Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 105 (2013) 466–473

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Trans/*cis* isomerization of [$RuCl_2$(diphosphine)(diamine)] complexes: Synthesis, X-ray structure and catalytic activity in hydrogenation

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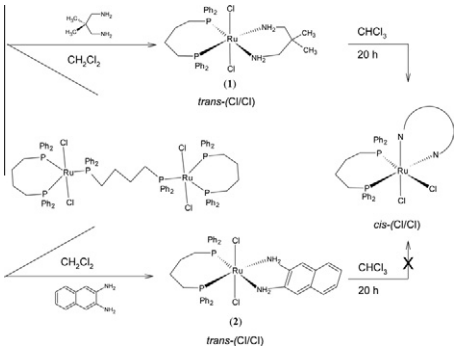
HIGHLIGHTS

- Two new ruthenium(II) complexes of type *trans*-[$RuCl_2$(dppb)(N—N)] were made available.
- *Trans* to *cis* isomerization reaction of complex **1** was monitored by $^{31}P\{^1H\}$ NMR.
- The thermodynamically favored *cis*-**1** isomer of complex **1** was confirmed by XRD crystal measurements.
- Synthesized complexes have showed very good catalytic activity in the hydrogenation of cinnamic aldehyde.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 September 2012
Received in revised form 6 November 2012
Accepted 30 November 2012
Available online 20 December 2012

Keywords:
Ruthenium(II) complexes
Trans/*cis* isomerism
Diamine
Diphosphine
Hydrogenation

ABSTRACT

The diamine (N—N) co-ligand 2,2-dimethyl-1,3-propanediamine and 2,3-diaminophathalene react individually with [$RuCl_2(dppb)_2$(μ-dppb)] to afford complexes with kinetically stable *trans*-[Cl_2-Ru(dppb)(N—N)] as the favoured isomer. The thermodynamically stable *cis*-[Cl_2Ru(dppb)(N—N)] isomer of complex **1** was formed from the *trans*-**1** isomer. The *trans* to *cis* isomerization reaction was conducted in $CHCl_3$ at RT and monitored by $^{31}P\{^1H\}$ NMR. The structures of the desired complexes were characterized via elemental analyses, IR and, UV–visible spectroscopy, FAB-MS and NMR. The structure of the *cis*-**1** isomer was determined by single crystal X-ray measurements. Both the *trans*-**1** and *cis*-**1** isomers were shown to have a significant catalytic role in selective hydrogenation reactions under mild conditions using cinnamic aldehyde as typical model reaction.

Introduction

A variety of phosphines and diphosphines have been studied recently due to their ability to chelate transition metals [1–18]. These studies, in turn, offer a broad framework for the design of new approaches for electro-catalysis, photolysis, bioinorganic chemistry, and asymmetrical catalytic hydrogenation [5–19]. Mixed-ligand [Ru(II)-(diamine)(phosphine)] complexes also serve as excellent hydrogen transfer catalysts [1–9]. The exchange of monodentate phosphine ligands, such as triphenylphosphine (PPh_3) or ether-phosphine (P–O), and bidentate phosphine ligands, such as 1,3-bis-diphenylphosphinepropane (dppp) or 1,1-bis(diphenylphosphino-methyl)ethane; (dppme), ligands of ruthenium(II) complexes with several types of diamine ligands to synthesize [Ru(II)-(diamine)(phosphine)] complexes represents one ongoing

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http://dx.doi.org/10.1016/j.saa.2012.11.108

area of investigation [1–5]. Due to their remarkable performance in the selective hydrogenation of unsaturated carbonyl compounds, mixed [Ru(II)-(diamine)(phosphine)] complexes have received considerable attention in recent years [7–18].

Improvements in catalytic reactivities can be achieved by the appropriate design of structural, electronic, and stereochemical features surrounding the coordination sphere of complexes, and dramatic changes in the catalytic activity in certain reactions can be attributed to small differences in the coordination sphere of the transition metals [19–21].

The *trans*/*cis* isomerism of ruthenium complexes of disubstituted-2,2′-bipyridine derivatives have been extensively investigated, although to date, bidentate biphosphine-based ligands with mixed diamine ligands have not been studied yet in details yet [22–24]. Due to the presence of the P-ligand in the backbone of such coordinated complexes, the *trans*/*cis* isomerism behavior during reaction processes can be easily monitored by $^{31}P\{^{1}H\}$ NMR [2–5].

As a part of our ongoing studies on the synthesis of new ligands and complexes for their structural coordination and studies of their applications [1–5,25–29], herein we report the synthesis and structural characterization of two new complexes and offer facile probing of structural isomerization of *trans*-**1** to *cis*-**1** via $^{31}P\{^{1}H\}$ NMR single-crystal X-ray crystallography. Both *cis* and *trans*-**1** isomeres were shown to have a significant catalytic role in the selective hydrogenation of the carbonyl group of cinnamic aldehyde under mild conditions.

