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Crystal structure of *cis*-dichloro(1,2-*R*,*R*-diaminocyclohexane)-bis[1,3-(diphenylphosphino)propane]ruthenium(II), $RuCl_2(C_{27}H_{26}P_2)(C_6H_{14}N_2)$

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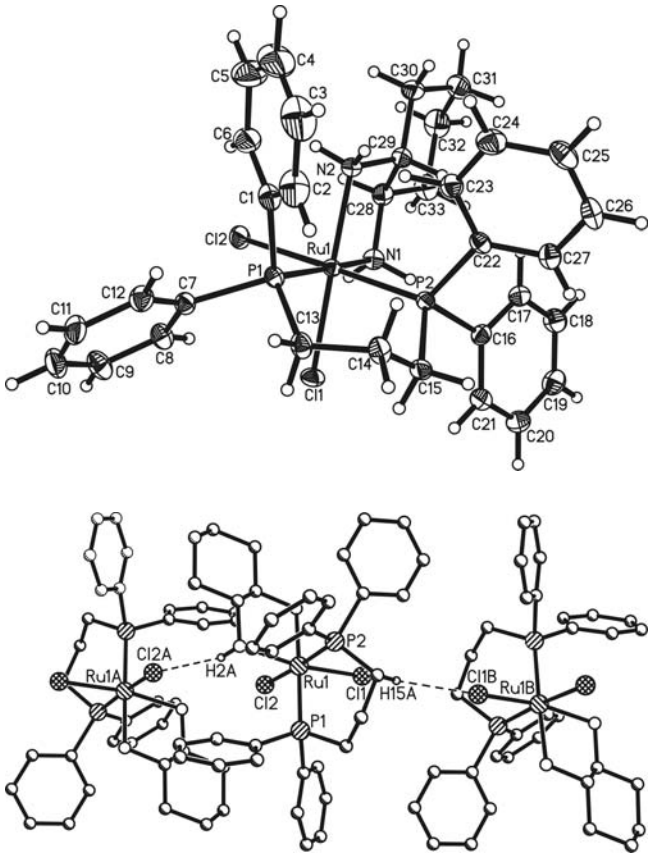

Abstract

$C_{33}H_{40}Cl_2N_2P_2Ru$, triclinic, $P\bar{1}$ (no. 2), a = 9.870(1) Å, b = 13.044(1) Å, c = 14.446(3) Å, α = 110.86(1)°, β = 100.55(1)°, γ = 107.657(9)°, V = 1565.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.067, 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. (1*R*,2*R*)-(–)-1,2-diaminocyclohexane (0.03 g, 0.27 mmol) was dissolved in 10 ml of dichloromethane and the solution was added dropwise to a stirred solution of $RuCl_2(dppp)_2$ (250 mg, 0.25 mmol) in 10 ml of dichloromethane within 5 min. The mixture was stirred for ca. 10 - 30 min at room temperature while the color changed from brown to yellow. After removal of any turbidity by filtration (P_4), the volume of the solution was concentrated to about 5 ml under reduced pressure. Addition of 40 ml of diethyl ether caused precipitation of a solid, which was filtered off (P_4). After recrystallization from dichloromethane/*n*-hexane the title compound was obtained as a yellow-brown powder in analytically pure form (yield 170 mg, 92 %; m.p. 296 °C). Elemental analysis — found: C, 56.33 %; H, 5.65 %; Cl, 10.23 %; N, 4.27 %; calculated for $C_{33}H_{40}Cl_2N_2P_2Ru$: C, 56.73 %; H, 5.77 %; Cl, 10.15 %; N, 4.01 %. ^{1}H NMR ($CDCl_3$), ^{31}P NMR, ^{13}C NMR and FAB-MS data are available in the CIF.

Experimental details

All H atoms were intially located in a difference Fourier map. The phenyl H atoms were then constrained to ideal geometrical parameters with d(C—H) = 0.95 Å and U_{iso}(H) =1.5 U_{eq}(C). The position of the amine H atoms was refined freely along with an isotropic displacement parameter. All other H atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with d(C—H) in the range 0.95 - 1.00 Å and U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

Diphosphines such dppp are of the most versatile ligands, since they can stablize metal-phosphorus bonds and at the same time [1-3], very different functionalization may be introduced by means of the groups bound to the phosphorus atom [4,5]. Metal complexes containing phosphorus ligands have always been important, due to their possible catalytic activity [2-6]. Recently, a ruthenium(II) complex system containing diphosphine and 1,2-diamine ligands of type $RuCl_2$/PP/NN was discovered, which in the presence of a base and 2-propanol, proved to be excellent catalysts for the hydrogenation of ketones under mild conditions [5,6]. Since that time large number of such complexes were made available for the same task [2,7].

