trans-Bis[bis(diphenylphosphino)methane-κ²P,P']-dichlororuthenium(II) dichloromethane disolvate acetone hemisolvate hemihydrate

The title compound, \([\text{RuCl}_2(\text{C}_{25}\text{H}_{22}\text{P}_2)_2] \cdot 2\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_3\text{H}_6\text{O} \cdot 0.5\text{H}_2\text{O}\), was obtained as unreacted starting material from our attempts to prepare acetylide complexes of ruthenium, based on 1,4-diethoxy-2,5-diethynylbenzene bridging ligands, in a route towards molecular wires. The complex is centrosymmetric.

Comment

The trans-[\text{RuCl}_2(\text{dppm})_2] complex [dppm is bis(diphenylphosphino)methane] is a useful starting material, commonly used for the preparation of mononuclear, as well as di- and polynuclear complexes (Faulkner et al., 1994). The title compound, (I), has been characterized previously by Chatt & Hayter (1961) and Mague & Mitchener (1972). Later, Mason et al. (1976) obtained the same complex using a modified synthesis strategy and different starting materials. The trans chloride geometry was proved by spectroscopic techniques only, namely \(^{31}\text{P}\) NMR in solution. The chemical behaviour of the cis- and trans-[\text{RuCl}_2(\text{dppm})_2] isomers has been thoroughly studied by Sullivan & Meyer (1982) and other authors (Zhu et al., 1997; Higgins et al., 2000). Four single-crystal structures containing the complex \([\text{RuCl}_2(\text{dppm})_2]\) have been published; while three of them contain the cis isomer – the first as the non-solvated form (Chakravarty et al., 1984), the second cocrystallized with the fac-[\text{RuCl}_3(\text{dppm})(\text{NO})] complex (Batista et al., 1999) and the third as a methanol solvate (Keller et al., 2003) – only one has a non-solvated trans configuration (Chakravarty et al., 1984). By recrystallization of trans-[\text{RuCl}_2(\text{dppm})_2], we obtained the title compound, (I).

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In the crystal structure of (I), the Ru$^{	ext{II}}$ atom (site symmetry $1$) has a distorted octahedral coordination via the four P atoms of the two chelating dppm ligands and the two chloride anions in $\text{trans}$ geometry (Fig. 1 and Table 1). The dichloromethane (DCM) solvent molecules interact with the chloride anions via weak C—H···Cl$^-$ bonds.

**Experimental**

Crystals of $\text{trans}[-\text{RuCl}_2(\text{dppm})_2]_2\text{DCM}$ were isolated as the unreacted product from the reaction between the unsolvated complex (0.665 g, 0.71 mmol), TIPF$_6$ (298 mg, 0.85 mmol) and 1,4-diethoxy-2,5-diethynylbenzene (51 mg, 0.24 mmol) in dried tetrahydrofuran (THF, 20 ml). After stirring for 6 d at room temperature under a nitrogen atmosphere, the solvent was removed under vacuum. Then, diethoxy-2,5-diethynylbenzene (51 mg, 0.24 mmol) in dried tetrahydrofuran (THF, 20 ml) was added and the mixture was stirred for a further 6 d, after which the resulting yellow solid was washed with dry diethyl ether and then more acetone (5 ml) was added and the mixture was stirred for a further 6 d, after which the unreacted product from the reaction between the unsolvated complex (0.665 g, 0.71 mmol), TIPF$_6$ (298 mg, 0.85 mmol) and 1,4-diethoxy-2,5-diethynylbenzene (51 mg, 0.24 mmol) in dried tetrahydrofuran (THF, 20 ml). After stirring for 6 d at room temperature under a nitrogen atmosphere, the solvent was removed under vacuum to yield a dark-brown solid which was extracted with THF and then with dichloromethane (15 ml). To the latter fraction, triethylamine (3 ml, 21 mmol) was added and the mixture was cooled to 253 K and held at that temperature for 7 d. The solution was filtered twice to remove a black oil that had formed and then more acetone (5 ml) was added. The mixture was allowed to stand for another 4 d at 253 K before it yielded bright-yellow crystals suitable for X-ray diffraction.

**Crystal data**

$\text{[RuCl}_2(\text{C}_2\text{H}_2\text{P}_2)_2]\text{CH}_2\text{Cl}_2$-0.5C$_2$H$_5$H.O

$M_r = 1170.61$

Triclinic, $P\overline{1}$

$\alpha = 10.9227 (3)$ Å

$\beta = 11.2603 (3)$ Å

$\gamma = 11.6768 (2)$ Å

$\beta = 105.098 (1)^\circ$

$\nu = 105.397 (1)^\circ$

$V = 1326.79 (6)$ Å$^3$

$Z = 1$

$D_x = 1.465$ Mg m$^{-3}$

Mo $K$-radiation

$\mu = 0.76$ mm$^{-1}$

$T = 173 (2)$ K

Block, yellow

0.30 × 0.30 × 0.25 mm

**Data collection**

Bruker–Nonius KappaCCD diffractometer

$\varphi$ and $\omega$ scans

9274 measured reflections

6011 independent reflections

5247 reflections with $I > 2\sigma(I)$

$R_{int} = 0.029$

$\theta_{max} = 27.4^\circ$

**Refinement**

Refinement on $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.066$

$wR(F^2) = 0.166$

$S = 1.09$

6011 reflections

316 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_c^2) + (0.0603P)^2 + 6.4786P]$

where $P = (F^2 + 2F_c^2)/3$

$\Delta F_{\text{max}} = 1.35$ e Å$^{-3}$

$\Delta F_{\text{min}} = -1.10$ e Å$^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<td>Ru1—P2</td>
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<td>Ru1—P3</td>
<td>2.3713 (11)</td>
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<td>Ru1—Cl4</td>
<td>2.4285 (10)</td>
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<td>P2—Ru1—P3</td>
<td>108.97 (4)</td>
<td>P3—Ru1—Cl4</td>
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<tr>
<td>P2—Ru1—Cl4</td>
<td>94.61 (4)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1**

The molecular structure showing the selected atom numbering and the solvent DCM molecules. Displacement ellipsoids are drawn at the 40% probability level.

The quite high residual electron density, not relating to the disolvated complex, was modelled as disordered acetone and water with partial occupancy ($\frac{1}{2}$ and $\frac{3}{4}$, respectively). The remaining residual electron density (1.35 e Å$^{-3}$) resides close to the DCM molecules and was not modelled. The deepest hole is located 0.53 Å from atom Cl27.

Data collection: COLLECT (Hooft, 1998); cell refinement: SCALEPACK; data reduction: DENZO and SCALEPACK (Otwinski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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**References**


metal-organic papers

L12.

Göttingen, Germany.