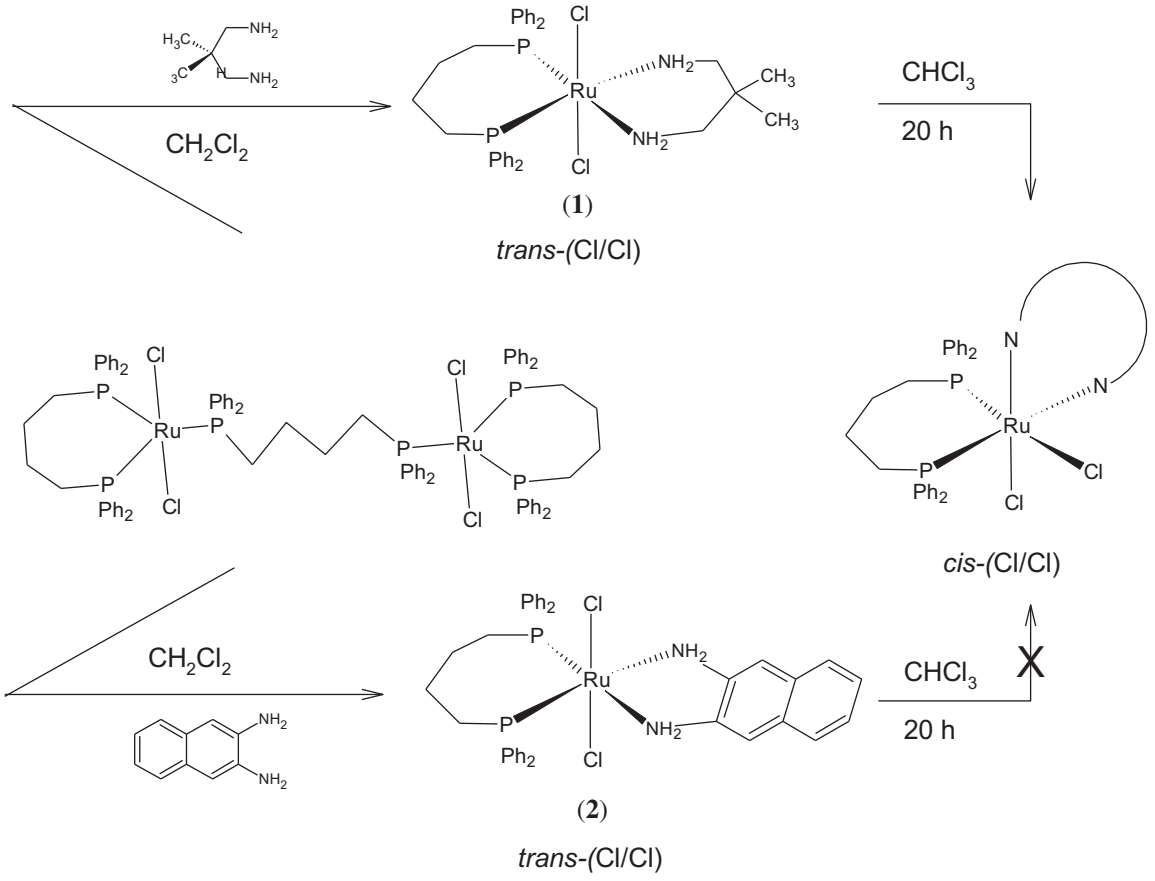
Experimental

Conditions, materials and physical measurements

All reactions were performed under an inert atmosphere (argon) using standard high vacuum and Schlenk-line techniques. The compounds 1,4-bis(diphenylphophino)butane (dppb), 2,2-dimethyl-1,3-propanediamine and 1,2-diaminphathaline were obtained from Merck and used as received. The [$RuCl_2(dppb)_2$-(μ-dppb)] was previously prepared in our lab. [30]. Elemental analyses were performed using an Elementar Varrio EL analyzer. High-resolution ^{1}H, $^{13}C\{_{1}H\}$, DEPT 135, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. FT-IR and FAB-MS data 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. The analyses of the hydrogenation experiments were performed on a GC 6000 Vega Gas 2 (Carlo Erba Instrument) with a FID and capillary columns PS 255 [10 m, carrier gas, He (40 kPa), integrator 3390 A (Hewlett–Packard)].

Synthesis of the [$RuCl_2$(dppb)diamine complexes]

The complex [$RuCl_2(dppb)_2$(μ-dppb)] was treated in situ with one equivalent of diamine ligands in chloroform under an inert atmosphere. The green color directly turned yellow or brown after the diamine addition. Air-sensitive mixed-ligand complexes



Scheme 1. Synthesis of complexes **1–2**.

{Ru(II)-(diamine)(bis-[diphenylphosphino] butane)} were obtained in good yields (Scheme 1).

General procedure for the preparation of the complexes

The corresponding diamine (at 10% excess) was dissolved in 10 mL of dichloromethane and the resulting solution was added drop-wise to a stirred solution of $[RuCl_2(dppb)_2(\mu\text{-}dppb)]$ in 10 mL of dichloromethane. The reaction mixture was stirred at room temperature under an inert atmosphere for 30 min until the green color of the solution changed. The resulting solution was concentrated by vacuum to 1 mL followed by the addition of 20 mL of *n*-hexane to precipitate compounds **1** and **2**. The resulting precipitates were washed three times with diethyl ether and *n*-hexane (10 mL each) to remove off the free ligands and other impurities.

