

Cis- & trans-isomerism in $[\text{Cl}_2\text{Ru}(\text{dppb})\text{N-N}]$ complexes: Synthesis, structural characterization and X-ray crystal structure of dichloromethane solvated cis-diaminebis(diphenylphosphinobutane)-ruthenium(II) complex

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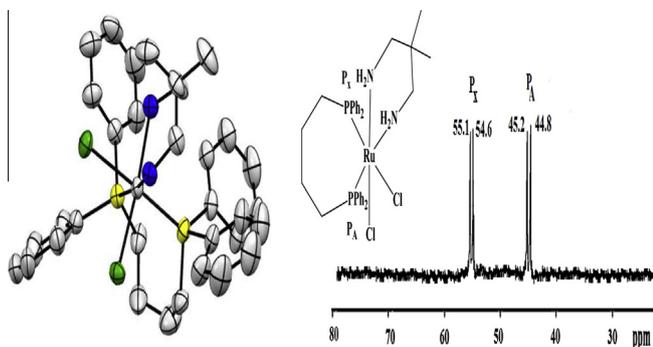
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HIGHLIGHTS

- Synthesis of *cis* & *trans* isomer of $[\text{RuCl}_2(\text{dppb})(\text{N-N})]$ complexes.
- Crystal structure of *cis*- $[\text{RuCl}_2(\text{dppb})(\text{N-N})]$ isomer.
- *cis* & *trans* isomerization is supported by ^{31}P NMR.

GRAPHICAL ABSTRACT



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ABSTRACT

Three diamine-bis(diphenylphosphinobutane)ruthenium(II) complexes, isolated from the reaction of $[\text{Cl}_2\text{Ru}(\text{dppb})]$ with diamines viz., 2,2-dimethyl-1,3-diaminopropane, 1,2-diaminocyclohexane and 1,8-diaminonaphthalene are reported. The synthesized complexes have been characterized on the basis of various physico-chemical studies viz., EDX, IR, FAB-MS, UV/Vis, NMR, TG-DTG and EXAFS studies. ^{31}P NMR investigations confirm that the complex **3** is in *cis* form while the complexes 1–2 appear in *trans* form. The structure of complex **3** has been additionally determined by single crystal X-ray diffraction showing solvated dichloromethane. Furthermore, complex **3** crystallizes as monoclinic unit cell with $P2(1)/n$ space group.

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Introduction

Phosphine ligands have been intensively used in coordination chemistry because of their electron donating properties [1–4]. Among them, diphosphines have received much attention due to their tendency to form more stable complexes than their non

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chelating phosphine analogs under the harsh reaction conditions required for catalysis [5–9]. In the last few years, lot of work has been reported on the dynamic behavior of transition metal complexes containing monodentate and bidentate ligands, and it still remains an active area of research interest [10,11]. In recent years, the chemistry of Ru(II) complexes possessing a chelating diphosphine (P-P) and diamine (N-N) ligands have been a topic of great interest, and represent an attractive class of compounds on account of their various catalytic and bioinorganic chemistry applications [3,11–16]. Furthermore, Noyori discovered that $[\text{RuCl}_2(\text{diphosphine})_2(\text{diamine})_2]$ complex can catalyze the hydrogenation of unfunctionalized ketones showing chemoselectivity on C=O bond over the more reactive C=C bond through a favored pericyclic transition state [11]. Moreover, the chelate diphosphine ligands decreased the number of isomers compared to monodentate phosphine ligands, which de-complicated the structural identification of synthesized complexes [17]. Therefore, in continuation of our ongoing interest in chemistry of various diamines diphosphineruthenium(II) complexes and their applications [17–20], herein, we have reported the synthesis of diamine[bis(diphenylphosphino)butane] ruthenium(II) complexes of general formula $[\text{RuCl}_2(\text{dppb})(\text{N-N})]$, obtained from the reaction of 1,4-bis(diphenylphosphino)butane with various diamines viz., 2,2-dimethyl-1,3-diaminopropane, 1,2-diaminocyclohexane and 1,8-diaminonaphthalene, and finally we got *cis*- and *trans*- $[\text{RuCl}_2(\text{dppb})(\text{N-N})]$ isomer complexes. The thermodynamically favoured isomer, *cis*- $[\text{RuCl}_2(\text{dppb})(\text{N-N})]$ with 2,2-dimethyl-1,3-propanediamine as diamine co-ligand, was confirmed by single crystal X-ray measurements.

