pletely spin pair the electrons. Similar results are obtained in other triketonates in which the copper atoms are 0.24 Å above and below the best plane.[6-8] While it does seem resonable to expect this nonplanarity to result in less efficient orbital overlap and, as a result, weaker magnetic exchange, the observed distortion is apparently a relatively small perturbation.

The electronic configuration in $(VO)_2(DANA)_2$ is somewhat less certain than in the analogous Cu(II) compound. However, it is certain that the unpaired electron on each VO^{2+} is not in a σ-symmetry orbital. Since the ground state of the homologous mononuclear 1,3-diketonates $VO(1,3\text{-diketonato})_2$ is considered to be d^1_{xy},[23] it is logical to believe that similar states are appropriate for each VO^{2+} in $(VO)_2(DANA)_2$. If the unpaired electrons are initially in d_{xy} orbitals, the possibility of a direct metal–metal interaction must be considered since d_{xy} is directed between the bridging oxygens. The distance between the vanadium is large (ca. 3.0–3.2 Å), and one would expect a weak exchange for the direct metal–metal interaction. Other superexchange mechanisms involving the bridging oxygen and metal orbitals are less convincing since they involve electron excitation into orbitals of appropriate symmetry followed by exchange in these excited states.[24]

Regardless of the details of the exchange mechanisms it is true that the strenght of the exchange as measured by the exchange constant, J, is about five times as large for $Co_2(DANA)_2(py)_2$ as for $(VO)_2(DANA)_2$. In these structurally similar molecules it is reasonable to attribute most of the difference to the spatial orientation of the exchanging electrons.

Acknowledgment is made to the National Science Foundation, Grant CHE-77-02664, and to the donors of the Petroleum Research Fund, administered by the American Chemical Sociiety, for support of this research.

Registry No. $(VO)_2(DANA)_2$, 75880-93-2; $Cu_2(DANA)_2$, 29745-69-5; $Cu_2(DANA)_2(py)_2$, 75880-94-3.

Supplementary Material Available: Listings of structure factor amplitudes and a packing diagram (18 pages). Ordering information is given on any current masthead page.

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(24) See, for example: Martin, R. L. "New Pathways in Inorganic Chemistry"; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: London, 1968; Chapter 9.

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Opening of the P–N Bond of Bicyclic Phosphoranes. X-ray Crystal and Molecular Structures of Four Rhodium(I) Complexes of Perhydro-1,3,6,2-dioxazaphosphocine Ligands[1]

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Received March 6, 1980

The structures of *cis*-$L^1Rh(CO)Cl$, *cis*-$L^2Rh(CO)Cl$, $[L_2{}^2Rh]Cl$, and $[L_2{}^2Rh]ClO_4$, where L^1 and L^2 are the perhydrodioxazaphosphocine ligands $C_6H_5\overline{POCH_2CH_2N(H)CH_2CH_2O}$ and $C_6H_5\overline{POCH_2C(CH_3)_2N(H)CH_2CH_2O}$, have been determined by three-dimensional X-ray diffraction studies. These compounds crystallize respectively in the space groups *Pbca* (a = 7.031 (1) Å, b = 11.509 (2) Å, c = 33.400 (9) Å, Z = 8), $P2_1/c$ (a = 11.692 (2) Å, b = 15.447 (4) Å, c = 9.202 (2) Å, β = 110.68 (2)°, Z = 4), $C2/c$ (a = 17.855 (3) Å, b = 13.567 (2) Å, c = 11.743 (2) Å, β = 107.60 (2)°, Z = 4), and $P\bar{1}$ (a = 9.856 (3) Å, b = 12.191 (5) Å, c = 12.469 (3) Å, α = 71.58 (3)°, β = 85.00 (3)°, γ = 77.69 (3)°, Z = 2). Diffraction data to respectively $2\theta_{max}$ = 60, 60, 72, and 72° (Mo Kα radiation) were collected on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer. The structures were solved by the heavy-atom method and refined by full-matrix least-squares procedures to conventional discrepancy indexes, respectively R = 0.0308 (1860 unique data), 0.0223 (2340), 0.0348 (2768), and 0.0586 (1464). For each case the configuration around Rh is square planar. The ligands L are in all cases of the bidentate P,N nature, with P···N distances in the range 2.788–2.853 Å, suggesting the lack of any dative $P \leftarrow N$ bond. The conformation of these ligands are of the chair-boat type with stronger deformations for the *gem*-dimethyl L^2 ligand. Some further deformations are indicated by the values observed for the Rh–P–C angles (ca. 125–130°) which deviate significantly from those reported for analogous phosphonites (ca. 118°). The complex $[L^2{}_2Rh]Cl$ presents a twofold axis which is in accordance with the occurrence of only one racemate in the crystal analyzed. In the complex $[L^2{}_2Rh]ClO_4$, only one oxygen atom of the perchlorate anion is asymmetrically bonded to the (N) hydrogens.

Introduction

The bicyclic phosphoranes **1** have attracted interest in the recent years owing to the possibility of equilibria with the tautomeric monocyclic structures **2**–**4** (Scheme I) containing now a P(III) site. Only compounds **1** are detected in solution[2] but, recently, the occurrence of form **2** has been evidenced in the gas phase by UPS.[3] Nevertheless, a reaction occurs with different transition-metal compounds leading to complexes where the monocyclic P,N form **2** is trapped and stabilized.[4,5]

For the rhodium(I) complexes, bidentate ligation is obtained and P(III) coordination is involved since ${}^1J_{^{103}Rh-^{31}P}$ coupling is observed. However, neither NMR nor IR spectroscopy

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(1) Paper 3 of this series. For papers 1 and 2, see ref 4 and 5.

(2) Houalla, D.; Brazier, J.-F.; Sanchez, M.; Wolf, R. *Tetrahedron Lett.* **1972**, 2969. Houalla, D.; Mouheich, T.; Sanchez, M.; Wolf, R. *Phosphorus* **1975**, *5*, 229.

(3) Houalla, D.; Sanchez, M.; Goubeau, D.; Pfister-Guillouzo, G. *Nouv. J. Chim.* **1979**, *3*, 509.

(4) Bondoux, D.; Tkatchenko, I.; Houalla, D.; Wolf, R.; Pradat, C.; Riess, J.; Mentzen, B. F. *J. Chem. Soc., Chem. Commun.* **1978**, 1022.

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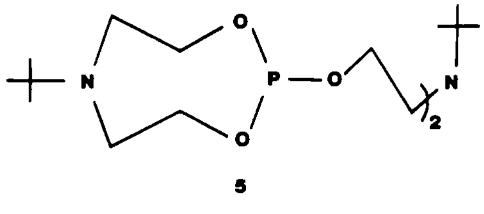
Table I. Summary of Crystal Data and Intensity Collection for **6a**, **6b**, **7a**, and **7b**

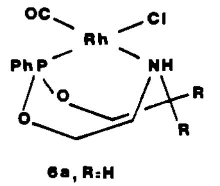
	6a	6b	7a	7b
(A) Crystal Parameters				
temp: 18 °C				
space group	*Pbca*	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	7.031 (1)	11.692 (2)	17.855 (3)	9.856 (3)
b, Å	11.509 (2)	15.447 (4)	13.567 (2)	12.191 (5)
c, Å	33.400 (9)	9.202 (2)	11.743 (2)	12.469 (3)
α, deg				71.58 (3)
β, deg		110.68 (2)	107.60 (2)	85.00 (3)
γ, deg				77.69 (3)
mol wt	377.57	405.63	616.87	680.87
ρ(calcd), g cm^{-3}	1.855 ($Z = 8$)	1.733 ($Z = 4$)	1.510 ($Z = 4$)	1.628 ($Z = 2$)
ρ(measd), g cm^{-3}	1.870	1.766	1.525	1.634
(B) Measurement of Intensity Data				
radiatn: Mo $K\bar{\alpha}$ (λ 0.710 73 Å)				
monochromator: graphite				
detector aperture				
horizontal ($A + B \tan \theta$): *A*, mm	1.50	1.40	1.40	1.40
B, mm	0.40	0.40	0.80	0.80
vertical: 4 mm				
rfltns measd	hkl	hkl, $hk\bar{l}$	hkl, $hk\bar{l}$	hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$
scan type: ω–2θ				
ω scan width, deg: $0.8 + 0.35 \tan \theta$				
bkgd: one-fourth additional scan at each end of scan				
scan rate				
max, deg/min	10.06	10.06	10.06	10.06
min, deg/min	2.52	2.24	2.87	2.87
no. of rfltns measd	4403	3786	5705	7853
data used ($F^2 > 2\sigma(F^2)$)	1860	2340	2768	1464
max 2θ, deg	60	60	72	72
cryst dimens, mm^3	0.4 × 0.25 × 0.25	0.44 × 0.44 × 0.45	0.32 × 0.25 × 0.25	0.30 × 0.20 × 0.20
μ, cm^{-1}	15.58	13.87	8.02	8.629
μ*R*	0.234	0.305	0.12	0.129
(C) Solution of the Structure				
method used: heavy-atom				
minimized function: $w(\lvert F_o\rvert - \lvert F_c\rvert)^2$				
weighting functions: first cycles $w = (2\lvert F_o\rvert_{min} + \lvert F_o\rvert + 2F_o^2/\lvert F_o\rvert_{max})^{-1}$ last cycles $w = (a + b\lvert F_o\rvert)^2$				
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0298	0.0263	0.0305	0.0505
weighted *R* (R_w) = $(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\Sigma w F_o^2))^{1/2}$	0.0308	0.0223	0.0348	0.0586
refined scale factor	0.1751 (5)	0.3987 (3)	0.6516 (8)	0.408 (4)
F(000)	1504	816	1272	700

could deduce the coordination of the nitrogen or of the oxygen moiety. Futhermore, different configurational isomers may arise from the reaction of **1** with, for example, $[Rh(CO)_2Cl]_2$, where the carbonyl ligand lies in cis or trans position to the P(III) atom. Besides, the reaction of **1b** with $[Rh(C_2H_4)_2Cl]_2$ giving a cationic complex which exhibits a rather low ν_{X-H} (X = N or O) vibration has also to be explained.[4] Finally, if the stabilized bidentate ligand has the structure **2**, it will be of interest to determine its conformation in order to compare it with that of compound **5** which has been recently reported.[6]

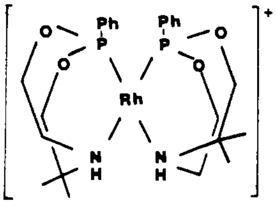


5

Single-crystal X-ray diffraction studies on **6a**, **6b**, **7a**, and **7b** have been carried out. In this paper structural evidences are presented that definitively establish the occurrence of the P(III),N(III) mode of ligation, which seems to be operative for oxidized group 8 metal species,[7] at variance with some group 6 metal species.[8] Preliminary results of this work have already been published.[4,5]



6a, R:H
6b, R:Me



7a, Y : Cl^-
7b, Y : ClO_4^-

Experimental Section

Compounds **6a**, **6b**, and **7a** were prepared as previously reported.[4,5] **7b** has been obtained by direct action of silver perchlorate on **7a** in acetonitrile solution. All the yellow crystals have been recrystallized in acetonitrile by slow evaporation under argon atomosphere at room temperature. The diffraction measurements for the four specimens were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. The unit cells were determined from 25 selected reflections by using the CAD-4 photo, center, index, and least-squares routines, and the

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(6) Devillers, J.; Houalla, D.; Wolf, R.; Bonnet, J.-J. *Nouv. J. Chim.* **1980**, *4*, 179.

