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Structure and Properties of *trans*-Rh(Cl)(CO)[P(2-C_5H_4N)$_3$]$_2$

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A new phosphine complex trans-*Rh(Cl)(CO)[P(2-pyl)$_3$]$_2$ was synthesized (P(2-pyl)$_3$ = tris(2-pyridyl)-phosphine). The complex crystallizes in space group $P2_1/c$ with two molecules in the unit cell of the following dimensions:* $a = 12.31(2)$, $b = 8.92(1)$, $c = 16.36(3)$ Å, $\beta = 123.05(8)°$, $V = 1506$ Å^3, $Z = 2$, $D_c = 1.54$, $D_m = 1.54$ g cm^{-3}. *Full-matrix least-squares refinement of the structure has led to a final value of the conventional factor 0.047 for the 1442 independent reflections with $I > 1.96\sigma(I)$. The phosphine ligands are in* trans *position. Owing to the fact that the rhodium atoms occupy special positions (symmetry centres), the chlorine atoms and CO groups in* trans *positions are statistically disordered.*

Introduction

Phosphine ligands are applied extensively in the chemistry of co-ordination compounds. The present work is the first where the pyridyl-phosphine ligand was used. Ligands, I, II, III, IV (Fig. 1) which according to information available, were not used until now for preparation of complex compounds, are interesting because of their strucures. Owing to the presence of pyridyl rings they should exhibit various donor and acceptor properties and thus render possible wide-range control of the M–P bond at practically constant geometric conditions, similar to those for triphenylphosphine. In the case of phosphines I and IV the coordination process may proceed as follows: via the phosphorus atom, via the nitrogen atom or simultaneously via phosphorus and nitrogen, so they might be bridging ligands. The chelating co-ordination is less probable because of the formation of a four-membered ring in this case (Fig. 2). The phosphine rhodium(I) complexes of the Rh(X)(CO)(PR$_3$)$_2$ type catalyze the olefin hydrogenation, hydroformylation and isomerisation reactions [1]. For that reason they have been thoroughly investigated in recent years [2]. The complex prepared by us is one of the first rhodium(I) compounds with pyridyl-phosphine ligands. A change in position of the nitrogen atom with respect to the phosphorus atom as well as a change in the number of pyridyl rings should lead to a change in the donor–acceptor properties of phosphorus with preservation of constant geometry. This should lead to changes in the catalytic properties of the complexes with these ligands.

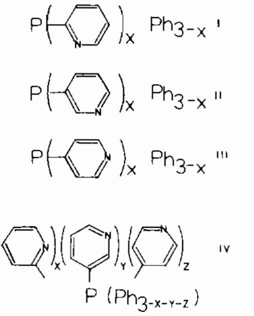

Fig. 1. Structure of the pyridyl-phosphine ligands.

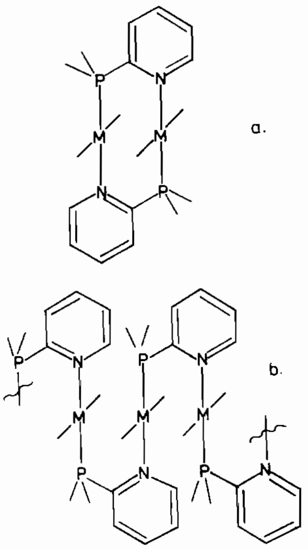

Fig. 2. Pyridyl-phosphine ligands as a bridging ligand. a) dimeric structure; b) polymeric structure.

Experimental

Rh(Cl)(CO)[P(2-pyl)$_3$]$_2$

Deaerated solution of tetracarbonyl-di-μ-chlorodirhodium(I) (0.02 g) in ethyl alcohol (1 ml) placed in a glass ampoule was treated with deaerated solution of tris-2pyridyl phosphine (0.09474 g) in ethyl alcohol (2.5 ml) (Rh:P ratio = 1:3.5). The ampoule was sealed and left for several days at room temperature until yellow crystals were precipitated. The precipitate was washed several times with ethyl alcohol and dried *in vacuo.* The yield was 70%. At a lower Rh:P ratio some unknown dark brown compounds are formed. Tris(2-pyridyl)phosphine was prepared as described in reference [9]. *Analytical data:* Calcd: %N = 12.15, %H = 3.42, %C = 53.14, %Cl = 5.07. Found: %N = 12.0, %H = 3.4, %C = 53.3, %Cl = 5.0. M.p. (°C) = 218. *IR spectrum* (in KBr): 306 vw, 390vw, 417w, 443w, 490m(sh), 498s, 508vs, 518vs, 528s(sh), 543w, 571m, 617vw, 710vw, 723w, 739m, 763s, 986s, 1043 w, 1083w, 1120vw, 1150w, 1232vw, 1275w, 1393w(sh), 1420vs, 1450vs, 1537w(sh), 1557s(sh), 1570vs, 1923w(sh), 1964vs, 1978vs(sh), 2980w, 3040m.

