Crystal structure of *trans*-dichloro-1,3-propanediamine-bis[(2-methoxyethyl)diphenylphosphine]ruthenium(II), $RuCl_2(C_3H_{10}N_2)(C_{15}H_{17}OP)_2$

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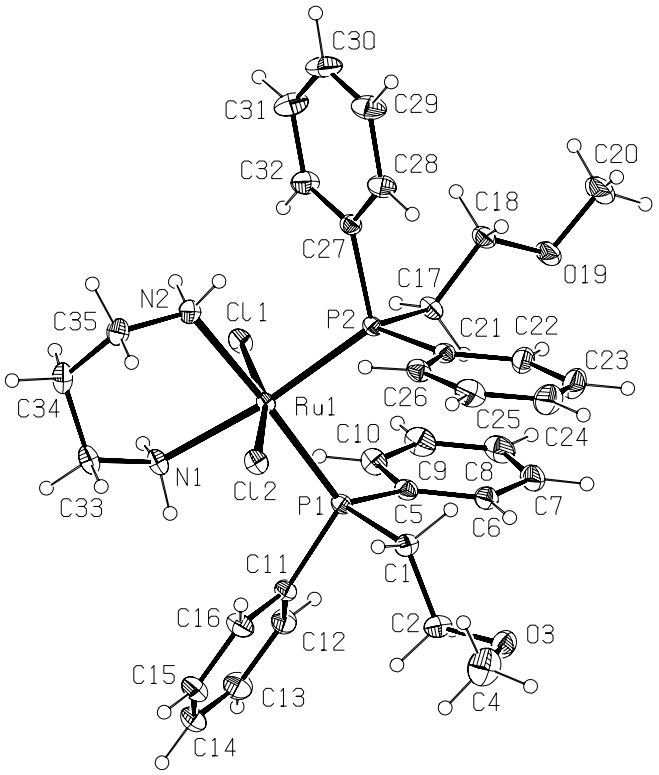

Abstract

$C_{33}H_{44}Cl_2N_2O_2P_2Ru$, monoclinic, $P12_1/c1$ (no. 14), a = 13.278(1) Å, b = 10.315(1) Å, c = 24.825(3) Å, β = 90.340(8)°, V = 3400.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.059, T = 173 K.

Source of material

All the reactions were performed using Schlenk-type flask under argon and standard high vacuum-line techniques. Solvents were of analytical grade and distilled under argon. The title compound was synthesized by treating $RuCl_2(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2$ complex with slightly excess 1.3-propanediamine ligand in dichloromethane as described previously [1]. The crystals were grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. They were re-crystallized from these two solutions. The desired complex was characterized by NMR, IR, and FAB-mass spectroscopy in addition to the elemental analysis [1,2].

Discussion

Nowadays, due to economical and environmental inciting, increasing attention is dedicated to catalysts and reagents [3,4]. An attractive strategy to consist in the homogenous catalysts by using dichloro(phosphine)diamineruthenium complexes in field of hydrogenation has been recently constructed [3-6]. The two hemilabile bidentate ether-phosphine ligands were coordinated the ruthenium(II) center atom via phosphor and oxygen atoms. The (ether) oxygen atom can easily be displaced by an incoming substrate such as diamine [1,2,7,8]. Thus, ether-phosphines are capable of making available and protecting vacant coordination sites which lead to an improvement in both stability and catalytic activity of the organometallic species [7,8].