(7) Bondoux, D.; Bonnet, M. C.; Nourian, N.; Tkatchenko, I., unpublished results.

(8) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem.*, submitted for publication.

Scheme I

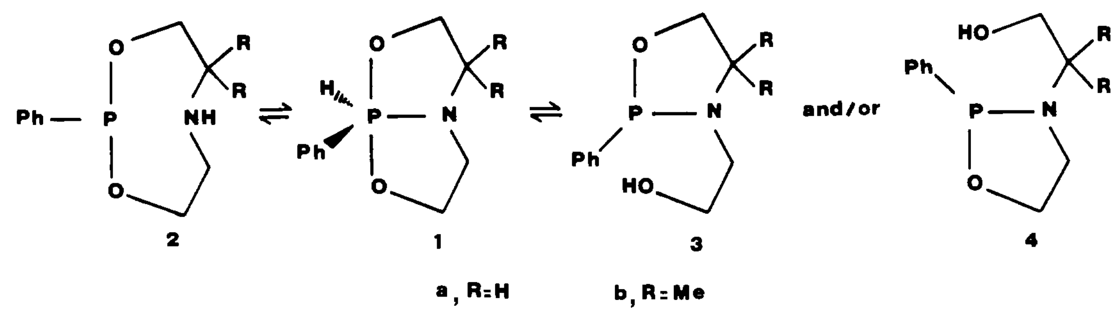

Table II. Final Positional and Thermal Parameters[a] and Their Estimated Standard Deviations[b] for $RhCl(CO)PO_2C_4H_8NH(C_6H_5)$ (6a)

atom	x/a	y/b	z/c	B_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{12}	U_{12}	U_{23}
Rh	0.49888 (4)	0.48565 (2)	0.09647 (1)	2.0	0.0339 (1)	0.0285 (1)	0.0215 (6)	0.0032 (1)	0.0011 (1)	0.0002 (2)
Cl	0.64309 (16)	0.39018 (8)	0.04072 (2)	2.4	0.0679 (6)	0.0570 (5)	0.0254 (6)	0.0264 (5)	0.0056 (4)	−0.0019 (4)
P1	0.33724 (8)	0.58570 (5)	0.13903 (2)	2.1	0.0345 (3)	0.0278 (3)	0.0243 (6)	0.0015 (2)	0.0025 (2)	0.0004 (2)
O11	0.11326 (24)	0.56853 (15)	0.13122 (5)	2.3	0.0339 (10)	0.0461 (10)	0.0305 (11)	0.0013 (8)	0.0046 (7)	0.0053 (8)
O12	0.36530 (28)	0.72259 (14)	0.13208 (5)	2.9	0.0529 (12)	0.0256 (7)	0.0350 (11)	−0.0000 (8)	0.0042 (8)	−0.0018 (6)
O	0.67633 (45)	0.33987 (25)	0.15886 (7)	2.9	0.0878 (22)	0.0656 (17)	0.0317 (11)	0.0332 (16)	−0.0051 (14)	0.0105 (10)
N1	0.34766 (32)	0.59796 (17)	0.05554 (6)	3.4	0.0485 (11)	0.0400 (9)	0.0401 (11)	0.0024 (9)	−0.0043 (10)	0.0012 (8)
C11	0.03800 (36)	0.61164 (26)	0.09373 (8)	2.9	0.0354 (17)	0.0493 (14)	0.0379 (11)	0.0030 (10)	−0.0046 (11)	0.0012 (8)
C12	0.13939 (42)	0.57199 (24)	0.05658 (8)	3.6	0.0420 (15)	0.0409 (15)	0.0350 (11)	−0.0051 (12)	−0.0059 (12)	0.0016 (10)
C13	0.47773 (46)	0.75748 (21)	0.09803 (8)	3.1	0.0545 (22)	0.0312 (11)	0.0339 (11)	−0.0060 (12)	0.0021 (14)	0.0039 (10)
C14	0.38625 (46)	0.72619 (22)	0.05870 (7)	2.8	0.0499 (18)	0.0333 (13)	0.0328 (11)	−0.0029 (12)	−0.0006 (12)	0.0076 (10)
C	0.61044 (53)	0.39622 (29)	0.13464 (9)	2.8	0.0479 (21)	0.0373 (17)	0.0288 (17)	0.0090 (15)	0.0012 (14)	−0.0066 (12)
CP11	0.34971 (33)	0.57082 (19)	0.19190 (6)	1.9	0.0317 (12)	0.0346 (11)	0.0271 (11)	0.0071 (9)	0.0030 (10)	−0.0002 (8)
CP12	0.40493 (38)	0.66259 (22)	0.21668 (7)	2.9	0.0384 (15)	0.0397 (13)	0.0379 (11)	0.0046 (11)	0.0030 (11)	−0.0047 (10)
CP13	0.41094 (42)	0.64718 (25)	0.25736 (7)	3.9	0.0402 (15)	0.0543 (15)	0.0390 (17)	0.0097 (12)	−0.0046 (12)	−0.0130 (12)
CP14	0.36447 (42)	0.54257 (26)	0.27420 (7)	2.9	0.0439 (15)	0.0744 (19)	0.0249 (11)	0.0096 (14)	0.0025 (11)	0.0051 (12)
CP15	0.31221 (41)	0.45027 (23)	0.25009 (8)	3.0	0.0462 (14)	0.0507 (14)	0.0356 (11)	−0.0004 (11)	0.0004 (12)	0.0095 (12)
CP16	0.30531 (37)	0.46477 (21)	0.20908 (7)	3.2	0.0424 (14)	0.0377 (13)	0.0356 (11)	−0.0028 (11)	−0.0017 (11)	0.0018 (10)

atom	x/a	y/b	z/c	B_{eq}, Å^2	atom	x/a	y/b	z/c	B_{eq}, Å^2
H111	0.0454 (53)	0.7077 (35)	0.0915 (10)	7 (2)	H142	0.2698 (41)	0.7743 (23)	0.0521 (7)	3 (1)
H112	−0.0947 (48)	0.5800 (28)	0.0912 (8)	4 (1)	HP12	0.4327 (45)	0.7278 (26)	0.2024 (9)	4.8 (1)
H121	0.1229 (45)	0.4882 (25)	0.0506 (8)	4 (1)	HP13	0.4406 (46)	0.7042 (27)	0.2757 (9)	6 (2)
H122	0.0796 (45)	0.6050 (27)	0.0327 (9)	5 (1)	HP14	0.3622 (41)	0.5355 (22)	0.3006 (8)	4 (1)
H131	0.6022 (29)	0.7210 (17)	0.1018 (5)	1.5 (7)	HP15	0.2854 (45)	0.3757 (26)	0.2623 (9)	5 (1)
H132	0.4736 (50)	0.8357 (33)	0.0998 (10)	5 (2)	HP16	0.2688 (45)	0.4067 (25)	0.1950 (9)	4 (1)
H141	0.4698 (34)	0.7480 (21)	0.0383 (8)	2.2 (9)	HN1	0.3908 (49)	0.5702 (28)	0.0274 (9)	5 (1)

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)$; the U_{ij} are related to the dimensionless β_{ij} employed during refinements as $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$. $B_{eq} = {}^4/_3(\beta_{11}a^2 + \ldots - 2\beta_{12}ab - \ldots)$. [b] The estimated standard deviations in the least significant figures are given in parentheses in this and in other tables.

space groups were established by inspecting the intensities of selected equivalent *hkl* triplets and checked from the systematic absences observed during the data collection.

All calculations were performed on the IBM 370-168 computers at Université Paris-Sud, Orsay, France, through the terminal of our institute. In addition to a local program library, we also used slightly modified programs of W. R. Busing, K. O. Martin, and H. A. Levy (ORNL-TM 305 and 306 reports). For graphical purposes Johnson's thermal ellipsoid plot program (ORNL-3794 report) was used. After data-reduction and corrections for Lorentz and polarization factors, the four structures were solved by the heavy-atom method. Salient data collections, crystal parametes, and formulas are given in Table I. Absorption corrections were negligible.

$C_{11}H_{14}O_3NClPRh$ (6a). A prismatic crystal of 0.4 × 0.25 × 0.25 mm^3 was mounted on a thin glass rod, in random orientation. Standard reflections monitored periodically showed an intensity fluctuation of nearly ±2% during data collection, and a linear rescale correction was applied. From a total of 4403 reflections, 1860 conformed to the relation $F^2 \geq 2.0\sigma(F_o^2)$. The structure was solved by conventional Patterson and difference-Fourier techniques, and for all the refinements, full-matrix least-squares methods were used. In the last stages of the refinements, the $w = (a + b|F_o|)^2$ function was introduced,[9] together with anisotropic thermal parameters for all nonhydrogen atoms. The residuals converged to $R = 0.0341$ and $R_w = 0.0356$. At this stage a difference-Fourier map revealed most of the hydrogen atoms; these were then introduced and isotropically refined together with the remaining heavier atoms. The final residuals dropped thus to $R = 0.0298$ and $R_w = 0.0308$. The eight largest peaks in the final difference-Fourier synthesis ranged from 0.21 to 0.11 e Å^{-3}. The final atomic coordinates and thermal parameters with their esd's are listed in Table II. The principal intra- and intermolecular distances and bond angles with their estimated standard deviations are given in Table VI. Tables for the structure factors corresponding to the four complexes investigated in the present work are available as supplementary material.