Trans-**1**: $[RuCl_2(dppb)_2(\mu\text{-}dppb)]$ (0.1 g, 0.069 mmol) was treated with the 2,2-dimethyl-1,3-propanediamine ligand (0.01 g, 0.07 mmol), to produce **1**. Yield (88%), yellow crystal, m.p. 276 °C (decomp.). IR (KBr, $\mu\ cm^{-1}$): 3350, 3150, 2870 and 315, 255 cm^{-1}, assigned to —NH_2, Ph—CH, alkyl—CH and Ru—Cl, respectively. ^1H NMR ($CDCl_3$ δ (ppm) 0.73 (s, 6H, CH_3), 1.48 (m, 4H, PCH_2-$C\underline{H}_2$), 2.47 (m, 4H, PCH_2), 2.74, 2.82 (b, 8H, CH_2N, NH_2), 7.19–7.60 (2 m, 20H, C_6H_5), $^{31}P\{^1H\}(CDCl_3)$: ∂ (ppm) 46.87. $^{13}C\{^1H\}$ NMR ($CDCl_3$): ∂ (ppm) 22.70 (s, $PCH_2\underline{C}H_2$), 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*) 700.4 [M^+]. Anal. Found: C, 56.26; H, 6.17; N, 3.87; Cl, 10.74. Calc. for $C_{33}H_{42}Cl_2N_2P_2Ru$: C, 56.57; H, 6.04; N, 4.00; Cl, 10.12%, UV–Vis $CHCl_3$: 330, 480 nm.

2-: $RuCl_2(dppb)_2(\mu\text{-}dppb)$ (0.1 g, 0.069 mmol) was treated with the 2,3-diaminophathalene ligand (0.012 g, 0.07 mmol), to produce **2** Yield (83%), yellow crystal, m.p. 305 °C. IR (KBr, $\mu\ cm^{-1}$): 3380, 3110, 2880 and 314, 254 cm^{-1}, assigned to —NH_2, Ph—CH, alkyl—CH and Ru—Cl, respectively. ^1H NMR ($CDCl_3$); δ (ppm) 1.52 (m, 4H, $PCH_2C\underline{H}_2$), 2.57 (m, 4H, PCH_2), 2.920(b, 4H, NH_2), 7.00–7.80 (3 m, 26H, C_6H_5), $^{31}P\{^1H\}(CDCl_3)$: ∂ (ppm) for *trans* ∂ (ppm) 46.87. $^{13}C\{^1H\}$ NMR ($CDCl_3$): ∂ (ppm) 23.80 (s, $PCH_2\underline{C}H_2$), 26.55 (m, PCH_2), 128.00–137.00 (8s, Ph), FAB-MS; (*m*/*z*) 756.1 [M^+]. Anal. Found: C, 60.52; H, 5.16; N, 3.55; Cl, 9.48. Calc. for $C_{38}H_{38}Cl_2N_2P_2Ru$: C, 60.32; H, 5.06; N, 3.70; Cl, 9.37. 62%; UV–Vis $CHCl_3$: 325, 495 nm.

*General procedure for the preparation of cis-**1** from trans-**1***

Trans-**1** (0.1 g, 1 mmol) was dissolved in 15 mL of $CHCl_3$. The reaction mixture was stirred at room temperature under an inert atmosphere for approximately 20 h. During the reaction, the samples were taken periodically and subjected to $^{31}P\{^1H\}$ NMR until all of the *trans*-**1** was converted to *cis*-**1**.

Cis-**1**-: m.p. 256 °C. IR (KBr, $\mu\ cm^{-1}$): 34250, 3120, 2890 and 315, 255 cm^{-1}, assigned to —NH_2, Ph—CH, alkyl—CH and Ru—Cl, respectively $^{31}P\{^1H\}(CDCl_3)$: δ (ppm) dd AX pattern δ_A = 45.8 and δ_X = 55.2 ppm (J_{PP} = 48.2 Hz).

General procedure for the catalytic studies

The respective complexes (0.02 mmol), and the co-catalysts (0.20 mmol) (KOH or K_2CO_3) and cinnamic aldehyde (2.0 mmol) were placed together in a 100 mL a Schlenk pressure tube. The solid mixture was stirred and warmed during the evacuation process, during which the Schlenk tube was filled and refilled with argon several times to assure an inert atmosphere, 2-propanol (40 mL) was added to the reaction mixture, which was then sonicated for 10 min to completely dissolve the reaction mixture. The mixture was vigorously stirred, degassed by two freeze–thaw cycles, and then pressurized with dihydrogen at 3 bars. The reaction mixture was vigorously stirred at RT for 1 h. During the hydrogenation process samples were taken from the reaction mixture after the gas was removed to control the conversion and turnover frequency. The samples were inserted into a gas chromatograph using a special glass syringe, and the various type of kind of reaction products were compared with authentic samples.

X-ray structural analyses for complexes

All measurements were performed in the $\omega/2\theta$-scan technique on a CAD4 (Nonius) automatic diffractometer with graphite monochromatized Mo Kα radiation [31]. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The details of the data collection and refinement are given in Table 1. The control of the intensity without appreciable decay (1.2%) yielded 7367 unique reflections, of which 6516 exhibited $I > 2.0(I)$. After Lorenz and polarization corrections, the absorption corrections were applied using -scans [32,33]. The structure was solved by direct methods using the program SIR-97 [24]. The non-hydrogen atoms were re-

Table 1
Crystal data and structure refinement for *cis*-**1**.

