

## Structure of *trans*-Carbonylchlorobis(methyldiphenylphosphine)rhodium(I), [RhCl(CO){PCH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>]

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**Abstract.**  $M_r = 566.3$ , monoclinic,  $C2/c$ ,  $a = 40.633$  (6),  $b = 9.854$  (2),  $c = 27.121$  (3) Å,  $\beta = 106.58$  (1)°,  $V = 10407.7$  (8) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.446$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.969$  mm<sup>-1</sup>,  $F(000) = 4608$ ,  $T = 293$  K. Full-matrix least-squares refinement based on 5878 reflections led to  $R$  and  $wR$  values of 0.045 and 0.058, respectively. The two independent molecules have similar conformations. Rh atoms are square-planar coordinated and phosphine ligands are almost eclipsed. The Rh–C–O bonding is effectively linear [178.1 (7) and 179.0 (7)°]. The Rh–Cl, Rh–P and Rh–C bond lengths are comparable with values in related complexes.

**Introduction.** Rh<sup>I</sup> square-planar  $d^8$  complexes of the type *trans*-[RhCl(CO)(PR<sub>3</sub>)<sub>2</sub>] show by <sup>31</sup>P{<sup>1</sup>H} NMR studies different conformers at slow exchange when  $R_3$  are bulky groups. This was exemplified when  $R_3 = (t\text{-Bu})_2\text{Me}$ ,  $(t\text{-Bu})_2\text{Et}$  or  $(n\text{-Pr})(t\text{-Bu})_2$  (Mann, Masters, Shaw & Stainbank, 1971), when  $R_3 = (n\text{-Pr})_2(t\text{-Bu})$ ,  $(p\text{-tolyl})(t\text{-Bu})_2$  or  $(t\text{-Bu})_2\text{Ph}$  (Mann, Masters & Shaw, 1971), and more recently when  $R_3 = (t\text{-Bu})_2\text{Me}$ ,  $(t\text{-Bu})_2\text{Ph}$  or  $(t\text{-Bu})_2\text{Cl}$  (Bushweller, Hoogasian, English, Miller & Lovrandos, 1981). In a previous work, phosphinezirconium [Cp<sub>2</sub>ZrCl(CH<sub>2</sub>PPh<sub>2</sub>)] was used (Choukroun & Gervais, 1982).

By slow diffusion of a mixture of hexane in a H<sub>4</sub>furan solution of the complex [Cp<sub>2</sub>ZrCl(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]-Rh(CO)Cl, we obtained a microcrystalline product which analyses show to be the expected heterometallic compound. Few crystals of suitable size were obtained, but were revealed to be the title compound complex, probably due to the adventitious presence of water from the solvents. The structure determination of the compound is reported herein.

**Experimental.** Yellow-orange parallelepiped crystals obtained from a H<sub>4</sub>furan–hexane solution of [Zr,Rh] complex kept at 243 K for a week. Crystal 0.80 × 0.45 × 0.40 mm, sealed in a Lindemann-glass capillary. CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$ , cell parameters from a least-squares fitting of 25 reflections with  $2\theta$  between 17 and 30°. 9273 unique reflections measured using  $\theta$ - $2\theta$  scans for  $2\theta$  from 3 to

50° ( $h$  –47 to 47,  $k$  0 to 11,  $l$  0 to 32), scan range (0.80 + 0.35tan $\theta$ )°. Intensities of three reflections (24,0,0, 040 and 0,0,14) measured every 2 h during data collection varied less than 2.5% and thus indicated crystal stability. Corrections for Lp but not for absorption. 7986 non-zero reflections. Heavy-atom method followed by Fourier and least-squares techniques using 5878 reflections having  $F_o^2 > 4\sigma(F_o^2)$ ,  $\sigma(F_o^2)$  based on counting statistics. Full-matrix least-squares

