ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 585 (1999) 290–293

Journal of Organometallic Chemistry

Complexes of Rh(I) with phosphite derivatives of codeine

K.N. Gavrilov [a,*], A.V. Korostylev [b], O.G. Bondarev [a], A.I. Polosukhin [b], V.A. Davankov [b]

[a] *Department of Chemistry, Ryazan State Pedagogic University, 46 Svoboda str., 390000 Ryazan, Russia*
[b] *Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov str., 117813 Moscow, Russia*

Received 15 February 1999; received in revised form 20 April 1999

Abstract

New complexes of Rh(I), $[RhCl(CO)(\mu\text{-}L)]_2$ and AcacRh(CO)L, have been obtained with L = 1,3,2-dioxaphosphorinane containing an exocyclic codeine fragment. The complexes were characterized by ^{1}H-, ^{13}C-, ^{31}P-NMR, IR spectroscopy, plasma desorption mass spectrometry, X-ray photoelectron spectroscopy and sedimentation analysis. It was found that the chlorocarbonyl rhodium complex is a dimer with the bridge-type P,N-bidentate ligands coordinated in the 'head to tail' mode. The same ligand in the acetylacetonate complex was found to be P-monodentate.

Keywords: Rhodium complexes; Chirality; Codeine derivatives; Phosphite ligands

1. Introduction

Phosphorylated alkaloids are known to be widely used in coordination synthesis and catalysis [1]. Earlier, we described the syntheses of 1,3,2-diazaphospholane and 1,3,2-dioxaphospholane on the base of codeine as well as their complexation with Pd(II) and Rh(I). In the complexation process, binuclear $[PdCl_2(\mu\text{-}L)]_2$ [2] and mononuclear AcacRh(CO)(η'-L) [3] complexes were formed. In the present paper, we report on a simple synthesis of phosphorylated codeine containing a more rigid dioxaphosphorinane cycle, and its rhodium complexes.

2. Experimental

All reactions were carried out under a dry argon atmosphere. All the solvents were distilled and carefully dehydrated before use. IR spectra were recorded on a Nicolet 750 instrument. ^{31}P- and ^{13}C-NMR spectra were recorded on a Bruker AMX-400 or Bruker AC-200 instrument (162.0 and 81.0 MHz with 85% H_3PO_4 in D_2O as an external standard for ^{31}P; 100.6 and 50.3 MHz with TMS as an external standard for ^{13}C). ^{1}H-NMR spectra were recorded on a Bruker WM-250 instrument (250.1 MHz; HMDS as an internal standard). The complete assignment of all resonances in ^{1}H- and ^{13}C-NMR spectra was achieved using homonuclear decoupling or DEPT technique, respectively. Literary data on ^{1}H- [4] and ^{13}C-NMR [5] spectroscopy of codeine have been used for the assignment of the resonances in NMR spectra of compounds **1**–**3**. Plasma-desorption mass spectrometry was performed on a time-of-flight MSVKh mass spectrometer with Cf-252 fission fragments as ionizing particles. The X-ray photoelectron spectra (XPS) were measured on a MAC-2 Riber spectrometer calibrated against Ag lines at 901.5 and 367.9 eV, correction for the sample charging was performed at C1s = 284.6 eV; the accuracy of the line maximum determination was $\pm$0.1 eV. Sedimentation analysis was performed on a MOM-3180 analytical ultracentrifuge, according to the literature technique [6–8]. Optical rotation was measured on a Jasco-Dip-360 polarimeter. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

* Corresponding author. Tel.: +7-091-2770162; fax: +7-095-1356471.
E-mail address: chem@ttc.ryazan.ru (K.N. Gavrilov)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00239-9

*2.1. 2-(7′,8′-didehydro-4′,5′-epoxy-3′-methoxy-N-methylmorphinoxy-6′)-1,3,2-dioxaphosphorinane (**1**)*