$C_{13}H_{18}O_3NClPRh$ (6b). A nearly cubic specimen of 0.44 × 0.44 × 0.45 mm^3 was mounted on a glass rod in random orientation and investigated on the CAD-4 diffractometer. All the observed reflections were consistent with the $P2_1/c$ space group, and from a total of 3786 reflections, 2340 were retained with the $F^2 \geq 2.0\sigma(F^2)$ criterion. The structure was solved as already described for **6a**. After all the hydrogen atoms were introduced, the final residuals converged to $R = 0.0263$ and $R_w = 0.0223$, and the eight largest peaks of the final difference-Fourier synthesis ranged from 0.18 to 0.10 e Å^{-3}. The positional and thermal parameters for the last refinement cycle are listed in Table III, and the interatomic distances and bond angles are given in Table VII.

$C_{24}H_{36}O_4N_2ClP_2Rh$ (7a). A specimen of 0.32 × 0.25 × 0.25 mm^3 dimensions has been selected and mounted on the CAD-4 goniometer head in a slightly titled orientation. Selection rules obeying $h + k$

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(9) Stout, G. H.; Jensen, L. H. "X-Ray Structure Determination, a Practical Guide"; Macmillan: New York, 1968; pp 454–458.

Table III. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $RhCl(CO)PO_2C_4H_6(CH_3)_2NH(C_6H_5)$ (**6b**)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.26272 (2)	0.40604 (1)	0.55541 (2)	2.2	0.0279 (1)	0.0328 (1)	0.0267 (1)	0.0009 (1)	0.0060 (0)	−0.0013 (1)
Cl	0.06208 (7)	0.42185 (5)	0.36762 (8)	3.9	0.0395 (5)	0.0667 (5)	0.0398 (3)	0.0157 (3)	−0.0027 (3)	−0.0083 (3)
P1	0.42668 (6)	0.39792 (4)	0.75827 (7)	2.2	0.0262 (4)	0.0343 (2)	0.0297 (3)	−0.0020 (3)	0.0077 (2)	0.0004 (2)
O11	0.40468 (17)	0.34150 (12)	0.89218 (20)	2.3	0.0276 (11)	0.0456 (10)	0.0398 (9)	0.0039 (8)	0.0135 (8)	0.0106 (7)
O12	0.45132 (16)	0.49270 (12)	0.83121 (20)	3.3	0.0295 (11)	0.0398 (10)	0.0406 (9)	−0.0015 (8)	0.0060 (8)	−0.0066 (7)
O	0.38730 (24)	0.35706 (16)	0.33856 (26)	2.7	0.0758 (17)	0.0708 (16)	0.0501 (12)	0.0136 (13)	0.0363 (12)	−0.0006 (11)
N1	0.19582 (12)	0.45856 (8)	0.73286 (14)	3.0	0.0416 (8)	0.0470 (7)	0.0418 (6)	0.0005 (6)	0.0124 (6)	−0.0008 (5)
C11	0.31652 (15)	0.36841 (13)	0.96009 (19)	2.0	0.0281 (10)	0.0511 (10)	0.0365 (8)	0.0016 (8)	0.0150 (7)	0.0058 (7)
C12	0.18844 (15)	0.38982 (10)	0.84723 (17)	2.2	0.0295 (10)	0.0430 (8)	0.0368 (8)	−0.0003 (7)	0.0130 (6)	0.0034 (6)
C13	0.37077 (17)	0.56068 (11)	0.77526 (21)	3.3	0.0400 (12)	0.0338 (7)	0.0476 (10)	−0.0026 (7)	0.0117 (8)	−0.0061 (7)
C14	0.25549 (17)	0.54171 (11)	0.80552 (20)	3.0	0.0392 (12)	0.0349 (8)	0.0428 (9)	0.0009 (7)	0.0127 (8)	−0.0069 (7)
C	0.33656 (27)	0.37319 (17)	0.42069 (30)	2.5	0.0447 (18)	0.0384 (12)	0.0350 (12)	0.0043 (12)	0.0111 (11)	−0.0005 (10)
CP11	0.57556 (14)	0.35807 (9)	0.77491 (16)	2.6	0.0293 (9)	0.0366 (7)	0.0362 (7)	−0.0033 (6)	0.0104 (6)	−0.0026 (5)
CP12	0.62955 (16)	0.28803 (11)	0.86730 (20)	2.5	0.0321 (12)	0.0430 (8)	0.0566 (10)	−0.0003 (7)	0.0175 (8)	0.0056 (7)
CP13	0.74697 (18)	0.26278 (12)	0.88100 (24)	2.6	0.0415 (13)	0.0502 (12)	0.0664 (12)	0.0075 (9)	0.0184 (9)	0.0072 (9)
CP14	0.80851 (19)	0.30778 (13)	0.80381 (24)	3.4	0.0289 (12)	0.0606 (12)	0.0775 (13)	0.0025 (9)	0.0237 (10)	−0.0036 (9)
CP15	0.75603 (19)	0.37728 (13)	0.71267 (24)	3.3	0.0428 (14)	0.0618 (11)	0.0669 (12)	−0.0074 (9)	0.0322 (10)	0.0015 (9)
CP16	0.63966 (17)	0.40237 (12)	0.69706 (19)	2.5	0.0403 (12)	0.0482 (8)	0.0504 (9)	−0.0016 (9)	0.0187 (7)	0.0075 (8)
C121	0.12766 (19)	0.31127 (12)	0.75323 (23)	3.1	0.0365 (12)	0.0456 (10)	0.0526 (10)	−0.0063 (8)	0.0174 (9)	0.0024 (8)
C122	0.11499 (20)	0.42216 (16)	0.94470 (24)	2.9	0.0385 (13)	0.0716 (15)	0.0447 (10)	0.0011 (10)	0.0197 (8)	0.0048 (9)

atom	x/a	y/b	z/c	B_{eq}, Å^2	atom	x/a	y/b	z/c	B_{eq}, Å^2
H111	0.3095 (16)	0.3221 (12)	1.0240 (21)	3.6 (8)	H1221	0.0375 (18)	0.4398 (12)	0.8829 (21)	3.4 (8)
H112	0.3489 (15)	0.4174 (11)	1.0237 (19)	2.8 (7)	H1222	0.1551 (22)	0.4744 (17)	1.0080 (28)	7 (1)
H131	0.3565 (15)	0.5695 (10)	0.6660 (20)	2.7 (7)	H1223	0.1152 (19)	0.3817 (13)	1.0125 (25)	4.6 (9)
H132	0.4079 (15)	0.6097 (11)	0.8300 (19)	3.0 (7)	HP12	0.5930 (17)	0.2572 (12)	0.9288 (20)	4.2 (8)
H141	0.2008 (15)	0.5884 (11)	0.7634 (18)	2.9 (7)	HP13	0.7778 (18)	0.2163 (13)	0.9417 (22)	4.8 (9)
H142	0.2739 (7)	0.5373 (12)	0.9177 (22)	3.9 (8)	HP14	0.8766 (19)	0.2883 (13)	0.8145 (22)	3.5 (9)
H1211	0.1124 (19)	0.2678 (14)	0.8207 (23)	4.4 (9)	HP15	0.7946 (20)	0.4099 (13)	0.6609 (25)	6 (1)
H1212	0.1733 (20)	0.2876 (15)	0.6948 (26)	3.6 (9)	HP16	0.6014 (14)	0.4496 (10)	0.6334 (17)	2.8 (6)
H1213	0.0468 (19)	0.3268 (13)	0.6741 (23)	4.4 (9)	HN1	0.1106 (20)	0.4729 (14)	0.6580 (25)	6 (1)

[a] See Table II.

Table IV. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh[PO_2C_4H_6(CH_3)_2(C_6H_5)NH]_2Cl$ (7a)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.0	0.22216 (2)	1/4	2.2	0.0354 (1)	0.0271 (1)	0.0362 (1)	0.0	0.0105 (1)	0.0
Cl	0.0	−0.09156 (6)	1/4	4.9	0.0716 (6)	0.0328 (4)	0.0894 (6)	0.0	0.0102 (5)	0.0
P1	0.09347 (3)	0.31683 (4)	0.23526 (4)	2.3	0.0389 (3)	0.0317 (2)	0.0434 (3)	−0.0005 (2)	0.0155 (2)	0.0011 (2)
O11	0.17592 (8)	0.29241 (10)	0.3367 (2)	3.4	0.0355 (7)	0.0382 (7)	0.0666 (13)	0.0018 (6)	0.0063 (6)	0.0231 (6)
O12	0.11452 (10)	0.2930 (1)	0.1135 (2)	2.9	0.0725 (10)	0.0404 (7)	0.0622 (13)	0.0026 (6)	0.0414 (8)	−0.0034 (6)
N1	0.0859 (1)	0.1114 (1)	0.2318 (2)	3.1	0.0549 (9)	0.0465 (8)	0.0698 (13)	0.0084 (7)	0.0216 (8)	0.0008 (8)
C11	0.2131 (1)	0.1982 (2)	0.3338 (3)	3.8	0.0414 (10)	0.0410 (9)	0.0997 (19)	0.0050 (7)	0.0154 (10)	0.0031 (8)
C12	0.1609 (1)	0.1093 (2)	0.3354 (2)	2.9	0.0446 (12)	0.0364 (9)	0.0743 (13)	0.0063 (8)	0.0154 (10)	0.0100 (8)
C13	0.0737 (2)	0.2086 (2)	0.0444 (2)	4.1	0.0924 (15)	0.0448 (9)	0.0514 (13)	−0.0049 (11)	0.0357 (10)	−0.0092 (8)
C14	0.0984 (2)	0.1119 (2)	0.1103 (3)	3.2	0.0778 (15)	0.0392 (9)	0.0755 (13)	0.0050 (9)	0.0415 (10)	−0.0077 (8)
C121	0.1359 (2)	0.1097 (2)	0.4482 (2)	4.0	0.0631 (15)	0.0625 (19)	0.0660 (13)	−0.0012 (12)	0.0048 (10)	0.0223 (15)
C122	0.2080 (2)	0.0150 (2)	0.3280 (3)	4.3	0.0704 (15)	0.0429 (9)	0.1498 (25)	0.0199 (12)	0.0183 (19)	0.0108 (15)
CP11	0.1003 (1)	0.4492 (1)	0.2399 (2)	2.3	0.0370 (9)	0.0331 (8)	0.0520 (13)	0.0005 (7)	0.0171 (8)	0.0015 (8)
CP12	0.0787 (2)	0.5023 (2)	0.1347 (2)	4.7	0.0613 (13)	0.0410 (9)	0.0641 (13)	−0.0056 (9)	0.0019 (10)	0.0046 (8)
CP13	0.0809 (2)	0.6056 (2)	0.1382 (3)	4.3	0.0719 (15)	0.0410 (9)	0.0952 (19)	0.0018 (11)	0.0106 (10)	0.0169 (15)
CP14	0.1043 (2)	0.6537 (2)	0.2473 (3)	3.5	0.0616 (15)	0.0392 (9)	0.1016 (19)	0.0019 (9)	0.0357 (10)	0.0008 (15)
CP15	0.1285 (2)	0.6000 (2)	0.3515 (3)	5.1	0.1203 (29)	0.0466 (9)	0.0857 (19)	0.0023 (12)	0.0492 (19)	−0.0162 (15)
CP16	0.1265 (2)	0.4982 (2)	0.3481 (2)	4.0	0.1145 (15)	0.0410 (9)	0.0578 (13)	0.0047 (12)	0.0376 (10)	−0.0054 (8)

