

Rhodium(III) and Rhodium(I) Complexes with Tripod Tetradentate Ligands

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Received June 26, 1982

Rhodium(III) complexes with the tripod tetradentate ligand tris(2-diphenylphosphinoethyl)amine, np_3 , of formula $[RhCl_2(np_3)]Y$ ($Y = Cl, PF_6, BPh_4$), have been prepared and characterized. One of the coordinated chlorine atoms in these compounds may be replaced by a molecule of acetonitrile. The hydrido complex $[RhHCl(Cynp_3)]BPh_4 \cdot (CH_3)_2CO$ has been obtained by reaction of rhodium trichloride hydrate with the tripod ligand tris(2-dicyclohexylphosphinoethyl)amine, $Cynp_3$, bearing bulky substituents on the phosphorus atoms. All of the above complexes are assigned six-coordinated structures, mainly on the basis of their 1H and ^{31}P n.m.r. spectra. The crystal structure of the hydrido complex has been determined by X-ray diffraction analysis. The np_3 derivatives are easily reduced to give five-coordinate rhodium(I) complexes with formulae $[RhH(np_3)]$ and $[RhCl(np_3)]$.

Introduction

The tripod tetradentate ligand tris(2-diphenylphosphinoethyl)amine, np_3 , has been found to stabilize first-row transition metal complexes with a wide range of interesting features [1]. The coordination geometry of these complexes is determined in part by the tripod ligand, which generally spans four coordination positions about the metal atom, but it is also influenced by the nature and number of the other ligands [2], as well as by the nature of the metal ion [3, 4].

Recently it has been found that the 'cone angle' [5] at the terminal phosphorus atoms plays an important role in determining the coordinating properties of tripod ligands. The reduction of such 'cone angle' going from np_3 to the ligand tris(2-dimethylphosphinoethyl)amine, $Menp_3$, which has the same inner skeleton as np_3 , allows the stabilization of poly-

nuclear species in which the ligand shares its donor atoms among two or three metal atoms [6]. On the other hand, the increase in the 'cone angle' at the phosphorus atoms in the ligand tris(2-dicyclohexylphosphinoethyl)amine, $Cynp_3$, producing a higher strain about the metal site, may result in detachment of a donor atom (P or N) and a consequent decrease in the coordination number with respect to the np_3 derivatives [7].

The behaviour of these ligands with platinum group metals has been poorly investigated, although many complexes of these metals with polydentate phosphines have been found to possess interesting properties in the activation of several reactions [8].

Here we report on the synthesis and characterization of Rh(III) and Rh(I) complexes with the tripod tetradentate ligands np_3 and $Cynp_3$. A complete X-ray analysis has been carried out on the hydrido complex $[RhHCl(Cynp_3)]BPh_4 \cdot (CH_3)_2CO$.

Experimental

All solvents were reagent grade and were used without further purification. The ligands tris(2-diphenylphosphinoethyl)amine, np_3 [9], and tris(2-dicyclohexylphosphinoethyl)amine, $Cynp_3$ [10], were prepared as already described. Rhodium trichloride hydrate and silver hexafluorophosphate were purchased from the Strem Chemicals Inc. and Fluka AG, respectively.

Physical Measurements

Conductivities, infrared spectra and X-ray powder diagrams were obtained as previously described [11]. 1H (at 80 MHz) and ^{31}P (at 32.19 MHz) n.m.r. spectra were measured on a Varian CFT 20 spectrometer equipped with proton noise decoupling and deuterium lock. 1H chemical shifts are quoted to tetramethylsilane, TMS = 0.0 ppm. ^{31}P chemical shifts are down-field relative to H_3PO_4 at 0.0 ppm.

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TABLE I. Analytical and Physical Data for the Complexes.

