COMPOSITION AND STRUCTURE OF THE NOVEL COMPLEX Rh(CO). (Ph2PNH2)3

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A novel complex of Rh is synthesized. Results of an x-ray structure analysis and IR and EPR spectroscopies demonstrated that it is a square-planar complex of zero-valent Rh, $Rh(CO) \cdot (Ph_2PNH_2)_3$.

It has previously been demonstrated [1-3] that $RhCl_3 \cdot (3-4)H_2O$ in ethanol solutions in the presence of phosphine ligands L readily forms Rh(I) complexes of formula $RhXL_3$ depending on the conditions. In the presence of a carbonylating agent [at certain Rh(III) and L concentrations this could even be ethanol] the complexes $RhClCOL_2$ form. In acetone solution, where dicarbonylrhodium(I) chloride does not form, the Rh(III) complex $RhCl_3COL_2$ is stabilized, especially if L is a phosphite. Large excesses of L lead to formation of $Rh_2Cl_2L_4$ [6]. Various other types of Rh complexes in lower oxidation states are formed in similar systems. In the present report, we discuss results of preliminary investigations of the structure and spectral properties of crystals of Rh complexes isolated from the system $RhCl_3 \cdot 4H_2O - EtOH HCOOH - Ph_2PNEt_2$.

EXPERIMENTAL

<u>Synthesis</u>. A weighed portion (0.28 g) of RhCl₃·4H₂O was dissolved in EtOH (15 ml). The diethylamide of diphenylphosphinous acid (Ph₂PNEt₂, 1.1 g) in the ratio Rh:P = 1:4 was added to the solution under an inert atmosphere (Kr) at room temperature. Concentrated HCO₂H (3 ml) was added to the reaction mixture, which was then heated to 80-90°C on a water bath. After 10 min the solution became yellowish-brown. The heating was stopped. After two weeks, bright yellow needlelike crystals that decomposed at 148°C were isolated from the solution, which had been kept under an inert atmosphere. Elemental analysis (mass %): Rh 14.3, C 53.7, H 4.8, N 4.1.

Infrared Spectra. IR absorption spectra in the range 400-4000 cm⁻¹ were recorded on an Specord IR-75 spectrometer. The remaining crystals of the batch from which those for the x-ray structure study were selected were prepared as pressed KBr pellets.

EPR Spectra. EPR spectra of the crystalline powder were recorded on an ESR-230 radiospectrometer at 9.3 GHz.

<u>X-Ray Structure Analysis.</u> Yellow prismatic single crystals suitable for structural studies were preliminarily examined by photographic methods. According to these data, they were assigned to the orthorhombic system. The unit-cell constants were refined on a Syntex P2₁ automated diffractometer to give a = 17.461(2), b = 18.598(3), c = 20.546(3)Å, $d_{calc} = 1.462$ g/cm³, Z = 8.

The intensities of 4738 reflections (1/8 of a sphere) were measured on the same diffractometer (CuK_{α}-radiation, $\theta/2\theta$ -scanning, $2\theta_{max} = 112^{\circ}$, scan rate 5 deg/min, crystal dimensions 0.2 × 0.2 × 0.3 mm). Absorption corrections were made empirically from an azimuthal scanning curve (μ CuK_{α} = 57.80 cm⁻¹). Calculations were performed using the YANX programs [7] in space group Pbca(D_{2h}^{15}) (weak systematically absent reflections of this space group were excluded from the calculations).

It must be noted that the studied crystal was of poor quality although the best of those at our disposal was selected for the data collection. Therefore, and possibly also due to the presence of statistically disordered water or solvent molecules not found in the structure solution, $F_{\rm obs}$ and $F_{\rm calc}$ systematically varied for the weak reflections and increased

