

cis-Dichloro[tris(diphenylphosphinoethyl)amine]ruthenium(II)–chloroform–water (1/2.5/1)Atilio Anzellotti,^{a*} Alexander Briceño,^a Gerzon Delgado,^b Graciela Díaz de Delgado^b and Bernardo Fontal^b^aCentro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela, and ^bDepartamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela
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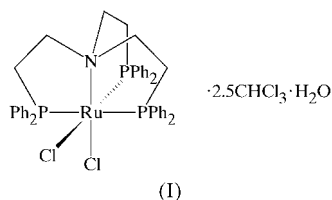
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In the title compound, $[\text{RuCl}_2(\text{C}_{42}\text{H}_{42}\text{NP}_3)] \cdot 2.5\text{CHCl}_3 \cdot \text{H}_2\text{O}$, the Ru atom is six-coordinated, to one tetradentate tris(diphenylphosphinoethyl)amine ligand and two Cl atoms, in a distorted octahedral arrangement. Molecules of chloroform and water stabilize the framework through intermolecular hydrogen bonds.

Comment

Tris(diphenylphosphinoethyl)amine (NP_3) is a very interesting polydentate ligand with chelating properties and mixed-donor functionality. Coordination compounds incorporating this ligand and several metal ions have been reported since its initial synthesis (Sacconi & Bertini, 1968). Either a tridentate or tetradentate form of coordination has been observed for NP_3 –metal compounds, although unusual mono- (Zank *et al.*, 1997) or bidentate coordination to the same metal can be achieved (Cecconi *et al.*, 1989; Ghilardi & Sacconi, 1975). Specifically for ruthenium– NP_3 complexes, only one structure has been reported previously, *viz.* $[\text{Ru}(\text{NP}_3)\text{Cl}\{\text{C}=\text{C}=\text{C}(\text{OMe})\text{CH}=\text{CPh}_2\}]$, (II) (Wolinska *et al.*, 1991), in which the NP_3 ligand exhibits a tetradentate coordination.



The title compound, (I), displays interesting catalytic properties, as shown by Fontal & Suarez (1985) in the case of hydrogenation and hydroformylation, as well as others (Dahlenbourg *et al.*, 1991), in 1-alkyne dimerization reactions, but in spite of a good spectroscopic characterization, especially through ^1H and ^{31}P NMR spectroscopic analyses, the crystal structure of (I) is hitherto unreported.

From a synthetic point of view, $\text{RuCl}_2(\text{NP}_3)$ is used as a starting material in the production of alkenyl–allenylidene compounds useful in the preparation of either metal-containing polymers or new polyunsaturated organic substrates (Wolinska *et al.*, 1991). It is interesting to note that the method of synthesis of (I) differs from that reported in the previous literature, where $\text{RuCl}_2(\text{NP}_3)$ was prepared from $\text{RuCl}_2(\text{PPh}_3)_3$ and the NP_3 ligand under reflux in toluene. Complex (I), in contrast, was obtained by reaction of $\text{RuCl}_2(\text{dmsO})_4$ (dmsO is dimethyl sulfoxide) and NP_3 in toluene solution. Also, it should be noted that the same reaction in acetone affords the $\text{RuCl}_2(\text{NP}_3)(\text{dmsO})$ compound, where NP_3 seems to act as a tridentate ligand (Taqui-Khan & Rama-Rao, 1988).

The asymmetric unit of (I) consists of one complex molecule, 2.5 chloroform molecules and one water molecule. The Ru atom is coordinated by two Cl atoms and one NP_3 ligand, which is bound through the N and P atoms to complete the octahedral environment of the Ru atom, as depicted in Fig. 1. The coordination geometry is distorted, with bond angles quite similar to those exhibited by analogous complex (II), with $\text{P1}–\text{Ru}–\text{P2} = 165.28(4)^\circ$, $\text{N}–\text{Ru}–\text{Cl1} = 176.1(1)^\circ$ and $\text{P3}–\text{Ru}–\text{Cl1} = 170.3(1)^\circ$. The $\text{Ru}–\text{P}$ distances involving the *trans* P atoms are longer than the distance involving the P atom *trans* to chlorine ($\text{Ru}–\text{P3}$; Table 1). When compared to those in analogous complex (II), the bond distances involving the *trans* P atoms are similar, but the $\text{Ru}–\text{P3}$ distance in (II) of 2.430(1) Å is unusually long. This can be attributed to a greater *trans* effect of the allene ligand due to its π -acceptor nature, compared to the Cl atom in (I). The Cl atoms are in a *cis* configuration, with longer bond distances compared to the mean value reported for the parent complex *cis*- $\text{RuCl}_2(\text{dmsO})_4$ [$\text{Ru}–\text{Cl}$ 2.420(2) Å; Alessio *et al.*, 1988; Attia & Calligaris, 1987]. The arrangement of the internal aromatic rings in the coordinated NP_3 ligand allows for π – π face-to-face interactions, with an average centroid–centroid distance of 3.672(8) Å.