Compound	Λ_M^a (cm ² /ohm mol)	% Calcd			% Found		
		C	H	N	C	H	N
[RhCl ₂ (np ₃)]Cl ^b	70	58.5	4.9	1.6	58.4	5.0	1.7
[RhCl ₂ (np ₃)]PF ₆ ^c	85	51.9	4.4	1.4	51.8	4.6	1.4
[RhCl ₂ (np ₃)]BPh ₄ ^d	55	69.1	5.5	1.2	68.9	5.7	1.2
[Rh(CH ₃ CN)Cl(np ₃)](PF ₆) ₂ ^e	140	47.1	4.0	2.5	47.2	4.1	2.7
[RhHCl(Cynp ₃)]BPh ₄ •(CH ₃) ₂ CO ^f	54	68.7	8.8	1.2	68.6	8.9	1.3
[RhCl(np ₃)] ^g		63.7	5.3	1.8	63.7	5.5	1.9
[RhH(np ₃)]		66.6	5.7	1.8	66.3	5.8	1.6

^aMolar conductance of ca. 10⁻³ solution in nitroethane at 20 °C.^bCalcd: Cl, 12.3; P, 10.8. Found: Cl, 12.1; P, 10.5.^cCalcd: P, 12.7. Found: P, 12.5.^dCalcd: Cl, 6.2; P, 8.1. Found: Cl, 5.9; P, 8.1.^eCalcd: Cl, 3.2; P, 13.8. Found: Cl, 3.1;P, 13.6. ^fCalcd: Cl, 2.9; P, 7.7. Found: Cl, 3.0; P, 7.9. ^gCalcd: Cl, 4.5. Found: Cl, 4.3.TABLE II. ³¹P{¹H} NMR Spectral Data for Rh(III) Complexes.

Compound	Solvent	Chemical shifts, J, Hz					Coord. chem. shift, Δ ^b	
		ppm ^a		J(P _a -Rh)	J(P _b -Rh)	² J(P _a -P _b)	shift, Δ ^b	
		P _a	P _b				ΔP _a	ΔP _b
[RhCl ₂ (np ₃)]Cl	CD ₂ Cl	29.8	21.2	116	91	22	48.8	40.8
[RhCl ₂ (np ₃)]PF ₆	CD ₂ Cl	29.2	21.1	116	91	22	48.8	40.7
[RhCl ₂ (np ₃)]BPh ₄	CD ₃ CN	29.1	21.2	116	91	22	48.6	40.8
[Rh(CH ₃ CN)Cl(np ₃)](PF ₆) ₂	CD ₃ CN	33.4	19.8	117	89	23	51.9	38.9
[RhHCl(Cynp ₃)]BPh ₄ •(CH ₃) ₂ CO	(CD ₃) ₂ CO	16.1	33.7	82	98	19	23.3	40.9

^a³¹P chemical shifts are relative to 85% H₃PO₄. Positive chemical shifts are downfield. ^bΔ = δP_{coord} - δP_{free ligand}.

Changes in chemical shifts on coordination are reported in ppm relative to the corresponding phosphorus in the free ligand.

Preparation of Compounds

The complexes were prepared under a protective nitrogen atmosphere; however, none of the rhodium(III) complexes showed any signs of instability towards air. Typical preparations are illustrated below. Analytical data (Table I) are in good agreement with the proposed formulae; n.m.r. data are reported in Table II.

[RhCl₂(np₃)Cl]

The solid ligand (1 mmol) was added to a rhodium trichloride hydrate (Rh 1 mmol) solution in ethanol (100 ml) and the resulting mixture was refluxed for 4 hours. After cooling, the reaction mixture was filtered and the yellow solution was concentrated until crystallization occurred. The yellow crystals of the complex were filtered off and dried *in vacuo*.

The complex was recrystallized from dichloromethane and ethanol (Yield 60%).

[RhCl₂(np₃)]Y, (Y = BPh₄, PF₆)

The reaction between the ligand and rhodium trichloride hydrate was carried out by the above procedure. The complexes were obtained by adding to the resulting yellow solution NaBPh₄ or [Bu₄N]-PF₆ (1 mmol) in ethanol (20 ml).