Single crystal X-ray data

$C_{30}H_{24}ClN_6OP_2Rh$: M = 696.5, monoclinic, a = 12.31(2), b = 8.92(1), c = 16.36(3) Å, β = 123.05(8)°, V = 1506 Å^3, D_m = 1.54 and D_c = 1.54 g cm^{-3}, Z = 2. Space group $P2_1/c$, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 7.9 cm^{-1}.

Intensity measurements

A crystal with dimensions 0.2 X 0.35 X 0.35 mm was mounted on a Syntex $P2_1$ diffractometer and 8 levels of the reciprocal lattice, 0kl–7kl, were collected in the range $8.0 \leqslant 2\theta \leqslant 52°$. Of 1848 reflections, 1442 with $I > 1.96\sigma(I)$ were used for structure solution and refinement.

Computations

All calculations were performed with the Syntex XTL structure-determination system. Neutral-atom scattering factors used were those listed in International Tables for X-ray Crystallography (1974).

Discussion of Results

Rhodium(I) *trans*-carbonylchloro-bis-(tris(2-pyridyl)phosphine) was prepared at room temperature in the reaction between tetra-carbonyl-di-μ-chlorodirhodium(I) with tris-(2-pyridyl)phosphine at the molar ratio of Rh:P = 1:3.5 in ethanol. The complex is relatively readily soluble in nitromethane, chloroform, methylene chloride, DMF, much less soluble in acetone, ethanol, methanol. It is stable in the air. Its structure was determined by X-ray analysis. The heavy-atom method was employed for phase determination. A three-dimensional Patterson synthesis gave a straightforward solution for the Rh and P positions. Difference Fourier syntheses after preliminary refinement of the heavy atoms showed the positions of all the remaining non-H atoms. Owing to the fact that the rhodium atoms are located in the symmetry centres, the chlorine atoms and CO groups are statistically disordered. Our investigation of this complex in solution suggests the equilibrium between monomer complex and dimeric or polymeric species, or the equilibrium between four-coordinate and five-coordinate complexes. Thus the statistical disorder of these groups results from lability of the complex.

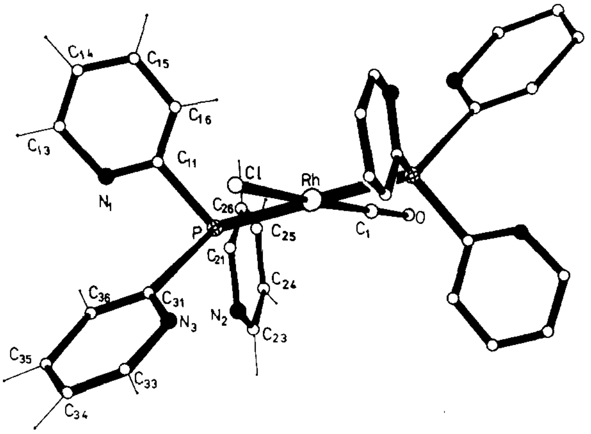

Fig. 3. Structure of the RhClCO[P(2-pyl)$_3$]$_2$.

The hydrogen atoms were placed in geometrically calculated positions at a distance of 1.0 Å. Further refinement reduced R to 0.047 and R_w to 0.056. A difference synthesis computed towards the end of the refinement process was featureless. Table I summarizes the position co-ordinates of the atoms and their thermal parameters. Table II summarizes principal interatomic distances and angles. Figure 3 shows the structure of Rh(Cl)(CO)[P(2-pyl)$_3$]$_2$.

The rhodium and phosphorus atoms and one of the three pyridyl rings of each phosphine lie on one plane which is perpendicular to the co-ordination plane determined by the chlorine, rhodium, phosphorus and carbon atoms from the CO group.

The Rh–C(1) bond length (1.82(3) Å) is comparable to the Rh–C bond length in Rh(Cl)(CO)(PPh$_3$)$_2$ [3] which is 1.86 Å. The Rh–P bond length as well as the angles C(11)–P–Rh, C(21)–P–Rh, C(31)–P–Rh are comparable to the corresponding values for the rhodium(I) complexes with *trans*-phosphine ligands [4]. The pyridyl ring in the P–Rh–P–C_{11} plane is more distorted than other rings (Table II).