An equimolar mixture of dry codeine (10^{-3} mol) and freshly distilled 2-diethylamino-1,3,2-dioxaphosphorinane was heated to 125°C under vigorous stirring. Then the mixture was stirred in vacuum (1 mmHg, 60°C) for 40 min in order to remove $HNEt_2$. Yellow solid, 97% yield. M.p. 55–56°C. $[\alpha]_D^{13} = -120.5$ ($c = 1$, $CHCl_3$). ^{31}P-NMR: δ_P 131.2 ppm ($CDCl_3$). Mass-spectrum m/z (I,%): $[M]^+$ 403 (64), $[M-OPO(CH_2)_3O]^+$ 282 (100), $[PO(CH_2)_3O]^+$ 105 (68). Found (%): C, 62.37; H, 6.32; P, 7.85. Calc. for $C_{21}H_{26}NO_5P$: C, 62.53; H, 6.45; P, 7.69.

*2.2. Bis-{μ-[2-(7′,8′-didehydro-4′,5′-epoxy-3′-methoxy-N-methylmorphinoxy-6′)-1,3,2-dioxaphosphorinane-P,N] chlorocarbonyl rhodium(I)} (**2**)*

A solution of compound **1** (0.081 g, 2×10^{-4} mol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of 0.039 g (10^{-4} mol) of $[Rh(CO)_2Cl]_2$ in the same solvent (20 ml) at 20°C. The reaction mixture was stirred at 20°C for 1 h. The excess of the solvent was then removed in vacuum (40 mmHg), and an ether–hexane mixture (1:1) was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (5 ml) and hexane (5 ml), and dried in vacuum (1 mmHg) to give the product **2** as a yellow solid (0.109 g, 96% yield). M.p. 154–156°C. Found (%): C, 46.81; H, 4.75; N, 2.33; P, 5.15. Calc. for $C_{22}H_{26}NO_6PClRh$: C, 46.40; H, 4.60; N, 2.46; P, 5.44.

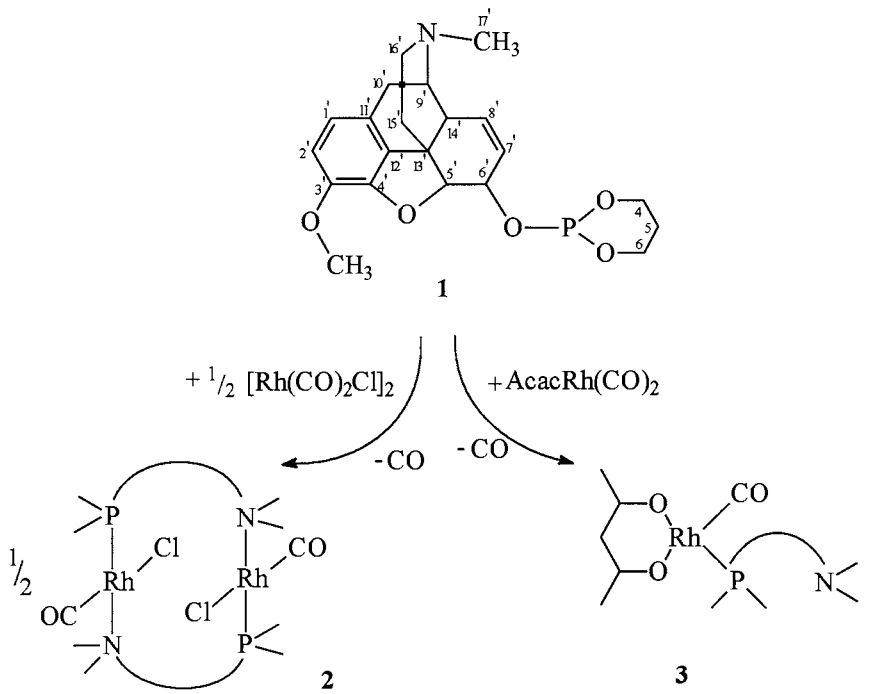
*2.3. Acetylacetone[2-(7′,8′-didehydro-4′,5′-epoxy-3′-methoxy-N-methylmorphinoxy-6′)-1,3,2-dioxaphosphorinane]carbonyl rhodium(I) (**3**)*