$C_{33}H_{40}Cl_2N_2P_2Ru\ CHCl_3$	V = 3621.18 (3) Å^3
M_r = 817.95	Z = 4
Monoclinic, $P2_1/n$	D_x = 1.504 g cm^{-3}
a = 12.377 (2) Å	Mo Kα radiation: (λ = 0.71073 Å)
b = 19.394 (3) Å	Cell parameters from 25 reflections
c = 15.427 (2) Å	θ = 2.0–27.0°
α = 90.00 (3)°	μ = 0.917 mm^{-1}
β = 102.012 (12)°	T = 173 K
γ = 90.00 (1)°	Crystal size = 0.8 × 0.4 × 0.4 mm^3
CAD4 (Nonius) diffractomer	R_{int} = 0.0216
$\omega/2\theta$ scan	θ_{max} = 2.10–25.25°
Absorption correction: numerical	$h = -1 \rightarrow 14$
T_{min} = NN, T_{max} = NN	$k = -23 \rightarrow 1$
7971 Measured reflections	$l = -18 \rightarrow 18$
7367 Independent reflections	3 Standard reflections
6545 Reflections with $I > 2\sigma(I)$	Every 100 reflections
Refinement on F^2	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)]$ = 0.048	Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 1.5015P]$ where $P = ((F_o^2 + 2(F_c^2)/3$
$wR(F^2)$ = 0.1255 (6545)	$(\Delta/\sigma)_{max}$ = 0.997
S = 1.093	$\Delta\rho_{max}$ = 1.74 e Å^{-1}
6545 Reflections	$\Delta\rho_{min}$ = −0.67 e Å^{-1}
429 Parameters	Extinction correction: SHELXL
CCDC number	784617

fined anisotropically by the full-matrix least-square techniques using the program SHELXL-97 [34]. 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 $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

Results and discussion

Synthesis of the complexes

Complexes **1** and **2** were isolated in good yield using a simple, 1 h, RT reaction of excess diamine with the green $RuCl_2(dppb)_2$-(μ-dppb) starting complex in chloroform under an inert atmosphere. The reaction was monitored by the green color change upon the addition of the diamine ligands, as well as by UV–Vis, IR and $^{31}P\{^1H\}$ NMR spectral analyses (Scheme 1).

IR spectral investigations

The IR spectra of the desired complexes were examined in comparison relative to the spectra of free ligands. The IR spectra of the $RuCl_2(dppb)_2$(μ-dppb) starting complex and complex **1** are shown in Fig. 1, $RuCl_2(dppb)_2$(μ-dppb) showed no peaks at 3400; and 1560 cm^{-1}, which are attributed to —NH_2, stretching and bending vibrations, respectively, as shown in Fig. 1a. The vibration of this functional group appeared upon the addition of diamine to $RuCl_2(dppb)_2$(μ-dppb) for the preparation of complex **1,** as shown in Fig. 1b. In particular, complexes **1** and **2** revealed four main sets of characteristic absorptions in the ranges of 3400–3200, 3190–3000, 2950–2820 and 270–285 cm^{-1}, which can be assigned to —NH_2, Ph—CH, alkyl—CH and Ru—Cl stretching vibrations, respectively. All other function group vibrations appeared at their expected positions as in Fig. 1.

Electronic absorption spectral studies

The electronic absorption spectra of green $RuCl_2(dppb)_2$(μ-dppb), and complexes **1** and **2** were acquired in chloroform at room temperature. To avoid any structural changes, the electronic absorption spectra of the [$RuCl_2(dppb)_2$(μ-dppb)] complexes were recorded before and after the direct addition of diamine to prepare complexes **1** and **2**, as in Fig. 2, the coordination process is visually detected by observing the change in color from green to yellow and brown upon addition of the diamine, consistent with the formation

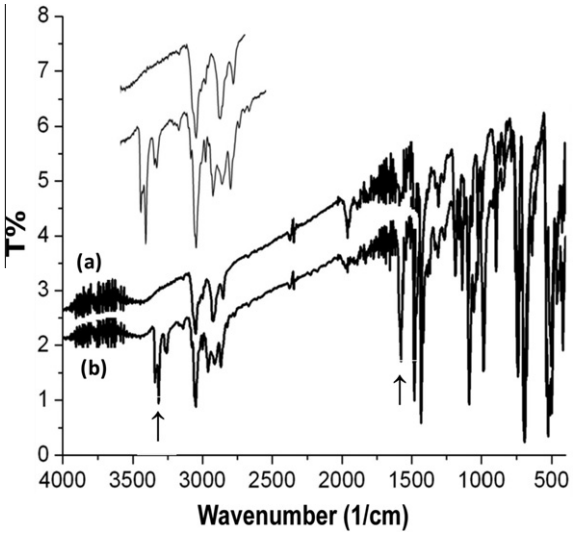


Fig. 1. IR-KBr disk spectra of (a) $RuCl_2(dppb)_2$(μ-dppb) and (b) complex **1**.

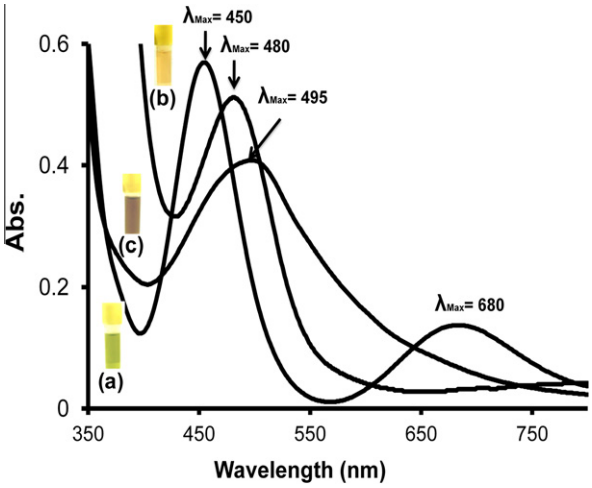


Fig. 2. UV–Vis spectra of (a) green Rucl2(dppb)2(μ-dppb), (b) yellow 1, (c) brown 2 complexes direct dissolved in $CHCl_3$ At RT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of complexes **1** and **2**, respectively. These complexes formed intensely colored solutions, and thus very low concentrations were used (10^{-4} M). The desired complexes displayed intense transitions in the UV–Vis region. Bands at the high-energy end at 200–340 nm range have been previously assigned to intra-ligand π–π^*/n–π^* transitions [22,29]. Base on the intensity and position, the lowest energy transitions in the visible region at 400–520 nm have been tentatively assigned to $M_{d\pi}$–L_{π^*} metal to ligand charge transfer transitions (MLCTs) [35,36]. Additionally, the $RuCl_2(dppb)_2$(μ-dppb) complex revealed a visible broad band at 680 nm, which can be primarily attributed to *d*–*d* electron transfer [36].