Experimental

Materials, and instrumentations

All reactions were carried out in argon atmosphere by using standard high vacuum and Schlenk-line techniques. 1,4-bis(diphenylphosphino)butane (dppb), $[\text{RuCl}_2(\text{PPh}_3)_2]$, 1,2-diaminocyclohexane, 2,2-dimethyl-1,3-diaminopropane and 1,8-diaminonaphthalene were available from Merck and used as received. Elemental analyses were carried out on Elementar Vario EL analyzer. High-resolution $\{^1\text{H}\}$, $\{^{13}\text{C}\{^1\text{H}\}\}$, and $\{^{31}\text{P}\{^1\text{H}\}\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR and FAB-MS spectra were obtained on a Bruker IFS 48 FT-IR spectrometer and Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (*m/z*), respectively.

Synthesis of diamine[bis(diphenylphosphino)butane]ruthenium(II)-complexes (1–3)

The precursor compound $[\text{RuCl}_2(\text{PPh}_2)_2\text{dppb}]$ was obtained by substitution reaction of equivalent amount of $[\text{RuCl}_2(\text{Ph}_3)_3]$ and dppb in dichloromethane in argon atmosphere. The precursor compound, $[\text{RuCl}_2(\text{PPh}_2)_2\text{dppb}]$ on treatment with corresponding diamines (10% excess) viz., 1,8-diaminonaphthalene, 1,2-diaminocyclohexane and 2,2-dimethyl-1,3-diaminopropane in equimolar ratio in dichloromethane leads to the color change in reaction from green to yellow. The volume of colored solution was concentrated to 1 ml under reduced pressure followed by the addition of 30 ml of diethyl ether to cause precipitation. The obtained precipitate was isolated and re-crystallized in dichloromethane-*n*-hexane mixture to obtain analytically pure compound. Crystals suitable for X-ray measurement were obtained for complex **3**. No crystal was found suitable for X-ray measurement for complexes **1** and **2**.