The title complex is crystallized as free solvated *trans*-dichloro-*cis*-phosphine isomers with approximate C_2 symmetry. The ruthenium atom is coordinated two chlorine species in *trans* form, one diamine co-ligand via the nitrogen atoms and two (2-methoxyethyl)(diphenyl)-phosphine ligands via the phosphorus atoms in *cis* forms. The complex exhibits mostly regular octahedron geometry around the ruthenium center atom with two Ru—N distances of 2.1993 Å and 2.1932 Å, two Ru—Cl distances of 2.4177 Å and 2.4244 Å and two Ru—P distances equal 2.2963 Å and 2.2910 Å. The diamine and ether-phosphine ligands are practically planar. (Deviations from the least-squares planes do not exceed 0.1 Å.) The coordination angle of the diamine chelate ring results in distinctly N–Ru–N angles of 84.71° departs from ideal value by up to approximately 5.3 Å, due to the six-membered ring chelating nature of 1,3-propanediamine ligand, while the P–Ru–P angle is equal 91.17°. The dichloro ligands are bent away from their axial positions toward the diamine ligand forming Cl–Ru–Cl angles of 165.61°, resonating to the steric effect of the phenyls in the ether-phosphine ligands. In the crystal structure there is a number of RuCl···H_2N contacts smaller than 3.0 Å at the same molecule, indicating the presence of unconventional intra-hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	yellow-brown prism, size 0.33 × 0.45 × 0.66 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.44 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	55.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22999, 7802
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7097
$N(param)_{refined}$:	382
Programs:	SHELXS-97 [9], SHELXL-97 [10]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2C)	4*e*	0.5245	0.6339	0.4966	0.032
H(2D)	4*e*	0.6131	0.7078	0.5155	0.032
H(1C)	4*e*	0.4963	0.7944	0.3463	0.036
H(1D)	4*e*	0.4415	0.6976	0.3787	0.036
H(13A)	4*e*	0.9103	0.7053	0.3899	0.032
H(13B)	4*e*	0.8701	0.8174	0.4285	0.032
H(14A)	4*e*	0.9749	0.7569	0.4975	0.039
H(14B)	4*e*	0.9958	0.6176	0.4715	0.039
H(15A)	4*e*	1.0290	0.9355	0.4192	0.087
H(15B)	4*e*	1.1479	0.9227	0.4287	0.087
H(15C)	4*e*	1.0731	0.9219	0.4791	0.087
H(2)	4*e*	0.9618	0.5005	0.3961	0.038
H(3)	4*e*	1.0009	0.2876	0.3710	0.049
H(4)	4*e*	0.8899	0.1189	0.3896	0.051
H(5)	4*e*	0.7413	0.1611	0.4361	0.048
H(6)	4*e*	0.7010	0.3724	0.4613	0.039
H(8)	4*e*	0.8099	0.4419	0.5378	0.039
H(9)	4*e*	0.8116	0.4678	0.6316	0.053
H(10)	4*e*	0.7909	0.6708	0.6701	0.056
H(11)	4*e*	0.7700	0.8521	0.6151	0.052
H(12)	4*e*	0.7686	0.8295	0.5214	0.042
H(28A)	4*e*	0.7854	0.4604	0.3260	0.031
H(28B)	4*e*	0.6705	0.4182	0.3317	0.031
H(29A)	4*e*	0.6481	0.3983	0.2425	0.036
H(29B)	4*e*	0.7322	0.5050	0.2286	0.036
H(30A)	4*e*	0.7265	0.2452	0.1843	0.096
H(30B)	4*e*	0.8449	0.2195	0.1906	0.096
H(30C)	4*e*	0.8052	0.3565	0.1688	0.096
H(17)	4*e*	0.8756	0.5870	0.2714	0.041
H(18)	4*e*	1.0079	0.7134	0.2396	0.055
H(19)	4*e*	0.9997	0.9381	0.2444	0.059
H(20)	4*e*	0.8594	1.0381	0.2823	0.050
H(21)	4*e*	0.7278	0.9129	0.3160	0.034
H(27)	4*e*	0.6515	0.7905	0.2222	0.039
H(26)	4*e*	0.5282	0.7862	0.1545	0.052
H(25)	4*e*	0.3845	0.6609	0.1645	0.057
H(24)	4*e*	0.3621	0.5404	0.2432	0.056
H(23)	4*e*	0.4873	0.5372	0.3095	0.042
H(33A)	4*e*	0.5351	0.8994	0.5043	0.039
H(33B)	4*e*	0.4700	0.8062	0.5420	0.039
H(32A)	4*e*	0.3694	0.7490	0.4652	0.046
H(32B)	4*e*	0.3592	0.8981	0.4817	0.046
H(31A)	4*e*	0.3714	0.8963	0.3900	0.041
H(31B)	4*e*	0.4776	0.9495	0.4114	0.041