Mass spectra

The observed molecular ion peak (s) at *m/z* 700.4 and 756.1 corresponding to complexes **1** and **2**, respectively, are consistent with the proposed molecular formula. The FAB-MS spectrum of complex **1** shows a molecular ion peak [M^+] *m/z* = 700.4, which corresponds to the molecular formula of its parent ion $[C_{31}H_{42}Cl_2N_2P_2Ru]^+$ at 50% of the base peak intensity. The main first three fragments that appeared in the spectrum correspond to *m/z* = 665.1 ($[C_{31}H_{38}ClN_2P_2Ru]^+$, 80%, [$M^+$]-Cl), and 629.9 ($[C_{31}H_{38}N_2P_2Ru]^+$, 50%, [$M^+$]-$HCl_2$) (Fig. 3).

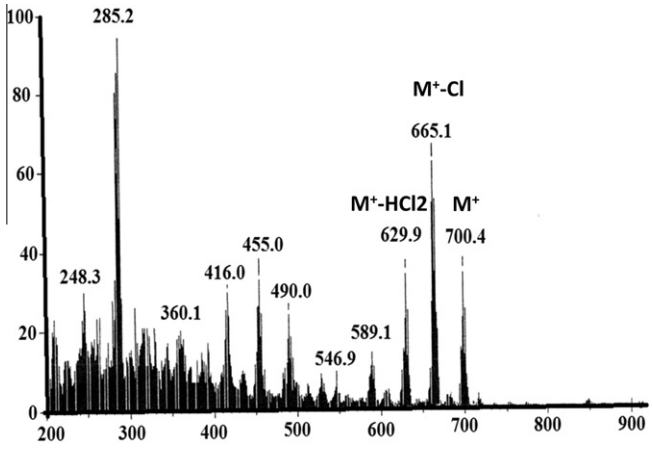


Fig. 3. FAB-MS spectrum of complex **1**.

NMR investigation

The NMR spectra also corroborate the structure of the desired complexes. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded directly after dissolving the complexes in $CDCl_3$ solution as described in 'Experimental'. Several characteristic sets of observed signals are attributed to the diamines and dppb ligands. The chemical shifts and integration of the DEPT 135 $^{13}C\{^{1}H\}$ and ^{1}H NMR resonances confirms the dppb to diamine coordination ratio which is in agreement with the structural composition, as shown in Fig. 4.

The $^{31}P\{^{1}H\}$ NMR spectra of direct dissolved complexes **1** and **2** in $CDCl_3$, showed only one signal at 46.87 and 47.15 ppm, respec-