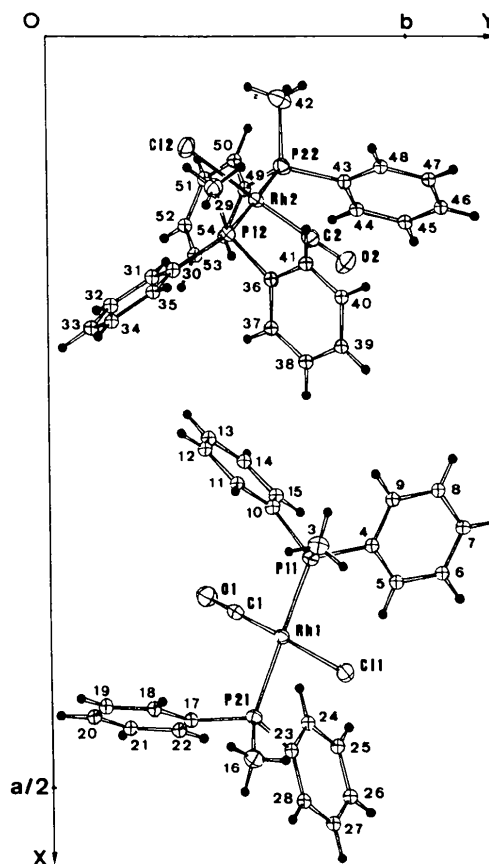


Fig. 1. ORTEP plot showing 30% probability thermal ellipsoids of the two independent molecules along the  $z$  axis. Isotropic atoms are drawn on an arbitrary scale.

refinement minimizing  $\sum w(|F_o| - |F_c|)^2$ , with anisotropic thermal parameters for Rh, Cl, P, CO and methyl carbons, isotropic rigid groups for phenyl rings ( $C-C = 1.380$ ,  $C-H = 0.95 \text{ \AA}$ ),  $U_H = 0.08 \text{ \AA}^2$  kept fixed.  $R = 0.045$ ,  $wR = 0.058$ , 241 variables,  $w = 3.94[\sigma^2(F_o) + (0.009F_o)^2]^{-1}$ . Mean and max. parameter

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors ( $\text{\AA}^2 \times 100$ ) with e.s.d.'s in parentheses*

$U_{eq}$  are defined by  $(U_1U_2U_3)^{1/3}$  where  $U_1$ ,  $U_2$  and  $U_3$  are the eigenvalues of the anisotropic-parameter tensor.

