta(P)$ 135.1 ppm) and the development of the high-field doublets $\delta(P)$ −38.1

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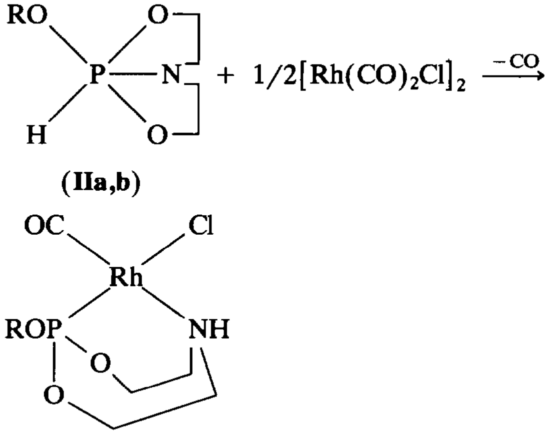
TABLE 1. IR spectral parameters for **IIIa,b**

Compound	Absorption bands, ν (cm^{-1})						
	ν(NH)	ν(C$_{ar}$H)	ν(CO)	ν(C=C$_{ar}$)	ν(PO–C$_{ar}$)	ν(PO–C$_{al}$)	$\nu^{as,s}$(PO–C$_{ar}$)
IIIa	3230	3050	2012	1592 1498	1204	1025 1010	938 706
IIIb	3148	–	2080 1996	–	–	1030 1015	–

and −39.6 ppm, ^1J(P,H) = 815.9 Hz, which corresponds to different isomers of the hydrophosphorane compound (**IIb**). It is interesting to note that the intensity of the signal δ(P) −38.1 ppm is essentially greater than the intensity of signal δ(P) −39.6 ppm. This fact apparently indicates that the two conformers of BAP have reacted with borneol at different rates yielding two isomers of **IIb**. We have also observed that the interaction of BAP with phenol also leads to the two new signals of compound **IIa**, δ(P) −33.7 and −43.8 ppm in the ^{31}P NMR spectrum of the resulting solution. Hydrophosphorane substances **IIa,b**, specially formed by us *in situ* in CH_2Cl_2, have reacted with [Rh(CO$_2$)Cl]$_2$ under mild conditions yielding chelate metallocomplexes (eqn. (2)):



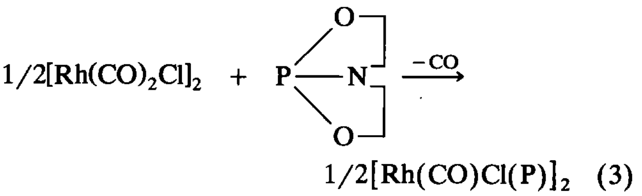
(**IIa,b**)

(2)

(**IIIa,b**)

The reaction was accompanied by intense evolution of gaseous carbon monoxide, a colour change from yellow to light yellow and precipitation of the brown product, **IIIa,b**. Addition of a quantity of [Rh(CO$_2$)Cl]$_2$ to a solution of **IIa,b** leads to the instantaneous disappearance of all starting signals in the ^{31}P NMR spectrum of the reaction solution and the development of new low-field doublets δ(P) 128.3 ppm, ^1J(P,Rh) = 291.0 Hz (**IIIa**) and δ(P) = 133.5 ppm, ^1J(P,Rh) = 262.0 Hz (**IIIb**). This indicates that the equilibrium of the proton transferring reaction (eqn. (1)) was rapidly displaced at the expense of complexation of rhodium(I) with compounds **IIa,b**. A clear difference in the ^1J(P,Rh) values of the complexes **IIIa,b** reflects a greater electronegative influence of the acyclic PhO-group in the case of system **IIIa** than the bornilo-group in the composition of complex **IIIb**.

We have also observed vital distinctions between the ^{31}P NMR spectral data of compounds **IIIa,b** and the model rhodium complex **IV**. This last substance was prepared independently (eqn. (3)).