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	e rarameter	<u>></u>		
Atom	x	y	z	^U eq
Rh	0,5684(1)	0.1197(1)	0,3094(1)	0,031(1)
P(1)	0,7016(4)	0,1262(4)	0,3181(3)	0,037(4)
P(2)	0,5761(5)	0,0715(4)	0,2042(3)	0,041(4)
P(3)	0,4370(4)	0,1006(3)	0,3121(4)	0,034(4)
N(1)	0,749(1)	0,092(1)	0,2630(8)	0,01(1)
N(2)	0,657(1)	0,047(1)	0,1763(8)	0,03(1)
N(3)	0,391(1)	0,099(1) 0.464(2)	0.2450(8)	0,02(1)
C	0,565(4)	0,104(2) 0.192(1)	0,330(1) 0.441(1)	0.07(1)
	0.737(1)	0.215(1)	0.328(1)	0,02(2)
C(1) C(2)	0.764(1)	0,252(1)	0,270(1)	0,04(2)
C(3)	0,785(2)	0,325(2)	0,275(2)	0,06(2)
C(4)	0,782(2)	0,360(2)	0,334(2)	0,07(2)
C(5)	0,760(2)	0,322(2)	0,390(2)	0,06(2)
C(6)	0,735(1)	0,250(1)	0,388(1)	0,03(2)
C(7)	0,737(2)	0,080(1)	0,393(1)	0,02(2)
C(8)	0,808(2)	0,093(1)	0,418(1)	0.04(2)
C(9)	0,828(2)	0,056(2)	0,476(2)	0,06(2)
C(10)	0,780(2)	0,013(2)	0,507(2)	0,06(2)
C(11)	0,708(2)	0,000(2)	0,484(2)	0,08(3)
C(12)	0,684(2)	0,035(1)	0,422(1)	0,04(2)
C(13)	0,518(2)	-0,012(2)	0,195(1)	0,05(2)
C(14)	0,542(2)	-0,064(2)	0,240(2)	0,09(3)
C(15)	0,498(2)	0,128(2)	0,237(2)	0,08(3)
C(16)	0,441(2)	-0,142(2)	0,195(2)	0,08(3)
C(17)	0,418(2)	-0,086(2)	0,146(2)	0,08(3)
C(18)	0.461(2)	-0,021(2)	0,151(2)	0,05(2)
C(19)	0.538(2)	0,132(2)	0,142(1)	0.05(2)
C(20)	0,492(2)	0,194(1)	0,157(1)	0,04(2)
C(21)	0,463(2)	0,237(2)	0,110(2)	0,08(3)
C(22)	0,476(2)	0,220(2)	0.041(2)	0,09(3)
C(23)	0.518(3)	0,159(2)	0,027(2)	0,08(3)
C(24)	0,545(2)	0,112(3)	0,077(2)	0,12(4)
. C(25)	0,413(1)	0,011(1)	0,348(1)	0,03(2)
C(26)	0,360(2)	0.035(2)	0,327(1)	0,05(2)
C(27)	0.346(2)	-0.100(2)	0,356(2)	0,06(2)
C(28)	0,396(2)	0,123(2)	0.406(2)	0,06(2)
C(29)	0,452(2)	0,073(2)	0,430(2)	0,07(2)
C(30)	0,462(2)	-0,003(2)	0,403(2)	0,05(2)
C(31)	0,377(1)	0.162(1)	0,362(1)	0,02(1)
C(32)	0,309(2)	0,144(2)	0,393(1)	0,06(2)
C(33)	0,266(2)	0,196(2)	0,421(1)	0,04(2)
C(34)	0,289(2)	0,269(2)	0,424(1)	0,04(2)
C(35)	0,360(2)	0,289(2)	0,392(2)	0,08(3)
C(36)	0,402(2)	0,236(2)	0,360(1)	0,05(2)

TABLE 1. Coordinates of Principal Atoms and Equivalent Temperature Parameters

the R-factor. In a subsequent report (the structure refinement will be continued), we will attempt to explain the nature of these discrepancies.

The structure was solved by the heavy-atom method. A Patterson synthesis revealed the coordinates of the Rh and three P atoms. Electron-density maps $\rho(xyz)$ and $\Delta\rho(xyz)$ were used to find all nonhydrogen atoms. The resulting model was refined by least-squares methods to 10.2% for 1982 unique reflections. The corresponding coordinates of the principal atoms and the equivalent temperature parameters are listed in Table 1; interatomic distances and intermolecular contacts, in Tables 2 and 3.

DISCUSSION

The results are best examined starting with the IR spectra of the ligand Ph_2PNEt_2 and the complex. These are shown in Fig. 1. It is noteworthy that the vibrational spectrum of

