Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

cis-Dichloridotetrakis(trimethylphosphane-κ*P*)ruthenium(II) benzene disolvate

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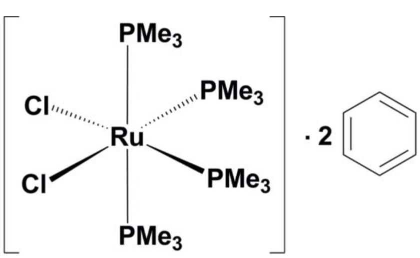
Received 19 November 2010; accepted 28 November 2010

Key indicators: single-crystal X-ray study; *T* = 173 K; mean σ(P–C) = 0.006 Å; *R* factor = 0.058; *wR* factor = 0.081; data-to-parameter ratio = 25.5.

The title compound, *cis*-$[RuCl_2(C_3H_9P)_4]\cdot 2C_6H_6$, contains a complex molecule with a crystallographic mirror plane passing through the Ru^{II} atom, the two *cis*-disposed Cl ligands and two P atoms of the two *cis*-disposed $P(CH_3)_3$ ligands. The Ru^{II} atom adopts a distorted octahedral $RuCl_2P_4$ coordination geometry with the two *trans*-disposed P atoms occupying the axial positions. The packing of the structure is accomplished through non-classical C—H···Cl hydrogen bonds between the benzene solvent molecule and one of the Cl ligands.

Related literature

For general background to *trans*-$[RuCl_2(P(CH_3)_3)_4]$, see: Csok *et al.* (2007); Gotzig *et al.* (1985); Hartwig *et al.* (1991); Hirano *et al.* (2010); Kohlmann & Werner (1993). For a related structure, see: Joo *et al.* (1994).



Experimental

Crystal data

$[RuCl_2(C_3H_9P)_4]\cdot 2C_6H_6$
M_r = 632.47
Orthorhombic, *Pnma*
a = 17.6243 (15) Å
b = 18.1889 (19) Å
c = 9.4610 (11) Å
V = 3032.9 (5) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.92 mm^{-1}
T = 173 K
0.18 × 0.12 × 0.06 mm

Data collection

Oxford Diffraction Gemini S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.949, T_{max} = 1.000
14352 measured reflections
3550 independent reflections
1653 reflections with $I > 2\sigma(I)$
R_{int} = 0.148

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.081
S = 0.82
3550 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ru1—P1	2.2690 (19)	Ru1—Cl1	2.479 (2)
Ru1—P2	2.297 (2)	Ru1—Cl2	2.5038 (19)
Ru1—P3	2.3819 (14)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4*S*—H4*SA*···Cl2	0.93	2.83	3.710 (5)	159

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors acknowledge financial support from the Young Talent Project of Department of Science & Technology of Fujian Province (grant No. 2007 F3095).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2431).

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supplementary materials

Acta Cryst. (2011). E**67**, m14 [**doi:10.1107/S1600536810049706**]

cis-Dichloridotetrakis(trimethylphosphane-*κP*)ruthenium(II) benzene disolvate

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Comment

The ruthenium(II) complex *trans*-[$RuCl_2(PMe_3)_4$], which can be readily prepared from the reaction of $RuCl_2(PPh_3)_3$ with PMe_3 in hexane at room temperature (Gotzig *et al.*, 1985), has proved to be a useful precursor for a wide variety of ruthenium compounds (Hartwig *et al.*, 1991; Kohlmann & Werner, 1993; Csok *et al.*, 2007; Hirano *et al.*, 2010). However, its geometrical isomer, *cis*-[$RuCl_2(PMe_3)_4$], has not been reported yet. During our preparation of ruthenium compounds with phosphine ligands using *trans*-[$RuCl_2(PMe_3)_4$] as the starting material, we found that the *trans*-isomer slowly isomerizes to the *cis*-isomer, the structure of which we report here as the benzene disolvate.