(3)

The ^{31}P NMR spectrum of the solution of complex **IV** in CH_2Cl_2 contained low-field doublets: δ(P) 128.3 ppm, ^1J(P,Rh) = 258.1 Hz and δ(P) 128.5 ppm, ^1J(P,Rh) = 256.1 Hz. In this case, the spectral signals are apparently due to the different isomers of **IV**.

Isolated compounds **IIIa,b** are fine, air-stable powders, insoluble in common organic solvents. The IR spectra (Table 1) of solid complexes contain ν(N–H) bands which correspond to the coordinated amino group [8]. The ν(CO) values correlated with the electronegative nature of the acyclic PhO-group and confirmed *trans*-position carbon monoxide and amino groups in square-planar rhodium complexes [19]. Note that the IR spectrum of **IIIa** has a series of characteristic absorption bands of the PhO-group. This is additional evidence for the formation of a Ph–O–P bond during the reaction. We have also observed the presence of strong ν(Rh–Cl) IR bands at 294 and 300 cm^{-1} characteristic of terminal Rh–Cl bonds in **IIIa,b**.

Table 2 shows the results of the X-ray electron spectroscopy investigation of **IIIa,b**. The energy of the

TABLE 2. X-Ray electron spectral data

Compound	Binding energy (eV)				
	Rh 3d$_{5/2}$	P 2p	N 1s	O 1s	Cl 2p
IIIa	308.5	134.0	399.4	532.5	197.7
IIIb	309.8	134.2	400.4	532.8	199.1

N 1s bond in **IIIa,b** (Table 2) is much greater than typical values for this spectral parameter for uncoordinated amino groups (397.8 eV) [20]. In addition, the values of binding the energies for IIIa are unusually low. This effect probably arises from donation of electron density of the aromatic ring to the rhodium atom.

A mass spectroscopy investigation of **IIIa,b** using the field-desorption technique revealed the presence of molecular ions M^+ with m/z 394 (intensity 74%) and 454 (80%), respectively, corresponding to the mononuclear metallocyclic species [Rh(CO)ClL] as well as products of its disintegration $M^+ - Cl$ with m/z 358 (3%) and 418 (5%).

As stated above, the compounds **IIIa,b** are insoluble in different mediums. They have limited solubility only in dimethylsulfoxide (DMSO) at 80°C, but this is accompanied by intensive destruction of the metallocomplexes. This probably arises from oxidation of the phosphorus ligand.

For example, the ^{31}P NMR spectrum of **IIIa** in DMSO contains only one line δ(P) 2.9 ppm, which corresponds to the product of the ligand's decay. The ^{31}P NMR spectrum of the compound **IIIb** in DMSO also contains high-field signals δ(P) 21.8 and -2.8 ppm, and their intensity rapidly increases with time. Incidentally, only immediately after dissolving, have we observed weak low-field broad doublets: δ(P) 136.1 ppm, ^1J(P,Rh) = 270 Hz and δ(P) 140.5 ppm, ^1J(P,Rh) = 243.0 Hz. This fact apparently indicates intensive solvation of **IIIb**.