1. $[\text{RuCl}_2(\text{PPh}_3)_2(\text{dppb})]$ precursor (0.1 g) was treated with the naphthalene-1,8-diamine ligand (0.06 g, 0.08 mmol). Yield (85%), yellow crystal, m.p. (decomp.). 355 °C. IR (KBr, ν cm^{-1}): 3360, 3140, 2870 and 314 cm^{-1} , assigned to $-\text{NH}_2$, Ph—CH, alkyl—CH and Ru—Cl, respectively. $\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 1.58 (m, 4H, PCH_2CH_2), 2.62 (m, 4H, PCH_2), 2.98 (b, 4H, NH_2), 7.00–7.80 (3 m, 26H, C_6H_5), $\{^{31}\text{P}\{^1\text{H}\}\}$ NMR (CDCl_3): δ (ppm) for *trans* δ (ppm) 48.2. $\{^{13}\text{C}\{^1\text{H}\}\}$ NMR (CDCl_3): δ (ppm) 23.90 (s, PCH_2CH_2), 26.70 (m, PCH_2), 129.00–138.00 (8s, Ph), FAB-MS; (*m/z*) 756.1 $[\text{M}^+]$. Anal. Found: C, 60.42; H, 5.08; N, 3.58; Cl, 9.51. Calc. for $\text{C}_{38}\text{H}_{38}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C, 60.32; H, 5.06; N, 3.70; Cl, 9.37. 62%; UV-Vis CHCl_3 : 210, 250, 280, 520 nm.
2. $[\text{RuCl}_2(\text{PPh}_3)_2(\text{dppb})]$ precursor (0.1 g) was treated with the 2-cyclohexane-1,2-diamine ligand (0.05 g, 0.07 mmol). Yield (90%), yellow-brown powder, m.p. 314 °C (dec.). $\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 0.88–2.14 (m, 10H, C_6H_{10}), 1.81 (m, 2H, CH_2), 2.49–2.81 (m, 8H, PCH_2 , PCH_2CH_2 , NH_2), 7.12–7.66 (m, 20H, C_6H_5). $\{^{31}\text{P}\{^1\text{H}\}\}$ NMR (CDCl_3): δ (ppm) 46.23. $\{^{13}\text{C}\{^1\text{H}\}\}$ NMR (CDCl_3): δ (ppm) 19.31 (s, CH_2), 24.96 (s, $\text{CH}_2\text{CH}_2\text{CH}$), 26.15 (m, PCH_2), 36.39 (s, NCHCH_2), 57.62 (s, NCHCH_2), 128.16 (m, *m*- C_6H_5), 129.15 (m, *p*- C_6H_5), 133.11 (m, *o*- C_6H_5). FAB-MS; (*m/z*): 712.1 (M^+). Anal. Found: C, 57.48; H, 5.86; Cl, 10.01; N, 4.07. Calc. for $\text{C}_{33}\text{H}_{40}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C, 57.30; H, 5.94; Cl, 9.95; N, 3.93%. UV-Vis CHCl_3 : 240, 280, 510 nm.
3. $[\text{RuCl}_2(\text{PPh}_3)_2(\text{dppb})]$ precursor (0.1 g) was treated with the 2,2-dimethyl-1,3-propanediamine ligand (0.02 g, 0.07 mmol). Yield (85%), yellow crystal, m.p. 272 °C (decomp.). IR (KBr, ν cm^{-1}): 3380–3270, 3180, 2900–2800 and 270–285 cm^{-1} , assigned to $-\text{NH}_2$, Ph—CH, alkyl—CH and Ru—Cl, respectively. $\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 0.83 (s, 6H, CH_3), 1.48 (m, 4H, PCH_2CH_2), 2.54 (m, 4H, PCH_2), 2.78, 2.80 (b, 8H, CH_2N , NH_2), 7.20–7.70 (2 m, 20H, C_6H_5), $\{^{31}\text{P}\{^1\text{H}\}\}$ NMR (CDCl_3): δ , *cis*, (ppm) (AX pattern with $\delta_A = 45.0$ and $\delta_X = 54.7$ ppm, coupling constant of P–P atoms, $J_{AX} = 48.8$ Hz) $\{^{13}\text{C}\{^1\text{H}\}\}$ NMR (CDCl_3): δ (ppm) 22.70 (s, PCH_2CH_2), 25.13 (s, CH_3), 26.03 (m, PCH_2), 49.92 (s, NCH_2), 128.13 (m, *m*- C_6H_5), 128.96 (s, *p*- C_6H_5), 133.92 (m, *o*- C_6H_5), 136.59 (m, *i*- C_6H_5). FAB-MS; (*m/z*) 700.1 $[\text{M}^+]$. Anal. Found: C, 56.46; H, 6.17; N, 3.97; Cl, 10.24. Calc. for $\text{C}_{33}\text{H}_{42}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C, 56.57; H, 6.04; N, 4.00; Cl, 10.12%. UV-Vis CH_2Cl_2 : 325, 495 nm.

X-ray structural analyses

All measurements were performed on $\omega/2\theta$ -scan technique on CAD4 (Nonius) automatic diffractometer, with graphite monochromatized Mo $\text{K}\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The control of the intensity without appreciable decay (1.2%) yielded 9022 unique reflections, of which 10558 exhibited $I > 2.0\sigma(I)$. After Lorenz and polarization corrections, the absorption corrections were applied using ψ -scans. The non-hydrogen atoms were refined anisotropically by the full-matrix least-square techniques using the program SHELXL97 [21]. All of the hydrogen atoms bonded to C atoms were geometrically located and treated using a riding model, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$.