As shown in Fig.1, the structure of the title complex possesses a crystallographic mirror plane passing through the Ru^{II} atom, the two *cis*-disposed Cl ligands and the two P atoms as well as two C atoms of the two *cis*-disposed PMe_3 ligands. Thus the asymmetric unit of the structure contains half of a molecule. The Ru^{II} atom adopts a distorted octahedral geometry with the two *trans*-disposed P atoms occupying the axial positions. The bond lengths of the two axial Ru—P bonds (2.3819 (14) Å), which are actually image-related, are slightly longer than those of the two equatorial Ru—P bonds which are *trans* to the Cl ligands (2.2690 (19) and 2.297 (2) Å, respectively). The two Ru—Cl bond lengths are 2.479 (2) and 2.5038 (19) Å, respectively, while the Cl(1)—Ru(1)—Cl(2) bond angle is 86.20 (7)°. These geometric values are similar to those reported for the only example of a sructurally characterized monodentate tetrakis(phosphine)-*cis*-dichlorido-ruthenium(II) complex, *viz*. [*cis*-$RuCl_2(PTA)_4$] (PTA = 1,3,5-triaza-7-phospha-adamantane-κP); 2.488 (2) and 2.503 (2) Å, 84.2 (1) °; Joo *et al.*, 1994).

The packing of the structure (Fig. 2) is accomplished through non-classical C—H···Cl hydrogen bonds between the benzene solvent molecule and one of the Cl ligands (Table 2).

Experimental

Route A: To a solution of $RuCl_2(PPh_3)_3$ (0.25 g, 0.24 mmol) in toluene (8 ml) under nitrogen atmosphere was added PMe_3 (0.27 ml, 2.5 mmol) and the resulting yellow solution was refluxed for 20 h. The solvent was removed under vacuum, and the solid residue was washed with n-hexane, and dried under vacuum to afford a white solid. Yield: 90 mg, 80%. Route B: A solution of *trans*-[$RuCl_2(PMe_3)_4$] (100 mg, 0.21 mmol) in benzene (5 ml) was refluxed for 12 h under nitrogen atmosphere. After the solution was cooled to ambient temperature, a white solid was precipitated, which was collected by filtration, washed with n-hexane, and dried under vacuum. Yield: 72 mg, 72%. Crystals suitable for X-ray analysis were obtained from standing a solution of *trans*-[$RuCl_2(PMe_3)_4$] in benzene at room temperature for 2 weeks.

Refinement

The benzene solvent molecule was treated as a rigid body. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically (C—H = 0.96 or 0.93 Å for methyl or phenyl H atoms, respectively) and were included in the refinement in the riding model approximation. The displacement parameters of methyl H atoms were set to $1.5U_{eq}$(C), while those of the phenyl H atoms were set to $1.2U_{eq}$(C). In the final Fourier map the highest peak is 0.04 Å from atom Ru1 and the deepest hole is 0.71 Å from atom Ru1.

Figures

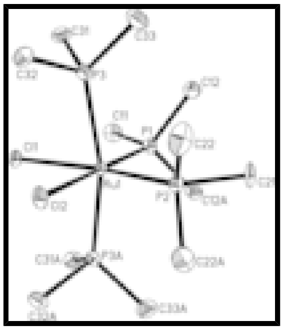

Fig. 1. The coordination of the Ru^{II} atom in the structure of *cis*-[$RuCl_2(P(CH_3)_3)_4$] with the atom labelling and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) x, -y+1/2, z.]

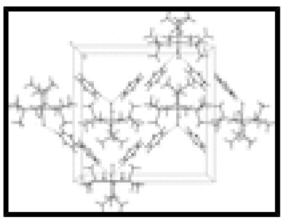

Fig. 2. The packing diagram of the structure viewed down the *c* axis, showing the non-classical C—H···Cl hydrogen bonds between the benzene solvent molecule and one of the Cl ligands of the complex molecule.

