# Crystal structure of *cis*-dichloro-1,2-ethylenediamine-bis(1,4-(diphenylphosphino)butane)-ruthenium(II) dichloromethane disolvate, $RuCl_2(C_2H_8N_2)(C_{28}H_{28}P_2) \cdot 2\,CH_2Cl_2$

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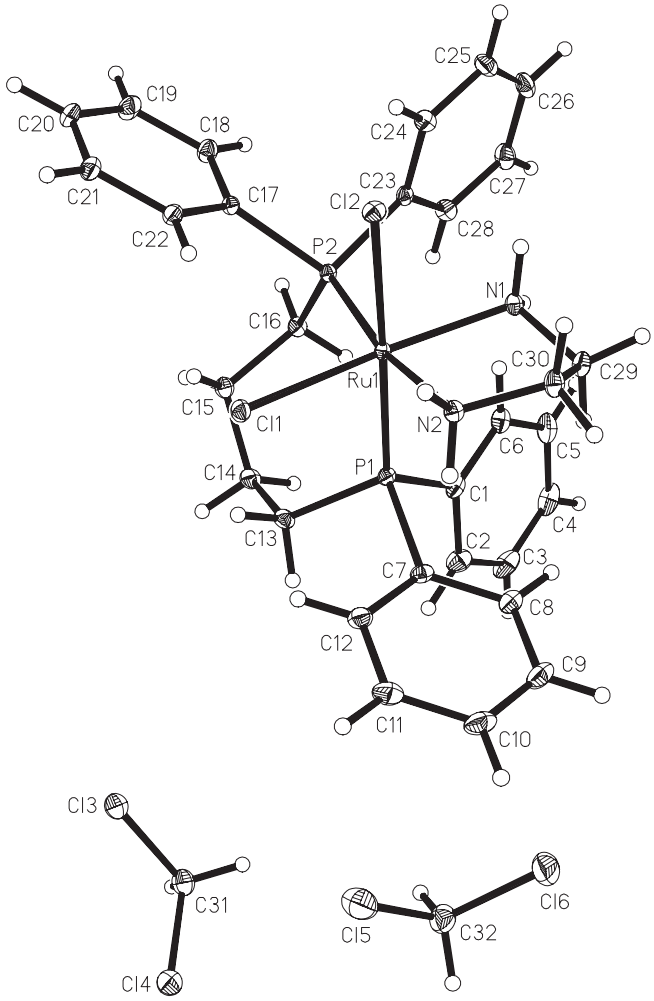


**Abstract**

$C_{32}H_{40}Cl_6N_2P_2Ru$, triclinic, $P\bar{1}$ (no. 2), $a$ = 10.338(6) Å, $b$ = 13.024(5) Å, $c$ = 14.491(5) Å, $\alpha$ = 81.02(2)°, $\beta$ = 87.65(3)°, $\gamma$ = 66.95(3)°, $V$ = 1772.9 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.075, $T$ = 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 prepared starting from *trans*-$RuCl_2(dppb)_2$. Mixing of ethylenediamine (0.012 g, 0.200 mmol) in dichloromethane (10 ml) dropwise with *cis*-$[RuCl_2(dppb)en]$ (0.200 g, 0.195 mmol) dissolved in the same solvent (15 ml). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, the residue was washed well with hexane then diethylether and dried, to give yellow powder. The crystals were grown by slow diffusion of diethylether into a solution of the complex in dichloromethane. NMR, IR, and FAB-mass spectroscopy data are available in the CIF. Elemental analysis – found: C, 54.57 %; H, 5.26 %; Cl, 10.84 %; N, 4.19 %; calc. for $C_{30}H_{36}Cl_2N_2P_2Ru$: C, 54.71 %; H, 5.51 %; Cl, 10.77 %; N, 4.25 %.