Molecule (I)	x	y	z	$U_{eq}/U_{iso}$
Rh(1)	0.52361 (1)	0.63908 (5)	0.40687 (2)	3.84 (1)
Cl(1)	0.56048 (5)	0.8133 (2)	0.4506 (7)	5.86 (6)
C(1)	0.4956 (2)	0.5114 (7)	0.3702 (3)	4.9 (2)
O(1)	0.4779 (1)	0.4319 (6)	0.3456 (3)	7.7 (2)
P(11)	0.48032 (4)	0.7231 (2)	0.43864 (6)	4.12 (5)
C(3)	0.4928 (2)	0.7441 (8)	0.5080 (3)	6.3 (2)
P(21)	0.56803 (4)	0.5581 (2)	0.37748 (6)	4.13 (5)
C(16)	0.6099 (2)	0.5550 (8)	0.4245 (3)	5.8 (2)
C(4)	0.4642 (1)	0.8919 (4)	0.4143 (2)	4.3 (2)
C(5)	0.4790 (1)	0.9596 (4)	0.3814 (2)	5.2 (2)
C(6)	0.4670 (1)	1.0861 (4)	0.3629 (2)	6.2 (2)
C(7)	0.4403 (1)	1.1450 (4)	0.3771 (2)	6.9 (2)
C(8)	0.4256 (1)	1.0773 (4)	0.4100 (2)	6.9 (2)
C(9)	0.4375 (1)	0.9508 (4)	0.4286 (2)	5.9 (2)
C(10)	0.4414 (1)	0.6182 (5)	0.4236 (1)	4.4 (2)
C(11)	0.4361 (1)	0.5213 (5)	0.4572 (1)	5.4 (2)
C(12)	0.4084 (1)	0.4342 (5)	0.4419 (1)	6.2 (2)
C(13)	0.3861 (1)	0.4440 (5)	0.3930 (1)	6.8 (2)
C(14)	0.3915 (1)	0.5409 (5)	0.3594 (1)	6.8 (2)
C(15)	0.4191 (1)	0.6281 (5)	0.3747 (1)	5.6 (2)
C(17)	0.5629 (1)	0.3829 (5)	0.3543 (2)	4.9 (2)
C(18)	0.5538 (1)	0.3495 (5)	0.3027 (2)	7.6 (2)
C(19)	0.5481 (1)	0.2157 (5)	0.2878 (2)	9.2 (3)
C(20)	0.5514 (1)	0.1153 (5)	0.3243 (2)	8.6 (3)
C(21)	0.5605 (1)	0.1487 (5)	0.3759 (2)	9.2 (3)
C(22)	0.5662 (1)	0.2825 (5)	0.3909 (2)	7.2 (2)
C(23)	0.5740 (1)	0.6602 (5)	0.3247 (2)	4.6 (2)
C(24)	0.5450 (1)	0.7079 (5)	0.2888 (2)	6.6 (2)
C(25)	0.5480 (1)	0.7880 (5)	0.2486 (2)	7.3 (2)
C(26)	0.5801 (1)	0.8204 (5)	0.2443 (2)	6.3 (2)
C(27)	0.6092 (1)	0.7727 (5)	0.2802 (2)	10.1 (3)
C(28)	0.6061 (1)	0.6925 (5)	0.3203 (2)	9.1 (3)
Molecule (II)				
Rh(2)	0.22598 (1)	0.58377 (5)	0.38844 (2)	4.03 (1)
Cl(2)	0.19268 (5)	0.3907 (2)	0.39346 (8)	6.53 (7)
C(2)	0.2506 (2)	0.7335 (8)	0.3861 (3)	4.8 (2)
O(2)	0.2661 (1)	0.8296 (6)	0.3850 (2)	7.3 (2)
P(12)	0.26949 (4)	0.5050 (2)	0.45742 (6)	3.99 (5)
C(29)	0.2562 (2)	0.4666 (8)	0.5146 (3)	5.7 (2)
P(22)	0.18234 (5)	0.6548 (2)	0.31790 (7)	4.92 (5)
C(42)	0.1394 (2)	0.6512 (9)	0.3257 (3)	7.4 (3)
C(30)	0.2899 (1)	0.3502 (5)	0.4448 (2)	4.4 (2)
C(31)	0.2799 (1)	0.2915 (5)	0.3966 (2)	6.5 (2)
C(32)	0.2963 (1)	0.1763 (5)	0.3868 (2)	8.2 (3)
C(33)	0.3227 (1)	0.1197 (5)	0.4251 (2)	7.3 (2)
C(34)	0.3327 (1)	0.1784 (5)	0.4733 (2)	7.0 (2)
C(35)	0.3163 (1)	0.2936 (5)	0.4832 (2)	5.8 (2)
C(36)	0.3060 (1)	0.6227 (4)	0.4789 (1)	3.9 (1)
C(37)	0.3311 (1)	0.6210 (4)	0.4537 (1)	4.9 (2)
C(38)	0.3569 (1)	0.7170 (4)	0.4652 (1)	5.6 (2)
C(39)	0.3576 (1)	0.8147 (4)	0.5020 (1)	5.9 (2)
C(40)	0.3325 (1)	0.8164 (4)	0.5272 (1)	6.6 (2)
C(41)	0.3067 (1)	0.7204 (4)	0.5157 (1)	5.4 (2)
C(43)	0.1860 (1)	0.8283 (6)	0.2971 (2)	6.8 (2)
C(44)	0.1901 (1)	0.8617 (6)	0.2498 (2)	8.7 (3)
C(45)	0.1949 (1)	0.9953 (6)	0.2383 (2)	10.8 (3)
C(46)	0.1956 (1)	1.0956 (6)	0.2741 (2)	11.1 (4)
C(47)	0.1915 (1)	1.0622 (6)	0.3214 (2)	12.8 (4)
C(48)	0.1867 (1)	0.9286 (6)	0.3329 (2)	10.3 (3)
C(49)	0.1803 (1)	0.5504 (5)	0.2616 (2)	4.8 (2)
C(50)	0.1499 (1)	0.5238 (5)	0.2243 (2)	6.6 (2)
C(51)	0.1498 (1)	0.4409 (5)	0.1832 (2)	7.1 (2)
C(52)	0.1801 (1)	0.3847 (5)	0.1794 (2)	7.6 (2)
C(53)	0.2105 (1)	0.4113 (5)	0.2167 (2)	7.0 (2)
C(54)	0.2106 (1)	0.4942 (5)	0.2578 (2)	5.9 (2)