cis-Dichloridotetrakis(trimethylphosphane-κ*P*)ruthenium(II) benzene disolvate

Crystal data

$[RuCl_2(C_3H_9P)_4]\cdot 2C_6H_6$	$F(000) = 1320$
$M_r = 632.47$	$D_x = 1.385$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo *K*α radiation, λ = 0.7107 Å
Hall symbol: -P 2ac 2n	Cell parameters from 1376 reflections
a = 17.6243 (15) Å	θ = 2.3–28.9°
b = 18.1889 (19) Å	μ = 0.92 mm^{-1}
c = 9.4610 (11) Å	*T* = 173 K
V = 3032.9 (5) Å^3	Block, colorless
Z = 4	0.18 × 0.12 × 0.06 mm

Data collection

Oxford Diffraction Gemini S Ultra diffractometer	3550 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1653 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.148$
Detector resolution: 16.1930 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
ω scans	$h = -22 \rightarrow 21$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)	$k = -23 \rightarrow 22$

T_{min} = 0.949, T_{max} = 1.000	l = −10→12
14352 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.058	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.081	H-atom parameters constrained
S = 0.82	$w = 1/[\sigma^2(F_o^2) + (0.0104P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3550 reflections	$(\Delta/\sigma)_{max}$ = 0.003
139 parameters	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ru1	0.54358 (3)	0.2500	0.30360 (7)	0.01803 (17)
Cl1	0.47805 (10)	0.2500	0.0718 (2)	0.0308 (6)
Cl2	0.41377 (9)	0.2500	0.4111 (2)	0.0347 (6)
P1	0.66211 (10)	0.2500	0.2100 (2)	0.0221 (5)
P2	0.57932 (10)	0.2500	0.5371 (2)	0.0233 (6)
P3	0.53321 (8)	0.37973 (7)	0.27518 (17)	0.0273 (4)
C11	0.6660 (4)	0.2500	0.0209 (8)	0.032 (2)
H11A	0.7178	0.2500	−0.0104	0.049*
H11B	0.6408	0.2069	−0.0142	0.049*
C12	0.7266 (2)	0.3256 (2)	0.2488 (6)	0.0303 (17)
H12A	0.7740	0.3175	0.2015	0.045*
H12B	0.7350	0.3282	0.3489	0.045*
H12C	0.7047	0.3709	0.2165	0.045*
C21	0.6769 (3)	0.2500	0.5976 (8)	0.036 (2)
H21A	0.6785	0.2500	0.6990	0.055*
H21B	0.7020	0.2069	0.5623	0.055*