[RhCl(CH₃CN)(np₃)](PF₆)₂

Solid AgPF₆ (2 mmol) was added to [RhCl₂(np₃)]Cl (1 mmol) dissolved in acetonitrile (30 ml). The resulting mixture was stirred vigorously for two hours at 50 °C and then filtered. The solution was concentrated until crystallization occurred.

[RhHCl(Cynp₃)]BPh₄

The hydride complex was prepared by the same procedure described for [RhCl₂(np₃)]BPh₄, using Cynp₃ instead of np₃.

[RhHCl(np₃)]

To the [RhCl₂(np₃)]Cl complex (1 mmol) dissolved in methylene chloride (20 ml) was added sodium tetrahydroborate (1 mmol) dissolved in ethanol (20 ml). The resulting solution was heated at *ca.* 40 °C until the color changed to red-brown; brown crystals of the complex were obtained by concentration. The precipitate was filtered, washed with ethanol, water, ethanol, light petroleum, and dried.

[RhH(np₃)]

Sodium tetrahydroborate (1 mmol) dissolved in ethanol (20 ml) was added to [RhCl₂(np₃)]Cl (0.5 mmol) in acetone (40 ml). The resulting solution was heated until formation of brown crystals occurred. The precipitate was filtered, washed with ethanol, water, ethanol, light petroleum and dried.

Crystal and Intensity Data

Intensity data for [RhHCl(Cynp₃)]BPh₄·(CH₃)₂CO were recorded on a Philips PW 1100 automated diffractometer using graphite-monochromated MoK α radiation, and a crystal of dimensions *ca.* 0.25 × 0.20 × 0.15 mm. Unit cell dimensions were determined from the angular measurements of 24 strong reflections with 20 < 2 θ < 30°. Intensity data were collected in the range 5 < 2 θ < 46° by the θ -2 θ scan technique, with a symmetric scan range of 0.80 + 0.30 tan θ and a scan speed of 4.0°/min in 2 θ . Background counts were measured at each end of the scan for a time equal to half the scan time. The intensities of three reflections well separated in reciprocal space were monitored periodically throughout data collection and showed only random variations (*ca.* 1%) from the mean values. Corrections for Lorentz and polarization effects were applied. Out of the 9728 intensities measured, 5399 independent observations having $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

Chlorohydridotris(2-dicyclohexylphosphinoethyl)-aminerhodium(III) Tetraphenylborate-Acetone, [RhHCl(Cynp₃)]BPh₄·(CH₃)₂CO,

C₆₆H₉₉BClNP₃Rh·C₃H₆O, $M = 1206.7$, monoclinic, $a = 18.555(7)$, $b = 24.725(9)$, $c = 14.251(6)$ Å, $\beta = 92.40^\circ$, $V = 6532.2$ Å³, $Z = 4$, $D_c = 1.227$ g cm⁻³, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu(\text{MoK}\alpha) = 4.10$ cm⁻¹, space group P2₁/n.

Solution and Refinement of the Structure

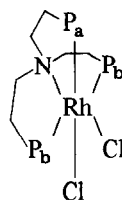
The structure was solved by heavy atom procedures and refined by blocked-cascaded least squares with blocks of *ca.* 270 parameters. In the least squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. Atoms heavier than carbon in the cation were assigned anisotropic temperature factors. All of the other non-hydrogen atoms in the structure were assigned iso-

tropic thermal parameters. Hydrogen atoms, except for the hydride ion bound to rhodium, were introduced in calculated positions (C-H = 1.00 Å), each with a temperature factor *ca.* 20% larger than that of the respective carbon atom. Refinement converged to the conventional R value of 0.068 ($R_w = 0.070$). Discrepancy indices are defined as follows: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. The position of the hydride ligand could not be unambiguously identified, although positive residual density (0.2 e Å⁻³) was confirmed by weighted difference-Fourier maps in the region where the hydride ligand was expected. The final ΔF Fourier showed no significant features (maximum peak height *ca.* 0.5 e Å⁻³). The atomic scattering factors were taken from Ref. [12] and anomalous dispersion terms for the metal atom were included in F_c [13]. All calculations were carried out with the programs listed in Ref. [14]. Fractional coordinates and temperature factors of the non-hydrogen atoms are listed in Table III. Important bond distances and angles within the cation appear in Table IV. A table of observed and calculated structure factors may be obtained from the authors on request.