atom	x/a	y/b	z/c	B_{eq}, Å^2	atom	x/a	y/b	z/c	B_{eq}, Å^2
H111	0.233 (1)	0.198 (1)	0.269 (2)	5.0	HP12	0.054 (1)	0.462 (1)	0.064 (2)	5.0
H112	0.258 (1)	0.197 (1)	0.406 (2)	5.0	HP13	0.057 (1)	0.653 (1)	0.060 (2)	5.0
H131	0.012 (1)	0.217 (1)	0.016 (2)	5.0	HP14	0.106 (1)	0.724 (1)	0.259 (2)	5.0
H132	0.092 (1)	0.206 (1)	−0.021 (2)	5.0	HP15	0.155 (1)	0.638 (1)	0.416 (2)	5.0
H141	0.060 (1)	0.058 (1)	0.046 (2)	5.0	HP16	0.154 (1)	0.456 (1)	0.424 (2)	5.0
H142	0.147 (1)	0.095 (1)	0.104 (2)	5.0	HN1	0.056 (1)	0.045 (1)	0.242 (2)	5.0

[a] See Table II.

$= 2n$ for hkl, $l = 2n$ ($h = 2n$) for $h0l$, and $k = 2n$ for $0k0$ reflections have been observed for the entire data collection, insuring thus the $C2/c$ space group. The measured specific weight indicates the presence of four rhodium atoms in the unit cell, and inspection of the observed F_0^2's with no extra conditions on the hkl triplets led to the localization of the Rh and Cl atoms on the twofold rotation axis, i.e., 0, y, $^1/_4$ and symmetry-related positions. The 5705 measured intensities were reduced to 2768 unique data, and the structure solution was done as already described. For this complex, all but the hydrogen atoms corresponding to the methyl groups were refined with a fixed thermal parameter of 5 Å^2. The final R and R_w residuals converged respectively to 0.0305 and 0.0348. In the last difference-Fourier map no peaks higher than 0.73 e Å^{-3} could be observed. The final atomic coordinates and the thermal parameters with their esd's are listed in Table IV. The principal interatomic contacts and bond angles are given in Table VIII.

Table V. Final Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh[PO_2C_4H_6(CH_3)_2(C_6H_5)NH]_2ClO_4$ (7b)[a]

atom	x/a	y/b	z/c	B_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.16829 (14)	0.24538 (8)	0.17305 (8)	4.3	0.0376 (19)	0.0378 (7)	0.0276 (7)	−0.0089 (6)	0.0029 (6)	−0.0152 (4)
Cl	−0.1244 (7)	0.3221 (3)	0.5077 (3)	6.4	0.0615 (85)	0.0626 (26)	0.0461 (28)	−0.0116 (28)	0.0121 (23)	−0.0245 (20)
P1	0.3219 (5)	0.3419 (3)	0.0806 (3)	4.6	0.0427 (56)	0.0397 (20)	0.0319 (21)	−0.0077 (22)	0.0023 (23)	−0.0163 (14)
P2	0.1358 (7)	0.1390 (3)	0.0723 (2)	4.9	0.0423 (75)	0.0411 (20)	0.0340 (21)	−0.0089 (22)	0.0006 (23)	−0.0177 (14)
O1	−0.0103 (12)	0.2357 (8)	0.4843 (8)	6.6	0.0455 (150)	0.0717 (65)	0.0659 (64)	0.0055 (55)	0.0115 (58)	−0.0360 (48)
O2	−0.1179 (16)	0.4316 (8)	0.4298 (9)	7.9	0.1615 (188)	0.0586 (65)	0.0850 (71)	−0.0221 (72)	0.0404 (58)	−0.0001 (54)
O3	−0.2525 (19)	0.2918 (13)	0.4969 (11)	16.1	0.0601 (249)	0.1629 (130)	0.1063 (71)	−0.0498 (111)	0.0231 (115)	−0.0822 (88)
O4	−0.1161 (13)	0.3225 (9)	0.6215 (8)	10.9	0.0765 (141)	0.1173 (65)	0.0638 (71)	0.0039 (72)	−0.0035 (69)	−0.0557 (61)
O11	0.4548 (10)	0.3177 (7)	0.1592 (6)	5.1	0.0216 (117)	0.0547 (52)	0.0340 (50)	−0.0055 (50)	−0.0017 (52)	−0.0245 (41)
O12	0.2647 (11)	0.4822 (7)	0.0549 (6)	4.9	0.0578 (127)	0.0371 (52)	0.0425 (50)	−0.0105 (50)	0.0069 (52)	−0.0129 (41)
O21	0.1706 (11)	0.0012 (6)	0.1451 (6)	4.9	0.0484 (122)	0.0430 (52)	0.0369 (50)	−0.0100 (50)	0.0092 (46)	−0.0183 (34)
O22	−0.0276 (15)	0.1594 (7)	0.0451 (7)	6.5	0.0451 (155)	0.0606 (52)	0.0376 (50)	−0.0177 (61)	−0.0006 (63)	−0.0204 (41)
N1	0.1826 (14)	0.3512 (8)	0.2888 (8)	6.2	0.0667 (150)	0.0521 (59)	0.0446 (57)	−0.0089 (61)	0.0017 (63)	−0.0177 (41)
N2	0.0178 (13)	0.1443 (8)	0.2850 (7)	4.8	0.0507 (146)	0.0463 (59)	0.0454 (57)	−0.0044 (55)	0.0075 (63)	−0.0136 (41)

atom	x/a	y/b	z/c	B_{eq}, Å^2	atom	x/a	y/b	z/c	B_{eq}, Å^2
C11	0.4441 (19)	0.3622 (11)	0.2541 (11)	3.7 (3)	CP11	0.4110 (18)	0.3406 (10)	−0.0515 (10)	3.0 (3)
C12	0.3282 (19)	0.3180 (11)	0.3410 (11)	3.3 (3)	CP12	0.3352 (17)	0.3916 (10)	−0.1504 (10)	3.4 (3)
C13	0.1348 (17)	0.4838 (10)	0.2351 (10)	3.3 (3)	CP13	0.4067 (20)	0.3880 (11)	−0.2537 (11)	3.9 (3)
C14	0.1275 (19)	0.5183 (11)	0.1059 (11)	3.5 (3)	CP14	0.5431 (21)	0.3328 (12)	−0.2532 (12)	4.6 (3)
C121	0.3610 (19)	0.1842 (12)	0.3908 (11)	4.2 (3)	CP15	0.6219 (21)	0.2796 (13)	−0.1601 (13)	5.0 (3)
C122	0.3256 (19)	0.3736 (11)	0.4384 (11)	4.1 (3)	CP16	0.5479 (20)	0.2839 (12)	−0.0515 (11)	4.1 (3)
C21	0.2060 (18)	−0.0270 (11)	0.2642 (11)	3.9 (3)	CP22	0.1320 (18)	0.1954 (11)	−0.1615 (11)	3.9 (3)
C22	0.0788 (17)	0.0136 (10)	0.3317 (10)	3.3 (3)	CP21	0.2097 (18)	0.1332 (10)	−0.0634 (10)	3.3 (3)
C23	−0.1256 (21)	0.1715 (11)	0.2361 (11)	3.4 (3)	CP23	0.2008 (20)	0.1903 (12)	−0.2676 (11)	4.4 (3)
C24	−0.1204 (19)	0.1162 (11)	0.1388 (11)	4.1 (3)	CP24	0.3299 (21)	0.1238 (13)	−0.2702 (12)	4.9 (4)
C221	−0.1704 (19)	0.3057 (11)	0.1921 (11)	4.1 (3)	CP25	0.4050 (22)	0.0616 (14)	−0.1751 (14)	5.9 (4)
C222	−0.2306 (20)	0.1188 (12)	0.3246 (13)	4.9 (3)	CP26	0.3376 (21)	0.0645 (13)	−0.0682 (12)	4.8 (3)

[a] See Table II.

$C_{24}H_{36}O_8N_2ClP_2Rh$ (7b). The mounted specimen had 0.3 × 0.2 × 0.2 mm^3 dimensions. The unit cell calculated from the 25 reflections in the reference list appeared to be triclinic, with two formula units per cell. A careful inspection of the Niggli values corresponding to the triclinic unit cell showed that the symmetry was definitely triclinic, and the intensities of several hkl, $\bar{h}\bar{k}\bar{l}$ pairs indicated a probable $P\bar{1}$ space group. Up to $2\theta = 72°$ we could observe only 1856 reflections (out of the 7853 measured) which were reduced to 1463 unique data. The structure was solved in the $P\bar{1}$ space group, and only the noncarbon atoms have been refined anisotropically. The final R and R_w converged to 0.0505 and 0.0586, and the thermal parameters listed in Table V together with the final atomic coordinates show that in **7b** the atoms have relatively high-temperature factors. In Table IX are gathered the relevant interatomic distances and bond angles. The first 30 peaks of the final difference-Fourier synthesis ranged between 0.55 and 0.34 e Å^{-3}, but owing to the lack of unique data, no attempt for localizing the hydrogen atoms has been undertaken.

Results and Discussion

Structures of the Neutral Complexes 6a and 6b. The crystal structures of $RhCl(CO)(C_{11}H_{14}O_3NP)$ **6a** and of $RhCl(CO)(C_{13}H_{18}ONP)$ **6b** consist of discrete molecules with no unusual intermolecular contacts. Stereoscopic drawings of the unit cells are respectively presented in Figures 1 and 2. Interatomic distances and angles for both molecules are given in Tables VI and VII.