C22	0.5445 (3)	0.3255 (3)	0.6447 (6)	0.057 (2)
H22A	0.5627	0.3200	0.7397	0.086*
H22B	0.4900	0.3252	0.6447	0.086*
H22C	0.5624	0.3713	0.6065	0.086*
C31	0.5557 (3)	0.4150 (3)	0.1015 (6)	0.0368 (16)
H31A	0.5499	0.4675	0.1010	0.055*
H31B	0.5221	0.3936	0.0331	0.055*
H31C	0.6072	0.4027	0.0781	0.055*
C32	0.4370 (2)	0.4140 (3)	0.2916 (7)	0.0447 (18)
H32A	0.4369	0.4664	0.2789	0.067*
H32B	0.4177	0.4023	0.3837	0.067*
H32C	0.4056	0.3916	0.2208	0.067*
C33	0.5837 (3)	0.4488 (3)	0.3798 (6)	0.046 (2)
H33A	0.5700	0.4971	0.3476	0.069*
H33B	0.6374	0.4420	0.3690	0.069*
H33C	0.5703	0.4436	0.4776	0.069*
C1S	0.2535 (3)	0.4577 (2)	0.8727 (8)	0.069 (3)
H1SA	0.2273	0.4919	0.9273	0.082*
C2S	0.3127 (4)	0.4177 (4)	0.9316 (4)	0.073 (3)
H2SA	0.3263	0.4251	1.0255	0.088*
C3S	0.3518 (2)	0.3667 (3)	0.8500 (8)	0.068 (3)
H3SA	0.3915	0.3399	0.8894	0.081*
C4S	0.3316 (3)	0.3557 (2)	0.7096 (8)	0.059 (2)
H4SA	0.3578	0.3215	0.6550	0.071*
C5S	0.2724 (3)	0.3957 (3)	0.6507 (4)	0.059 (2)
H5SA	0.2589	0.3883	0.5567	0.071*
C6S	0.23327 (19)	0.4467 (3)	0.7323 (8)	0.064 (3)
H6SA	0.1936	0.4735	0.6929	0.076*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.0145 (3)	0.0200 (3)	0.0196 (4)	0.000	−0.0017 (4)	0.000
Cl1	0.0333 (12)	0.0318 (13)	0.0275 (14)	0.000	−0.0146 (10)	0.000
Cl2	0.0154 (11)	0.0489 (14)	0.0398 (15)	0.000	−0.0001 (10)	0.000
P1	0.0212 (10)	0.0254 (12)	0.0197 (14)	0.000	0.0015 (11)	0.000
P2	0.0181 (11)	0.0330 (14)	0.0187 (14)	0.000	0.0012 (10)	0.000
P3	0.0230 (8)	0.0249 (8)	0.0339 (11)	0.0015 (7)	−0.0029 (8)	−0.0031 (8)
C11	0.029 (5)	0.036 (6)	0.032 (6)	0.000	0.012 (4)	0.000
C12	0.026 (3)	0.029 (3)	0.036 (5)	0.002 (3)	0.003 (3)	0.000 (3)
C21	0.023 (5)	0.073 (7)	0.013 (5)	0.000	−0.004 (4)	0.000
C22	0.059 (4)	0.081 (5)	0.032 (4)	0.027 (4)	−0.006 (4)	−0.018 (4)
C31	0.048 (4)	0.027 (3)	0.035 (4)	−0.003 (3)	−0.002 (3)	0.008 (3)
C32	0.039 (4)	0.031 (3)	0.064 (5)	0.009 (3)	−0.008 (4)	−0.001 (4)
C33	0.039 (4)	0.033 (4)	0.066 (6)	−0.007 (3)	0.003 (3)	−0.013 (4)
C1S	0.085 (6)	0.053 (6)	0.067 (7)	−0.029 (5)	0.050 (5)	−0.019 (6)
C2S	0.099 (7)	0.091 (8)	0.029 (5)	−0.066 (5)	−0.019 (5)	0.026 (6)
C3S	0.039 (4)	0.063 (6)	0.101 (9)	−0.009 (4)	−0.006 (5)	0.041 (6)

C4S	0.056 (5)	0.026 (4)	0.097 (8)	−0.004 (3)	0.049 (5)	−0.009 (5)
C5S	0.087 (6)	0.059 (6)	0.033 (5)	−0.050 (4)	−0.003 (5)	0.007 (5)
C6S	0.035 (4)	0.037 (5)	0.119 (10)	−0.007 (3)	0.010 (5)	0.029 (6)

Geometric parameters (Å, °)

