Synthesis and Crystal Structure of *cis*-Dichloro[1,4-bis(diphenylphosphino)-butane](ethylenediamine)Ruthenium Complex

Ismail WARAD,*† Nizam DIAB, Saud AL-RESAYES,***

***Department of Chemistry, King Saud University, Riyadh-11451, Kingdom of Saudi Arabia*

****Department of Chemistry, Arab American University-Jenin, P.O. Box 240 Jenin, Palestine*

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The crystal structure of *cis*-dichloro[1,4-bis(diphenylphosphino)butane](ethylenediamine)ruthenium, *cis*-[$RuCl_2$(dppb)en] has been synthesized and determined by X-ray diffraction. This compound found to crystallize with two dichloromethane solvent molecules in a Triclinic system, space group P-1, with the following cell parameters: a = 10.338(6) Å, b = 13.024(5) Å, c = 14.491(5) Å, α = 81.017(16) (°). β = 87.650(3) (°), γ = 66.950(3) (°). V = 1773.0(13) $Å^3$, Z = 2 and D_{calc} = 1.552 mg/m^3. The crystal structure was solved by Patterson method and refined on F^2 by full-matrix least squares to final value R = 0.0282 and wR = 0.0720 with 9430 reflections. The Ru(II) ion is octahedrally coordinated to one of dppb and en ligands as well as two chloride ions in full *cis*-configuration form.

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* To whom correspondence should be addressed

E-mail: ismeilkw@yahoo.com

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] 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.[2-4] 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] and there has been much interest in the chemistry of Ru(II) complexes bearing chiral diphosphine ligands such as BINAP ligand.[6] We have also studied Ru(II) complexes containing both separated P- and N-donor ligands.[3, 4, 7-9] These complexes proved to be excellent catalysts in the hydrogenation of α,ß-unsaturated ketones under mild condition.[4, 7] The source of the transferred hydrogen atom was attributed to a metal̄centered hydride. Generally, the most widely accepted theory is that at least one NH and a RuH unit is intimately involved in the hydride transfer process.[2]

The title compound which schemed in Fig 1 was prepared using published procedure,[3] but using trans-$RuCl_2(dppb)_2$ as starting precursor. Analysis from $C_{30}H_{36}Cl_2N_2P_2Ru$: Calcd: C, 54.71; H, 5.51; Cl, 10.77; N, 4.25%. Found: C, 54.57; H, 5.26; Cl, 10.84; N, 4.19%. Solution NMR spectra confirmed the *trans*-$RuCl_2$ isomer formation with no dichloromethane binding molecules. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 45.20. ^1H NMR ($CDCl_3$): δ (ppm) 1.52 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.63 (br, 4H, NH_2), 2.78 (br, 8H, PCH_2, NCH_2) 7.10-7.70 (m, 20H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 20.09 (s, $CH_2(CH_2)_2CH_2$), 26.81 (m, PCH_2), 44.44 (s, NCH_2), 129.07 (m, *m*-C_6H_5), 130.04 (s, *p*-C_6H_5), 132.21 (m, *i*–C_6H_5), 133.88 (br, *o*–C_6H_5). FAB–MS; *(m/z)*: 658.1 (M^+). The X-ray data of the yellow crystal of *cis*-$[RuCl_2(dppb)en].2CH_2Cl_2$ were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex, crystal and experimental data were listed in Table 1. A selected crystal was mounted on a Siemens P4 four-circle diffractometer by using a perfluorinated polyether as protecting agent. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used for the measurement of intensity data in the ω-scan mode at a temperature of 173(2) K. The intensity data was corrected for polarization and Lorentz effects. Structure solution and refinement were carried out using the Bruker

SHELXTL package. The structures were solved by Patterson synthesis, followed by identification of non-hydrogen atoms in successive Fourier maps. Refinement was carried out with full-matrix least-squares methods based on F^2, with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model. The molecular structure is shown in Fig. 2. atomic coordinates and temperature factors in Table 2, and selected bond distances and angles are listed in Table 3.

The ruthenium center is in a distorted octahedral environmental with a five-membered diamine ring coordinated in *cis* form *via* N1 and N2, a seven-membered bis(phosphine) ring coordinated in *cis* form *via* P1 and P2 as well as *cis*-dichloro atoms-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. Ru-N1 distance *trans* to Cl1 shorter than Ru-N2 distance *trans* to P2, 2.1213 Å and 2.1825 Å, respectively. Ru-P1 distance *trans* to Cl2 slightly shorter than Ru-P2 distance *trans* to N2, 2.2656 Å and 2.2782 Å, respectively. Ru-Cl1 distance *trans* to N1 shorter than Ru-Cl2 distance *trans* to P1 by 0.0337 Å.