The molecular structures of compounds **6a** and **6b** are illustrated in Figures 3 and 4. The geometries about the rhodium centers are square planar with the organic ligand in the P,N mode of coordination and the P and Cl atoms in trans positions. The distances of the Rh, Cl, P1, N1, and C atoms to the least-square mean planes 1 (complex **6a**) and 2 (complex **6b**) are collected in Table X. According to the reported values, the square plane in **6b** is more distorted than in **6a**. Inspection of Figures 1 and 2 and of Tables VI and VII suggests that the stronger deformatin for the complex **6b** has its origin in the *gem*-dimethyl group located on carbon C12. This is confirmed by the larger O11–P1–O12 and C12–N1–C14 angles observed for **6b**. Interestingly, the corresponding

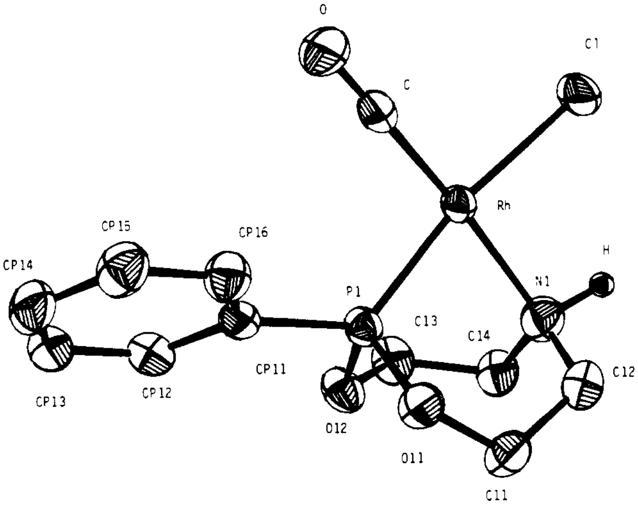

Figure 3. ORTEP diagram of **6a** showing 50% probability ellipsoids.

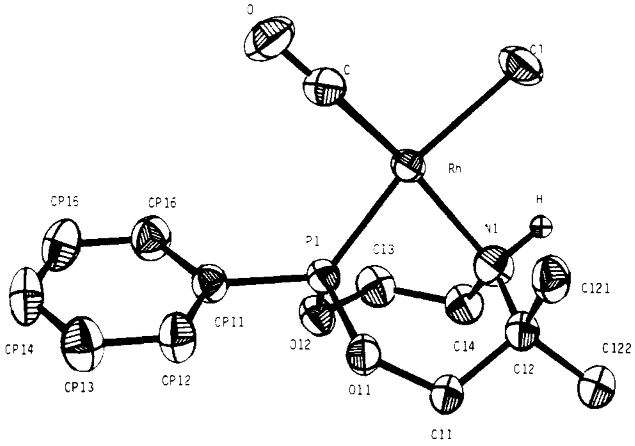

Figure 4. ORTEP diagram of **6b** showing 50% probability ellipsoids.

Table VI. Principal Interatomic Distances (Å) and Bond Angles (Deg) with Esd's for $C_{11}H_{14}O_3NPClRh$ (6a)

(A) Intramolecular Distances and Angles

Rh–Cl	2.388 (1)	N1–H	1.04 (3)
Rh–P1	2.1536 (7)	Cl···N1	3.206 (2)^b
Rh–N1	2.161 (2)	Cl···H	2.76 (3)
Rh–C	1.817 (3)	O11···CP16	3.164 (3)^b
C–O	1.136 (4)	O11···CP11	2.622 (3)
P1–O11	1.608 (2)	O12···CP12	2.922 (3)^b
P1–O12	1.605 (2)	O12···CP11	2.656 (3)
P1–CP11	1.776 (2)	O12···CP16	3.104 (3)^b
O11···O12	2.507 (3)	CP11–CP12	1.397 (3)
O11–C11	1.447 (3)	CP11–CP16	1.384 (3)
O12–C13	1.442 (3)	CP12–CP13	1.371 (3)
C11–C12	1.502 (4)	CP13–CP14	1.368 (4)
C12–N1	1.495 (4)	CP14–CP15	1.383 (4)
C13–C14	1.506 (4)	CP15–CP16	1.381 (4)
C14–N1	1.504 (3)	P1···N1	2.793 (2)
Cl–Rh–P1	169.98 (3)	O12–C13–C14	112.8 (2)
Cl–Rh–C	95.9 (1)	C13–C14–N1	111.9 (2)
Cl–Rh–N1	89.48 (6)	Rh–N1–C14	117.0 (2)
P1–Rh–C	93.9 (1)	Rh–N1–C12	110.3 (2)
P1–Rh–N1	80.68 (6)	Rh–N1–H	104 (2)
N1–Rh–C	174.4 (1)	C14–N1–C12	111.8 (2)
Rh–C–O	178.5 (3)	C14–N1–H	108 (2)
Rh–P1–O11	110.12 (7)	C12–N1–H	104 (2)
Rh–P1–O12	111.38 (7)	Cl···H–N1	106 (2)
Rh–P1–CP11	125.35 (8)	P1–CP11–CP12	122.0 (2)
CP11–P1–O11	101.4 (1)	P1–CP11–CP16	119.1 (2)
CP11–P1–O12	103.4 (1)	CP12–CP11–CP16	118.9 (2)
O11–P1–O12	102.6 (1)	CP11–CP12–CP13	119.9 (2)
P1–O11–C11	117.1 (2)	CP12–CP13–CP14	120.9 (3)
P1–O12–C13	117.1 (2)	CP13–CP14–CP15	120.0 (2)
O11–C11–C12	115.9 (2)	CP14–CP15–CP16	119.6 (2)
C11–C12–N1	115.0 (2)	CP15–CP16–CP11	120.7 (2)

(B) Intermolecular Contacts ($d \leqslant 3.35$ Å)

atom 1	atom 2	dist, Å	symmetry code^a	translation
Cl	N1	3.219 (2)^b	v	1 1 0
Cl	H	2.33 (3)	v	1 1 0
O	C13	3.308 (4)^b	vi	1 −1 0
CP14	CP16	3.274 (4)	viii	0 0 0

^{a} Codification for equipoints are as follows. v: $-x, -y, -z$; vi: $^1/_2 - x, {}^1/_2 + y, z$; viii: $^1/_2 + x, y, {}^1/_2 - z$. ^{b} Possible hydrogen bonds.

angles for the "opened" structure **5** are only slightly different from those of the P,N ligand of **6a** (respectively 101.3 (2) and 111.8 (5)°).[6]

The Cl–Rh–P1 as well as the N1–Rh–C angles in both complexes are not very far from strict linearity. The deformation could be due (i) to the occurrence of a Cl···H–N hydrogen bond, (ii) to the repulsion between the carbonyl group and the P and Cl atoms, and/or (iii) to the geometrical constraints of the bidentate ligand. Inspection of Tables VI and VII suggests that the last explanation seems to be the most plausible. The N1···Cl distances in **6a** and **6b** indicate the presence of normal Cl···H–N hydrogen bonds (normally accepted values for such hydrogen bonds are 3.16–3.26 Å[10]). Futhermore, the N1–Rh–Cl angles are very similar to the angle (89.5 (4)°) observed for the complex $RhCl(CO)(C_2H_4)(NHEt_2)$,[11] although the N–Rh–C angle in this complex (179.5 (8)°) does not suggest a deformation within the Rh(N, Cl, C) moiety. The distortion of the square plane, which is greater for **6b** than for **6a**, agrees well with the stronger deformation of the Cl–Rh–P1 and N1–Rh–C angles observed for **6b** over **6a**.

Table VII. Principal Interatomic Distances (Å) and Bond Angles (Deg) with Esd's for $C_{13}H_{18}O_3NPClRh$ (6b)

(A) Intramolecular Distances and Angles

Rh–Cl	2.3845 (7)	Cl···N1	3.217 (2)^b
Rh–P1	2.1559 (6)	Cl···H	2.65 (2)
Rh–N1	2.199 (2)	C12–C121	1.514 (2)
Rh–C	1.815 (3)	C12–C122	1.528 (3)
C–O	1.141 (5)	O11···CP11	2.597 (3)
P1–O11	1.603 (2)	O12···CP11	2.620 (3)
P1–O12	1.602 (2)	O11···CP12	2.841 (3)^b
P1–CP11	1.801 (2)	O12···CP16	3.104 (3)^b
O11···O12	2.544 (3)	CP11–CP12	1.383 (2)
O11–C11	1.443 (3)	CP11–CP16	1.387 (3)
O12–C13	1.450 (3)	CP12–CP13	1.389 (3)
C11–C12	1.527 (2)	CP13–CP14	1.366 (3)
N1–C12	1.519 (2)	CP14–CP15	1.367 (3)
C13–C14	1.498 (3)	CP15–CP16	1.373 (3)
N1–C14	1.501 (2)	P1···N1	2.788 (2)
N1–H	1.02 (2)		
Cl–Rh–P1	168.48 (2)	C11–C12–C122	106.9 (1)
Cl–Rh–C	96.7 (1)	C121–C12–C122	110.4 (1)
Cl–Rh–N1	89.05 (4)	O12–C13–C14	112.6 (1)
P1–Rh–C	94.8 (1)	C13–C14–N1	113.0 (1)
P1–Rh–N1	79.59 (4)	Rh–N1–C14	114.5 (1)
N1–Rh–C	171.7 (1)	Rh–N1–C12	112.3 (1)
Rh–C–O	175.8 (3)	Rh–N1–H	96 (1)
Rh–P1–O11	111.24 (8)	C14–N1–C12	114.9 (1)
Rh–P1–O12	109.00 (7)	C14–N1–H	108 (1)
Rh–P1–CP11	129.10 (6)	C12–N1–H	110 (1)
CP11–P1–O11	99.3 (1)	Cl···H–N1	115 (1)
CP11–P1–O12	100.5 (1)	P1–CP11–CP12	122.5 (1)
O11–P1–O12	105.1 (1)	P1–CP11–CP16	118.0 (1)
P1–O11–C11	120.6 (1)	CP12–CP11–CP16	119.4 (2)
P1–O12–C13	117.9 (1)	CP11–CP12–CP13	119.8 (2)
O11–C11–C12	116.5 (2)	CP12–CP13–CP14	119.7 (2)
C11–C12–N1	109.9 (1)	CP13–CP14–CP15	120.9 (2)
N1–C12–C121	107.1 (1)	CP14–CP15–CP16	120.0 (2)
N1–C12–C122	111.1 (1)	CP15–CP16–CP11	120.2 (2)
C11–C12–C121	111.4 (1)		

(B) Intermolecular Contacts ($d \leqslant 3.20$ Å)

atom 1	atom 2	dist, Å	symmetry code^a	translation
Cl	H	2.54 (2)	iii	0 1 1
O	O11	3.102 (3)	iv	0 0 0
O12	O12	2.921 (4)	iii	1 1 2

^{a} Codification for equipoints is as follows. iii: $-x, -y, -z$; iv: $x, {}^1/_2 - y, {}^1/_2 + z$. ^{b} Possible hydrogen bonds.