Bond	d, Å	Bond	d, Å		
Rh-P(1)	2,336(7)	P(1) - N(1)	1.54(2)		
-P(2)	2,344(7)	P(2) - N(2)	1.59(2)		
P(3)	2,322(7)	P(3) - N(3)	1,63(2)		
C	1,85(2)	CO	1,17(3)		
P(1) - C(1)	1,78(2)	P(1)-C(7)	1,87(2)		
C(1) - C(2)	1,45(3)	C(7) - C(8)	1,36(4)		
C(1) - C(6)	1,39(3)	C(7)—C(12)	1,38(4)		
C(2) - C(3)	1,41(4)	C(8)-C(9)	1,42(4)		
C(3) - C(4)	1,38(5)	C(9)—C(10)	1,32(5)		
C(4) - C(5)	1,40(5)	C(10)—C(11)	1,36(5)		
C(5) - C(6)	1,41(4)	C(11)—C(12)	1,49(5)		
P(2)-C(13)	1,86(3)	P(2)C(19)	1,83(3)		
C(13) - C(14)	1,40(5)	C(19)—C(20)	1,44(4)		
C(13) - C(18)	1,35(4)	C(19)—C(24)	1,39(5)		
C(14) - C(15)	1,42(5)	C(20) - C(21)	1,35(4)		
C(15) - C(16)	1,34(5)	C(21)—C(22)	1,47(6)		
C(16) - C(17)	1,50(5)	C(22)—C(23)	1,38(6)		
C(17) - C(18)	1,43(5)	C(23)—C(24)	1,43(6)		
P(3) - C(25)	1,87(2)	P(3) - C(31)	1,86(2)		
C(25) - C(26)	1,33(4)	C(31)—C(32)	1,39(5)		
C(25) - C(30)	1,44(4)	C(31)—C(36)	1,44(4)		
C(26) - C(27)	1,37(5)	C(32)—C(33)	1,35(5)		
C(27) - C(28)	1,41(5)	C(33)—C(34)	1,42(5)		
C(28) - C(29)	1,44(5)	C(34)—C(35)	1,45(5)		
C(29) - C(30)	1,43(5)	C(35)—C(36)	1,39(5)		
P(1)—Rh— $P(2)$	91,9(3)	Rh-P(1)-C(1)	113,8(7)		
P(1)—Rh— $P(3)$	171,8(3)	Rh-P(1)-C(7)	111,6(1,1)		
P(1)—Rh—C	87,7(1,1)	Rh-P(1)-N(1)	117,2(8)		
P(2)-Rh- $P(3)$	91,2(3)	C(1) - P(1) - C(7)	102,6(1,0)		
P(2)-Rh-C	176,1(1,1)	C(1) - P(1) - N(1)	106, 3(1, 0)		
P(3)-Rh-C	89,8(1,1)	N(1) - P(1) - C(7)	103,8(1,1)		
Rh - P(2) - C(13)	112,4(9)	Rh - P(3) - C(25)	111,5(6)		
Rh - P(2) - C(19)	112,9(9)	Rh - P(3) - C(31)	118,4(7)		
rh - P(2) - N(2)	119,5(7)	Rh - P(3) - N(3)	117,9(7)		
C(13) - P(2) - C(19)	104.1(1,4)	C(25) - P(3) - C(31)	101,8(9)		
N(2) - P(2) - C(13)	102.0(1.2)	N(3) - P(3) - C(25)	102.5(9)		
N(2) - P(2) - C(19)	104,3(1,3)	N(3) - P(3) - C(31)	402.3(9)		

TABLE 2. Principal Bond Lengths d (Å) and Bond Angles ω (deg)

any phosphine or phosphite complex is basically that of the ligand itself with slight changes of the vibrations compared with those in the free phosphine (or phosphite) [8]. A comparison of the two IR spectra unambiguously indicates that the ligand undergoes substantial composition changes. The absorption bands at 417, 445, 658, 935, 1380, 1465, 2870, 2930, and 2976 cm⁻¹ disappear in the spectrum of the coordinated ligand. According to the literature [9], these bands are characteristic of $v_{P-Caliph}$, δ_{CH_3} and δ_{CH_2} , and $v_{C-Haliph}$. This suggests that the ethyl groups are lost during the synthesis. New bands in the spectrum of the complex are claerly evident at 2003, 1628, 1000, 730, 755, and 570 cm⁻¹. The first unambiguously indicates the presence of a carbonyl ligand in the complex. The others can be assigned to deformations of the NH₂ group. The presence of this group is confirmed by the appearance of a broad band at 3450 cm⁻¹, which is not shown in Fig. 1, in the IR spectrum of the complex. The value $v_{CO} = 2003$ cm⁻¹ is consistent with Rh(I) in the complex [4, 6].

Unfortunately, the elemental analysis does not correspond to any acceptable formula for a complex with Ph_2PNH_2 . It was necessary to solve the x-ray crystal structure in order to determine the composition of the complex.

The structure solution, elemental analysis, and spectra are consistent with the formula $Rh(CO) \cdot [Ph_2PNH_2]_3$ for the complex.

The crystal structure is comprised of discrete molecules of this composition. The molecules, which are reflected through the a glide-plane, are situated at approximately the same z level and are bonded to each other by a rather strong H-bond N(1)...N(3) (2.49 Å) and normal van der Waals contacts ($d_{min} = 3.50$ Å). This forms infinite chains parallel to [100]. Neighboring chains interact through a series of contacts. These are listed in Table 3.



Fig. 1. IR spectra of Ph_2PNEt_2 (1) and $Rh(CO)(Ph_2PNH_2)_3$ (2) as KBr pellets.



Fig. 2. Principal structural fragment, an infinite chain of discrete $Rh(CO)(Ph_2PNH_2)_3$ molecules related by N-H...N H-bonds (dashed lines). Atoms of the central molecule are labeled according to Table 1. In the phenyl rings, the C atom in the P coordination sphere is labeled.