**Discussion**

The synthesis and chemistry of Ru(II) complexes possessing a chelating, ditertiary phosphine (P-P) and diamine (N-N) ligands remains a topic of interest, the main impetus being the potential of such complexes as catalysts [1-5]. Recently ruthenium homogenous hydrogenation catalysts have been proven to be some of most useful catalytic hydrogenation of polar double bonds such as C=O or C=N due to their favorable reactivity and selectivity [3-6]. The use of chiral Ru(II)(P-P)*(N-N)* complexes for asymmetric catalysis have been tremendously successful, especially in enantioselective hydrogenation of functionalized carbonyl compounds [2,5-8], and there has been much interest in the chemistry of Ru(II) complexes bearing chiral diphosphine ligands such as BINAP [9]. Such complexes proved to be excellent catalysts in the hydrogenation of functionalized carbonyl compounds under mild condition [2-11].

The title complex $[RuCl_2(dppb)en]$ crystallizes with two $CH_2Cl_2$ solvated molecules in full *cis* form with lost of the $C_2$ symmetry. The *cis*-$[RuCl_2(dppb)en]$ thermodynamical isomer is structurally favored over the *trans*-$[RuCl_2(dppb)en]$ kinetic isomer [4,11,12], while the opposite was observed in solution and some solid state studies [3,6-8,13]. The ruthenium center is in a distorted octahedral environment with a five-membered diamine ring coordinating in *cis* form via N1 and N2, a seven-membered bis(phosphine) ring coordinating in *cis* form via P1 and P2 as well as *cis*-dichloro coordination. The bis(phosphine) ring allows for P–Ru–P angle to be larger than the ideal value of 94.13°, the smaller 1,2-diamine enforces N–Ru–N angle that is 10.85° less than the ideal value, while the Cl–Ru–Cl was found to be 89.61° which is very close to the ideal value. The Ru—N1 distance *trans* to Cl1 is shorter than the Ru—N2 distance *trans* to P2, 2.1213 Å and 2.1825 Å, respectively. The Ru—P1 distance *trans* to Cl2 slightly shorter than Ru—P2 distance *trans* to N2, 2.266 Å and 2.278 Å, respectively. The Ru—Cl1 distance *trans* to N1 is slightly shorter than the Ru—Cl2 distance *trans* to P1 by 0.034 Å, and found to be 2.489 Å and 2.455 Å, respectively. In the crystal structure there are a number of RuCl···H2N contacts smaller than 3.0 Å, indicating the presence of unconventional intra-hydrogen bonds [7,13].