Results and Discussion

The reaction of rhodium trichloride hydrate with the ligand np₃ in ethanol affords the complex [RhCl₂(np₃)]Cl. The complexes [RhCl₂(np₃)]Y, Y = BPh₄, PF₆, are obtained by adding sodium tetraphenylborate or tetrabutylammonium hexafluorophosphate to a solution of [RhCl₂(np₃)]Cl. The complexes, which are scarcely soluble in common organic solvents, behave as 1:1 electrolytes (Table I).

The ³¹P{¹H} n.m.r. spectra of the complexes (Table II) are not affected by the nature of the anion (Cl, BPh₄, PF₆) and exhibit a typical AB₂X pattern. This pattern and the steric requirements of the tetradentate ligand allow us to assign the coordination geometry of the complex in solution as octahedral (I). In analogy with the structure of the [CoCl₂(np₃)]⁺ cation in the solid state [2], the tripod ligand may be assumed to span two adjacent faces of the octahedron and the chlorine atoms to coordinate in a *cis* position with respect to each other.



(I)

TABLE III. Positional Parameters and Temperature Factors for $[\text{RhHCl}(\text{Cynp}_3)]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$.^{a,b}

Atom	x/a	y/b	z/c	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Rh	0.18352(4)	0.19539(3)	0.11688(5)	0.0324(4)	0.0237(4)	0.0254(4)	-0.0075(4)	-0.0041(3)	0.0024(4)
Cl	0.2805(1)	0.2571(1)	0.1329(2)	0.042(1)	0.033(1)	0.046(1)	-0.014(1)	-0.003(1)	0.004(1)
P1	0.1417(1)	0.2115(1)	0.2671(2)	0.040(1)	0.031(1)	0.027(1)	-0.009(1)	-0.004(1)	0.002(1)
P2	0.2407(1)	0.1419(1)	0.0084(2)	0.037(1)	0.027(1)	0.033(1)	-0.004(1)	-0.003(1)	-0.003(1)
P3	0.1072(1)	0.2573(1)	0.0234(2)	0.037(1)	0.031(1)	0.031(1)	-0.004(1)	-0.004(1)	0.002(1)
N	0.0960(4)	0.1396(3)	0.1024(5)	0.027(4)	0.027(4)	0.030(4)	-0.001(3)	-0.002(3)	-0.002(3)
Atom	x/a	y/b	z/c	U ₁ Å ²	Atom	x/a	y/b	z/c	U ₁ Å ²
C1	0.0677(5)	0.1237(4)	0.1969(6)	0.040(2)	C61	0.0932(5)	0.3276(4)	0.0673(6)	0.039(2)
C2	0.0593(5)	0.1701(4)	0.2640(7)	0.039(2)	C62	0.1513(6)	0.3676(4)	0.0427(7)	0.051(3)
C3	0.1197(5)	0.0871(4)	0.0582(6)	0.039(2)	C63	0.1437(6)	0.4211(4)	0.0952(8)	0.059(3)
C4	0.1665(5)	0.0956(4)	-0.0238(7)	0.041(2)	C64	0.0695(6)	0.4448(4)	0.0797(8)	0.059(3)
C5	0.0352(5)	0.1614(4)	0.0403(6)	0.037(2)	C65	0.0114(6)	0.4047(4)	0.1016(8)	0.064(3)
C6	0.0232(5)	0.2231(4)	0.0487(6)	0.035(2)	C66	0.0190(6)	0.3517(4)	0.0460(8)	0.059(3)