Acknowledgements

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Table 1 Crystal and experimental data

Formula: $C_{32}H_{40}Cl_6N_2P_2Ru$
Formula weight: 828.37
Crystal system: Triclinic
space group: P-1 Z = 2
A = 10.338(6) Å $\alpha = 81.017(16)^o$
B = 13.024(5) Å $\beta = 87.65(3)^o$
C = 14.491(5) Å $\gamma = 66.95(3)^o$
V= 1773.0(13) $Å^3$
D_{calc} = 1.552 mg/m^3
No. of reflections used = 9430
Crystal size = 0.2 x 0.4 x 0.3 mm
$2\theta = 55.0^o$ with Mo-K_α
Max. and min. transmission = 0.4853 and 0.4037
Final R indices [I>2sigma(I)] R1 = 0.0282, wR2 = 0.0720
R indices (all data) R1 = 0.0325, wR2 = 0.0746
Measurement: Siemens P4
Program system: Bruker xscans
Structure determination: Patterson method (SHELXL-97)
Refinement method: Full-matrix on F^2 (SHELXL-97)
Largest diff. peak and hole ($eÅ^3$) 0.688 and -0.691

Table 2 Atomic coordinates and equivalent isotopic displacement parameters ($Å^2$ x 10^3)

Atom	*x*	*y*	*z*	*Ueq*
Ru(1)	8626(1)	9592(1)	7199(1)	16(1)
Cl(1)	10857(1)	9558(1)	7752(1)	25(1)
Cl(2)	8568(1)	11070(1)	5867(1)	24(1)
P(1)	8887(1)	8166(1)	8387(1)	19(1)
P(2)	7043(1)	10939(1)	7962(1)	17(1)
N(1)	7054(2)	9481(1)	6369(1)	21(1)
N(2)	9921(2	8468(1)	6251(1)	21(1)
C(1)	7448(2)	7704(2)	8769(1)	25(1)
C(2)	7686(3)	6767(2)	9459(2)	36(1)
C(3)	6571(3)	6443(2)	9748(2)	44(1)
C(4)	5243(3)	7035(2)	9357(2)	44(1)
C(5)	4993(3)	7961(2)	8684(2)	38(1)
C(6)	6096(2)	8291(2)	8393(2)	29(1)
C(7)	10258(2)	6831(2)	8126(1)	24(1)
C(8)	9926(3)	6046(2)	7737(2)	31(1)
C(9)	10993(3)	5090(2)	7477(2)	40(1)
C(10)	12384(3)	4908(2)	7585(2)	43(1)
C(11)	12728(3)	5690(2)	7953(2)	39(1)
C(12)	11674(2)	6646(2)	8224(2)	31(1)
C(13)	9596(2)	8223(2)	9524(1)	26(1)
C(14)	8598(2)	8948(2)	10194(1)	28(1)
C(15)	7942(2)	10221(2)	9851(1)	28(1)
C(16)	6649(2)	10595(2)	9194(1)	22(1)
C(17)	7339(2)	12229(2)	8046(1)	21(1)
C(18)	8626(1)	13145(2)	8378(2)	30(1)
C(19)	10857(1)	14061(2)	8545(2)	36(1)
C(20)	8568(1)	14082(2)	8375(2)	34(1)
C(21)	8887(1)	13187(2)	8029(2)	31(1)
C(22)	7043(1)	12263(2)	7864(1)	25(1)
C(23)	7054(2)	11535(2)	7410(1)	21(1)
C(24)	9921(2)	12231(2)	6543(2)	27(1)
C(25)	7448(2)	12636(2)	6079(2)	35(1)
C(26)	7686(3)	12344(2)	6466(2)	36(1)
C(27)	6571(3)	11653(2)	7321(2)	36(1)
C(28)	5243(3)	11260(2)	7798(2)	29(1)
C(29)	4993(3)	8410(2)	5974(2)	26(1)
C(30)	6096(2)	8284(2)	5562(2)	29(1)
Cl(3)	10258(2)	9328(1)	6021(1)	42(1)
Cl(4)	9926(3)	6876(1)	6555(1)	44(1)
Cl(5)	10993(3)	4746(1)	5685(1)	65(1)
Cl(6)	12384(3)	4165(1)	4634(1)	86(1)
C(31)	12728(3)	8044(2)	6257(2)	37(1)
C(32)	11674(2)	4075(2)	5741(2)	45(1)

Table 3 Selected bond lengths (Å) and bond angles (°)

Ru(1)-N(1)	2.1213(19)	P(2)-C(16)	1.840(2)
Ru(1)-N(2)	2.1825(17)	P(2)-C(17)	1.845(2)
Ru(1)-P(1)	2.2656(9)	P(2)-C(23)	1.848(2)
Ru(1)-P(2)	2.2782(10)	N(1)-C(29)	1.483(3)
Ru(1)-Cl(1)	2.4551(14)	N(2)-C(30)	1.485(3)
Ru(1)-Cl(2)	2.4888(9)	C(13)-C(14)	1.531(3)
P(1)-C(7)	1.846(2)	C(14)-C(15)	1.531(3)
P(1)-C(1)	1.847(2)	C(15)-C(16)	1.543(3)
P(1)-C(13)	1.854(2)	C(29)-C(30)	1.513(3)
N(1)-Ru(1)-N(2)	79.15(7)	P(1)-Ru(1)-Cl(1)	86.58(3)
N(1)-Ru(1)-P(1)	100.71(5)	P(2)-Ru(1)-Cl(1)	101.21(4)
N(2)-Ru(1)-P(1)	93.82(6)	N(1)-Ru(1)-Cl(2)	82.06(5)
N(1)-Ru(1)-P(2)	93.51(6)	N(2)-Ru(1)-Cl(2)	82.38(5)
N(2)-Ru(1)-P(2)	170.07(5)	P(1)-Ru(1)-Cl(2)	174.84(18)
P(1)-Ru(1)-P(2)	94.13(4)	P(2)-Ru(1)-Cl(2)	90.03(4)
N(1)-Ru(1)-Cl(1)	163.10(5)	Cl(1)-Ru(1)-Cl(2)	89.61(3)
N(2)-Ru(1)-Cl(1)	85.21(6)		