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**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | yellow chunk, size 0.3 × 0.4 × 0.2 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 10.11 $cm^{-1}$ |
| Diffractometer, scan mode: | Bruker P4, $\omega$ |
| $2\theta_{max}$: | 55° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 9430, 8079 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 7344 |
| $N(param)_{refined}$: | 389 |
| Programs: | SHELXS-97 [14], SHELXL-97 [15] |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1A) | 2*i* | 0.6291 | 0.9507 | 0.6730 | 0.025 |
| H(1B) | 2*i* | 0.6760 | 1.0084 | 0.5893 | 0.025 |
| H(2A) | 2*i* | 1.0509 | 0.8776 | 0.5940 | 0.025 |
| H(2B) | 2*i* | 1.0470 | 0.7785 | 0.6591 | 0.025 |
| H(2) | 2*i* | 0.8598 | 0.6351 | 0.9731 | 0.043 |
| H(3) | 2*i* | 0.6734 | 0.5808 | 1.0219 | 0.052 |
| H(4) | 2*i* | 0.4500 | 0.6801 | 0.9553 | 0.052 |
| H(5) | 2*i* | 0.4076 | 0.8374 | 0.8418 | 0.046 |
| H(6) | 2*i* | 0.5917 | 0.8933 | 0.7927 | 0.035 |
| H(8) | 2*i* | 0.8970 | 0.6164 | 0.7649 | 0.037 |
| H(9) | 2*i* | 1.0754 | 0.4556 | 0.7222 | 0.048 |
| H(10) | 2*i* | 1.3102 | 0.4252 | 0.7409 | 0.051 |
| H(11) | 2*i* | 1.3687 | 0.5576 | 0.8020 | 0.047 |
| H(12) | 2*i* | 1.1921 | 0.7175 | 0.8479 | 0.038 |
| H(13A) | 2*i* | 1.0022 | 0.7440 | 0.9859 | 0.031 |
| H(13B) | 2*i* | 1.0367 | 0.8492 | 0.9392 | 0.031 |
| H(14A) | 2*i* | 0.9120 | 0.8821 | 1.0787 | 0.034 |
| H(14B) | 2*i* | 0.7828 | 0.8680 | 1.0336 | 0.034 |
| H(15A) | 2*i* | 0.8663 | 1.0452 | 0.9518 | 0.033 |
| H(15B) | 2*i* | 0.7661 | 1.0621 | 1.0399 | 0.033 |
| H(16A) | 2*i* | 0.5893 | 1.1266 | 0.9391 | 0.027 |
| H(16B) | 2*i* | 0.6297 | 0.9982 | 0.9254 | 0.027 |
| H(18) | 2*i* | 0.5378 | 1.3140 | 0.8489 | 0.035 |
| H(19) | 2*i* | 0.5850 | 1.4675 | 0.8778 | 0.044 |
| H(20) | 2*i* | 0.8067 | 1.4707 | 0.8495 | 0.041 |
| H(21) | 2*i* | 0.9824 | 1.3205 | 0.7904 | 0.037 |
| H(22) | 2*i* | 0.9369 | 1.1654 | 0.7626 | 0.029 |
| H(24) | 2*i* | 0.5775 | 1.2429 | 0.6267 | 0.033 |
| H(25) | 2*i* | 0.3591 | 1.3116 | 0.5494 | 0.041 |
| H(26) | 2*i* | 0.1777 | 1.2617 | 0.6145 | 0.043 |
| H(27) | 2*i* | 0.2133 | 1.1445 | 0.7584 | 0.043 |
| H(28) | 2*i* | 0.4294 | 1.0801 | 0.8392 | 0.034 |
| H(29A) | 2*i* | 0.6977 | 0.8426 | 0.5484 | 0.032 |
| H(29B) | 2*i* | 0.7736 | 0.7765 | 0.6470 | 0.032 |
| H(30A) | 2*i* | 0.9520 | 0.7518 | 0.5393 | 0.034 |
| H(30B) | 2*i* | 0.8905 | 0.8840 | 0.4987 | 0.034 |
| H(31A) | 2*i* | 0.3223 | 0.7935 | 0.5700 | 0.045 |
| H(31B) | 2*i* | 0.2992 | 0.8079 | 0.6779 | 0.045 |
| H(32A) | 2*i* | 0.7998 | 0.3271 | 0.6013 | 0.054 |
| H(32B) | 2*i* | 0.6730 | 0.4431 | 0.6155 | 0.054 |