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	4*e*	0.629822(9)	0.68875(1)	0.411012(4)	0.02227(7)	0.01569(6)	0.01716(6)	−0.00094(4)	0.00210(4)	−0.00014(4)
Cl(1)	4*e*	0.53881(3)	0.48512(4)	0.41365(2)	0.0356(2)	0.0229(2)	0.0272(2)	−0.0094(2)	0.0058(2)	−0.0019(1)
Cl(2)	4*e*	0.68341(3)	0.91181(3)	0.41971(2)	0.0338(2)	0.0169(2)	0.0289(2)	−0.0025(2)	0.0031(2)	−0.0004(1)
P(1)	4*e*	0.78245(3)	0.62380(4)	0.44561(2)	0.0258(2)	0.0188(2)	0.0174(2)	−0.0003(2)	−0.0002(2)	0.0012(1)
P(2)	4*e*	0.68179(3)	0.64474(4)	0.32510(1)	0.0224(2)	0.0196(2)	0.0166(2)	0.0002(2)	0.0008(1)	0.0009(1)
O(3)	4*e*	1.0737(1)	0.7602(1)	0.43775(5)	0.0292(7)	0.0412(7)	0.0463(7)	−0.0024(6)	0.0015(6)	−0.0041(6)
O(19)	4*e*	0.7883(1)	0.3321(1)	0.24706(5)	0.0455(8)	0.0489(8)	0.0325(7)	0.0189(7)	−0.0071(6)	−0.0196(6)
N(1)	4*e*	0.5612(1)	0.7082(1)	0.49075(5)	0.0341(8)	0.0234(6)	0.0226(6)	−0.0001(6)	0.0081(6)	−0.0009(5)
N(2)	4*e*	0.4857(1)	0.7661(1)	0.38095(6)	0.0274(7)	0.0320(7)	0.0304(7)	0.0044(6)	0.0001(6)	−0.0040(6)
C(1)	4*e*	0.8915(1)	0.7255(2)	0.42746(6)	0.0266(8)	0.0271(7)	0.0269(8)	−0.0036(7)	−0.0014(6)	0.0043(6)
C(2)	4*e*	0.9856(1)	0.7105(2)	0.46312(7)	0.0317(9)	0.0346(9)	0.0321(8)	−0.0044(7)	−0.0071(7)	0.0020(7)
C(4)	4*e*	1.0815(2)	0.8952(2)	0.4415(1)	0.055(2)	0.043(1)	0.076(2)	−0.012(1)	0.011(1)	0.007(1)
C(5)	4*e*	0.8266(1)	0.4588(2)	0.43101(6)	0.0307(9)	0.0242(7)	0.0205(7)	0.0035(7)	−0.0027(6)	0.0004(6)
C(6)	4*e*	0.9164(1)	0.4321(2)	0.40413(7)	0.0313(9)	0.0353(9)	0.0274(8)	0.0052(7)	−0.0024(7)	−0.0030(7)
C(7)	4*e*	0.9396(2)	0.3051(2)	0.38912(8)	0.041(1)	0.047(1)	0.0357(9)	0.0180(9)	−0.0031(8)	−0.0110(8)
C(8)	4*e*	0.8742(2)	0.2049(2)	0.40046(8)	0.058(1)	0.0285(9)	0.042(1)	0.0131(9)	−0.009(1)	−0.0099(8)
C(9)	4*e*	0.7859(2)	0.2301(2)	0.42765(8)	0.057(1)	0.0221(8)	0.042(1)	0.0012(8)	−0.0022(9)	−0.0015(7)
C(10)	4*e*	0.7621(2)	0.3560(2)	0.44271(7)	0.041(1)	0.0233(8)	0.0325(8)	0.0017(7)	0.0015(8)	0.0014(6)
C(11)	4*e*	0.7890(1)	0.6328(2)	0.51982(6)	0.0273(8)	0.0308(8)	0.0199(7)	0.0013(7)	0.0003(6)	0.0010(6)
C(12)	4*e*	0.8017(1)	0.5257(2)	0.55309(7)	0.034(1)	0.0366(9)	0.0264(8)	0.0029(8)	0.0007(7)	0.0074(7)
C(13)	4*e*	0.8026(2)	0.5414(2)	0.60912(7)	0.047(1)	0.060(1)	0.0249(8)	0.004(1)	0.0000(8)	0.0161(8)