Results and discussion

Earlier, we reported ruthenium complexes of diphenylphosphinobutane, dppb with three different diamine co-ligands viz., 1,3-diaminopropane, 2-methyl-1,2-ethanediamine, and 1,4-diaminobutane, and we isolated single crystal of ruthenium complex with 1,3-diaminopropane as *trans*- Cl_2Ru -isomer without solvent. Unfortunately, we could not find suitable crystal structure of the remaining complexes [17]. Furthermore, in the synthesis of $[\text{RuCl}_2(\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{PPh}_2)_2)(\text{diamine})]$ complexes, we used

diphosphine as 1,3-diphosphine ligand with C=C function group ($\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{PPh}_2)$), and that was complete different system [18]. Herein this article, reported mixed ligand *cis/trans* complexes were obtained by the reaction of $[\text{RuCl}_2(\text{PPh}_3)_2(\text{dppb})]$ with excess amount of the entirely different diamines viz., 1,2-diaminocyclohexane, 2,2-dimethyl-1,3-diaminopropane and 1,8-diaminonaphthalene (Scheme 1) in dichloromethane. Different bidentate diamine used as co-ligands in complex synthesis were used to stabilize both *cis* and *trans*- $[\text{Cl}_2\text{Ru}(\text{dppb})(\text{N-N})]$ isomer complexes. All the desired complexes were characterized on the basis of elemental analyses, EDX, IR, FAB-MS, UV/Vis, NMR, TG-DTG and EXAFS studies. Additionally, one of the complex with 2,2-dimethyl-1,3-diaminopropane was determined by single crystal X-ray diffraction showing complex exists as *cis*- Cl_2Ru -isomer with one molecule of dichloromethane. Unfortunately, we could not find other crystals suitable for single crystal X-ray diffraction. Furthermore, we introduced EXAF in the current work as a power tool to confirm the coordination number while we did not use it in our previous work.

EDX analysis

Formation of complexes was confirmed by EDX measurements indicating the number of signals coming from Ru, P, Cl, N and C atoms are consistent with the proposed molecular formula of the complexes [Fig. 1S].

Mass spectra

The FAB-MS molecular ion peak(s) $[\text{M}^+]$ m/z observed at 756.1, 712.1 and 700.1 were consistent with the proposed molecular formulae of their respective complexes **1**, **2** and **3**, respectively. The

FAB-MS spectrum of complex **3** showed a molecular ion peak of $[\text{M}^+]$ $m/z = 700.1$, corresponding to the molecular formula of its parent ion $[\text{C}_{33}\text{H}_{42}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}]^+$ at 100% of the base peak intensity. The main first three fragments that appeared in the spectrum correspond to $[\text{M}^+]$ $m/z = 664.1$ $[\text{C}_{33}\text{H}_{41}\text{ClN}_2\text{P}_2\text{Ru}]^+$, 40%, $([\text{M}^+]-\text{HCl})$, and 628.2 $[\text{C}_{33}\text{H}_{40}\text{N}_2\text{P}_2\text{Ru}]^+$ 20%, $([\text{M}^+]-\text{H}_2\text{Cl}_2)$ [Fig. 2S].