The title complex is crystallized as solvent-free in full *cis* form with lost of the C_2 symmetry. The *cis*-[$RuCl_2$(dppp)NN] thermodynamical isomer is structurally favored over the *trans*-[$RuCl_2$(dppp)NN] kinetic isomer [3], while the opposite was observed in solution and some solid state studies [2,8]. The ruthenium center is in a distorted octahedral environment with a five-membered diamine ring coordinating in *cis* form via N1 and N2, a six-membered bis(phosphine) ring coordinating in *cis* form via P1 and P2 as well as *cis*-dichloro coordination (figure, top). The six-membered ring of the dppp ligand allows ∠P–Ru–P = 91.35° very close to ideal value, the smaller 1,2-diamine enforces ∠N–Ru–N = 79.14°, that is 10.86° less than the ideal value; while the ∠Cl–Ru–Cl was found to be 90.37°, which is very close to the ideal value. The d(Ru—N2) = 2.147 Å *trans* to Cl1 is shorter than the d(Ru—N1) = 2.174 Å *trans* to P1. The d(Ru—P2) = 2.253 Å *trans* to Cl2 is slightly shorter than d(Ru—P1) = 2.275 Å *trans* to N1. The d(Ru—Cl1) *trans* to N2 is slightly shorter than the

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d(Ru—Cl2) *trans* to P2, 2.418 Å and 2.493 Å, respectively. The molecular packing in the crystal structure (figure, bottom) is stabilized by two weak H-bond intermolecular interactions, in which chloride atoms works as acceptor. In each molecule there are two types of donors which interact with Cl2 and Cl1. The distance Cl2A···H2A of the amino group is 2.576 Å and the angle ∠Ru1A–Cl2A···H2A is 142.35°. The distance Cl1B···H15A of the PCH group of the dppp ligand is 2.716 Å and the angle ∠Ru1B–Cl1B···H15A is 159.49°.

Table 1. Data collection and handling.

Crystal:	red plate, size 0.15 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.00 cm^{-1}
Diffractometer, scan mode:	Siemens CCD, ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8075, 6869
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6081
$N(param)_{refined}$:	362
Programs:	SHELXS-97, SHELXL-97 [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.9033	0.7293	0.6516	0.024
H(1B)	2*i*	1.0481	0.8045	0.7398	0.024
H(2A)	2*i*	0.8263	0.9159	0.8964	0.021
H(2B)	2*i*	0.6852	0.8884	0.8161	0.021
H(2)	2*i*	0.6003	1.1703	0.7434	0.045
H(3)	2*i*	0.4216	1.1683	0.8298	0.065
H(4)	2*i*	0.4581	1.1442	0.9827	0.067
H(5)	2*i*	0.6777	1.1285	1.0547	0.057
H(6)	2*i*	0.8547	1.1244	0.9670	0.036
H(8)	2*i*	1.2045	1.1998	0.8363	0.028
H(9)	2*i*	1.4065	1.3860	0.9059	0.037
H(10)	2*i*	1.3651	1.5619	0.9593	0.038
H(11)	2*i*	1.1223	1.5530	0.9461	0.035
H(12)	2*i*	0.9200	1.3673	0.8795	0.029
H(13A)	2*i*	0.7985	1.2205	0.6845	0.027
H(13B)	2*i*	0.9084	1.1674	0.6358	0.027
H(14A)	2*i*	0.5989	1.0243	0.5898	0.027
H(14B)	2*i*	0.6586	1.0807	0.5158	0.027
H(15A)	2*i*	0.8140	0.9649	0.4972	0.025
H(15B)	2*i*	0.6370	0.8875	0.4399	0.025
H(17)	2*i*	0.6151	0.5966	0.5343	0.026
H(18)	2*i*	0.6430	0.4310	0.4198	0.032
H(19)	2*i*	0.7780	0.4518	0.3057	0.034
H(20)	2*i*	0.8805	0.6370	0.3041	0.034
H(21)	2*i*	0.8555	0.8037	0.4194	0.030
H(23)	2*i*	0.5500	0.9100	0.7216	0.026
H(24)	2*i*	0.2971	0.8673	0.7044	0.035
H(25)	2*i*	0.1103	0.7227	0.5453	0.034
H(26)	2*i*	0.1790	0.6265	0.4032	0.031
H(27)	2*i*	0.4323	0.6723	0.4186	0.026
H(28)	2*i*	0.9547	0.7770	0.8599	0.027
H(29)	2*i*	0.6654	0.7029	0.7145	0.025
H(30A)	2*i*	0.5636	0.6978	0.8482	0.033
H(30B)	2*i*	0.7261	0.7361	0.9275	0.033
H(31A)	2*i*	0.5934	0.5266	0.8588	0.040
H(31B)	2*i*	0.5657	0.5129	0.7414	0.040
H(32A)	2*i*	0.7674	0.4595	0.7873	0.044
H(32B)	2*i*	0.8545	0.5858	0.8890	0.044
H(33A)	2*i*	0.9606	0.5948	0.7576	0.036
H(33B)	2*i*	0.7987	0.5530	0.6759	0.036