Ru1—P1	2.2690 (19)	C22—H22B	0.9600
Ru1—P2	2.297 (2)	C22—H22C	0.9600
Ru1—P3^{i}	2.3819 (14)	C31—H31A	0.9600
Ru1—P3	2.3819 (14)	C31—H31B	0.9600
Ru1—Cl1	2.479 (2)	C31—H31C	0.9600
Ru1—Cl2	2.5038 (19)	C32—H32A	0.9600
P1—C11	1.790 (8)	C32—H32B	0.9600
P1—C12	1.821 (4)	C32—H32C	0.9600
P1—C12^{i}	1.821 (4)	C33—H33A	0.9600
P2—C21	1.812 (6)	C33—H33B	0.9600
P2—C22	1.816 (5)	C33—H33C	0.9600
P2—C22^{i}	1.816 (5)	C1S—C2S	1.3900
P3—C31	1.808 (5)	C1S—C6S	1.3900
P3—C32	1.813 (4)	C1S—H1SA	0.9300
P3—C33	1.831 (5)	C2S—C3S	1.3900
C11—H11A	0.9600	C2S—H2SA	0.9300
C11—H11B	0.9598	C3S—C4S	1.3900
C12—H12A	0.9600	C3S—H3SA	0.9300
C12—H12B	0.9600	C4S—C5S	1.3900
C12—H12C	0.9600	C4S—H4SA	0.9300
C21—H21A	0.9600	C5S—C6S	1.3900
C21—H21B	0.9599	C5S—H5SA	0.9300
C22—H22A	0.9600	C6S—H6SA	0.9300
P1—Ru1—P2	97.07 (8)	H21A—C21—H21B	109.5
P1—Ru1—P3^{i}	91.52 (4)	P2—C22—H22A	109.5
P2—Ru1—P3^{i}	97.45 (4)	P2—C22—H22B	109.5
P1—Ru1—P3	91.52 (4)	H22A—C22—H22B	109.5
P2—Ru1—P3	97.45 (4)	P2—C22—H22C	109.5
P3^{i}—Ru1—P3	164.31 (8)	H22A—C22—H22C	109.5
P1—Ru1—Cl1	94.79 (8)	H22B—C22—H22C	109.5
P2—Ru1—Cl1	168.14 (7)	P3—C31—H31A	109.5
P3^{i}—Ru1—Cl1	82.20 (4)	P3—C31—H31B	109.5
P3—Ru1—Cl1	82.20 (4)	H31A—C31—H31B	109.5
P1—Ru1—Cl2	179.01 (9)	P3—C31—H31C	109.5
P2—Ru1—Cl2	81.94 (7)	H31A—C31—H31C	109.5
P3^{i}—Ru1—Cl2	88.61 (4)	H31B—C31—H31C	109.5
P3—Ru1—Cl2	88.61 (4)	P3—C32—H32A	109.5
Cl1—Ru1—Cl2	86.20 (7)	P3—C32—H32B	109.5
C11—P1—C12	100.2 (2)	H32A—C32—H32B	109.5
C11—P1—C12^{i}	100.2 (2)	P3—C32—H32C	109.5
C12—P1—C12^{i}	98.0 (3)	H32A—C32—H32C	109.5

C11—P1—Ru1	115.2 (2)	H32B—C32—H32C	109.5
C12—P1—Ru1	119.71 (17)	P3—C33—H33A	109.5
C12^{i}—P1—Ru1	119.71 (17)	P3—C33—H33B	109.5
C21—P2—C22	98.3 (2)	H33A—C33—H33B	109.5
C21—P2—C22^{i}	98.3 (2)	P3—C33—H33C	109.5
C22—P2—C22^{i}	98.3 (4)	H33A—C33—H33C	109.5
C21—P2—Ru1	124.3 (3)	H33B—C33—H33C	109.5
C22—P2—Ru1	116.5 (2)	C2S—C1S—C6S	120.0
C22^{i}—P2—Ru1	116.5 (2)	C2S—C1S—H1SA	120.0
C31—P3—C32	99.3 (3)	C6S—C1S—H1SA	120.0
C31—P3—C33	98.1 (3)	C3S—C2S—C1S	120.0
C32—P3—C33	99.9 (2)	C3S—C2S—H2SA	120.0
C31—P3—Ru1	115.93 (18)	C1S—C2S—H2SA	120.0
C32—P3—Ru1	113.76 (17)	C2S—C3S—C4S	120.0
C33—P3—Ru1	125.57 (19)	C2S—C3S—H3SA	120.0
P1—C11—H11A	110.1	C4S—C3S—H3SA	120.0
P1—C11—H11B	109.1	C3S—C4S—C5S	120.0
H11A—C11—H11B	109.5	C3S—C4S—H4SA	120.0
P1—C12—H12A	109.5	C5S—C4S—H4SA	120.0
P1—C12—H12B	109.5	C6S—C5S—C4S	120.0
H12A—C12—H12B	109.5	C6S—C5S—H5SA	120.0
P1—C12—H12C	109.5	C4S—C5S—H5SA	120.0
H12A—C12—H12C	109.5	C5S—C6S—C1S	120.0
H12B—C12—H12C	109.5	C5S—C6S—H6SA	120.0
P2—C21—H21A	110.1	C1S—C6S—H6SA	120.0
P2—C21—H21B	109.1		

Symmetry codes: (i) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4S—H4SA···Cl2i	0.93	2.83	3.710 (5)	159

Symmetry codes: i.