**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* | 0.86255(2) | 0.95915(1) | 0.71985(1) | 0.01645(8) | 0.01740(8) | 0.01422(8) | –0.00737(6) | 0.00206(5) | –0.00403(5) |
| Cl(1) | 2*i* | 1.08570(5) | 0.95577(4) | 0.77520(3) | 0.0203(2) | 0.0253(2) | 0.0302(2) | –0.0099(2) | –0.0009(2) | –0.0066(2) |
| Cl(2) | 2*i* | 0.85681(5) | 1.10702(4) | 0.58672(3) | 0.0292(2) | 0.0242(2) | 0.0203(2) | –0.0119(2) | 0.0048(2) | –0.0018(2) |
| P(1) | 2*i* | 0.88870(5) | 0.81658(4) | 0.83868(3) | 0.0224(2) | 0.0182(2) | 0.0170(2) | –0.0080(2) | 0.0014(2) | –0.0031(2) |
| P(2) | 2*i* | 0.70432(5) | 1.09385(4) | 0.79624(3) | 0.0178(2) | 0.0189(2) | 0.0159(2) | –0.0070(2) | 0.0015(2) | –0.0048(2) |
| N(1) | 2*i* | 0.7054(2) | 0.9481(1) | 0.6369(1) | 0.0219(8) | 0.0261(8) | 0.0179(7) | –0.0114(7) | 0.0025(6) | –0.0060(6) |
| N(2) | 2*i* | 0.9921(2) | 0.8468(1) | 0.6251(1) | 0.0211(8) | 0.0240(8) | 0.0182(7) | –0.0084(6) | 0.0035(6) | –0.0063(6) |
| C(1) | 2*i* | 0.7448(2) | 0.7704(2) | 0.8769(1) | 0.034(1) | 0.026(1) | 0.0208(9) | –0.0165(8) | 0.0091(8) | –0.0086(7) |
| C(2) | 2*i* | 0.7686(3) | 0.6767(2) | 0.9459(2) | 0.046(1) | 0.030(1) | 0.032(1) | –0.017(1) | 0.008(1) | –0.0014(9) |
| C(3) | 2*i* | 0.6571(3) | 0.6443(2) | 0.9748(2) | 0.070(2) | 0.036(1) | 0.036(1) | –0.034(1) | 0.022(1) | –0.008(1) |
| C(4) | 2*i* | 0.5243(3) | 0.7035(2) | 0.9357(2) | 0.058(2) | 0.056(2) | 0.039(1) | –0.043(1) | 0.025(1) | –0.023(1) |
| C(5) | 2*i* | 0.4993(3) | 0.7961(2) | 0.8684(2) | 0.039(1) | 0.057(2) | 0.031(1) | –0.029(1) | 0.014(1) | –0.021(1) |
| C(6) | 2*i* | 0.6096(2) | 0.8291(2) | 0.8393(2) | 0.034(1) | 0.037(1) | 0.023(1) | –0.020(1) | 0.0080(8) | –0.0104(8) |
| C(7) | 2*i* | 1.0258(2) | 0.6831(2) | 0.8126(1) | 0.029(1) | 0.0189(9) | 0.0202(9) | –0.0059(8) | 0.0034(8) | –0.0016(7) |
| C(8) | 2*i* | 0.9926(3) | 0.6046(2) | 0.7737(2) | 0.037(1) | 0.026(1) | 0.030(1) | –0.0127(9) | 0.0044(9) | –0.0063(8) |
| C(9) | 2*i* | 1.0993(3) | 0.5090(2) | 0.7477(2) | 0.054(2) | 0.026(1) | 0.040(1) | –0.014(1) | 0.007(1) | –0.013(1) |
| C(10) | 2*i* | 1.2384(3) | 0.4908(2) | 0.7585(2) | 0.049(2) | 0.026(1) | 0.041(1) | –0.001(1) | 0.006(1) | –0.008(1) |
| C(11) | 2*i* | 1.2728(3) | 0.5690(2) | 0.7953(2) | 0.030(1) | 0.034(1) | 0.042(1) | –0.001(1) | 0.001(1) | –0.004(1) |
| C(12) | 2*i* | 1.1674(2) | 0.6646(2) | 0.8224(2) | 0.034(1) | 0.024(1) | 0.032(1) | –0.0062(9) | –0.0014(9) | –0.0050(8) |
| C(13) | 2*i* | 0.9596(2) | 0.8223(2) | 0.9524(1) | 0.029(1) | 0.027(1) | 0.0193(9) | –0.0070(8) | –0.0035(8) | –0.0027(7) |
| C(14) | 2*i* | 0.8598(2) | 0.8948(2) | 1.0194(1) | 0.035(1) | 0.029(1) | 0.0169(9) | –0.0096(9) | –0.0023(8) | –0.0029(8) |
| C(15) | 2*i* | 0.7942(2) | 1.0221(2) | 0.9851(1) | 0.036(1) | 0.028(1) | 0.0199(9) | –0.0118(9) | –0.0030(8) | –0.0068(8) |
| C(16) | 2*i* | 0.6649(2) | 1.0595(2) | 0.9194(1) | 0.025(1) | 0.0253(9) | 0.0163(8) | –0.0096(8) | 0.0041(7) | –0.0062(7) |
| C(17) | 2*i* | 0.7339(2) | 1.2229(2) | 0.8046(1) | 0.025(1) | 0.0206(9) | 0.0186(9) | –0.0094(7) | –0.0015(7) | –0.0041(7) |
| C(18) | 2*i* | 0.6288(2) | 1.3145(2) | 0.8378(2) | 0.027(1) | 0.028(1) | 0.036(1) | –0.0107(9) | 0.0031(9) | –0.0112(9) |
| C(19) | 2*i* | 0.6567(3) | 1.4061(2) | 0.8545(2) | 0.036(1) | 0.025(1) | 0.047(1) | –0.0075(9) | 0.004(1) | –0.017(1) |
| C(20) | 2*i* | 0.7878(3) | 1.4082(2) | 0.8375(2) | 0.044(1) | 0.023(1) | 0.040(1) | –0.017(1) | –0.004(1) | –0.0082(9) |
| C(21) | 2*i* | 0.8923(2) | 1.3187(2) | 0.8029(2) | 0.031(1) | 0.027(1) | 0.038(1) | –0.0158(9) | –0.0008(9) | –0.0048(9) |
| C(22) | 2*i* | 0.8652(2) | 1.2263(2) | 0.7864(1) | 0.025(1) | 0.0223(9) | 0.027(1) | –0.0099(8) | 0.0007(8) | –0.0049(8) |
| C(23) | 2*i* | 0.5270(2) | 1.1535(2) | 0.7410(1) | 0.0199(9) | 0.0214(9) | 0.0221(9) | –0.0059(7) | 0.0015(7) | –0.0102(7) |
| C(24) | 2*i* | 0.5039(2) | 1.2231(2) | 0.6543(2) | 0.026(1) | 0.029(1) | 0.024(1) | –0.0071(8) | 0.0017(8) | –0.0063(8) |
| C(25) | 2*i* | 0.3737(3) | 1.2636(2) | 0.6079(2) | 0.035(1) | 0.034(1) | 0.026(1) | –0.0020(9) | –0.0072(9) | –0.0083(9) |
| C(26) | 2*i* | 0.2659(2) | 1.2344(2) | 0.6466(2) | 0.025(1) | 0.040(1) | 0.039(1) | –0.0015(9) | –0.0086(9) | –0.018(1) |
| C(27) | 2*i* | 0.2868(2) | 1.1653(2) | 0.7321(2) | 0.023(1) | 0.044(1) | 0.043(1) | –0.014(1) | 0.0020(9) | –0.015(1) |
| C(28) | 2*i* | 0.4165(2) | 1.1260(2) | 0.7798(2) | 0.023(1) | 0.031(1) | 0.029(1) | –0.0085(8) | 0.0034(8) | –0.0065(8) |