Table 2. *Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses*

Rh(1)—Cl(1)	2.363 (2)	Rh(2)—Cl(2)	2.361 (2)
Rh(1)—C(1)	1.795 (7)	Rh(2)—C(2)	1.795 (2)
Rh(1)—P(11)	2.321 (2)	Rh(2)—P(12)	2.311 (2)
Rh(1)—P(21)	2.313 (2)	Rh(2)—P(22)	2.315 (2)
Cl(1)—Rh(1)—C(1)	176.6 (2)	Cl(2)—Rh(2)—C(2)	178.1 (2)
Cl(1)—Rh(1)—P(11)	89.6 (1)	Cl(2)—Rh(2)—P(12)	90.1 (1)
Cl(1)—Rh(1)—P(21)	88.8 (1)	Cl(2)—Rh(2)—P(22)	88.6 (1)
C(1)—Rh(1)—P(11)	91.6 (2)	C(2)—Rh(2)—P(12)	90.0 (2)
C(1)—Rh(1)—P(21)	90.0 (2)	C(2)—Rh(2)—P(22)	91.5 (2)
P(11)—Rh(1)—P(21)	178.2 (1)	P(12)—Rh(2)—P(22)	177.9 (1)
C(1)—O(1)	1.142 (8)	C(2)—O(2)	1.141 (8)
Rh(1)—C(1)—O(1)	178.1 (7)	Rh(2)—C(2)—O(2)	179.0 (7)
P(11)—C(3)	1.816 (7)	P(12)—C(29)	1.820 (6)
P(11)—C(4)	1.839 (4)	P(12)—C(30)	1.815 (5)
P(11)—C(10)	1.835 (4)	P(12)—C(36)	1.842 (4)
Rh(1)—P(11)—C(3)	114.1 (2)	Rh(2)—P(12)—C(29)	114.5 (2)
Rh(1)—P(11)—C(4)	114.8 (1)	Rh(2)—P(12)—C(30)	114.5 (1)
Rh(1)—P(11)—C(10)	114.4 (2)	Rh(2)—P(12)—C(36)	113.9 (2)
C(3)—P(11)—C(4)	103.5 (3)	C(29)—P(12)—C(30)	104.4 (3)
C(3)—P(11)—C(10)	105.2 (3)	C(29)—P(12)—C(36)	105.6 (3)
C(4)—P(11)—C(10)	103.5 (2)	C(30)—P(12)—C(36)	102.6 (2)
P(21)—C(16)	1.811 (6)	P(22)—C(42)	1.816 (7)
P(21)—C(17)	1.828 (5)	P(22)—C(43)	1.820 (6)
P(21)—C(23)	1.822 (5)	P(22)—C(49)	1.824 (5)
Rh(1)—P(21)—C(16)	115.5 (2)	Rh(2)—P(22)—C(42)	115.7 (3)
Rh(1)—P(21)—C(17)	114.9 (2)	Rh(2)—P(22)—C(43)	115.4 (2)
Rh(1)—P(21)—C(23)	111.9 (1)	Rh(2)—P(22)—C(49)	111.3 (1)
C(16)—P(21)—C(17)	102.6 (3)	C(42)—P(22)—C(43)	102.7 (3)
C(16)—P(21)—C(23)	104.7 (3)	C(42)—P(22)—C(49)	105.7 (3)
C(17)—P(21)—C(23)	106.2 (2)	C(43)—P(22)—C(49)	105.0 (2)

shifts  $0.76\sigma$  and  $1.92\sigma$  respectively. Max. and min. height in final  $\Delta F$  map  $0.9$  and  $-0.52 e \text{ \AA}^{-3}$ . Scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974) and from Stewart, Davidson & Simpson (1965) for H. DPS-8 computer, *SHELX76* (Sheldrick, 1976) and *ORFFE* (Busing, Martin & Levy, 1964) programs.\*