TABLE I. Positional and Thermal Parameters of the Atoms of $Rh(CO)Cl[P(C_5H_4N)_3]_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0	0	0	3.08(10)	2.45(3)	2.89(3)	0.26(5)	1.72(3)	0.18(4)
Cl*	0.1227(7)	–0.1057(8)	0.1608(6)	2.9(5)	5.2(3)	3.5(4)	1.2(3)	2.0(3)	0.8(3)
P	0.1807(3)	–0.0227(3)	–0.0071(2)	2.96(21)	2.00(9)	2.91(8)	0.51(9)	1.92(9)	0.26(7)
C(11)	0.2363(12)	–0.2193(9)	0.0011(6)	2.4(9)	2.7(4)	4.3(4)	0.6(5)	2.8(5)	0.1(3)
N(1)	0.3361(12)	–0.2367(9)	–0.0057(8)	7.7(10)	3.4(4)	14.3(9)	1.3(6)	9.7(8)	1.6(5)
C(13)	0.3811(15)	–0.3821(15)	0.0002(12)	8.5(12)	5.6(7)	20.0(14)	4.1(7)	13.3(11)	2.2(7)
C(14)	0.3181(18)	–0.5003(12)	0.0099(8)	10.2(14)	2.1(4)	7.6(6)	0.3(8)	4.0(7)	1.0(6)
C(15)	0.2147(12)	–0.4793(11)	0.0160(8)	2.3(10)	3.9(5)	7.6(6)	0.0(5)	4.3(6)	0.2(4)
C(16)	0.1733(11)	–0.3337(9)	0.0129(6)	3.3(7)	2.8(4)	5.1(5)	0.6(4)	3.2(5)	0.1(3)
C(21)	0.1682(9)	0.0426(8)	–0.1195(6)	1.3(6)	3.3(4)	3.8(4)	0.5(4)	2.5(4)	0.5(3)
N(2)	0.1941(8)	0.1873(8)	–0.1182(5)	4.5(6)	3.2(4)	4.5(4)	–0.5(4)	2.7(4)	0.6(3)
C(23)	0.1779(11)	0.2427(11)	–0.2013(8)	5.5(8)	4.5(5)	5.2(6)	–0.1(5)	2.8(5)	2.1(4)
C(24)	0.1356(13)	0.1600(14)	–0.2820(7)	6.9(9)	7.0(7)	3.6(5)	0.2(6)	2.5(5)	2.2(5)
C(25)	0.1073(12)	0.0136(14)	–0.2825(6)	6.5(8)	6.9(6)	3.2(4)	0.6(7)	2.7(5)	–0.2(5)
C(26)	0.1224(10)	–0.0479(9)	–0.1997(7)	3.3(7)	3.7(4)	4.4(5)	0.2(4)	3.1(5)	0.0(3)
C(31)	0.3325(11)	0.0765(9)	0.0876(6)	–0.5(7)	3.1(4)	4.2(4)	0.4(5)	2.5(4)	0.6(3)
N(3)	0.3158(10)	0.1561(10)	0.1511(7)	4.6(7)	6.1(5)	6.8(5)	–1.3(5)	3.7(5)	–3.0(4)
C(33)	0.4213(16)	0.2324(17)	0.2186(10)	4.7(11)	10.5(9)	7.9(8)	–4.1(10)	4.0(9)	–5.5(7)
C(34)	0.5329(16)	0.2329(15)	0.2264(9)	4.9(11)	6.7(7)	4.4(6)	–1.7(8)	0.7(7)	–1.4(5)
C(35)	0.5455(11)	0.1568(15)	0.1627(9)	1.0(8)	7.9(7)	6.8(7)	–0.1(6)	2.0(6)	1.4(6)
C(36)	0.4399(13)	0.0750(12)	0.0891(7)	0.2(8)	6.7(6)	5.7(5)	–0.3(6)	3.6(6)	–0.9(4)
O*	–0.148(2)	0.114(3)	–0.199(2)	4.9(6)					
C(1)*	–0.091(3)	0.071(3)	–0.125(2)	3.0(6)					
H(13)	0.459	–0.399	–0.003	5.0					
H(14)	0.351	–0.604	0.013	5.0					
H(15)	0.169	–0.568	0.022	5.0					
H(16)	0.098	–0.313	0.019	5.0					
H(23)	0.201	0.350	–0.202	5.0					
H(24)	0.125	0.206	–0.342	5.0					
H(25)	0.075	–0.048	–0.342	5.0					
H(26)	0.101	–0.156	–0.198	5.0					
H(33)	0.417	0.291	0.269	5.0					
H(34)	0.609	0.291	0.278	5.0					
H(35)	0.631	0.156	0.167	5.0					
H(36)	0.447	0.018	0.039	5.0					

The form of the anisotropic ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
*The occupancy factors of Cl, C(1) and O atoms are 0.5.

