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## Structure of Tetrakis(dimethylphenylphosphine)rhodium(I) Chloride

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### Abstract

The monomeric cation  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$  exhibits a four-coordinate distorted square-planar coordination geometry about the Rh atom. The chloride counter ion is not coordinated to the rhodium metal [Rh...Cl distance 3.984(3) Å].

### Comment

The coordination number and geometry of the phosphine complexes of rhodium(I) are of interest because of the catalytic activity of these complexes (Nomura, Saito & Shimoda, 1989). The monomeric complexes most commonly have coordination numbers of four, but a few five-coordinate monomeric complexes have been reported (Burk & Harlow, 1990). It is possible that a four-coordinate cationic rhodium(I) complex may become five coordinate in the presence of a coordinating anion. Previous workers have characterized the cation of  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{BF}_4 \cdot \text{C}_4\text{H}_2\text{O}$  as four coordinate but the  $\text{BF}_4$  anion is generally non-coordinating (Lundquist, Streib & Caulton, 1989). This work characterizes  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{Cl}$  in which the chloride counter ion could act as a coordinating ligand. The structure reported here is four coordinate, even in the presence of the coordinating anion. The presence of a coordinating anion does not increase the coordination number of the metal in the solid state for this particular complex. The structure of the  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$  cation is similar to those previously reported for the cations  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]^+$  and  $[\text{Rh}(\text{PMe}_3)_4]^+$  (Blum, Calabrese, Frolow & Milstein, 1990).

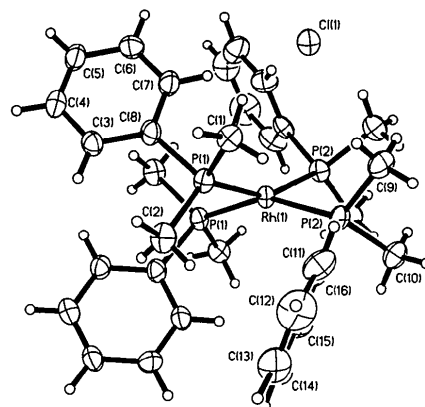


Fig. 1. Thermal ellipsoid plot (50% probability) of  $[\text{Rh}(\text{PMe}_2\text{Ph})_4]\text{Cl}$ . H atoms are drawn as spheres of arbitrary radius.

### Experimental

#### Crystal data

$[\text{Rh}(\text{C}_8\text{H}_{11}\text{P})_4]^+ \cdot \text{Cl}^-$

$M_r = 691.0$

Orthorhombic

$C222_1$

$a = 14.754$  (3) Å

$b = 14.805$  (5) Å

$c = 15.277$  (4) Å

$V = 3337$  (2) Å<sup>3</sup>

$Z = 4$

$D_x = 1.375$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 16.99$ – $28.58^\circ$

$\mu = 0.792$  mm<sup>-1</sup>

$T = 197$  K

Plate

$0.40 \times 0.18 \times 0.02$  mm

Orange

#### Data collection

Siemens  $R3m/V$  diffractometer

$\omega$  scans

Absorption correction:

Semi-empirical

$T_{\min} = 0.9159$ ,  $T_{\max} =$

0.9645

1670 measured reflections

1662 independent reflections

1662 observed reflections

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.00^\circ$

$h = -17 \rightarrow 0$

$k = -18 \rightarrow 0$

$l = -19 \rightarrow 0$

3 standard reflections

frequency: 97 min

intensity variation: 1%

#### Refinement

Refinement on  $F$

Final  $R = 0.0501$

$wR = 0.0512$

$S = 1.0197$

1662 reflections

174 parameters

Calculated weights  $w =$

$1/[\sigma^2(F) + 0.00100F^2]^2$

$(\Delta/\sigma)_{\text{max}} = 0.0104$

$\Delta\rho_{\text{max}} = 0.6100$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -1.0120$  e Å<sup>-3</sup>

Extinction correction:

Lorentzian isotropic (Larson, 1967)

Extinction coefficient:

0.00034 (6)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Siemens  $P3VAX$  version 3.4. Data reduction: *REFRED* (Reibenspies, 1992). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | x           | y           | z           | $U_{eq}$   |
|-------|-------------|-------------|-------------|------------|
| Rh(1) | -0.0761 (1) | 0           | 0           | 0.0224 (1) |
| Cl(1) | 0           | -0.0110 (2) | -1/4        | 0.0352 (1) |
| P(1)  | -0.1847 (1) | 0.0879 (1)  | -0.0672 (1) | 0.0275 (1) |
| P(2)  | 0.0306 (1)  | 0.1135 (1)  | -0.0025 (2) | 0.0276 (1) |
| C(1)  | -0.1467 (5) | 0.1577 (4)  | -0.1589 (5) | 0.0325 (2) |
| C(2)  | -0.2569 (4) | 0.1684 (4)  | -0.0093 (7) | 0.0359 (2) |
| C(3)  | -0.3593 (5) | 0.0213 (5)  | -0.1152 (5) | 0.0330 (2) |
| C(4)  | -0.4151 (5) | -0.0371 (6) | -0.1635 (5) | 0.0413 (2) |
| C(5)  | -0.3797 (5) | -0.0988 (5) | -0.2200 (5) | 0.0386 (2) |
| C(6)  | -0.2858 (5) | -0.1030 (5) | -0.2309 (5) | 0.0382 (2) |
| C(7)  | -0.2291 (5) | -0.0441 (5) | -0.1850 (5) | 0.0368 (2) |
| C(8)  | -0.2647 (4) | 0.0161 (5)  | -0.1258 (5) | 0.0309 (2) |
| C(9)  | 0.0905 (6)  | 0.1500 (5)  | -0.1009 (5) | 0.0387 (3) |
| C(10) | 0.1254 (5)  | 0.0983 (5)  | 0.0733 (5)  | 0.0376 (2) |
| C(11) | -0.0290 (5) | 0.2972 (4)  | -0.0064 (8) | 0.0455 (3) |
| C(12) | -0.0730 (7) | 0.3707 (5)  | 0.0277 (7)  | 0.0623 (4) |
| C(13) | -0.1062 (6) | 0.3689 (5)  | 0.1130 (7)  | 0.0547 (3) |
| C(14) | -0.0934 (6) | 0.2919 (5)  | 0.1625 (6)  | 0.0522 (3) |
| C(15) | -0.0514 (5) | 0.2158 (6)  | 0.1272 (5)  | 0.0420 (3) |
| C(16) | -0.0184 (5) | 0.2176 (4)  | 0.0420 (5)  | 0.0301 (2) |