Molecules of chloroform and water are incorporated in the lattice as crystallization solvents; hydrogen-bond analysis, performed with PLATON (Spek, 1999), showed a series of inter- and intramolecular contacts (Table 2). A further analysis provided evidence that the chloroform and water molecules interact with the Cl atoms of the complex *via* $\text{C}–\text{H} \cdots \text{Cl}$ and $\text{O}–\text{H} \cdots \text{Cl}$ hydrogen bonds, respectively. Each coordinated Cl atom (Cl1 and Cl2) serves as an acceptor of four hydrogen bonds; additionally, direct $\text{C72} \cdots \text{Cl2}$ and $\text{C91} \cdots \text{Cl2}$ interactions between complex molecules were observed. These hydrogen bonds may account for the molecular packing and the stability of the structure. Intramolecular interactions could contribute to the distorted environment around the Ru atom also.

In addition, all three chloroform molecules are disordered. This disorder was modelled with two set of positions for molecules 1 (containing atom C1) and 2 (containing atom C2), with refined occupation factors of 0.70:0.30 and 0.60:0.40, respectively. Disorder in the third molecule (containing atom C3) was completely modelled with two set of positions.

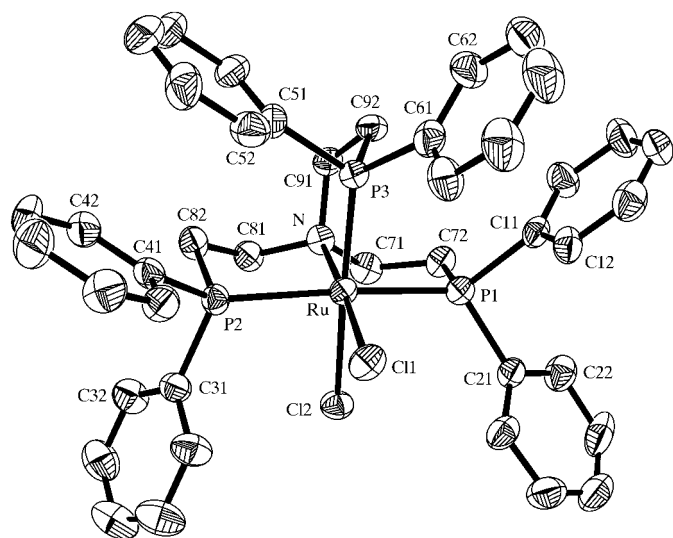


Figure 1
View of the title compound, showing the labelling of the non-H atoms and ellipsoids at the 40% probability level.

Refinement of the occupation factor of this molecule reveals a partial occupation of 0.5, distributed between 0.2 and 0.3 for the two orientations.

Experimental

The synthesis of (I) was carried out under a nitrogen atmosphere by refluxing a solution of *cis*-RuCl₂(dms_o)₄ (484.53 mg, 1 mmol) with tris(diphenylphosphinoethyl)amine (653.75 mg, 1 mmol) in stirred toluene for 3 h. The resulting orange–yellow mixture was vacuum filtered and evaporated. The yellow solid obtained was washed with ether (yield 85%). ³¹P NMR (CDCl₃, recorded on a Bruker 300 MHz spectrometer, p.p.m.): δ -27.2 (*d*), -47.9 (*t*). Elemental analysis, calculated for C₄₂H₄₂Cl₂NP₃Ru: C 61.0, H 5.09, Cl 8.58, N 1.69, P 11.26%; found: C 60.1, H 5.22, Cl 8.19, N 1.61, P 10.20%. Crystals of (I) were obtained by slow evaporation of a chloroform solution of the complex at room temperature.