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)	2*i*	0.90248(2)	0.94329(1)	0.74093(1)	0.01245(8)	0.01570(9)	0.01506(8)	0.00602(6)	0.00499(6)	0.00778(6)
Cl(1)	2*i*	1.07847(6)	0.98988(5)	0.65056(4)	0.0188(2)	0.0285(3)	0.0246(2)	0.0094(2)	0.0119(2)	0.0141(2)
Cl(2)	2*i*	1.11497(6)	1.02809(5)	0.90648(4)	0.0192(2)	0.0253(3)	0.0204(2)	0.0048(2)	0.0013(2)	0.0107(2)
P(1)	2*i*	0.87686(6)	1.11926(5)	0.77396(4)	0.0128(2)	0.0162(2)	0.0192(2)	0.0058(2)	0.0040(2)	0.0080(2)
P(2)	2*i*	0.72024(6)	0.85099(4)	0.58393(4)	0.0141(2)	0.0161(2)	0.0154(2)	0.0050(2)	0.0045(2)	0.0076(2)
N(1)	2*i*	0.9460(2)	0.7844(2)	0.7210(1)	0.0203(9)	0.0214(9)	0.0222(9)	0.0106(7)	0.0079(7)	0.0105(7)
N(2)	2*i*	0.7726(2)	0.8759(2)	0.8259(1)	0.0177(8)	0.0190(8)	0.0181(8)	0.0078(7)	0.0072(7)	0.0089(7)
C(1)	2*i*	0.7442(2)	1.1434(2)	0.8446(2)	0.017(1)	0.018(1)	0.029(1)	0.0070(8)	0.0080(8)	0.0057(8)
C(2)	2*i*	0.6156(3)	1.1594(2)	0.8055(2)	0.026(1)	0.034(1)	0.046(2)	0.018(1)	0.009(1)	0.008(1)
C(3)	2*i*	0.5098(3)	1.1591(3)	0.8576(3)	0.024(1)	0.048(2)	0.076(2)	0.021(1)	0.018(1)	0.006(2)
C(4)	2*i*	0.5318(4)	1.1458(3)	0.9486(3)	0.044(2)	0.047(2)	0.074(2)	0.017(1)	0.042(2)	0.011(2)
C(5)	2*i*	0.6608(4)	1.1348(3)	0.9904(2)	0.054(2)	0.044(2)	0.051(2)	0.021(1)	0.037(2)	0.018(1)
C(6)	2*i*	0.7665(3)	1.1329(2)	0.9383(2)	0.032(1)	0.028(1)	0.033(1)	0.013(1)	0.018(1)	0.011(1)
C(7)	2*i*	1.0411(2)	1.2641(2)	0.8490(2)	0.0173(9)	0.019(1)	0.0179(9)	0.0056(8)	0.0031(8)	0.0084(8)
C(8)	2*i*	1.1870(2)	1.2711(2)	0.8583(2)	0.018(1)	0.023(1)	0.029(1)	0.0070(9)	0.0036(8)	0.0119(9)
C(9)	2*i*	1.3074(3)	1.3820(2)	0.8997(2)	0.018(1)	0.029(1)	0.039(1)	0.0031(9)	0.003(1)	0.017(1)
C(10)	2*i*	1.2828(3)	1.4866(2)	0.9318(2)	0.027(1)	0.023(1)	0.029(1)	–0.002(1)	–0.001(1)	0.0096(9)
C(11)	2*i*	1.1391(3)	1.4814(2)	0.9240(2)	0.037(1)	0.018(1)	0.025(1)	0.008(1)	0.008(1)	0.0047(9)
C(12)	2*i*	1.0185(3)	1.3705(2)	0.8836(2)	0.025(1)	0.023(1)	0.024(1)	0.0104(9)	0.0082(9)	0.0082(9)
C(13)	2*i*	0.8207(2)	1.1481(2)	0.6602(2)	0.021(1)	0.018(1)	0.023(1)	0.0048(8)	0.0011(8)	0.0102(8)