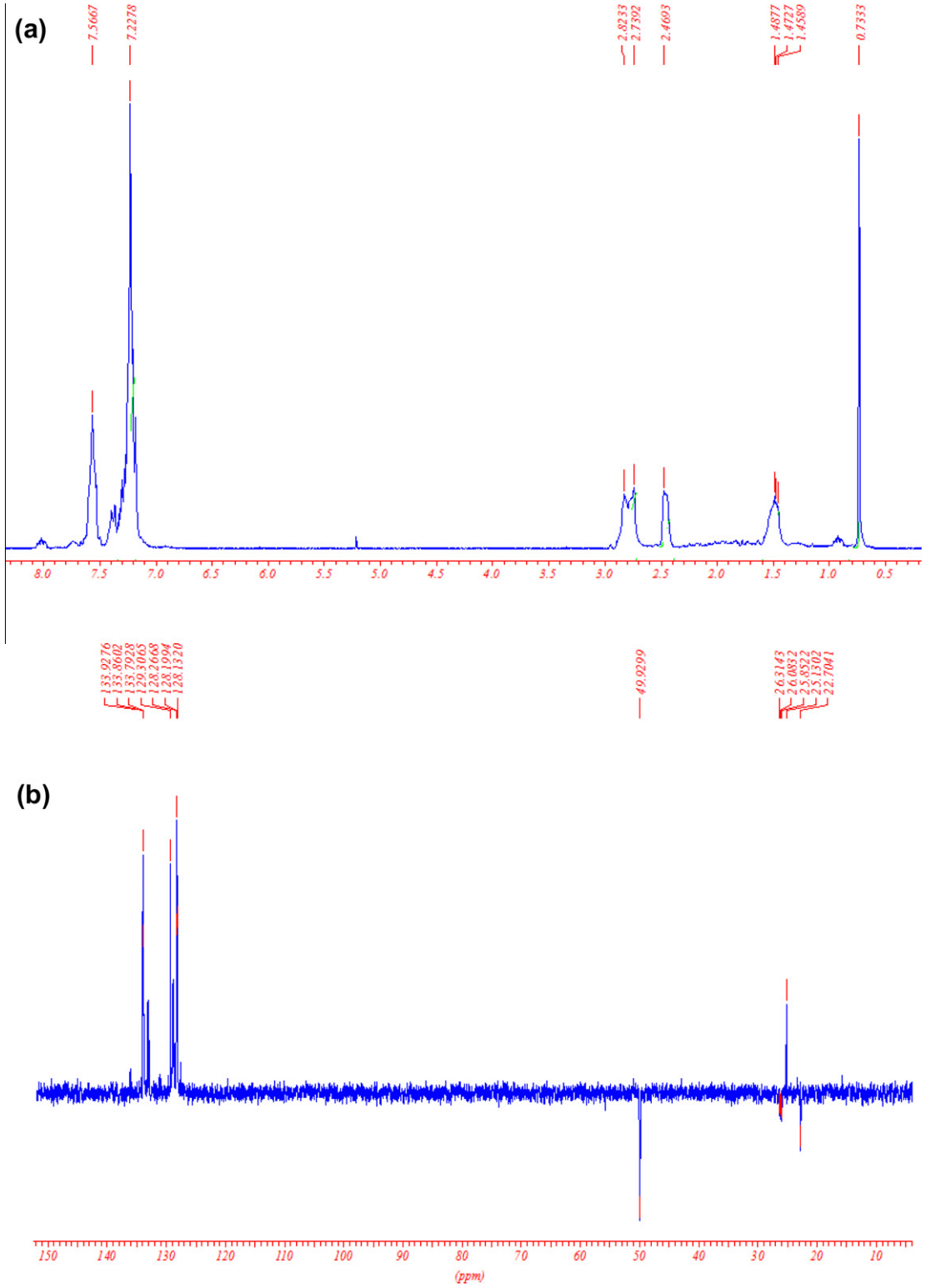


Fig. 4. (a) ^{1}H and (b) 135 dept $^{13}C\{^{1}H\}$ NMR spectra corroborates the structure of *trans*-**1** in $CDCl_3$ at RT.