The IR spectrum of the $Rh(Cl)(CO)[P(2\text{-pyl})_3]_2$ complex over the 300–4000 cm^{-1} region exhibits a large number of bands which result mainly from phosphine ligand vibrations, slightly shifted as a result of co-ordination. The bands resulting from the valence ν_{CO} frequencies appear at 1964 vs and 1978 vs(sh) cm^{-1} and ν_{Rh-Cl} at 306 cm^{-1} as for other complexes of the $Rh(X)(CO)(PR_3)_2$ type [5].

The UV–Vis diffuse reflectance spectrum exhibits two bands at 32600 and 25800 cm^{-1} corresponding to the $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_1$ transitions, respectively. It is therefore similar to the absorption spectrum of the $Rh(Cl)(CO)(PPh_3)_2$ complex [6]. The absorption spectrum of the complex under investigation was measured in chloroform. It differs considerably from those of the $Rh(X)(CO)(PR_3)_2$ complexes [5] and from the diffuse reflectance spectrum. There are three bands I 21000 cm^{-1} (ϵ = 462), II 27000 cm^{-1} (ϵ = 362) and III 37900 cm^{-1} ($\epsilon = 2.81 \times 10^3$) corresponding to transitions I, II $^1A_1 \rightarrow {}^1B_1$ (for the C_{2v} symmetry) or I $^1A_1' \rightarrow {}^1E'$ (for the D_{3h} symmetry), II $^1A_1 - {}^1B_1$ and III inside the ligand. The band shift to lower energies is characteristic of rhodium(I) square-planar complexes with the Rh–Rh bond [7] or may be expected for the five-coordinate complexes [11]. No such changes in the absorption spectrum are observed for a similar rhodium(I) complex with tris-(3-pyridyl)phosphine, $Rh(Cl)(CO)[P(3\text{-pyl})_3]_2$ [8]. The absorption spectrum of this compound in chloroform solution exhibits three bands at I 27400 cm^{-1} (ϵ = 425), II 34500 cm^{-1} (sh), III 38900 cm^{-1} ($\epsilon = 2.37 \times 10^3$) resulting from transitions I $^1A_1 \rightarrow {}^1B_1$, II $^1A_1 \rightarrow {}^1B_2$ and transition III inside the ligand. Thus

TABLE II. Bond Lengths (Å) and Angles (°) in $Rh(CO)Cl[P(C_5H_4N)_3]_2$.

Rh–Cl	2.399(7)	Rh–C(1)	1.82(3)
Rh–P	2.298(4)	C(1)–O	1.09(3)
P–C(11)	1.86(1)	C(11)–N(1)	1.30(3)
N(1)–C(13)	1.39(2)	C(13)–C(14)	1.37(3)
C(14)–C(15)	1.34(3)	C(15)–C(16)	1.38(2)
P–C(21)	1.85(1)	C(21)–N(2)	1.33(1)
N(2)–C(23)	1.35(2)	C(23)–C(24)	1.35(2)
C(24)–C(25)	1.35(2)	C(25)–C(26)	1.38(2)
P–C(31)	1.87(1)	C(31)–N(3)	1.36(2)
N(3)–C(33)	1.34(2)	C(33)–C(34)	1.31(3)
C(34)–C(35)	1.32(2)	C(35)–C(36)	1.40(2)
P–C(11)–C(16)	120(1)	P–C(11)–N(1)	116(1)
C(16)–C(11)–N(1)	124(2)	C(11)–N(1)–C(13)	118(2)
N(1)–C(13)–C(14)	120(2)	C(13)–C(14)–C(15)	121(2)
C(14)–C(15)–C(16)	118(2)	C(15)–C(16)–C(11)	119(2)
P–C(21)–C(26)	122(1)	P–C(21)–N(2)	114(1)
C(26)–C(21)–N(2)	124(1)	C(21)–N(2)–C(23)	116(1)
N(2)–C(23)–C(24)	124(2)	C(23)–C(24)–C(25)	120(2)
C(24)–C(25)–C(26)	119(2)	C(25)–C(26)–C(21)	118(1)
P–C(31)–C(36)	123(1)	P–C(31)–N(3)	112(1)
C(36)–C(31)–N(3)	124(2)	C(31)–N(3)–C(33)	114(2)
N(3)–C(33)–C(34)	125(2)	C(33)–C(34)–C(35)	119(2)
C(34)–C(35)–C(36)	119(2)	C(35)–C(36)–C(31)	118(2)
C(11)–P–C(21)	101.3(5)	Cl–Rh–C(1)	176.8(9)
C(11)–P–C(31)	102.9(5)	Rh–C(1)–O	178(3)
C(21)–P–C(31)	100.2(5)		