**Discussion.** The final positional and equivalent or isotropic thermal parameters are listed in Table 1. The thermal ellipsoid plot (Johnson, 1965) of the two independent  $[\text{RhCl}(\text{CO})(\text{PMePh}_2)_2]$  molecules is shown as a (001) projection in Fig. 1 with the atomic numbering. Bond lengths and angles are listed in Table 2.

The two molecules have similar conformations. The Rh atoms exhibit the expected square-planar coordination with slight distortions. The two phosphine ligands are *trans* to one another. The Rh—Cl, Rh—P and Rh—C bond lengths are comparable with those found in *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  (Ceriotti, Ciani &

\* Lists of structure factors, anisotropic thermal parameters, hydrogen parameters and least-squares-planes' equations and deviations from them have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42023 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

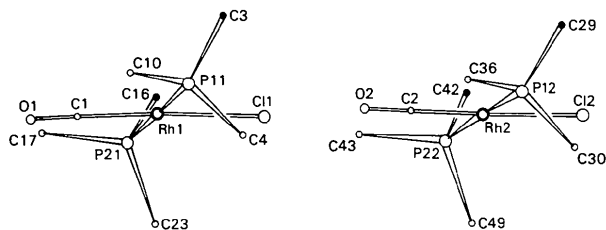


Fig. 2. A view of the two  $[\text{RhCl}(\text{CO})(\text{PMePh}_2)_2]$  molecules approximately along the P...P direction. Methyl carbons are drawn in black.

Sironi, 1983) or in  $[\text{Rh}(\text{SH})(\text{CO})(\text{PPh}_3)_2]$  (Gaffney & Ibers, 1982). The Rh—C—O angles,  $178.1(7)$  and  $179.0(7)^\circ$  show that these interactions are linear. The Rh, P, P, Cl, C and O atoms are coplanar, with nevertheless significant deviations of the carbonyl atoms from the planes:  $0.079(7)$  and  $0.165(7)$  Å for C(1) and O(1),  $0.051(7)$  and  $0.101(6)$  Å for C(2) and O(2).

The bond parameters within the methyl-diphenylphosphine groups are normal with P—C distances in the range  $1.815(5)$ – $1.842(4)$  Å, mean  $1.828(5)$  Å, and average Rh—P—C and C—P—C angles of  $114.4(2)$  and  $104.1(3)^\circ$ .

The only slight difference between the two  $[\text{RhCl}(\text{CO})(\text{PMePh}_2)_2]$  molecules lies in the stereochemistry of the two phosphine ligands which are more eclipsed in molecule (II) than in molecule (I) (Fig. 2). Along the P—P direction, the angles between methyls

and phenyl pivots have the values  $10.4$ ,  $10.9$  and  $12.6^\circ$  in molecule (I),  $5.8$ ,  $5.8$  and  $7.5^\circ$  in molecule (II).

Intermolecular distances do not indicate any interaction stronger than normal van der Waals forces.

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## Structure de (Diméthyl-5,5 Diphényl-1,9 Tétraaza-3,4,6,7 Nonatétraène-1,3,6,8 Diolato-1,9-O,O',N,N')nickel(II), $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_2)]$

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**Abstract.**  $M_r = 393.1$ , monoclinic,  $P2_1/c$ ,  $a = 9.674(8)$ ,  $b = 17.423(13)$ ,  $c = 10.709(9)$  Å,  $\beta = 100.20(7)^\circ$ ,  $V = 1776.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.44(4)$ ,  $D_x = 1.47$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu =$

$1.113$  mm<sup>-1</sup>,  $F(000) = 816$ , room temperature,  $R = 0.042$ ,  $wR = 0.044$  for 1734 unique diffractometer data. The macrocycle is coordinated to the Ni atom as a tetradentate ligand with a *cis* N<sub>2</sub>O<sub>2</sub> donor set in a