C(14)	4*e*	0.7906(2)	0.6616(2)	0.63203(7)	0.043(1)	0.078(2)	0.0193(8)	0.005(1)	0.0015(8)	−0.0007(9)
C(15)	4*e*	0.7780(2)	0.7688(2)	0.59943(7)	0.047(1)	0.055(1)	0.0290(9)	0.006(1)	−0.0008(8)	−0.0146(8)
C(16)	4*e*	0.7772(2)	0.7553(2)	0.54361(7)	0.046(1)	0.0345(9)	0.0249(8)	0.0042(8)	−0.0036(7)	−0.0034(7)
C(17)	4*e*	0.7168(1)	0.4750(2)	0.31142(6)	0.0362(9)	0.0225(7)	0.0194(7)	0.0038(7)	0.0011(6)	−0.0014(6)
C(18)	4*e*	0.7157(1)	0.4313(2)	0.25251(6)	0.036(1)	0.0308(8)	0.0232(7)	0.0059(7)	−0.0025(7)	−0.0064(6)
C(20)	4*e*	0.7915(2)	0.2847(3)	0.19359(9)	0.064(2)	0.083(2)	0.045(1)	0.032(1)	−0.012(1)	−0.039(1)
C(21)	4*e*	0.7871(1)	0.7367(2)	0.29660(6)	0.0238(8)	0.0297(8)	0.0179(6)	−0.0016(7)	−0.0009(6)	0.0037(6)
C(22)	4*e*	0.8718(1)	0.6788(2)	0.27386(7)	0.0272(9)	0.043(1)	0.0326(9)	0.0038(8)	0.0033(7)	0.0038(7)
C(23)	4*e*	0.9504(2)	0.7540(2)	0.25480(8)	0.028(1)	0.065(1)	0.045(1)	0.001(1)	0.0080(8)	0.004(1)
C(24)	4*e*	0.9458(2)	0.8870(2)	0.25779(9)	0.037(1)	0.065(1)	0.045(1)	−0.021(1)	0.0080(9)	0.007(1)
C(25)	4*e*	0.8627(2)	0.9463(2)	0.28033(7)	0.050(1)	0.039(1)	0.0349(9)	−0.0179(9)	0.0036(9)	0.0034(8)
C(26)	4*e*	0.7842(1)	0.8716(2)	0.30003(6)	0.0322(9)	0.0305(8)	0.0227(7)	−0.0040(7)	0.0012(7)	0.0034(6)
C(27)	4*e*	0.5830(1)	0.6626(2)	0.27262(6)	0.0264(8)	0.0236(7)	0.0220(7)	0.0032(6)	−0.0024(6)	−0.0028(6)
C(28)	4*e*	0.5935(2)	0.7376(2)	0.22642(7)	0.041(1)	0.0299(8)	0.0269(8)	−0.0009(8)	−0.0067(7)	0.0039(7)
C(29)	4*e*	0.5195(2)	0.7359(2)	0.18619(8)	0.058(1)	0.037(1)	0.0339(9)	0.005(1)	−0.0171(9)	0.0059(8)
C(30)	4*e*	0.4345(2)	0.6622(2)	0.19204(9)	0.052(1)	0.042(1)	0.048(1)	0.005(1)	−0.029(1)	−0.0050(9)
C(31)	4*e*	0.4218(2)	0.5897(2)	0.23849(9)	0.039(1)	0.048(1)	0.053(1)	–0.010(1)	–0.017(1)	–0.0021(9)
C(32)	4*e*	0.4961(2)	0.5888(2)	0.27822(7)	0.036(1)	0.0382(9)	0.0316(9)	–0.0062(8)	–0.0053(7)	0.0010(7)
C(33)	4*e*	0.4951(2)	0.8185(2)	0.50489(7)	0.041(1)	0.0289(8)	0.0289(8)	0.0033(7)	0.0118(7)	–0.0042(6)
C(34)	4*e*	0.4059(2)	0.8326(2)	0.46677(8)	0.032(1)	0.040(1)	0.043(1)	0.0049(8)	0.0132(8)	–0.0040(8)
C(35)	4*e*	0.4334(1)	0.8723(2)	0.41001(7)	0.0300(9)	0.0336(9)	0.0384(9)	0.0097(8)	0.0019(7)	–0.0033(7)