Crystal data

[RuCl₂(C₄₂H₄₂NP₃)]·2.5CHCl₃·H₂O
M_r = 1140.88
 Monoclinic, *P*2₁/*c*
a = 17.541 (2) Å
b = 12.112 (1) Å
c = 24.950 (3) Å
 β = 109.26 (1)°
V = 5004.1 (9) Å³
Z = 4

D_x = 1.514 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 80 reflections
 θ = 10–20°
 μ = 0.95 mm⁻¹
T = 293 (2) K
 Plate, yellow
 0.5 × 0.3 × 0.2 mm

Data collection

Nicolet P3/F (Crystal Logic) diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.718, *T_{max}* = 0.827
 10 018 measured reflections
 8811 independent reflections
 4795 reflections with *I* > 2σ(*I*)

R_{int} = 0.039
 θ_{max} = 25.0°
h = 0 → 20
k = -8 → 14
l = -29 → 28
 3 standard reflections every 97 reflections
 intensity decay: 10%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.080
wR(*F*²) = 0.223
S = 1.05
 8811 reflections
 533 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0838P)^2 + 23.3179P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.01 e Å⁻³
 Δρ_{min} = -1.11 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ru–N	2.188 (7)	P2–C82	1.820 (8)
Ru–P3	2.254 (2)	P2–C41	1.827 (10)
Ru–P2	2.346 (2)	P2–C31	1.828 (9)
Ru–P1	2.355 (2)	P3–C51	1.842 (9)
Ru–Cl1	2.447 (2)	P3–C61	1.848 (10)
Ru–Cl2	2.479 (2)	P3–C92	1.849 (9)
P1–C72	1.844 (9)	N–C71	1.494 (11)
P1–C21	1.846 (9)	N–C81	1.507 (10)
P1–C11	1.850 (9)	N–C91	1.524 (11)
N–Ru–P3	84.5 (2)	P2–Ru–Cl1	93.41 (8)
N–Ru–P2	84.55 (19)	P1–Ru–Cl1	98.81 (8)
P3–Ru–P2	96.44 (9)	N–Ru–Cl2	88.2 (2)
N–Ru–P1	82.68 (19)	P3–Ru–Cl2	171.89 (9)
P3–Ru–P1	92.61 (8)	P2–Ru–Cl2	86.38 (8)
P2–Ru–P1	163.56 (8)	P1–Ru–Cl2	82.92 (8)
N–Ru–Cl1	176.6 (2)	Cl1–Ru–Cl2	88.93 (8)
P3–Ru–Cl1	98.47 (9)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C2B–H2B···Cl1 ⁱ	0.98	2.38	3.349 (7)	171
C26–H26···Cl1	0.93	2.78	3.635 (12)	153
C66–H66···Cl1	0.93	2.71	3.521 (11)	146
C71–H712···Cl2	0.97	2.58	3.216 (10)	122
C72–H721···Cl2 ⁱⁱ	0.97	2.62	3.455 (10)	144
C91–H911···Cl2 ⁱⁱⁱ	0.97	2.79	3.666 (11)	151
C46–H46···Cl1	0.93	2.88	3.698 (9)	148
C15–H15···Cl2 ⁱⁱⁱ	0.93	2.89	3.511 (11)	126
C66–H66···Cl3 ^{iv}	0.93	2.89	3.590 (18)	133
C54–H54···Cl2 ^{iv}	0.93	2.73	3.545 (15)	146
C54–H54···Cl13 ^v	0.93	2.87	3.50 (2)	126
O–H1O···Cl21	0.85	2.78	3.56 (2)	151
O–H2O···Cl2 ⁱ	0.85	2.46	3.31 (2)	176

Symmetry codes: (i) -*x*, 1 - *y*, -*z*; (ii) -1 - *x*, ½ + *y*, -½ - *z*; (iii) *x* - 1, 1 + *y*, *z* - 1; (iv) *x*, ½ - *y*, *z* - ½; (v) *x*, 1 + *y*, *z*.

All H atoms were placed in calculated positions and allowed for riding (C–H = 0.93–0.98 Å). Disorder of the chloroform molecules was modelled with two sites for each molecule, and these were refined isotropically constraining C–Cl distances to 1.750 (2) Å. The occupation factors of chloroform molecules 1 and 2 were refined with *SHELXTL* (Siemens, 1994), using the *PART* option. The best model for the third chloroform molecule was obtained by free refinement of the occupation factor for each set of positions, which gives a partial occupation of 0.5. These occupations were fixed during the final refinements. The H atoms of the water molecule were not located in the density map, but were calculated using the *HYDROGEN* program (Nardelli, 1999).

Data collection: *COLLECT* in *UCLA Crystallographic Package* (Strouse, 1988); cell refinement: *LEAST* in *UCLA Crystallographic Package*; data reduction: *REDUCE* in *UCLA Crystallographic Package*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1568). Services for accessing these data are described at the back of the journal.

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