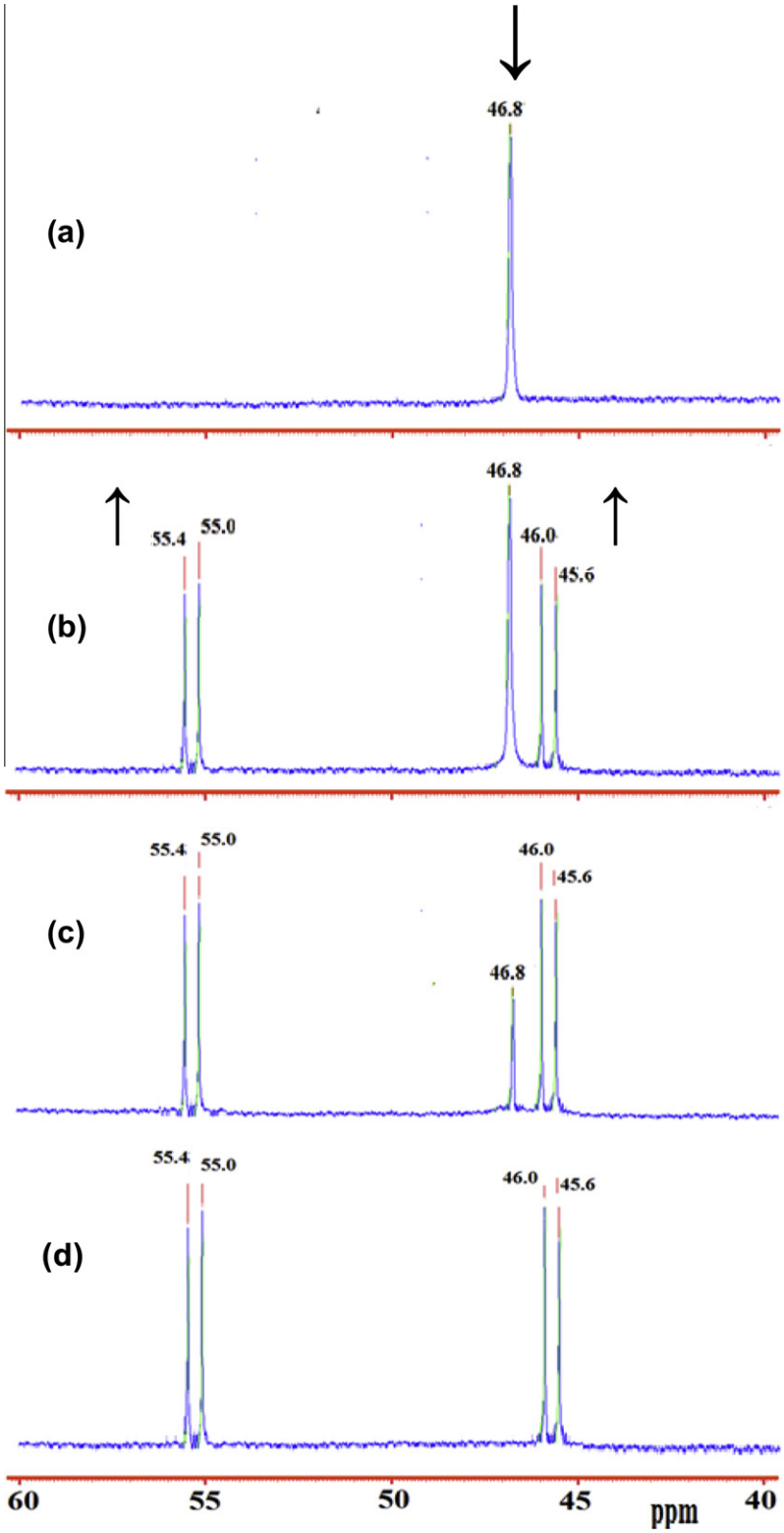


Fig. 5. Time-dependent $^{31}P\{^{1}H\}$ NMR spectroscopic of: (a) *trans*-**1** complex with C_2v equivalent P atoms at δp = 46.8 ppm, direct dissolved in $CDCl_3$ (b) after 2 h of stirring, mixture of *trans*-**1** and *cis*-**1** isomers with *trans*-**1** predominate, (c) after 12 h, mixture of *trans*-**1** and *cis*-**1** isomers with dd in-equivalent P atoms *cis*-**1** predominate isomer, (d and c) after 20 h, only *cis*-**1** isomer was recorded.

tively as shown in Fig. 5. This result is expected for a kinetically favored *trans*-**1** configuration with C_2v symmetrical arrangements of the P atoms, where the nitrogen atoms are *trans* to the phosphorus atoms, as shown in Scheme 1. In our studies of such complexes, we demonstrated that the *trans*-Cl_2Ru isomer, which the nitrogen atoms *trans* to the phosphorus atoms (*trans* effect) is chemically and structurally favoured over any other isomers.

It is interesting to point out that the process of isomerization the from *trans* to the *cis* isomer was first observed through $^{31}P\{^{1}H\}$ NMR experiments. In the case of the spectrum for *trans*-**1**

a fresh solution of complex **1** in $CHCl_3$ showed one singlet at 46.87 ppm for the kinetically favored *trans*-**1** isomer. The intensity of this singlet decreased with time as the complex became dynamic in the chloroform solution. Two doublets indicating the formation of *cis*-**1** (the thermodynamically favored isomer) with unequivalent number of phosphorus atoms were observed by $^{31}P\{^{1}H\}$ NMR at room temperature (AX pattern with $\delta_A = 45.8$ and $\delta_X = 55.2$ ppm, coupling constant of P—P atoms, $J_{AX} = 48.2$ Hz) (Fig. 5). The ^{31}P chemical shifts and the ^{31}P—31P coupling constants are consistent with a *cis* arrangement of the P atoms in dppb.

To verify the spatial molecular structure of the *cis*-**1** isomer, obtained from *trans*-**1**, we performed an X-ray structure analysis for crystal of complex **1**.

*X-ray structure determination of complex **1***

A suitable single crystal of *cis*-**1** was obtained by evaporating the concentrated parent solution of full *cis*-**1,** as confirmed by ^{31}P NMR, using a soft-vacuum desiccator, several trials were performed until suitable crystals were collected. A yellow crystal of *cis*-**1** having approximate dimensions of $0.8 \times 0.4 \times 0.4\ mm^3$ was mounted on a glass fiber.

The structure shows two independent diamine and diphosphine ligands and one solvated chloroform molecule per asymmetric unit. The orientations of the diamine and diphosphine ligands are different which indicates that the structure belongs to the *cis*-Cl_2Ru isomer. The diphosphine portion of atomic numbering scheme is shown in Fig. 6.

The geometry surrounding the Ru(II) center has an octahedral environment formed by two chlorine atoms in the *cis* geometric configuration and two P—P and N—N ligands. The Ru—Cl bond distances are 2.4404(4) and 2.5264(3) Å. The Ru—N bond distances, which in range from 2.1268(3) to 2.1978(3) Å are similar to those of Ru—N in the *trans*-Cl_2Ru(P—P)(N—N)] complex with a range 2.1994(19)–2.2030(2) Å, where N—N′ is an analogs of N—N (the P—P ligand is the same for both complexes) [29].

In the molecular structure of *cis*-**1**, the two central phenyl rings of the two P atoms coordinated to the Ru metal form dihedral angles of 34.8(5) and 68.8(6)° for C7—P1---P2—C23 and C1—P1---P2—C27, respectively. We note a slight deformation around Ru1; where the angles are different from 96°[N1—Ru1— N2 = 84.21(6)°, N1—Ru1—P1 = 94.72(9)°, N1—Ru1— P2 = 98.78(10)°, N2—Ru1—P1 = 170.16(10)°, N2—Ru1—P2 = 96.78(9)°, and Cl1—Ru1—Cl2 = 90.74(5)°]. The deviation in this octahedral geometry is also confirmed by the angles of the atoms in *trans* positions, which are consistent different from 180°; P1—Ru1—N2 = 170.16(1)° and P2—Ru1—Cl2 = 176.35(1)°. The crystal structure of the title complex is stabilized by inter- and intra-molecular C—H. . .Cl—CCl_2H type-hydrogen bonding interactions that form a 3D network. The packing and hydrogen bonding interactions are illustrated in Fig. 7.

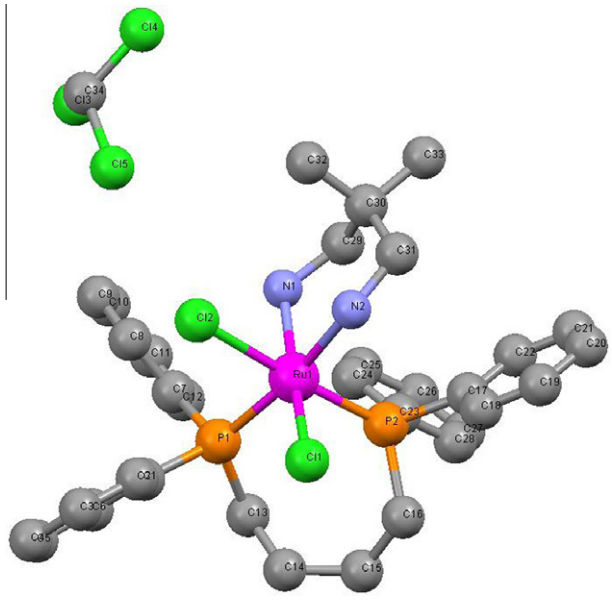


Fig. 6. ORTEP view of the *cis*-**1** with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms were omitted for clarity.