C11	0.1085(5)	0.2770(4)	0.3162(6)	0.036(2)	C71	0.8895(5)	0.0807(4)	0.3419(6)	0.041(2)
C12	0.1711(5)	0.3169(4)	0.3305(7)	0.047(3)	C72	0.9583(5)	0.0660(4)	0.3796(7)	0.048(3)
C13	0.1441(6)	0.3715(4)	0.3652(8)	0.058(3)	C73	0.9907(6)	0.0928(5)	0.4603(8)	0.059(3)
C14	0.1037(6)	0.3653(5)	0.4547(8)	0.063(3)	C74	0.9540(6)	0.1359(5)	0.4984(8)	0.065(3)
C15	0.0413(6)	0.3257(4)	0.4412(8)	0.057(3)	C75	0.8872(6)	0.1507(5)	0.4662(8)	0.064(3)
C16	0.0691(6)	0.2705(4)	0.4064(7)	0.048(3)	C76	0.8521(6)	0.1234(4)	0.3865(7)	0.055(3)
C21	0.2001(5)	0.1844(4)	0.3656(7)	0.042(2)	C81	0.8549(5)	0.0899(4)	0.1545(6)	0.039(2)
C22	0.1938(6)	0.1234(4)	0.3793(8)	0.058(3)	C82	0.8564(5)	0.1471(4)	0.1621(7)	0.046(3)
C23	0.2413(6)	0.1058(5)	0.4633(9)	0.079(4)	C83	0.8490(6)	0.1802(4)	0.0806(7)	0.056(3)
C24	0.3176(6)	0.1214(5)	0.4591(9)	0.071(4)	C84	0.8414(6)	0.1579(4)	-0.0082(7)	0.056(3)
C25	0.3258(6)	0.1809(4)	0.4425(8)	0.064(3)	C85	0.8417(6)	0.1017(4)	-0.0173(8)	0.060(3)
C26	0.2799(5)	0.1994(5)	0.3552(7)	0.053(3)	C86	0.8490(5)	0.0684(4)	0.0625(7)	0.051(3)
C31	0.3168(5)	0.1001(4)	0.0543(7)	0.046(3)	C91	0.8951(5)	-0.0076(4)	0.2324(6)	0.041(2)
C32	0.2925(8)	0.0521(6)	0.1095(11)	0.103(5)	C92	0.9536(5)	-0.0103(4)	0.1749(7)	0.047(3)
C33	0.3620(9)	0.0169(7)	0.1410(13)	0.129(6)	C93	0.9940(6)	-0.0595(4)	0.1668(7)	0.057(3)
C34	0.4186(9)	0.0487(6)	0.1932(11)	0.111(5)	C94	0.9750(6)	-0.1034(4)	0.2178(8)	0.059(3)
C35	0.4371(8)	0.0970(6)	0.1453(11)	0.102(5)	C95	0.9193(6)	-0.1020(4)	0.2749(8)	0.060(3)
C36	0.3713(6)	0.1310(5)	0.1150(8)	0.067(3)	C96	0.8781(5)	-0.0542(4)	0.2832(7)	0.045(2)
C41	0.2701(5)	0.1645(4)	-0.1075(6)	0.038(2)	C101	0.7656(5)	0.0389(4)	0.2652(6)	0.040(2)
C42	0.2845(6)	0.1163(4)	-0.1744(7)	0.056(3)	C102	0.7122(6)	0.0451(4)	0.1931(8)	0.060(3)
C43	0.3046(6)	0.1375(5)	-0.2718(8)	0.059(3)	C103	0.6383(7)	0.0325(5)	0.2084(9)	0.078(4)
C44	0.3695(6)	0.1761(5)	-0.2630(8)	0.068(3)	C104	0.6187(7)	0.0145(5)	0.2969(9)	0.075(4)
C45	0.3581(6)	0.2225(4)	-0.1960(7)	0.057(3)	C105	0.6709(6)	0.0086(5)	0.3676(8)	0.069(3)
C46	0.3375(5)	0.2007(4)	-0.0994(7)	0.047(3)	C106	0.7439(5)	0.0212(4)	0.3524(7)	0.053(3)
C51	0.1052(5)	0.2563(4)	-0.1081(6)	0.041(2)	B	0.8515(6)	0.0506(4)	0.2471(8)	0.040(3)
C52	0.1671(6)	0.2889(4)	-0.1485(7)	0.055(3)	O	0.3158(6)	0.4871(4)	0.2610(8)	0.124(4)