A solution of compound **1** (0.081 g, 2×10^{-4} mol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of 0.052 g (2×10^{-4} mol) of $AcacRh(CO)_2$ in the same solvent (20 ml) at 20°C. The reaction mixture was stirred at 20°C for 1 h. The excess of the solvent was then removed in vacuum (40 mmHg), and a ether-hexane mixture (1:1) was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2 × 5 ml), and dried in vacuum (1 mmHg) to give the product **3** as a dark-yellow solid (0.119 g, 94% yield). M.p. 136–138°C. ^{13}C-NMR (δ_C, ppm): CH 101.0, CH_3 27.4 and 27.1 ($CDCl_3$). Found (%): C, 51.35; H, 5.42; N, 2.07; P, 4.66. Calc. for $C_{27}H_{33}NO_8PRh$: C, 51.18; H, 5.25; N, 2.21; P, 4.89.

3. Results and discussion

Coordination of phosphite **1** has been found to proceed according to the general scheme shown in Scheme 1.

The dimeric structure of complex **2** and *trans*-arrangement of two P,N-bidentate-bound ligands **1**

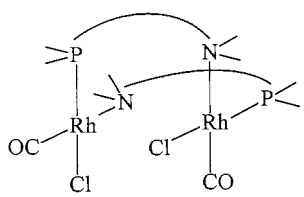


Scheme 1.

Table 1
^{13}C-NMR data for solutions of compounds **1**–**3** in $CDCl_3$, δ_C (ppm) (J(C,P), Hz)

Carbon atom	Compound		
	1	**2**	**3**
1′	118.7	120.2	118.9
2′	114.6	115.7	113.9
3′	142.1	143.3	142.1
4′	147.6	147.9	147.4
5′	91.5	91.3	90.7
6′	68.4 (19.6)	71.6	70.6 (4.4)
7′	133.4	132.1	133.4
8′	129.4	128.6	128.8
9′	58.6	60.5	58.8
10′	20.5	22.0	20.4
11′	127.4	126.7	127.3
12′	131.2	131.7	130.8
13′	43.5	43.5	43.4
14′	41.1	42.5	40.7
15′	35.7	37.1	35.5
16′	46.4	54.8	46.3
17′	43.1	47.2	43.0
OCH_3	57.0	57.8	56.7
4	60.0	67.1	64.9 (11.1)
5	28.6	28.5	27.7
6	59.5	65.9	64.6 (13.3)

(in the 'head to tail' mode) can be proven by ^{31}P-NMR (δ_P 128.9 ppm, ^1J(P,Rh) 252.0 Hz), ^{13}C-NMR (δ_C 184.1 ppm, ^1J(C,Rh) 80.5 Hz, ^2J(C,P) 20.4 Hz) spectroscopy data, and by IR spectroscopy data (ν(CO) 1996 cm^{-1}, ν(Rh–Cl) 310 cm^{-1}) on the reaction product dissolved in $CDCl_3$. It should be noted that similar spectral parameters are characteristic of *iso*-structural complexes of phosphorylated 1,3- and 1,6-aminoalcohols [9,10]. Comparing ^{13}C-NMR spectra of compounds **1** and **2** (see Table 1), we arrived at the conclusion that phosphite **1** in complex **2** is bound to rhodium atoms only via phosphorus and nitrogen donor centers. Considerable coordination shifts: $\Delta\delta_C$ 3–7 and 2–8 ppm, respectively, are observed for the very carbon atoms that are directly connected to these donor centers. The conclusion is also proven by ^{1}H-NMR data (see Table 2); considerable $\Delta\delta_H$ for protons neighboring to phosphorus (0.8–1 ppm) and nitrogen (0.3–0.5 ppm) atoms are observed. Unfortunately, because of the complicated structure of the spectra and broadening of resonances (in the case of compound **2**) only few J(H,H) constants have been determined. In spite of this, chemical shifts for all protons in compounds **1** and **2** have been defined rather exactly. Therefore, it is correct to compare these shifts. Interestingly, some amount (4%) of the *cis*-isomer **2a** can be found in the reaction solution. Its structure appears from the characteristic value of ^1J(P,Rh) [11]: δ_P 127.7 ppm, ^1J(P,Rh) 273.1 Hz ($CDCl_3$).