The P···N distances are shorter than the sum of the van der Waals radii of P and N (3.4 Å). These values are smaller than the values (ca. 3.1 Å) reported by Verkade and his co-workers for $H_3B\cdot P(OCH_2CH_{12})_3N$[12] and $S{=}P(OCH_2CH_2)_3N$.[13] The observed value for compound **5** (2.870 (5) Å)[6] agrees well with the present determinations since one can expect that coordination of both P and N atoms to Rh(I) will result in a closer P···N distance. However, there is no direct P···N interaction as in $[HP(OCH_2CH_2)_3N]BF_4$[14] where a dative P←N bond (1.986 Å) is demonstrated.

Inspection of Tables VI and VII shows that the bond distances to rhodium in both structures are comparable to those encountered in related compounds. Thus, Rh–Cl distance are slightly longer than those reported for chlororhodium–phosphine complexes (e.g., 2.373 Å in $RhCl(PPh_3)_3$,[15] 2.386 Å in

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Table VIII. Principal Interatomic Distances (Å) and Bond Angles (Deg) with Esd's for $C_{24}H_{36}O_4N_2P_2ClRh$ (7a)

(A) Intramolecular Distances and Angles

Rh-P1	2.1540 (6)	C11–C12	1.528 (4)
Rh-N1	2.203 (2)	C12–C121	1.520 (4)
Rh···H	2.62 (1)	C12–C122	1.548 (4)
Rh···Cl	4.2562 (7)	C13–C14	1.519 (4)
Cl···H	2.12 (2)	C121···C122	2.530 (5)
Cl···N1	3.190 (2)	CP11–CP12	1.380 (3)
N1-H	1.07 (2)	CP12–CP13	1.402 (4)
P1-O11	1.623 (2)	CP13–CP14	1.385 (5)
P1-O12	1.617 (3)	CP14–CP15	1.377 (5)
O11···O12	2.517 (3)	CP15–CP16	1.382 (4)
P1–CP11	1.800 (2)	CP11–CP16	1.384 (3)
O11–C11	1.445 (3)	CP11···CP11^{ii}	3.661 (4)
O12–C13	1.464 (3)	CP14···CP14^{ii}	3.744 (7)
N1-C12	1.513 (2)	P1···N1	2.790 (3)
N1–C14	1.509 (4)		

P1-Rh-N1	79.62 (5)	C14-N1-H	109 (1)
P1-Rh-N1^{ii}	173.45 (5)	O11–C11–C12	114.3 (2)
P1-Rh-P1^{ii}	106.79 (2)	O12–C13–C14	112.0 (2)
Cl···H-N1	180.0 (7)	N1–C14–C13	112.5 (2)
H···Cl···H^{ii}	58.2 (7)	N1–C12–C11	111.7 (2)
Rh-P1–O11	111.85 (7)	N1–C12–C121	106.2 (2)
Rh-P1–O12	110.16 (7)	N1–C12–C122	109.5 (2)
Rh-P1–CP11	129.76 (6)	C11–C12–C121	110.4 (2)
O11-P1-O12	101.91 (9)	C11–C12–C122	107.9 (2)
O11-P1-CP11	98.24 (9)	C121–C12–C122	111.1 (2)
O12-P1–CP11	101.22 (9)	P1–CP11–CP12	119.7 (2)
P1–O11–C11	119.0 (2)	P1–CP11–CP16	120.5 (2)
P1–O12–C13	115.9 (2)	CP12–CP11–CP16	119.8 (2)
Rh-N1–C12	114.1 (1)	CP11–CP12–CP13	119.8 (2)
Rh-N1–C14	113.3 (1)	CP12–CP13–CP14	119.7 (3)
Rh-N1-H	100 (1)	CP13–CP14–CP15	119.9 (3)
C12-N1–C14	114.3 (2)	CP14–CP15–CP16	120.3 (3)
C12-N1-H	104 (1)	CP15–CP16–CP11	120.3 (3)

(B) Intermolecular Nonhydrogen Contacts ($d \leqslant 3.8$ Å)

atom 1	atom 2	dist, Å	symmetry code[a]	translation
O12	CP15	3.478 (4)	iv	0 1 −1
C13	Cl	3.668 (2)	iv	0 0 −1
C13	CP15	3.765 (5)	iv	0 1 −1
C14	C121	3.726 (4)	iv	0 0 −1
CP12	CP12	3.540 (6)	iii	0 1 0
CP12	CP16	3.714 (4)	iv	0 1 −1

[a] Codification for equipoints is as follows. i: x, y, z; ii: $-x, y, \frac{1}{2}-z$; iii: $-x, -y, -z$; iv: $x, -y, \frac{1}{2}+z$.

$RhCl(CS)(PPh_3)_2$,[16] and 2.381 Å in $RhCl(PhP(CH_2CH_2CH_2PPh_2)_2$[17]). The Rh-P1 distances are intermediate between those reported for $Rh_2(P(OPh)_3)_2(C_8H_{12})Cl_2$[18] (2.146 and 2.138 Å) and $(RhCl(CO)PMe_2Ph)_2$[19] (2.235 and 2.221 Å). This could be explained by considering the P(III) donor as a phosphonite ligand, $PhP(OCH-)_2$, which should be a better π acceptor than a phosphine and a poorer π acceptor than a phosphite. Significant π interaction of diethyl phenylphosphonite which, on the electronic standpoint, is close to the P(III) arm of the ligand under consideration has been mentioned for iron(II),[20] nickel(II),[21] and ruthenium(II)[22] complexes. Nevertheless, these Rh–P distances are shorter than that (2.265 Å) found in the complex (*trans*-H(NC)C═C(CN)H)(P(OPh)$_3$)Rh(*p*-MeOC$_6$H$_4$NC)$_2$;[23] however, the very different nature of the other ligands for this Rh(I) complex precludes any direct comparison. The Rh–N distances are similar to the Rh–N distance (2.168 Å) reported for $RhCl(CO)(C_2H_4)NHEt_2$ where the N atom is also trans to the carbonyl ligand.[11] The significative lengthening in going from **6a** to **6b** is certainly related to the occurrence of the *gem*-dimethyl group on C12 of **6b** (vide supra). This is experimentally sustained by the slower rate of formation of **6b** from the reaction of **1b** with $[Rh(CO)_2Cl]_2$ as judged from the rate of evolution of carbon monoxide.[24] The Rh–C distances are slightly longer than that reported (1.788 Å)[11] for $RhCl(CO)(C_2H_4)NHEt_2$. Interestingly, the reversed trend is observed for the C–O distances (respectfully 1.136, 1.141, and 1.186 Å), suggesting a weaker back-donation from rhodium(I) in complexes **6a** and **6b**.

The bond angles around the nitrogen atom indicate a slightly distorted tetrahedral environment. Inspection of Tables VI and VII shows that, except or the Rh–N1–H angles (respectively 104 and 96°), the observed values do not deviate drastically from those reported for the ligand **5** (118.5, 116.0, and 115.0°).[6] Furthemore, the Rh–N1–C12 and Rh–N1–C14 angles are quite comparable to those observed for $RhCl(CO)(C_2H_4)NHEt_2$[11] (113.0 and 112.3°).

The bond angles around the phosphorus atom reveal a stronger deformation from the ideal tetrahedral coordination. Comparison with the mean values reported for diethyl phenylphosphonite complexes of iron(II),[20] nickel(II),[21] and ruthenium(II)[22] (Table XI) shows the same trend for the M–P–O, C–P–O, M–P–C, and O–P–O angles, i.e., the expansion of two angles and the contraction of two angles relative to the tetrahedral value suggesting thus that this behavior already reported for phosphites is also a general feature of phosphonite complexes. However, inspection of Table XI indicates consistent differences with the diethyl phenylphosphonite ligand. This is mainly the case for the M–P–C angles which are significantly larger for **6a** and **6b** and for the M–P–O angles which are significantly smaller for **6a** and **6b**. These deformations may arise from rehybridization at the P atom as a result of the constraints at the perhydrodioxazaphosphocine ring. The oxygen atoms engaged in this ring are no longer participating in the ligand "breathing" accompanying the coordination to rhodium(I). Furthermore, the occurrence of a *gem*-dimethyl group in **6b** induces a significant expansion of the Rh–P1–CP11 and also of the O11–P1–O12 angles. A rehybridization at the phosphorus may also be reflected by the contraction of the P–C bond relative to the mean values observed for the reported diethyl phenylphosphonite complexes.[20-22]

The cone angles of the two ligands in complexes **6a** and **6b** have been calculated to be 112 and 111° by assuming that the van der Waals radii of oxygen and (aromatic) carbon atoms are respectively 1.40 and 1.85 Å.[25] These cone angles are smaller than those calculated according to Tolman[26,27] by taking either $P(OCH_2)_3CMe$ and PPh_3 (calculated value of 116°) or $P(OEt)_3$ and PPh_3 (calculated value 121°). As Tolman's values are determined for a metal to phosphorus distance of 2.28 Å, the cone angles we calculated should be even smaller.