the positions of bands I and II are the same as for $Rh(Cl)(CO)(PPh_3)_2$ in chloroform [6]. The presence of two bands in the spectrum of $Rh(Cl)(CO)[P(2\text{-}pyl)_3]_2$ probably results: a) from the equilibrium in solution between the monomeric form dealt with in the solid state for which the $^1A_1 \rightarrow {}^1B_1$ transition lies at 27000 cm^{-1} and the dimeric or polymeric form with a band corresponding to that transition at 21000 cm^{-1}. b) From the equilibrium in solution between tetracoordinate and five-coordinate complexes, where the fifth position is occupied by the solvent molecule or by the nitrogen atom of the pyridyl ring. In dimeric or polymeric complexes of rhodium(I) which exhibit the Rh–Rh type interaction, a lower band corresponding to the transition from the d_{z^2} metal orbital to b_1 ligand orbital ($^1A_1 \rightarrow {}^1B_1$ transition for the C_{2v} symmetry) is shifted to lower energies (Fig. 4) [7]. The low-spin d^8 pentacoordinate complexes (trigonal bipyramids) should exhibit two bands corresponding to the transitions: the low-energy transition $(e'')^4(e')^4 \rightarrow (e'')^4(e')^3(a')^1$ *i.e.* $^1A_1' \rightarrow {}^1E'$ (dipole-allowed) and the high energy transition $(e'')^4(e')^4 \rightarrow (e'')^3(e')^4(a')^1$ *i.e.* $^1A_1' \rightarrow {}^1E''$ (dipole-forbidden) [10]. In the case of rhodium(I) pentacoordinate complexes with polydentate phosphine ligands (in comparison to Ni(II) and Pd(II) complexes) most probably the low-energy transition should be observed below 20000 cm^{-1} [10] but in the case of monodentate ligands the low-energy band should be observed above 20000 cm^{-1} [11]. The band at 21000 cm^{-1} results probably from the transition $^1A_1' \rightarrow {}^1E'$ for the D_{3h} symmetry (five-coordinate complex) and the band at 27000 cm^{-1} from $^1A_1 \rightarrow {}^1B_1$ transition for the C_{2v} symmetry (four-coordinate complex). Thus the difference in the absorption

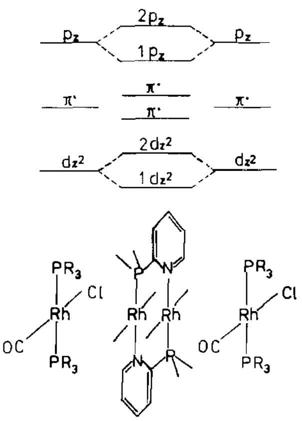

Fig. 4. A partial MO orbital diagram for the dimeric or polymeric rhodium(I) complexes, with pyridyl-phosphine ligands.

spectra of the complex under investigation and $Rh(Cl)(CO)[P(3\text{-}pyl)_3]_2$ and $Rh(Cl)(CO)(PPh_3)_2$ may be explained as due to the equilibria:

a) $n\ Rh(Cl)(CO)[P(2\text{-}pyl)_3]_2 = [Rh(Cl)(CO)P(2\text{-}pyl)_3]_n + n\ P(2\text{-}pyl)_3$

b) tetracoordinate complex = pentacoordinate complex.

Now it is impossible to define which case, a or b, is true. Further investigation should solve this problem.

The spectrum of compound under investigation should also exhibit a band at 34000 cm^{-1} corresponding to the $^1A_1 \rightarrow {}^1B_2$ transition (C_{2v} symmetry) which is probably masked by a strong band resulting from the transition inside the ligand at 37900 cm^{-1}.

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