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|                              |            |                   |            |
|------------------------------|------------|-------------------|------------|
| Rh(1)—P(1)                   | 2.306 (2)  | C(3)—C(8)         | 1.408 (9)  |
| Rh(1)—P(2)                   | 2.302 (2)  | C(4)—C(5)         | 1.362 (11) |
| Rh(1)—P(1) <sup>i</sup>      | 2.306 (2)  | C(5)—C(6)         | 1.396 (10) |
| Rh(1)—P(2) <sup>i</sup>      | 2.302 (2)  | C(6)—C(7)         | 1.396 (11) |
| P(1)—C(1)                    | 1.829 (7)  | C(7)—C(8)         | 1.375 (11) |
| P(1)—C(2)                    | 1.827 (8)  | C(11)—C(12)       | 1.371 (12) |
| P(1)—C(8)                    | 1.824 (7)  | C(11)—C(16)       | 1.401 (11) |
| P(2)—C(9)                    | 1.826 (8)  | C(12)—C(13)       | 1.392 (15) |
| P(2)—C(10)                   | 1.829 (8)  | C(13)—C(14)       | 1.382 (12) |
| P(2)—C(16)                   | 1.833 (7)  | C(14)—C(15)       | 1.395 (12) |
| C(3)—C(4)                    | 1.403 (10) | C(15)—C(16)       | 1.389 (11) |
| P(1)—Rh(1)—P(2)              | 93.2 (1)   | C(10)—P(2)—C(16)  | 99.8 (3)   |
| P(1)—Rh(1)—P(1) <sup>i</sup> | 92.0 (1)   | C(4)—C(3)—C(8)    | 119.2 (6)  |
| P(2)—Rh(1)—P(1) <sup>i</sup> | 153.4 (1)  | C(3)—C(4)—C(5)    | 121.4 (7)  |
| P(1)—Rh(1)—P(2) <sup>i</sup> | 153.4 (1)  | C(4)—C(5)—C(6)    | 119.1 (7)  |
| P(2)—Rh(1)—P(2) <sup>i</sup> | 93.7 (1)   | C(5)—C(6)—C(7)    | 120.5 (7)  |
| P(1)—Rh(1)—P(2) <sup>i</sup> | 93.2 (1)   | C(6)—C(7)—C(8)    | 120.4 (7)  |
| Rh(1)—P(1)—C(1)              | 116.6 (2)  | P(1)—C(8)—C(3)    | 123.6 (5)  |
| Rh(1)—P(1)—C(2)              | 123.9 (3)  | P(1)—C(8)—C(7)    | 117.0 (5)  |
| C(1)—P(1)—C(2)               | 100.4 (4)  | C(3)—C(8)—C(7)    | 119.3 (6)  |
| Rh(1)—P(1)—C(8)              | 109.8 (2)  | C(12)—C(11)—C(16) | 121.4 (9)  |
| C(1)—P(1)—C(8)               | 98.7 (3)   | C(11)—C(12)—C(13) | 120.5 (9)  |
| C(2)—P(1)—C(8)               | 103.9 (3)  | C(12)—C(13)—C(14) | 118.7 (8)  |
| Rh(1)—P(2)—C(9)              | 124.1 (3)  | C(13)—C(14)—C(15) | 121.0 (9)  |
| Rh(1)—P(2)—C(10)             | 115.0 (2)  | C(14)—C(15)—C(16) | 120.2 (7)  |
| C(9)—P(2)—C(10)              | 100.8 (4)  | P(2)—C(16)—C(11)  | 123.8 (7)  |
| Rh(1)—P(2)—C(16)             | 109.7 (2)  | P(2)—C(16)—C(15)  | 118.0 (5)  |
| C(9)—P(2)—C(16)              | 104.3 (3)  | C(11)—C(16)—C(15) | 118.1 (7)  |

Symmetry code: (i) x, -y, -z.

A suitable crystal was chosen and mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in an  $N_2$  cold stream. Inspection of axial photographs about each of the three axes confirmed axis length and Laue symmetry.  $\omega$  scans of several intense reflections indicated acceptable crystal quality. The  $\theta$  scan width was  $1.2^\circ$  with a scan rate variable between 2.0 and  $14.6^\circ \text{ min}^{-1}$  in  $\theta$ . The background was measured by the stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time. Intensities were corrected by a peak-profiling method (Diamond, 1969). Carbon-bound H atoms were placed in idealized positions [ $C-H = 0.96 \text{ \AA}$ ,  $U(H) = 0.08 \text{ \AA}^2$  (fixed)]. The H atom parameters were not refined. The absolute configuration was determined (Rogers, 1981). The structure of the title compound

and the numbering scheme used are shown in Fig. 1. The title compound was obtained from Dr C. Ovalles and S. Taboada (INTEVEP, SA, Venezuela).

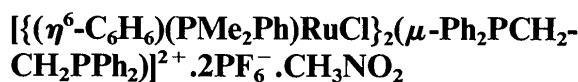
The X-ray diffraction and crystallographic computing system was purchased from funds provided by the National Science Foundation (USA) grant CHE-8513273.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55534 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1031]

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## Abstract

In the title compound, [ $\mu$ -ethylenebis(diphenylphosphine)-bis( $(\eta^6$ -benzene)chloro(dimethylphenylphosphine)ruthenium(II))] bis(hexafluorophosphate) nitromethane solvate, the cation is crystallographically centrosymmetric about the midpoint of the  $\text{CH}_2\text{—CH}_2$  bond. The diphosphine ligand adopts a bridging function between the two  $\text{Ru}^{\text{II}}$  centres.