The only marked difference between **6a** and **6b** lies in the relative positions of the mean-square and phenyl planes (Table

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Table IX. Principal Interatomic Distances (Å) and Bond Angles (Deg) with Esd's for $C_{24}H_{36}O_8N_2P_2ClRh$ (7b)

(A) Intramolecular Distances and Angles

Rh-P1	2.146 (2)	Rh···O1	4.087 (7)	O12-C13	1.483 (9)	C22-C222	1.53 (1)
Rh-P2	2.154 (2)	Rh···O2	4.867 (8)	O21···O22	2.528 (7)	C221···C222	2.51 (1)
Rh-N1	2.249 (6)	N2···P2	2.816 (5)	O22-C24	1.470 (8)	CP11-CP12	1.39 (1)
Rh-N2	2.236 (6)	N2···O21	3.005 (7)	O21-C21	1.452 (9)	CP11-CP16	1.38 (1)
Cl-O1	1.446 (6)	N2···O22	2.950 (7)	O1···O2	2.304 (7)	CP12-CP13	1.42 (1)
Cl-O2	1.391 (5)	N2···O1	2.999 (8)	O1···O3	2.345 (11)	CP13-CP14	1.37 (1)
Cl-O3	1.42 (1)	N2-C23	1.518 (7)	O1···O4	2.345 (8)	CP14-CP15	1.36 (1)
Cl-O4	1.430 (6)	N2-C22	1.517 (12)	O2···O3	2.29 (1)	CP15-CP16	1.49 (1)
Cl···N1	3.891 (7)	N1···O2	3.430 (9)	O2···O4	2.339 (7)	CP21-CP22	1.409 (9)
P1-O11	1.625 (6)	C11-C12	1.56 (1)	O3···O4	2.30 (1)	CP21-CP26	1.37 (1)
P1-O12	1.619 (4)	C12-C121	1.523 (9)	N1···P1	2.853 (6)	CP22-CP23	1.44 (1)
P1-CP11	1.801 (7)	C11-C122	1.56 (1)	N1···O11	3.028 (8)	CP23-CP24	1.36 (1)
P2-O21	1.625 (8)	C14-C13	1.535 (9)	N1···O12	2.985 (6)	CP24-CP25	1.37 (1)
P2-O22	1.616 (4)	C121···C122	2.51 (1)	N1···O1	3.115 (8)	CP25-CP26	1.44 (1)
P2-CP21	1.799 (7)	C24-C23	1.53 (1)	N1-C12	1.55 (1)	CP11···CP21	3.57 (1)
O11···O12	2.530 (6)	C21-C22	1.56 (1)	N1-C14	1.527 (7)	CP14···CP24	3.69 (1)
O11-C11	1.438 (9)	C22-C221	1.529 (9)				

P1-Rh-P2	104.90 (8)	CP12-CP11-CP16	122.2 (7)	Rh-P1-O12	110.4 (2)	CP26-CP26-CP21	121.3 (8)
P1-Rh-N1	80.9 (2)	CP11-CP12-CP13	117.2 (7)	Rh-P1-CP11	130.6 (3)	C11-C12-C121	110.8 (6)
P1-Rh-N2	174.3 (2)	CP12-CP13-CP14	120.3 (7)	O11-P1-O12	102.5 (3)	C11-C12-N1	113.4 (6)
P2-Rh-N1	174.1 (2)	CP13-CP14-CP15	125.5 (8)	O11-P1-CP11	99.5 (3)	C11-C12-C122	107.1 (6)
P2-Rh-N2	79.8 (2)	CP14-CP15-CP16	114.6 (8)	O12-P1-CP11	100.0 (3)	C121-C12-C122	108.7 (6)
N1-Rh-N2	94.5 (2)	CP15-CP16-CP11	120.2 (7)	Rh-P2-O22	109.8 (2)	C121-C12-N1	106.8 (6)
O1-Cl-O2	108.6 (4)	P2-CP21-CP22	119.4 (5)	Rh-P2-O21	111.3 (2)	N1-C12-C122	109.9 (6)
O1-Cl-O3	109.9 (4)	P2-CP21-CP26	119.0 (6)	Rh-P2-CP21	129.7 (3)	C21-C22-N2	109.8 (6)
O1-Cl-O4	109.2 (4)	CP22-CP21-CP26	121.6 (7)	O22-P2-O21	102.5 (3)	C21-C22-CG221	110.7 (6)
O2-Cl-O3	109.1 (5)	CP21-CP22-CP23	116.0 (7)	O22-P2-CP21	100.9 (3)	C21-C22-C222	106.9 (6)
O2-Cl-O4	111.9 (4)	CP22-CP23-CP24	121.0 (7)	O21-P2-CP21	99.1 (3)	N2-C22-C221	107.4 (6)
O3-Cl-O4	108.0 (4)	CP23-CP24-CP25	123.1 (8)	P1-CP11-CP12	118.0 (5)	N2-C22-C222	111.7 (6)
Rh-P1-O11	110.3 (2)	CP24-CP25-CP26	116.6 (8)	P1-CP11-CP16	119.7 (6)	C221-C22-C222	110.3 (7)

(B) Intermolecular Nonhydrogen Contacts ($d \leqslant 3.9$ Å)

atom 1	atom 2	dist, Å	symmetry code[a]	translation	atom 1	atom 2	dist, Å	symmetry code[a]	translation
Cl	C23	3.893 (6)	ii	0 0 1	O3	CP14	3.67 (1)	i	−1 0 1
O11	C221	3.72 (1)	i	1 0 0	O4	C14	3.35 (1)[b]	ii	0 1 1
O11	C222	3.807 (9)	i	1 0 0	O4	C122	3.715 (8)	ii	0 1 1
O12	C221	3.388 (7)[b]	ii	0 1 0	O4	C24	3.700 (9)	ii	0 0 1
O12	CP16	3.70 (1)	ii	1 1 0	O4	C23	3.892 (9)	ii	0 0 1
O22	CP15	3.551 (9)	ii	1 0 0	O4	CP14	3.57 (1)	i	−1 0 1
O21	C13	3.735 (7)	ii	0 1 0	O4	CP15	3.58 (1)	i	−1 0 1
O1	C23	3.340 (7)[b]	ii	0 0 1	O4	CP22	3.548 (9)	i	0 0 1
O1	CP23	3.71 (1)	i	0 0 1	O4	CP23	3.38 (1)[b]	i	0 0 1
O2	C122	3.51 (1)	ii	0 1 1	C11	CP13	3.65 (1)	ii	1 1 0
O2	CP13	3.62 (1)	ii	0 1 0	C11	CP14	3.74 (1)	ii	1 1 0
O3	C24	3.610 (8)	ii	0 0 1	C24	CP25	3.87 (1)	ii	1 0 0
O3	C23	3.775 (9)	ii	0 0 1	C222	CP24	3.57 (1)	ii	0 0 0

[a] Codification for equipoints. i: x, y, z; ii: $-x, -y, -z$. [b] Possible hydrogen bonds.

X). This is easily seen from Figures 5 and 6. In the case of **6a**, the CP12 atom is close to O12 and the CP16 atom is away from O11; the reverse situation is observed for **6b** (Tables VI and VII). This situation leads to dihedral angles of 122.1 and 61.8°, respectively. This difference arises probably from the crystal packing since no drastic change occurs in the molecular environment of the phenyl plane on going from **6a** to **6b**.

The arrangements of the carbon atoms of the phenyl group in both structures are close to a regular hexagon: all the bond distances and bond angles are respectively in the range 1.368–1.397 Å and 118.9–120.9° for **6a** and 1.366–1.389 Å and 119.4–120.9° for **6b**. The largest distance of a carbon atom to the least-squares mean plane of the phenyl groups is 0.007 Å in **6a** (Table X).

The conformation of the eight-membered ring is similar to that observed for compound **5**; i.e., it is better described as a chair-boat combination. This is readily observed on Figures 5–7 which represent the stereoscopic drawings of the P,N ligand bound to rhodium(I) and ligand **5** in the same prjection along the P,N axis. The *gem*-dimethyl group is located on the $PhNC_2OP$ moiety with the chair conformation. As already reported, the presence of the *gem*-dimethyl group opens the O11–P1–O12 and the C12–N1–C14 angles; however, there is practically no modification of the tetrahedral environment at C12 (mean angle 109.47°). The C–C, C–N, and C–O distances (Tables VI and VII) within the organic ligand are not significantly different from those of ligand **5**.[6] The small lengthening of the C11–C12 and C12–N1 bonds in complex **6b** is a consequence of the occurrence of a *gem*-dimethyl group at C12.

The shortest distances between nonbonding atoms in the complexes **6a** and **6b** show that most of these contacts involve hydrogen bonds (Tables VI and VII). The intermolecular contacts are of the normal van der Waals type. In the same tables, further intermolecular hydrogen bonds which contribute to the cohesion of the crystals are cited. The shortest nonhydrogen intermolecular contact is 2.92 Å.

Structures of the Cationic Complexes 7a and 7b. The crystal structures of $Rh(C_{13}H_{18}O_2NP)_2Cl$ (**7a**) and of $Rh(C_{13}H_{18}O_2NP)_2ClO_4$ (**7b**) consist of discrete molecules with no unusual intermolecualr contacts. The unit cell packing of **7a** consists of four molecules; that of **7b** consists of two molecules. Stereoscopic drawings of the unit cells are respectively represented in Figures 8 and 9. Interatomic distances and angles for both

Table X. Least-Squares Mean Planes with Esd's and Dihedral Angles for Compounds **6a**, **6b**, **7a**, and **7b**

atom	dev, Å	atom	dev, Å	dihedral angle, deg
Plane 1 (for **6a**): Rh–Cl–N1–P1–C				
$-0.7551X - 0.6540Y - 0.0458Z + 6.4274 = 0^a$				
Rh	−0.042(3)	P1	0.0159(6)	
Cl	0.014(1)	C	−0.002(4)	
N1	−0.004(2)			
Plane 2 (for **6a**): CP11–CP12–CP13–CP14–CP15–CP16				
$0.9558X - 0.2858Y - 0.0692Z - 0.0357 = 0$				
CP11	−0.007(2)	CP14	−0.005(3)	
CP12	0.005(3)	CP15	0.003(3)	
CP13	0.002(3)	CP16	0.004(3)	planes 1-2 122.1
Plane 3 (for **6b**): Rh–Cl–N1–P1–C				
$0.2985X + 0.9399Y - 0.1661Z - 5.5098 = 0$				
Rh	−0.309(2)	P1	−0.0635(6)	
Cl	−0.0509(8)	C	0.073(3)	
N1	0.072(1)			
Plane 4 (for **6b**): CP11–CP12–CP13–CP14–CP15–CP16				
$-0.1051X - 0.6089Y - 0.7862Z + 9.0548 = 0$				
CP11	−0.001(1)	CP14	0.000(2)	
CP12	−0.002(2)	CP15	−0.003(2)	
CP13	0.003(2)	CP16	0.004(2)	planes 3-4 −61.8
Plane 5 (for 7a): Rh–Cl–N1–P1–C				
$-0.1098X - 0.9939Z + 2.6837 = 0$				
Rh	0.0	N1	0.027(2)	
P1	−0.0251(4)	$N1^{ii}$	−0.027(2)	
$P1^{ii}$	0.0251(4)			
Plane 6 (for 7a): CP11–CP12–CP13–CP14–CP15–CP16				
$0.9991X - 0.0157Y - 0.0397Z - 0.7518 = 0$				
CP11	−0.016(2)	CP14	−0.018(4)	
CP12	0.007(4)	CP15	0.009(4)	
CP13	0.010(4)	CP16	0.009(4)	planes 5-6 98.6; planes 6-6^{ii} 2.01
Plane 7 (for **7b**): Rh–P1–P2–N1–N2				
$-0.6395X + 0.6031Y - 0.4768Z + 0.4199 = 0$				
Rh	0.015(1)	N1	0.041(12)	
P1	−0.046(4)	N2	−0.048(11)	
P2	0.039(5)			
Plane 8 (for **7b**): CP11–CP12–CP13–CP14–CP15–CP16				
$0.4749X + 0.8745Y - 0.0983Z - 5.7411 = 0$				
CP11	0.013(12)	CP14	0.014(16)	
CP12	−0.012(14)	CP15	−0.001(17)	
CP13	0.005(15)	CP16	−0.007(16)	planes 7-8 −74.3
Plane 9 (for **7b**): CP21–CP22–CP23–CP24–CP25–CP26				
$0.5815X + 0.8112Y - 0.0627Z - 2.4766 = 0$				
CP21	0.025(15)	CP24	−0.005(18)	
CP22	−0.016(16)	CP25	0.013(20)	
CP23	0.006(17)	CP26	−0.023(18)	planes 7-9 −81.5; planes 8-9 7.4

[a] The orthogonalized coordinates *X*, *Y*, and *Z* are for each plane those corresponding to the unit cell of the related compound.

molecules are given in Tables VIII and IX.