C(14)	2*i*	0.6859(2)	1.0488(2)	0.5658(2)	0.021(1)	0.020(1)	0.024(1)	0.0057(9)	–0.0003(8)	0.0125(9)
C(15)	2*i*	0.7162(2)	0.9388(2)	0.5092(2)	0.021(1)	0.022(1)	0.019(1)	0.0048(8)	0.0049(8)	0.0124(8)
C(16)	2*i*	0.7317(2)	0.7177(2)	0.4887(2)	0.019(1)	0.021(1)	0.0163(9)	0.0080(8)	0.0047(8)	0.0076(8)
C(17)	2*i*	0.6695(2)	0.6055(2)	0.4878(2)	0.023(1)	0.023(1)	0.021(1)	0.0096(9)	0.0079(8)	0.0110(8)
C(18)	2*i*	0.6861(3)	0.5067(2)	0.4197(2)	0.031(1)	0.020(1)	0.030(1)	0.0105(9)	0.010(1)	0.0115(9)
C(19)	2*i*	0.7658(3)	0.5189(2)	0.3518(2)	0.032(1)	0.026(1)	0.025(1)	0.015(1)	0.0097(9)	0.0062(9)
C(20)	2*i*	0.8272(3)	0.6289(2)	0.3514(2)	0.029(1)	0.031(1)	0.024(1)	0.011(1)	0.0143(9)	0.0090(9)
C(21)	2*i*	0.8115(2)	0.7282(2)	0.4197(2)	0.024(1)	0.024(1)	0.025(1)	0.0062(9)	0.0097(9)	0.0093(9)
C(22)	2*i*	0.5189(2)	0.7961(2)	0.5724(2)	0.0156(9)	0.017(1)	0.023(1)	0.0063(8)	0.0056(8)	0.0117(8)
C(23)	2*i*	0.4750(2)	0.8526(2)	0.6563(2)	0.018(1)	0.024(1)	0.022(1)	0.0072(8)	0.0052(8)	0.0099(8)
C(24)	2*i*	0.3243(3)	0.8268(2)	0.6466(2)	0.024(1)	0.038(1)	0.033(1)	0.017(1)	0.014(1)	0.017(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(25)	2*i*	0.2135(3)	0.7417(2)	0.5521(2)	0.018(1)	0.032(1)	0.040(1)	0.0103(9)	0.0100(9)	0.019(1)
C(26)	2*i*	0.2546(2)	0.6846(2)	0.4679(2)	0.019(1)	0.019(1)	0.034(1)	0.0041(9)	–0.0001(9)	0.0119(9)
C(27)	2*i*	0.4057(2)	0.7116(2)	0.4773(2)	0.021(1)	0.019(1)	0.024(1)	0.0079(8)	0.0048(8)	0.0093(8)
C(28)	2*i*	0.8825(2)	0.7303(2)	0.7867(2)	0.025(1)	0.022(1)	0.021(1)	0.0088(9)	0.0043(8)	0.0119(8)
C(29)	2*i*	0.7359(2)	0.7454(2)	0.7882(2)	0.022(1)	0.020(1)	0.020(1)	0.0058(8)	0.0066(8)	0.0094(8)
C(30)	2*i*	0.6617(3)	0.6911(2)	0.8530(2)	0.034(1)	0.024(1)	0.024(1)	0.005(1)	0.013(1)	0.0124(9)
C(31)	2*i*	0.6374(3)	0.5592(2)	0.8138(2)	0.042(1)	0.024(1)	0.032(1)	0.004(1)	0.011(1)	0.017(1)
C(32)	2*i*	0.7862(3)	0.5455(2)	0.8157(2)	0.047(2)	0.027(1)	0.038(1)	0.013(1)	0.007(1)	0.021(1)
C(33)	2*i*	0.8614(3)	0.5997(2)	0.7508(2)	0.036(1)	0.024(1)	0.036(1)	0.015(1)	0.011(1)	0.016(1)

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