2a

Table 2
^{1}H-NMR data for solutions of compounds **1** and **2** in $CDCl_3$

Hydrogen atom	Compound			
	1		**2**	
	δ_H (ppm)	$J_{H,H}$ (Hz)	δ_H (ppm)	$J_{H,H}$ (Hz)
H1′	6.55 d	$J_{1',2'}$ 8.1	6.55 d	$J_{1',2'}$ 8.2
H2′	6.67 d	$J_{5',6'}$ 6.3	6.67 d	$J_{5',6'}$ 6.7
H5′	4.87 d	$J_{7',8'}$ 9.9	5.08 d	$J_{7',8'}$ 9.9
H6′	4.58 m	$J_{10'a,10'e}$ 18.9	5.63 m	$J_{15'e,15'a}$ 12.0
H7′	5.75 m	$J_{15'e,15'a}$ 13.4	5.93 m	$J_{5e,5a}$ 14.5
H8′	5.34 m	$J_{16'e,16'a}$ 12.3	5.26 m	
H9′	3.45 br	$J_{5e,5a}$ 14.6	3.75 br	
H10′a	2.37 m		2.42 m	
H10′e	3.04 m		3.05 m	
H14′	2.77 m		3.00 m	
H15′e	1.89 d		2.08 d	
H15′a	2.12 d		2.35 d	
H16′a	2.43 m		2.95 m	
H16′e	2.68 m		3.08 m	
N–CH_3	2.49 s		2.91 s	
O–CH_3	3.87 s		3.82 s	
$POCH_2$	4.80 m, 4.60 m, 3.85 m, 3.83 m		5.73 m, 5.38 m, 4.81 m, 4.50 m	
CH_2	2.44 d, 1.59 d		2.50 d, 1.76 d	

Table 3
XPS data for compounds **1** and **2** (E_b (eV))

Compound	P2p	N1s	Rh3d5/2	Cl2p
1	133.1	399.3		
2	133.5	399.9	308.9	198.4

^{31}P-NMR (δ_P 128.1 ppm, ^1J(P,Rh) 272.0 Hz) and IR (ν(CO) 2012 cm^{-1}, ν(acac) 1570 and 1524 cm^{-1}) data for the reaction solution of **3** in $CDCl_3$ indicate that ligand **1** in this complex **3** acts as a P-monodentate. This conclusion is also proven by ^{13}C-NMR data, since the coordination shifts $\Delta\delta_C$ (2–5 ppm) are demonstrated by the carbon atoms neighboring the phosphorus center (see Table 1).

Being isolated from solutions, complexes **2** and **3** are stable powders well soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. They maintain their structure in the solid state. The last statement is proven by IR data: ν(CO) 1987 cm^{-1}, ν(Rh–Cl) 303 cm^{-1} for **2** and ν(CO) 1990 cm^{-1}, ν(acac) 1568, 1520 cm^{-1} for **3**. The P,N-bidentate coordination of **1** in complex **2** is also substantiated by a considerable increase in E_b P2p (by 0.4 eV) and N1s (by 0.6 eV) in the XPS spectrum of **2**, as compared to **1** (see Table 3). A plasma desorption mass spectral investigation of complex **2** confirms its dimeric nature, since the following fragment ions have been detected, m/z (I, %): $[M–CH_3]^+$ 1124 (4), $[M–L–CH_3]^+$ 721 (8), $[M–L\text{-}2Cl–CH_3]^+$ 650 (6), $[1/2M–CO]^+$ 542 (15), $[L–CH_3]^+$ 388 (20), $[L–OPO(CH_2)_3O]^+$ 282 (100), $[PO(CH_2)_3O]^+$ 105 (70). Sedimentation analysis in a DMF solution has given the molecular mass value for **2** of 1204 Da, which stands in good agreement with the calculated value for the dimer **2** (1175).