The molecular structures of compounds **7a** and **7b** are illustrated by Figures 10 and 11. The geometries about the rhodium centers are square planer with two cis phosphorus atoms. Complex **7a** possess a twofold rotation axis which is contained in the least-squares mean plane. However the square plane in **7a** is more distorted than in **7b** as judged from the distances of the Rh, P1, P2, N1, and N2 atoms to the least-squares mean planes (Table X). This is also reflected by the sum of the angles around the rhodium atom (respectively 372.82 and 360.10°).

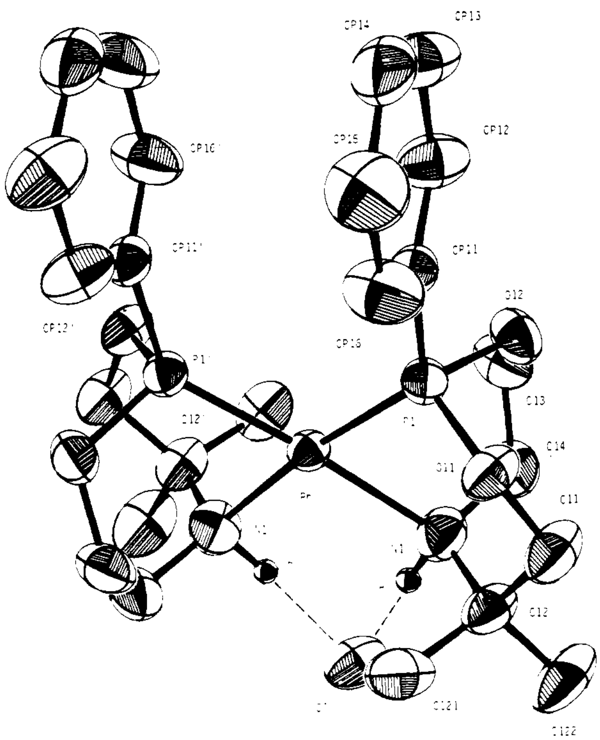

Figure 10. ORTEP diagram of **7a** showing 50% probability ellipsoids.

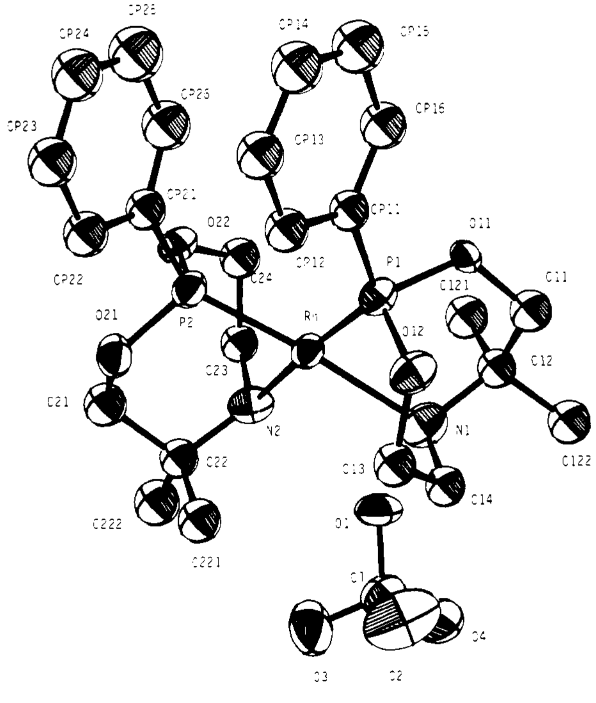

Figure 11. ORTEP diagram of **7b** showing 50% probability ellipsoids.

The Rh···Cl and Rh···O1 distances respectively in **7a** and **7b** indicate an ionic character for these compounds. The shorter intramolecular contacts between the N and Cl atoms of **7a** with respect to the neutral complexes **6a** and **6b** reflect the better hydrogen bonding in the former complex and explain the important red shift of the NH stretching frequency for this compound ($\Delta\nu$ = 118 cm^{-1} [24]). The N1–O1 and N2–O1 distances in complex **7b** also indicate the occurrence of hydrogen bonding (accepted values lie between 2.73 and 3.22 Å[10]). The lack of reference complexes does not allow a direct evaluation of their strength. As oxygen is more electronegative than chlorine, one can expect stronger H bonds with oxygen atoms which withdraw further electron density from the ni-

Table XI. Selected Bond Angles (Deg) and Interatomic Distances (Å) for Different Coordinated Phosphonite Ligands

complex	M-P-O	M-P-C	C-P-O	O-P-O	P-C	P-O	cone angle θ	ref
6a	110.75	125.35	102.4	102.6	1.776	1.607	112	this work
6b	110.12	129.10	99.9	105.1	1.801	1.603	111	this work
7a	111.01	129.76	99.7	101.91	1.800	1.620	110	this work
7b	110.08	130.15	99.88	102.5	1.800	1.621	110	this work
cis-$H_2Fe[PPh(OEt)_2]_4$	118.55	119.45	100.3, 94.6	101.1	1.838	1.630		20
$Ni(CN)_2[PPh(OEt)_2]_3$	114.67	117.33	101.7	105.57	1.82	1.62		21
trans-$H_2Ru[PPh(OEt)_2]_4$	123.5	119.4	100.4, 95.4	100.4	1.826	1.615		22

trogen atoms. The Rh–N distances for **7b** are significantly longer than Rh–N distances determined for **7a**. This bond lengthening could be explained by the weaker σ donation from the nitrogen atoms in **7b**, owing to this electronic drain toward the perchlorate anion.

The shorter Rh–N distances together with the larger chlorine radius may explain the opening of the N1–Rh–N2 angle of **7a** and the deformation observed for the rhodium plane. Besides, a $Rh^{\delta+}\cdots Cl^{\delta-}$ interaction may also particpate in such a deformation.

The symmetrical sharing of the chlorine anion between the two N–H moieties locks the two P,N ligands in such a way that a twofold axis occurs in the molecule of **7a**. The prefered precipitation of only one racemate of **7a** is of interest with respect to the use of the corresponding optically resolved compounds for asymmetric catalytic reactions.[25]

Only one of the oxygen atoms of the perchlorate anion is shared between the two NH moieties of **7b**, but the two hydrogen bonds are no longer symmetrical: the symmetry of the anion is distorted toward C_{3v}.

The P···N and Rh–P distances in both complexes as well as the bond angles around the P(III) atoms (Tables VIII and IX) are similar to those observed in **6b** (Tables VII and XI). Interestingly, the phenyl rings in complex **7a** are now nearly parallel, with a distance between the centers of the two rings of 3.703 Å. No further opening of the Rh–P–C angles is observed. The carbon atoms of the phenyl rings in both structures are very close to perfect hexagons. All the bond distances and bond angles are similar to those already reported for the phenyl group in complex **6b**. The largest distance of a carbon atom to the least-squares mean plane of these phenyl rings is 0.025 Å in **7b** (Table X).

The bond angles around the nitrogen atoms, except for the angles which involve the hydrogen atom, are very similar to those reported for complex **6b**. Inspection of Table VIII suggests that the occurrence of the strong hydrogen bonds with the chlorine anion is associated with a significant bonding of the hydrogen outward from the rhodium and only the contraction of the C12–N1–H angle.

The conformation of the eight-membered rings is similar to that observed for compound **6b**. This is clearly demonstrated by the comparison of Figures 12 and 13 which represent the stereoscopic drawings of the P,N ligand bound to the rhodium(I) and Figure 6. The C–C, C–N, and C–O distances within the organic ligand are not significantly different from those reported for the complex **6b**. In both complexes, the dihedral angles between the phenyl ring and the mean-squares plane of the rhodium already reported for **6b** are no longer retained. The tendency toward orthogonality may be explained by the steric repulsions between the two phenyl groups as noted for other phenylphosphonite complexes.[22]

The shortest distances between nonbonding atoms show that most of these contacts involve hydrogen bonds (Tables VIII and IX). The intermolecular contacts are of the normal van der Waals type. In the same tables, further intermolecular hydrogen bonds are cited, which contribute to the cohesion of the crystals. The shortest nonhydrogen intermolecular contact is 3.34 Å.

Acknowledgment. We thank Professor J. G. Riess for the gift of phosphoranes which enabled us to prepare the complexes **6a**, **6b**, **7a**, and **7b** and Dr. D. Houalla for providing us with structural data from ref 6 prior to publication. This work was supported by the DGRST and CNRS.

Registry No. **6a**, 69229-14-7; **6b**, 69229-15-8; **7a**, 70428-74-9; **7b**, 75790-02-2.

Supplementary Material Available: Listings of structure factor amplitudes and thermal parameters and Figures 1 and 2 (stereoscopic drawings of the unit cells of **6a** and **6b**), 5–7 (stereoscopic drawings of the P,N ligand bound to Rh(I) and **5**), 8 and 9 (stereoscopic drawings of the unit cells of **7a** and **7b**), and 12 and 13 (stereoscopic drawings of the P,N ligand bound to Rh(I) and **6** (45 pages). Ordering information is given on any current masthead page.