IR spectral investigations

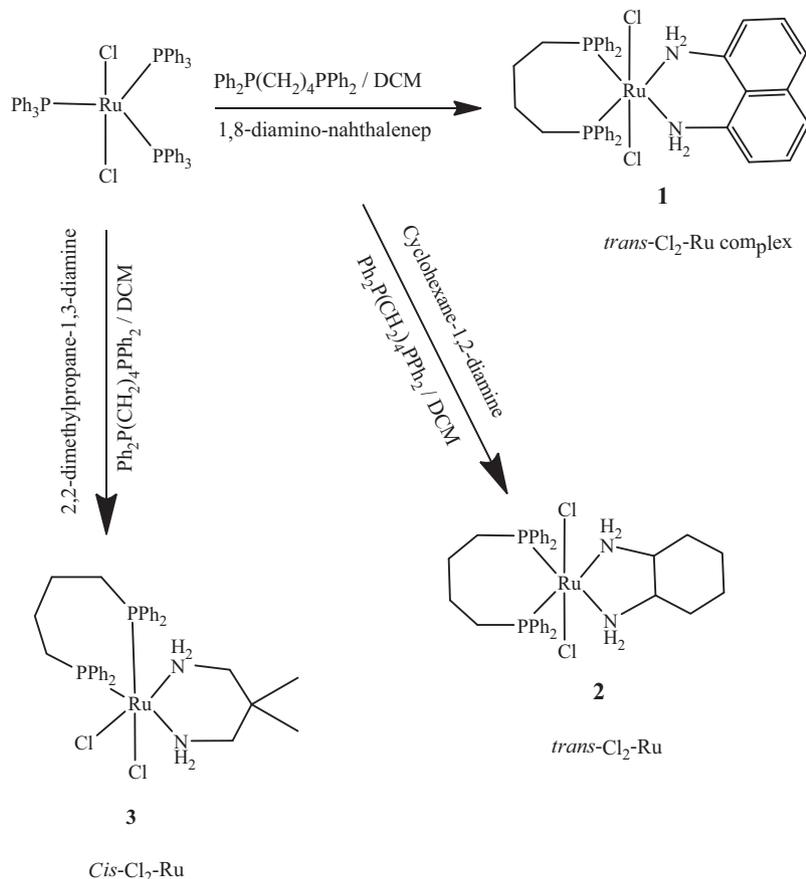
Preliminary identification of the synthesized complexes has been obtained from IR spectra which revealed four main sets of characteristic absorptions in the ranges of 3380–3270, 3180, 2900–2800 and 270–285 cm^{-1} , assigned to $-\text{NH}_2$, $\text{Ph}-\text{CH}$, alkyl- CH and $\text{Ru}-\text{Cl}$ stretching vibrations, respectively. All other function group vibrations appeared at their expected positions [Fig. 3S].

Electronic absorption spectral

The electronic absorption spectra of the reported complexes, recorded in dichloromethane at room temperature, showed intense transitions in the UV/Vis region. The UV bands observed at 200–300 nm range have been assigned to intra-ligand $\pi-\pi^*/n-\pi^*$ transitions [22,23], while the bands observed at ~ 510 nm have been tentatively assigned to M-L charge transfer transitions (MLCT) [Fig. 4S] [24].

EXAFS measurement

EXAFS of complex **1** was carried out to support structural formula of the synthesized complex as well as to determine the bond lengths between the Ruthenium center and the coordinating P, N,



Scheme 1. Schematic representation of synthesis of Ru(II) complexes.

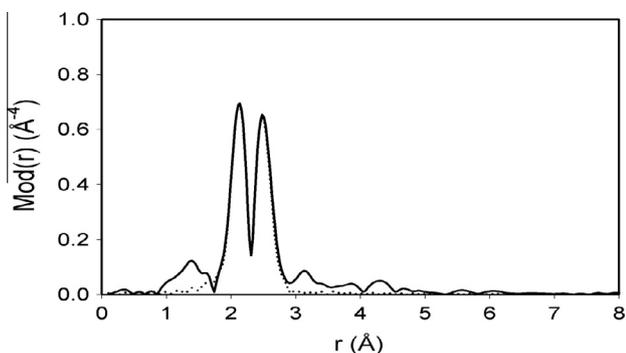


Fig. 1. Experimental (solid line) and theoretical (dotted line) Fourier Transform plot of the desired complex **1**.

and Cl atoms of the ligands. The k^3 weighted EXAFS function of complex can be described by six different atom shells. For the most intense peak of the Fourier Transform, two equivalent phosphorus, two nitrogen atoms and two chlorine atoms with Ru–P, Ru–N and Ru–Cl bond distances of 2.27, 2.18 and 2.42 Å, respectively, are reported [Fig. 1].