It is important to note that in a DMF solution complex **2** is represented exclusively by its *trans* isomer: δ_P 128.6 ppm, ^1J(P,Rh) 251.0 Hz; ν(CO) 1984 cm^{-1}, while in a $CHCl_3$ solution, again, the *cis* isomer **2a** (3%) can also be detected. In a DMSO solution, the *cis* isomer prevails, as in the ^{31}P-NMR spectrum both doublet resonances of **2**: δ_P 128.4 ppm, ^1J(P,Rh) 249.4 Hz (45%) and that of **2a**: δ_P 125.7 ppm, ^1J(P,Rh) 262.5 Hz (55%) are observed. The reduced value of ^1J(P,Rh) constant in the case of **2a** is supposed to be due to coordination of the DMSO molecule into the fifth coordination site of the rhodium atom. Similar data on reducing of ^1J(P,Rh) constant in DMSO solutions were also observed in the past [10,12]. Thus, the coordination behavior of ligand **1** closely resembles that of other aminophosphites [9,10] and aminophosphines [13,14] containing two distant donor centers.

Acknowledgements

The authors wish to thank G.V. Tcherkaev, M.G. Ezernitskaya and P.V. Petrovskii (Institute of Organoelement Compounds, Moscow) for their assistance in characterizing the products, and D.V. Lechkin (Ryazan State Pedagogic University) for his help with the synthesis of compound **1**.

References

[1] K.N. Gavrilov, D.V. Lechkin, Koord. Khim. 24 (1998) 3 in Russian.
[2] K.N. Gavrilov, D.V. Lechkin, Zh. Neorg. Khim. 42 (1997) 1847 in Russian.
[3] K.N. Gavrilov, D.V. Lechkin, L.A. Lopanova, G.I. Timofeeva, Koord. Khim. 22 (1996) 472 in Russian.
[4] De-hua Wang, Xiao-Long Xu, G.C. Levy, Acta Chim. Sin. 47 (1989) 756.
[5] F.I. Carroll, C.G. Moreland, G.A. Brine, J.A. Kepler, J. Org. Chem. 41 (1976) 996.
[6] W.D. Lansing, E.O. Kraemer, J. Am. Chem. Soc. 57 (1935) 1389.
[7] R.T. van Holde, R.L. Baldvin, J. Phys. Chem. 62 (1958) 734.
[8] H.G. Elias, Ultracentrifugen-Methoden. Beckman-Instruments Gmbh, Munchen, 1961 S. 96.
[9] K.N. Gavrilov, Zh. Neorg. Khim. 39 (1994) 459 in Russian.
[10] K.N. Gavrilov, Koord. Khim. 20 (1994) 853 in Russian.
[11] K.N. Gavrilov, Zh. Neorg. Khim. 41 (1996) 1857 in Russian.
[12] A.T. Teleshev, K.N. Gavrilov, A.R. Bekker, N.N. Nevsky, E.E. Nifantyer, Zh. Obshch. Khim. 62 (1992) 2470 in Russian.
[13] M. Grassi, G. De Munno, F. Nicolo, S. Lo Schiavo, J. Chem. Soc. Dalton Trans. (1992) 2367.
[14] C.R. Langrick, D. Parker, Inorg. Chim. Acta 111 (1986) 29.