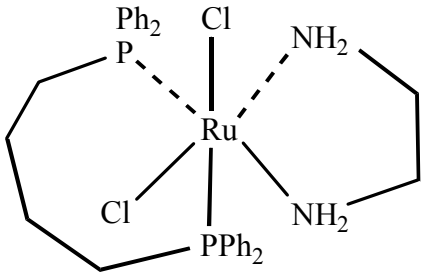

Fig. 1 Chemical structure of the present compound.

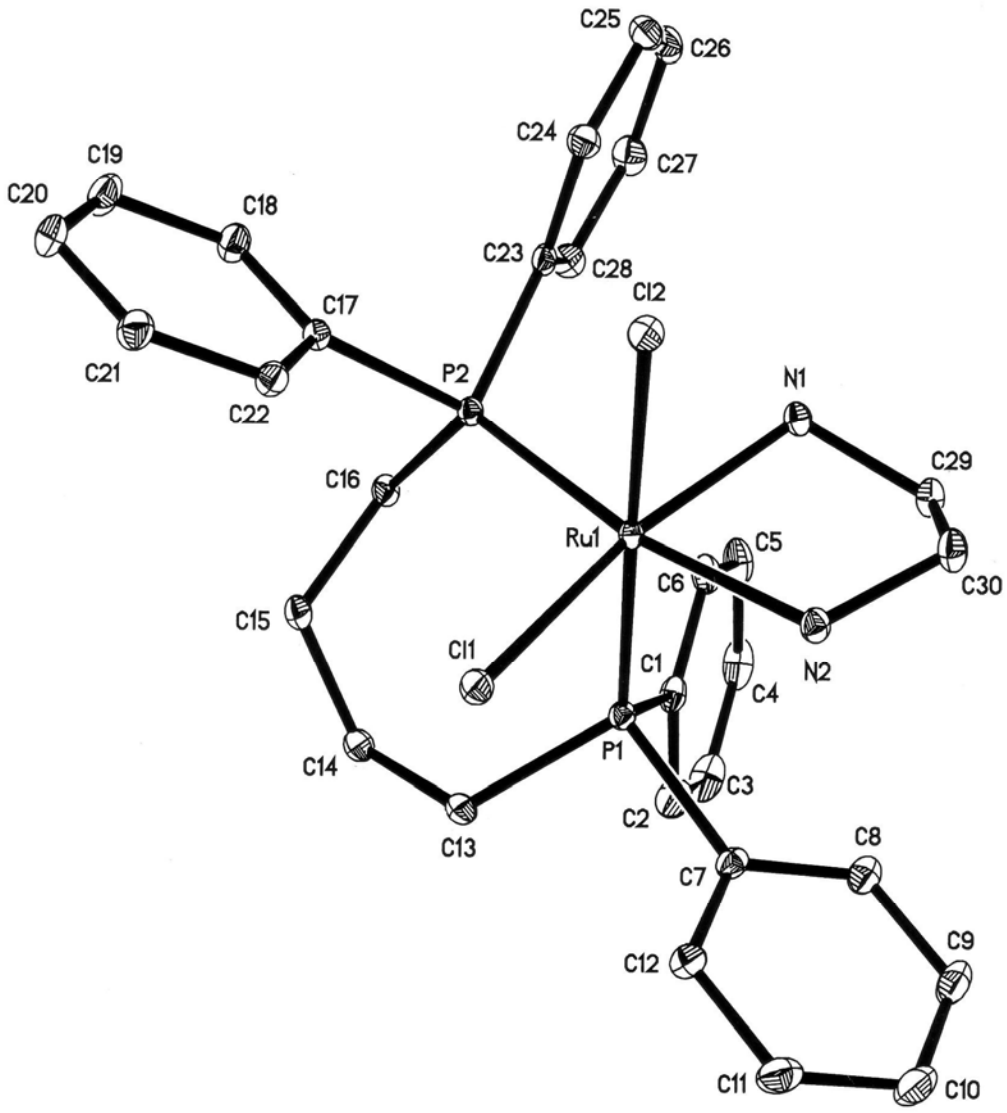

Fig. 2 Molecular structure of *cis*-[$RuCl_2$(dppb)en]. H atoms and CH_2Cl_2 solvent molecules are omitted for clarity.