C53	0.1706(7)	0.2784(5)	-0.2552(8)	0.072(4)	C111	0.3367(7)	0.4566(5)	0.1991(9)	0.072(3)
C54	0.1000(6)	0.2929(5)	-0.3044(8)	0.070(3)	C112	0.3267(7)	0.3970(5)	0.2089(9)	0.076(4)
C55	0.0378(6)	0.2648(5)	-0.2647(8)	0.067(3)	C113	0.3727(7)	0.4775(5)	0.1177(9)	0.087(4)
C56	0.0344(6)	0.2734(5)	-0.1566(7)	0.055(3)					

^aStandard deviations on the last significant digits are in parentheses. Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2 \theta)/\lambda^2]$ and anisotropic temperature factors are of the form $\exp[-2\pi^2 (U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$. ^bAtoms O–C113 belong to the acetone molecule.

TABLE IV. Selected Bond Distances (Å) and Angles (°).

Rh–Cl	2.364(2)	P2–C31	1.85(1)
Rh–P1	2.341(2)	P2–C41	1.85(1)
Rh–P2	2.324(3)	P3–C6	1.82(1)
Rh–P3	2.442(2)	P3–C51	1.87(1)
Rh–N	2.134(7)	P3–C61	1.87(1)
P1–C2	1.84(1)	N–C1	1.52(1)
P1–C11	1.88(1)	N–C3	1.52(1)
P1–C21	1.86(1)	N–C5	1.50(1)
P2–C4	1.84(1)		
Cl–Rh–N	179.9(1)	Rh–P2–C31	116.5(3)
P1–Rh–P2	152.0(1)	Rh–P2–C41	125.6(3)
P1–Rh–P3	100.7(1)	C4–P2–C31	107.1(4)
P2–Rh–P3	105.3(1)	C4–P2–C41	102.2(4)
Cl–Rh–P1	94.7(1)	C31–P2–C41	103.6(4)
Cl–Rh–P2	93.7(1)	Rh–P3–C6	94.7(3)
Cl–Rh–P3	94.0(1)	Rh–P3–C51	121.7(3)
N–Rh–P1	85.3(2)	Rh–P3–C61	119.1(3)
N–Rh–P2	86.2(2)	C6–P3–C51	102.2(4)
N–Rh–P3	86.0(2)	C6–P3–C61	103.5(4)
Rh–P1–C2	101.0(3)	C51–P3–C61	110.4(4)
Rh–P1–C11	127.9(3)	Rh–N–C1	111.8(5)
Rh–P1–C21	115.1(3)	Rh–N–C3	111.1(5)
C2–P1–C11	101.7(4)	Rh–N–C5	112.0(5)
C2–P1–C21	105.9(4)	C1–N–C3	105.4(6)
C11–P1–C21	102.7(4)	C1–N–C5	109.6(6)
Rh–P2–C4	99.4(3)	C3–N–C5	106.6(6)