One of these chains, the principal structural fragment, is shown in Fig. 2. The structure of a single complex is also clearly visible. Thus, the coordination of the Rh is close to square planar but noticeably distorted, apparently owing to steric hindrances between the bulky phenyl ligands. The atoms Rh, P(1), P(2), P(3), C, and O, which comprise the mean-square plane, deviate noticeably from it by -0.03, 0.22, -0.18, 0.03, -0.04, and -0.04 Å, respectively. The angles around Rh of 87.7, 91.9, 171.8, and 176.1° also deviate from the ideal values of 90 and 180°.

The P atoms are tetrahedrally surrounded by the Rh atom, two C atoms from two phenyl rings, and the N atom. Although the angles around P significantly vary (102.6-117.2°), their average is approximately constant at 109.2°.

The six phenylphosphine groups of the ligands are practically planar. The maximal deviation of the atoms from the plane is 0.06 Å for C(27). The average C-C bond length in the phenyl rings (1.39-1.41 Å) agrees well with the standard value. The most important bond lengths and bond angles, which are shown in Fig. 2, are comparable to those in analogous Rh(I)complexes [8-13].

The presence of short intra- and intermolecular N...N istances indicates that the NH₂ group is involved in N-H...N H-bonds. This explains why the $v_{\rm NH}$ and $\delta_{\rm NH_2}$ absorption bands are broad and not narrow. However, the composition found for the complex implies that the Rh is zero-valent. Therefore, the complex should be paramagnetic. Indeed, the powdered complex gives an EPR signal with $g_1 = 2.102$, $g_2 = 2.030$, and $g_3 = 1.987$. The value $v_{\rm CO} = 2003$ cm⁻¹ according to all known data is consistent with the vibrational frequency of CO in Rh(I) complexes. Since we are not aware of any previously reported Rh(0) carbonyls, the results

Contacts in the chain parallel to [100]		Contacts between chains		
$\begin{array}{c} N(1) - N(3) \\ - C(26) \\ - C(31) \\ - C(32) \\ N(2) - C(32) \\ N(3) - C(1) \\ - C(2) \\ - C(8) \\ C(2) - C(31) \\ - C(35) \\ - C(35) \\ - C(36) \\ C(3) - C(35) \\ C(8) - C(18) \\ C(9) - C(18) \end{array}$	$\begin{array}{c c} 2.49(2) \\ 3.57(4) \\ 3.65(3) \\ 3.50(3) \\ 3.51(4) \\ 3.74(3) \\ 3.62(3) \\ 3.62(3) \\ 3.61(3) \\ 3.75(3) \\ 3.79(4) \\ 3.61(3) \\ 3.73(5) \\ 3.69(5) \\ 3.78(5) \end{array}$	$\begin{array}{c} 0C(22) \\C(23) \\C(28) \\C(29) \\C(31) \\ C(3)C(14) \\ C(4)C(12) \\C(17) \\ C(5)C(17) \\ C(11)C(28) \\C(29) \\C(30) \\C(30) \\C(32) \\ C(15)C(36) \\ C(16)C(36) \\ C(16)C(28) \\ C(21)C(28) \\ C(22)C(35) \end{array}$	$\begin{array}{c} 3.05(4)\\ 3.39(4)\\ 3.46(4)\\ 3.47(4)\\ 3.70(3)\\ 3.73(5)\\ 3.77(4)\\ 3.66(5)\\ 3.62(5)\\ 3.69(5)\\ 3.57(5)\\ 3.57(5)\\ 3.77(5)\\ 3.69(5)\\ 3.66(5)\\ 3.66(5)\\ 3.73(5)\\ 3.60(5)\\ 3.67(5)\\ \end{array}$	
		C(27)-C(34)	3,67(5)	

TABLE 3. Intermolecular Contacts <3.80 Å

suggest that v_{CO} in Rh(0) complexes are close to those in Rh(I) compounds whereas the EPR parameters may correspond to square-planar d⁹ Rh(0) complexes.* The discrepancy of the experimental elemental analysis and that calculated for Rh(CO)·(Ph₂PNH₂)₃ indicates that the isolated complex contains several types of complexes, of which Rh(CO)·(Ph₂PNH₂)₃ forms the best crystals.

As mentioned in the introduction, Rh(I) compounds are formed in the system $RhCl_3 \cdot (3-4) \times H_2O-EtOH$ and are stabilized in the presence of PR_3 and $P(OR)_3$ ligands. It seems reasonable that also adding a strong reductant and the carbonyl source HCO_2H [4] further reduces Rh(I) to Rh(O). Obviously, the Ph_2PNH_2 ligand is formed from Ph_2PNEt_2 during the synthesis.

The investigation of this type of compounds will continue.

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^{*}The last conclusion is probabilistic in nature owing to the similarity of the obtained g_1 , g_2 , and g_3 and the EPR parameters of Rh(III) complexes [14].