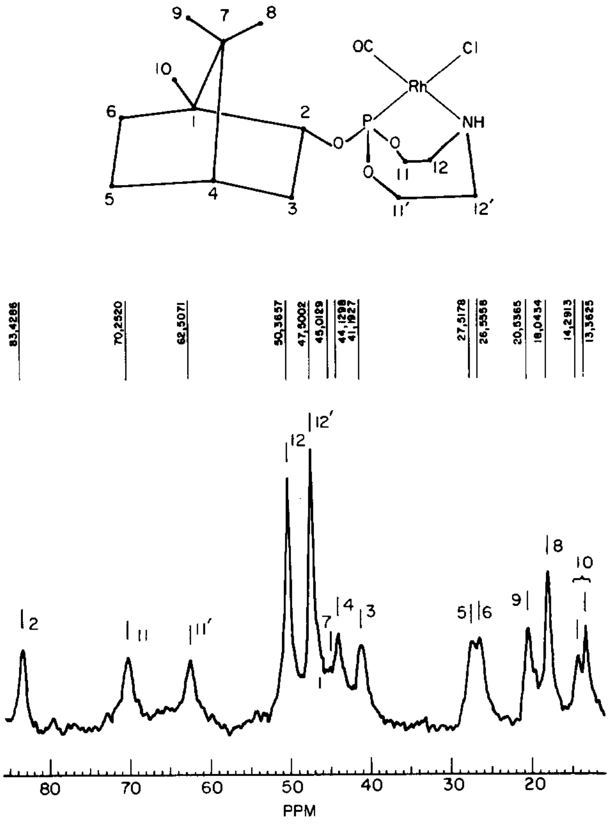


Fig. 1.

A solid-state ^{13}C NMR study of the complexes **IIIa,b** confirmed the part structure of their ligands. The spectrum of compound **IIIa** is given by a series of signals, δ(C) 150.5 ($C_{arom}O$); 132.3 and 130.8 (C_{meta}); 126.3 (C_{para}); 123.0 and 122.2 (C_{ortho}); 69.2 and 62.5 ($POCH_2$); 51.2 and 47.6 (CH_2N) ppm. It is interesting to note the spectral inequality of the *ortho*-, *meta*- and chelate ring carbon atoms. These probably arise from asymmetry of the chelate "basket" which distorts the geometry of the complex. Figure 1 shows the ^{13}C NMR spectrum of the ligand part **IIIb**.

3. Experimental details

IR spectra were recorded on Specord M 80 instruments in KBr disks or in Nujol between CsI plates. ^{31}P NMR spectra were run on a Bruker WP 80 instrument at 32.4 MHz versus 85% H_3PO_4 in D_2O. ^{13}C cross-polarization spectra using the magic angle technique were obtained at 75.5 MHz on a Bruker MSL-300 spectrometer. Mass spectra using the field-desorption technique were obtained on a Varian-MAT 731 spectrometer. X-Ray electron spectroscopy data were collected on a MAC-2 Riber spectrometer calibrated with Ag (lines at 901.5 and 367.9 eV); the samples were charged at 284.6 eV. The precision in determining the maximum of an individual spectral line was 0.1 eV.

All manipulations were carried out under an atmosphere of dry argon. Solvents were distilled from molecular sieves under argon. The BAP was prepared by the literature method [21].

3.1. *Synthesis of neutral chlorocarbonyl rhodium(I) complex*

Appropriate reagent ROH (R = Ph, Bornil) (2×10^{-3} mol) in 30 ml of CH_2Cl_2 was added dropwise, with stirring, to a solution of BAP (2×10^{-3} mol) in 30 ml of CH_2Cl_2 at 20°C. The reaction mixture was stirred for 1 h. Then the resulting solution was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ in 30 ml of CH_2Cl_2.

A fine brown precipitate was separated by centrifugation, washed with ether and pentane, and dried in air *in vacuo* (1 mmHg).

(2-Phenoxy-6-aza-1,3,2-dioxaphosphocan)rhodiumcarbonylchloride (**IIIa**). Bright-yellow powder. Yield 96%, m.p. 284°C with dec. Anal. Found: C, 33.4; H, 3.6; P, 8.1. $C_{11}H_{12}NO_4PClRh$ calcd.: C, 33.6; H, 3.6; P, 7.9%.

(2-Borniloxy-6-aza-1,3,2-dioxaphosphocan)rhodiumcarbonylchloride (**IIIb**). Yellow powder. Yield 93%, m.p. 252–254°C with dec. Anal. Found: C, 39.6; H, 5.9; P, 7.0. $C_{15}H_{26}NO_4PClRh$ calcd.: C, 39.7; H, 5.8; P, 6.8%.

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