Fig. 1

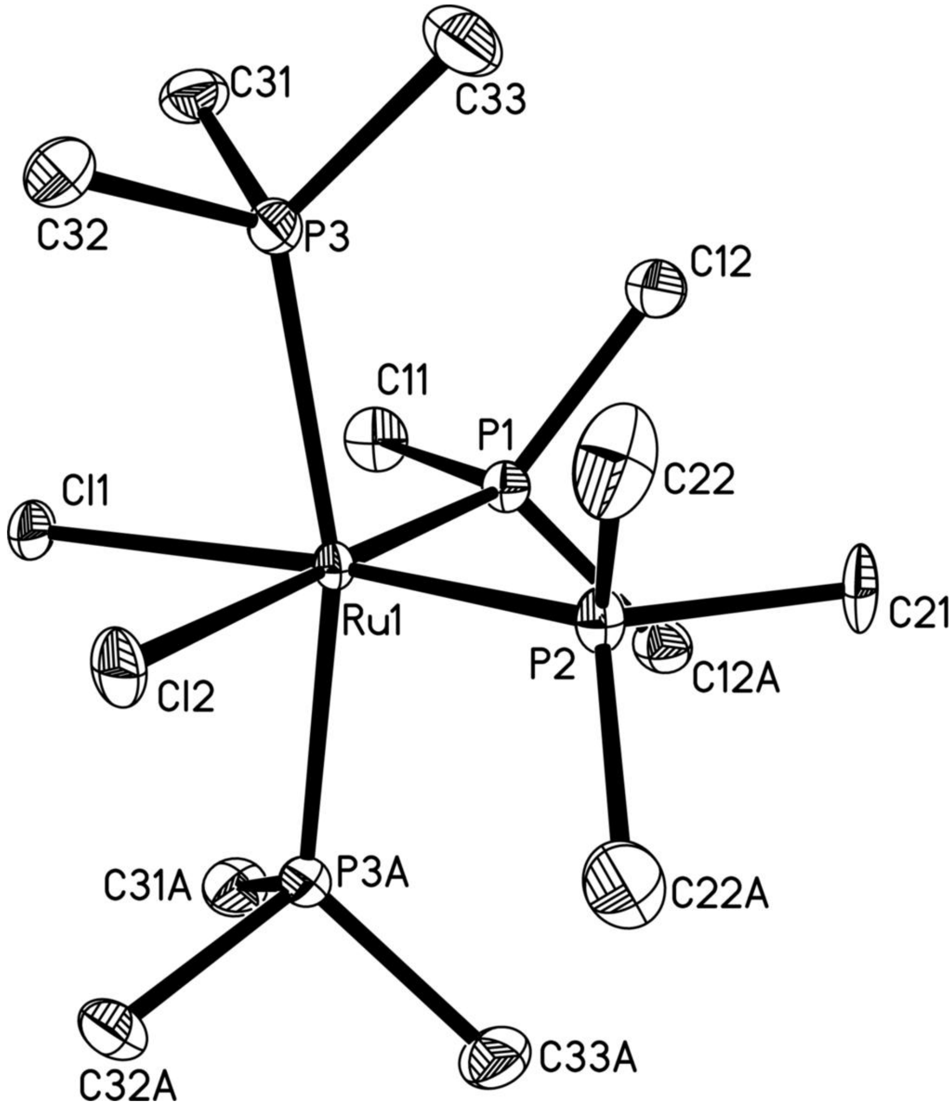
C31
C33
C32
P3
C12
C11
P1
C22
Cl1
Ru1
P2
C21
C12A
Cl2
C31A
P3A
C22A
C32A
C33A

Fig. 2