NMR investigation

Structure of the reported complexes was further supported by $\{^1\text{H}\}$, $\{^{13}\text{C}\{^1\text{H}\}$ NMR and $\{^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies. The $\{^1\text{H}\}$ NMR spectra Ru(II) complexes have been recorded in CDCl_3 , and their assignments are given in experimental part. Several characteristic sets of signals attributed to the dppb and diamine ligands are observed. The integration of the $\{^1\text{H}\}$ resonances confirm that dppb and diamine ratio is in agreement with the structural composition of *cis*- and *trans*- $[\text{Cl}_2\text{Ru}(\text{dppb})(\text{N-N})]$ complexes. $\{^{31}\text{P}\}$ NMR

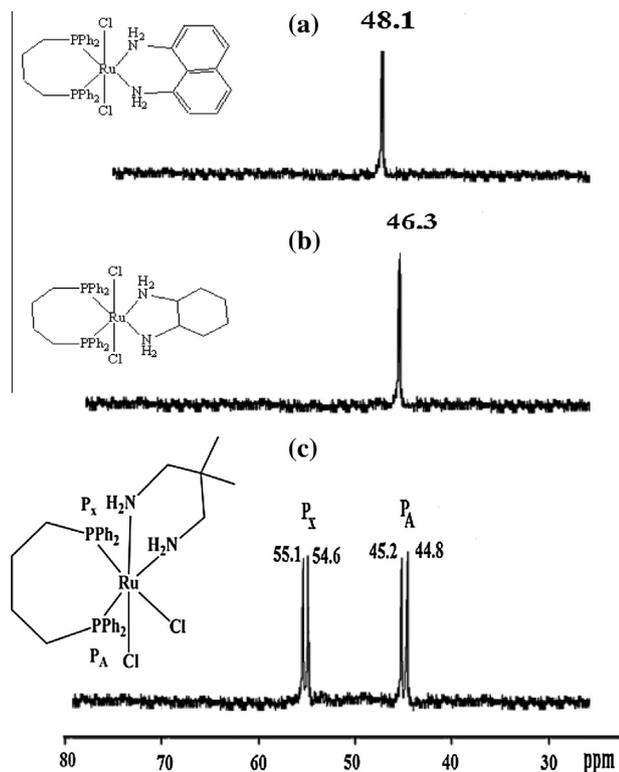


Fig. 2. $\{^{31}\text{P}\{^1\text{H}\}$ NMR spectra showing of singlet *trans*- Cl_2Ru (a) and (b), and (c) dd *cis*- Cl_2Ru with inequivalent P atoms.

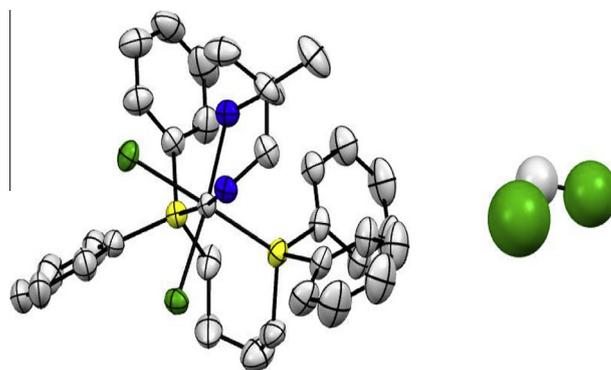


Fig. 3. ORTEP view of complex **3**, *cis*- $[\text{Cl}_2\text{Ru}(\text{dppb})(\text{N-N})]\cdot\text{H}_2\text{Cl}_2$. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms were omitted for clarity.