**Table 3.** Continued.

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| C(29) | 2*i* | 0.7627(2) | 0.8410(2) | 0.5974(2) | 0.028(1) | 0.030(1) | 0.026(1) | –0.0148(9) | 0.0040(8) | –0.0121(8) |
| C(30) | 2*i* | 0.9040(2) | 0.8284(2) | 0.5562(2) | 0.029(1) | 0.036(1) | 0.025(1) | –0.0144(9) | 0.0056(8) | –0.0150(9) |
| Cl(3) | 2*i* | 0.38813(7) | 0.93281(5) | 0.60206(5) | 0.0377(3) | 0.0420(3) | 0.0491(4) | –0.0170(3) | –0.0090(3) | –0.0054(3) |
| Cl(4) | 2*i* | 0.52654(7) | 0.68761(5) | 0.65548(5) | 0.0412(3) | 0.0419(3) | 0.0487(4) | –0.0141(3) | –0.0042(3) | –0.0086(3) |
| Cl(5) | 2*i* | 0.86922(9) | 0.47457(7) | 0.56853(7) | 0.0574(5) | 0.0610(5) | 0.0797(6) | –0.0337(4) | –0.0176(4) | 0.0147(4) |
| Cl(6) | 2*i* | 0.6830(1) | 0.41654(8) | 0.46336(7) | 0.145(1) | 0.0558(5) | 0.0616(5) | –0.0466(6) | –0.0494(6) | 0.0076(4) |
| C(31) | 2*i* | 0.3649(3) | 0.8044(2) | 0.6257(2) | 0.032(1) | 0.045(1) | 0.039(1) | –0.019(1) | 0.001(1) | –0.009(1) |
| C(32) | 2*i* | 0.7511(3) | 0.4075(2) | 0.5741(2) | 0.061(2) | 0.042(1) | 0.038(1) | –0.026(1) | –0.001(1) | –0.005(1) |

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