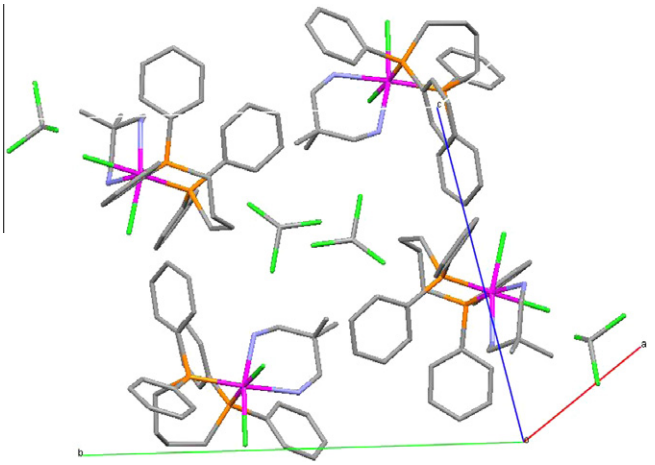


Fig. 7. View of packing of *cis*-**1** in the unitcell.

Catalytic activity of complexes in the hydrogenation of cinnamic aldehyde

Cinnamic aldehyde (*trans*-4-phenyl-3-propene-2-al) was selected to determine the hydrogenation selectivity and activity of the desired complexes. Three different regio-selective hydrogenation was expected [1,29].

The hydrogenation reaction using the complexes as the catalysts were perform under identical conditions: 40 °C with a molar substrate: to catalyst (TON, S/C) ratio of 1000/1; 3 bar of hydrogen pressure, 40 ml of 2-propanol; Ru: co-catalysts (KOH, *t*-BOK or K_2CO_3): cinnamic aldehyde ratio of [1:10:1000]. Data regarding the reduction of cinnamic aldehyde to *trans*-4-phenyl-3-propene-2-ol are presented in Table 2.

The hydrogenation reactions under the above condition using complex **1** with both isomers (*trans*-1 and *cis*-1) as catalysts were

Table 2
Hydrogenation of cinnamic aldehyde using Ru(II) cat. in 2-propanol at 40 °C with a molar substrate: catalyst (TON, S/C) ratio of 1000/1, under 3 bar of hydrogen pressure, for 1 h.

Trial	Catalyst	Conversion (%)[a]	Co-cat.	TOF[b]
1	*Trans*-**1**	>99	KOH	995
2	*Cis*-**1**	>99	KOH	990
3	*Trans*-**1**	>99	*t*-KOBu	980
4	*Trans*-**1**	20[c]	KOH	200
5	*Trans*-**1**	7[d]	K_2CO_3	7
6	**2**	0[d]	KOH	0
6	$RuCl_2(dppb)_2(\mu\text{-dppb})$	0[d]	KOH	0

[a] Yield and selectivity were determined by GC.
[b] TOF: turnover frequency ($mol_{sub}\ mol^{-1}{}_{cat}\ h^{-1}$).
[c] EtOH instead of 2-propanol solvent.
[d] 10 h reaction.

completed within 1 h which enhanced the TOF number. Both the *trans*-**1** and *cis*-**1** isomers of complex 1 showed approximately the same degree of catalytic activity and were only effective in the presence of excess hydrogen in 2-propanol and a strong basic co-catalyst such as KOH and *t*-BOK. When the weak base K_2CO_3, was used as co-catalyst, *trans*-**1** lost 93% of activity even when the reaction was conducted for 10 h instead of 1 h. When the solvent 2-propanol was replaced by EtOH, the reaction was conducted for 10 h, *trans*-**1** lost 80% of it activity. The selectivity for the hydrogenation of the C=O bond (in cinnamic aldehyde) by complex **1** isomers was as high as 99%. In comparison, complex **2** and [$RuCl_2(dppb)_2(\mu\text{-}dppb)$] were inactive under identical conditions, because we were not able to increase the pressure to more than 3 bar due to technical problem in our lab; therefore, these complexes were classified as weak hydrogenation catalysts.

Conclusion

In conclusion, the coordination geometry and isomerization of *trans*-(Cl/Cl)-[$RuCl_2$(dppb)(diamine)]; were established by single-crystal X-ray crystallography and $^{31}P\{^1H\}$ NMR. The desired complexes were shown to be highly active and excellent in the selective hydrogenation of C=O over C=C in cinnamic aldehyde under mild basic conditions. However, this catalytic activity has encouraged us to prepare new chiral mixed-ligand ruthenium–diphospine–diamine complexes that are strongly wanted strongly required for the industrial chiral hydrogenation of pro-chiral ketones designated for pharmaceutical used.

Acknowledgment

The project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

Appendix A. Supplementary material

Crystallographic data corresponding to the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 784617 for complex {[*cis*-Cl2Ru(P—P)-(N—N)]·$HCCl_3$}. 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.saa.2012.11.108.

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