spectra revealed the formation of the kinetic favoured *trans*-isomer with equivalent number of phosphorus atoms (P *trans* to N) singlet $\{^{31}\text{P}\delta \sim 46.2$ ppm and 48.1 ppm for complex **1** and **2** at room temperature, respectively [Fig. 2a and b] [17,22–24]. The $\{^{31}\text{P}\}$ NMR spectrum of complex **3** revealed two doublets indicating the formation of thermodynamically favoured *cis*-isomer with an unequal number of phosphorus atoms at room temperature (AX pattern with $\delta_A = 45.0$ and $\delta_X = 54.7$ ppm, coupling constant of P–P atoms, $J_{AX} = 48.8$ Hz) [Fig. 3c]. The $\{^{31}\text{P}\}$ chemical shifts and the $\{^{31}\text{P}\}$ – $\{^{31}\text{P}\}$ coupling constants are consistent with a *cis* arrangement of P atoms in dppb in complex **3**. The $\{^{31}\text{P}\}$ chemical shifts ~ 45 ppm which sited to P_A belongs to P *trans* to N, while P *trans* to Cl (P_X) sited to higher chemical shift ~ 55 ppm [18,25].

TGA/DTG studies

The TGA/DTG studies of the complexes were investigated at temperature 25–900 °C at a heating rate of 10 °C/min. The TGA/DTG graph clearly shows that there is no weight loss up to 25–295 °C, thus indicating the absence of coordinated or uncoordinated water. All the three complexes undergo one step decomposition with weight loss experimentally at 82.5%, thus showing that coordinated chlorides, diamine, dppb ligands have been de-structured at temperature 300–400 °C with exothermic DTG peaks at

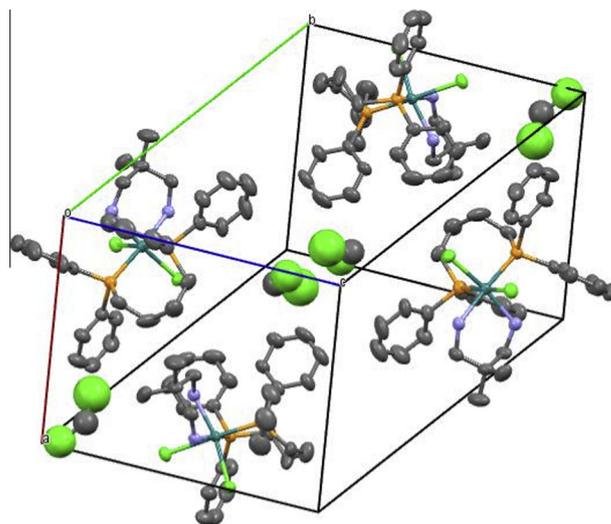


Fig. 4. View of packing of *cis*- $[\text{Cl}_2\text{Ru}(\text{dppb})(\text{N-N})]$, complex **3** in the unitcell.

Table 1
Crystal data and structure refinement for the complex.

Empirical formula	C ₃₄ H ₄₄ Cl ₄ N ₂ P ₂ Ru	
Formula weight	785.6	
Temperature	191(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 12.260(3)$ Å	$\alpha = 90^\circ$
	$b = 20.879(3)$ Å	$\beta = 98.999(13)^\circ$
	$c = 14.8783(11)$ Å	$\gamma = 90^\circ$
Volume	3761.5(10) Å ³	
Z	4	
Density (calculated)	1.312 Mg/m ³	
Absorption coefficient	0.739 mm ⁻¹	
F(000)	1532	
Crystal size	0.60 × 0.50 × 0.50 mm ³	
Theta range for data collection	3.05–28.00°	
Index ranges	–16 ≤ h ≤ 16, –1 ≤ k ≤ 27, –1 ≤ l ≤ 19	
Reflections collected	10,558	
Independent reflections	9022 [R(int) = 0.0371]	
Completeness to theta = 28.00°	96.5%	
Absorption correction	Psi-Scan	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	9022/0/541	
Goodness-of-fit on F ²	1.077	
Final R indices [I > 2σ(I)]	R1 = 0.0541, wR2 = 0.1536	
R indices (all data)	R1 = 0.0927, wR2 = 0.1733	
Largest diff. peak and hole	1.342 and –0.849 e Å ⁻³	

340.71 °C [Fig. 5S]. The final residue was analyzed by IR spectra and identified as ruthenium oxide (RuO).