The values of the $J(P_a-Rh)$, $J(P_b-Rh)$, and $J(P_a-P_b)$ coupling constants, of 116, 91, and 22 Hz respectively, are in the range found for *mer* Rh(III) neutral complexes with monodentate phosphines [15]. The coupling constant with Rh of the P atom *trans* to Cl is larger than that of the P atoms lying *trans* to each other. The P_a resonance is more deshielded with respect to the P_b resonance as found for rhodium(III) complexes formed by monodentate phosphines. The coordination chemical shifts of both P_a and P_b phosphorus atoms (Table II), are higher than the downfield shifts on coordination reported for the octahedral *mer* $RhCl_3(PEtPh_2)_3$ [15], which has similar cone angles at the phosphorus atoms as the present compounds. Such differences in the coordination chemical shifts cannot be accounted for solely by the ionic nature of the $[RhCl_2(np_3)]Y$ complexes. They are better rationalized by allowing for ring contributions [16] in the case of the present compounds, where the phosphorus atoms are involved in five-membered chelate rings. It should be noted that similar values of the coordination chemical shifts have been found for other rhodium(III) cationic complexes with the bidentate 'mixed' ligands $R_2P(CH_2)_2NR'_2$, having the same donor atoms and similar geometric requirements to those of the chains of the np_3 ligand. On the other hand, the $R_2P(CH_2)_3NR'_2$ ligands, forming

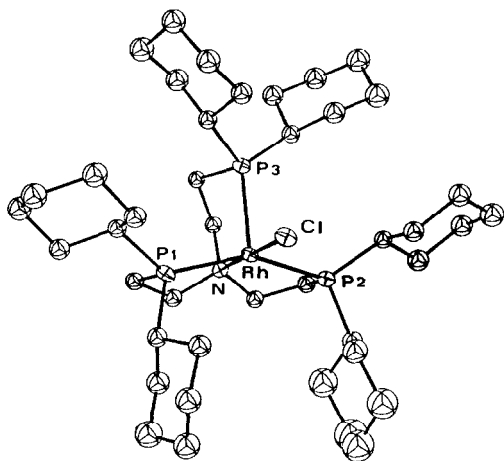


Fig. 1. Structure of the $[\text{RhHCl}(\text{Cynp}_3)]^+$ cation.

six-membered chelate rings, exhibit smaller coordination chemical shifts [17].

The addition of two equivalents of silver hexafluorophosphate to the acetonitrile solution of $[\text{RhCl}_2(\text{np}_3)]\text{Cl}$ gives the dicationic complex with formula $[\text{Rh}(\text{CH}_3\text{CN})\text{Cl}(\text{np}_3)](\text{PF}_6)_2$. The conductivity (Table I) is in accordance with the proposed formula. The CN stretching vibrations of the coordinated acetonitrile molecule (2138 and 2190 cm^{-1}) are in the range found for related solvate complexes [18], indicating that one chlorine atom in the parent compound has been replaced by a molecule of coordinating acetonitrile. The second chlorine atom in the coordination sphere cannot be removed even by refluxing the complex in acetonitrile with a large excess of silver hexafluorophosphate. The $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectrum of the above complex in acetonitrile solution (Table II) shows a typical AB_2X pattern: the overall coordination geometry should therefore be similar to that of the $[\text{RhCl}_2(\text{np}_3)]^+$ cation. The P_a resonance for this dicationic complex is downfield shifted from that of the corresponding P atom in the monocationic $[\text{RhCl}_2(\text{np}_3)]^+$ complexes, whereas the P_b resonance is slightly upfield shifted (Table II).

The reaction of rhodium trichloride hydrate with the ligand Cynp_3 yields by addition of sodium tetraphenylborate the compound $[\text{RhHCl}(\text{Cynp}_3)]\text{PBh}_4 \cdot (\text{CH}_3)_2\text{CO}$. A band at 2008 cm^{-1} in the I.R. spectrum of the compound is assigned as the $\text{Rh}-\text{H}$ stretching vibration. The structure of the compound has been investigated by X-ray diffraction methods in order to obtain precise information on the coordination geometry and on the possible role of steric effects in stabilizing such hydride.