References

1. Lindner, E.; Warad, I.; Eichele, K.; Mayer, H. A.: Supported organometallic complexes Part 34: Synthesis and structures of an array of diamine(ether-phosphine)ruthenium(II) complexes and their application in the catalytic hydrogenation of *trans*-4-phenyl-3-butene-2-one. Inorg. Chim. Acta **350** (2003) 49-56.
2. Nachtigal, C.; Al-Gharabli, S.; Eichele, K.; Lindner, E.; Mayer, H. A.: Structural studies of an array of mixed diamine phosphine ruthenium(II) complexes. Organometallics **21** (2002) 105-112.
3. Noyori, R.: Asymmetric catalysis in organic synthesis. J. Wiley and Sons, New York 1994.
4. Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A.; Ikariya, T.; Noyori, R.: *Trans*-[$RuCl_2$(phosphane)$_2$(1,2-diamine)] and chiral *trans*-[RuCl2(diphosphane)(1,2-diamine): shelf-stable precatalysts for the rapid, productive, and stereoselective hydrogenation of ketones. Angew. Chem., Int. Ed. Engl. **37** (1998) 1703-1707.
5. Lindner, E.; Mayer, H. A.; Warad, I.; Eichele, K.: Supported organometallic complexes Part 35. Synthesis, characterization, and catalytic application of a new family of diamine(diphosphine)ruthenium(II) complexes. J. Organomet. Chem. **665** (2003) 176-185.
6. Abdur-Rashid, K.; Faatz, M.; Lough, A. J.; Morris, H. R.: Catalytic cycle for the asymmetric hydrogenation of prochiral ketones to chiral alcohols: Direct hydride and proton transfer from chiral catalysts *trans*-$Ru(H)_2$(diphosphine)(diamine) to ketones and direct addition of dihydrogen to the resulting hydridoamido complexes. J. Am. Chem. Soc. **123** (2001) 7473-7474.
7. Warad, I.; Lindner, E.; Eichele, K.; Mayer, A. H.: Supported organometallic complexes part 39: Cationic diamine(ether-phosphine)ruthenium(II) complexes as precursors for the hydrogenation of *trans*-4-phenyl-3-butene-2-one. Inorg. Chim. Acta **357** (2004) 1847-1853.
8. Bader, A.; Lindner, E.: Coordination chemistry and catalysis with hemilabile oxygen-phosphorus ligands. Coord. Chem. Rev. **108** (1991) 27-110.
9. Sheldrick, G. M.: SHELXS-90. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1990.
10. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.