X-ray structure determination of the complex

The molecular structure of complex **3** has been determined by single crystal X-ray diffraction, and the ORTEP diagram and packing mode is given in Figs. 3 and 4, respectively. Complex crystallizes in the monoclinic system with space group P2(1)/n. The crystal data and structure refinement is summarized in Table 1. Ruthenium center being coordinated by two bidentate ligands in a distorted octahedral geometry as shown by the angles around the metal ion, listed in Table 2. The selected bond distances are also given in Table 2. The structure shows two independent diamine and diphosphine ligands and one solvated dichloromethane molecule per asymmetric unit. The orientations of the ligands are different from those of complexes **1** and **2** showing complex exists in cis-[RuCl₂(dppb)(N-N)] isomeric form. The distorted octahedral

Table 2
Selected bond lengths (Å) and angles (°) for the complex.

Ru1	Cl1	2.517(1)	N1 Ru1 N2	84.5(1)
Ru1	Cl2	2.429(1)	Cl1 Ru1 Cl2	89.43(4)
Ru1	P1	2.271(1)	N1 Ru1 P2	171.7(1)
Ru1	P2	2.286(1)	N2 Ru1 Cl2	165.9(1)
Ru1	N1	2.194(4)	Cl1 Ru1 P1	176.58(4)
Ru1	N2	2.128(4)	N1 Ru1 P1	96.1(1)
N1	C3	1.476(6)	P1 Ru1 P2	92.21(4)
N2	C1	1.488(6)	Cl2 Ru1 P1	88.04(4)
P1	C11	1.847(6)	Cl2 Ru1 P2	96.80(4)
P1	C101	1.843(5)	N1 Ru1 Cl2	83.7(1)
P2	C14	1.837(6)	N2 Ru1 Cl1	81.2(1)
P2	C211	1.853(5)	N2 Ru1 P2	93.8(1)
P2	C201	1.836(4)	P1 Ru1 P2	92.21(4)

coordination environment around the ruthenium centre exists with two Ru–N distances of 2.194 Å and 2.128 Å, two Ru–Cl distances of 2.517 Å and 2.429 Å and two Ru–P distances equal to 2.271 Å and 2.286 Å. The coordination angle of the diamine chelate ring results in a distinct N–Ru–N angle of 84.5°, departing from ideal value by up to approximately 5.5°, due to six-membered ring chelating nature of dppb ligand. The P–Ru–P angle is equal to 92.2° departing from ideality due to seven-membered ring chelating nature of the dppb ligand. The dichloro Cl–Ru–Cl angle was found to be 89.43°. In the crystal structure, there are a number of RuCl₂···HN contacts smaller than 3.0 Å, indicating the presence of unconventional intra-hydrogen bonds [25].

Conclusion

In this work, we reported the synthesis of three thermodynamically favoured isomers of general formula, [Cl₂Ru(dppb)(N-N)], and characterized them by various spectroscopic studies viz., IR, UV/Vis, FAB-MS, TG-DTA, EXAF, EDX and NMR. Additionally, complex **3** was established by single crystal X-ray measurements. *Cis*- and *trans*- isomerism in the complexes were established by ³¹P NMR and single crystal X-ray diffraction measurements. The X-ray crystal structure determination confirms that complex **3** is *cis*-dichloro type isomer. The structure shows two independent diamine and diphosphine ligands and one solvated dichloromethane molecule per asymmetric unit. The orientations of the diamine and diphosphine ligands are different which indicates that complex **3** structure belongs to the *cis* isomer, which is further supported by two doublets indicating the formation of the thermodynamically favoured *cis*-isomer with an unequivalent number of phosphorus atoms at room temperature. Furthermore, ³¹P NMR spectra clearly reveal that both complex **1** and **2** exists as *trans* isomers showing singlet at room temperature. Moreover, it is anticipated that these type of complexes might be strong candidates for various types of catalytic activities.

Acknowledgments

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Appendix A. Supplementary material

Crystallographic data corresponding to the structural analysis have been deposited within the Cambridge Crystallographic Data Centre, CCDC No. 953474 for complex {[*cis*-Cl₂Ru(P-P)(N-N)]·H₂CCl₂}. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2014.08.039>.

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