The structure consists of $[\text{RhHCl}(\text{Cynp}_3)]^+$ cations, of tetraphenylborate anions and of solvate acetone molecules. A view of the complex cation is

shown in Fig. 1. The rhodium atom is coordinated by the nitrogen and the three phosphorus atoms of the Cynp_3 ligand, by the chlorine atom, which lies *trans* to nitrogen, and by the hydride ligand. The arrangement of the non-hydrogen atoms is distorted square pyramidal with appreciable axial elongation ($\text{Rh}-\text{P}_3 = 2.442(2)\text{ \AA}$, vs. $\text{Rh}-\text{P}_1 = 2.341(2)\text{ \AA}$ and $\text{Rh}-\text{P}_2 = 2.324(3)\text{ \AA}$). Although the position of the hydride was not clearly detectable from ΔF Fourier maps (see experimental part) there is enough space to accommodate such ligand in *trans* position to P_3 . Moreover, the presence of hydride is unambiguously indicated by the spectral and magnetic properties of the compound, which are typical of a six coordinated d^6 low spin chromophore. The proposed coordination geometry is also consistent with the previous observation that ligands with π -acceptor properties are more favourably accommodated *trans* to hydrogen than are ligands with σ -donor properties, due to the competition of the latter with the hydride for σ -bonding orbitals [19].

The proton noise decoupled ^{31}P n.m.r. spectrum of the complex (Table II), which does not vary between -50 and $+50^\circ\text{C}$, shows a typical AB_2X pattern. A significant feature of the spectrum is the coordination chemical shift of the phosphorus atom *trans* to the hydride ligand which is smaller than the downfield shift of the two phosphorus atoms *cis* to the hydride. The ^1H n.m.r. spectrum of the complex exhibits two quartets, with intensity ratio 1:1, centered at 9.95δ . Each quartet originates from the coupling of the hydride ligand with the two equivalent phosphorus atoms and with rhodium ($J(\text{H}-\text{P}) = J(\text{H}-\text{Rh}) = 12\text{ Hz}$); the coincidence of these coupling constants to give pseudomultiplets has been stated previously for other rhodium complexes [20]. The doubled quartet originates from the coupling of hydrogen with the *trans* phosphorus atom ($J(\text{H}-\text{P}) = 182\text{ Hz}$). Such coupling is known to be larger than the $J(\text{H}-\text{P}_{\text{cis}})$ one. The present value is even larger than those reported before [21]. The stabilization of the hydrido complex $[\text{RhHCl}(\text{Cynp}_3)]\text{BPh}_4$ when the Cynp_3 ligand is employed may be attributed to the steric hindrance of the substituent groups on the phosphorus atoms, which prevents coordination by ligands larger than hydride. Effects of such crowding have been evidenced for iron(II), cobalt(II), and nickel(II) complexes with the Cynp_3 ligand, where one of the polyphosphine donor atoms may be uncoordinated [7]. Formation of the hydride with no detachment of donor atoms in the present case may be due to the stability of the low-spin d^6 configuration in a six-coordinate environment.

The $[\text{RhCl}_2(\text{np}_3)]^+$ cation when treated with sodium tetrahydroborate yields different products depending on the reaction conditions. When it is dissolved in acetone and is reacted with an excess of sodium tetrahydroborate a compound of formula

[RhH(np₃)] is obtained. The Rh—H stretching vibration is located at 1925 cm⁻¹. On the other hand, by reacting the parent compound in methylene chloride with sodium tetrahydroborate, a compound of formula [RhCl(np₃)] is obtained. Due to the poor solubility of both Rh(I) complexes it was not possible to obtain information on the stereochemistry of the compounds in solution.

The X-ray powder diagrams clearly show that the two compounds are isomorphous to the corresponding cobalt derivatives [CoH(np₃)] and [CoCl(np₃)], which have been found to have trigonal pyramidal geometry with the nitrogen and the hydrogen (or chlorine) atoms in the axial positions [22]. The same geometry is therefore assigned to the rhodium derivatives in the solid state.

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