SYNTHESIS AND CHARACTERIZATION OF 1,3-DIAMINE(PHOSPHINE)-RUTHENIUM(II) COMPLEXES USING MONODENTATE AND BIDENTATE PHOSPHINE LIGANDS

Ismail Warad
Department of Chemistry, College of Science, King Saud University,
P.O. Box 2455, Riyadh 11751, Saudi Arbia
warad@ksu.edu.sa
(Received 19th Oct. 2006; Accepted 27th Dec. 2006)

معقدات الروثنيوم الثنائي المتعادلة ذوات متصلات: أحادي الفسفين أو ثنائي الفسفين مع ٣،١-ثنائي الأمين من صيغة [$RuCl_2(PP)(NN)$]، تم تحضيرها بناتج جيد جداً وبطريقة سهلة في وسط خامل مستخدمين ثنائي كلورو ميثان كمذيب ترغبه جميع المتفاعلات. للمرة الأولى يتم تحضير كل من معقدات **2** و **4** و **6** عند درجة حرارة الغرفة باستخدام معقدات **1** و **3** و **5** على التوالي كمواد أولية.

متشكلة (*trans*-$RuCl_2$) ثنائي الكلور المرتبط بالكرة التناسقية لأيون الروثنيوم متضاد لنفسه و ذرتي النيتروجين في متصلة ثنائي الأمين مرتبطة بالروثنيوم بشكل متضاد لذرتي الفسفور في متصلة الفسفين أو ثنائي الفسفين، هذه الظواهر الشكلية تم رصدها ومراقبتها بواسطة طيف الرنين النووي المغناطيسي لنظيرالفسفور^{31} حيث أن هذه الشكل الفراغي هو المفضل حركياً من الناحية النظرية.

المعقدات المشيدة في هذه الدراسة تم تحليها والتأكد من تركيبها بواسطة الرنين النووي المغناطيسي لكل من نظيرالفسفور^{31} والكربون^{13} الدبتي والهيدروجين^{1} بالإضافة إلى كل من طيف الأشعة تحت الحمراء وطيف الكتلة الفابي و التحليل الأولي.

The neutral Ru(II), chelating phosphine or diphosphine with 1,3-diamine (1,3-diamino-2-propanol) of type [$RuCl_2(PP)(NN)$], are readily synthesized in very good yields at an inert atmosphere using dichloromethane as solvent. For the first time, the ruthenium(II) complexes: [*trans*-dichloro-(bis(triphenylphosphine)(1,3-diamino-2-propanol)ruthenium(II)] (**2**), [*trans*-dichloro(1,3-bis(diphenyl-phosphino)propane)(1,3-diamino-2-propanol)ruthenium(II)] (**4**) and [*trans*-dichloro(bis(ether-phosphine)-(1,3-diamino-2-propanol)ruthenium(II)] (**6**) have been prepared at room temperature starting from [$RuCl_2(PPh_3)_3$], [$RuCl_2(Ph_2PCH_2CH_2OCH_3)_2$] and [$RuCl_2(dppp)_2$], respectively.
Trans-$RuCl_2$ with nitrogen atoms are *trans* to phosphorus atoms are structurally favored (kinetic) isomer. This structural phenomenon has been monitored by $^{31}P\{^1H\}$ NMR in CD_2Cl_2. All the mentioned complexes were fully characterized by NMR, IR, and FAB-MS as well as elemental analysis.

INTRODUCTION

Phosphine ligands have been intensively used in coordination chemistry because of their electron-donating power [1-9]. Diphosphine ligands have received particular attention, because in general they form more stable complexes than their non-chelating phosphine analogues under the harsh reaction conditions required for catalysis [10-20]. Although dynamic behavior of transition metal complexes containing monodentate and bidentate ligands has been often investigated in the last few years, it remains an area of active research interest [1, 3, 21-23]. We are partially interested in fluxional processes of ruthenium(II) and palladium(II) complexes containing mono-dentate (P~0) and bidentate (P^0) ether-phosphines because of their potential in synthesis and catalysts [1, 3-9]. These ligands form a close metal-phosphorus contact and only weaker metal-oxygen bonds which may be cleaved reversibly. In these complexes the oxygen atom is incur-porated in open-chained or cyclic ether moieties [1, 3-8, 21-23]. Recently we demonstrated a novel procedure to exchange the two monodentate (P~0) from $RuCl_2(P\sim0)_2$(diamine) complexes by one bidentate diphosphine ligand (dppp) to form $RuCl_2$dppp(diamine) under mild condition [24].

Intensive studies have recently been focused on the hydrogenation of ketones to obtain alcohols, owing to the exceedingly mild reaction conditions and technical simplicity variety of transition-metal complexes are now known to show catalytic activity in the hydrogenation of ketones, but effective catalysts are strictly limited to ruthenium complexes with various kinds of diamine and phosphine ligands [5-12, 14-20]. The most general and efficient catalyst for this reaction was pioneered by Noyori, who showed that ruthenium complexes of the type [(diphosphine)-$RuCl_2$(diamine)], used in the presence of a base in 2-propanol, are extremely efficient and selective catalysts for the asymmetric reduction of unfunctionalized ketones [14-19]. Much less effort has been dedicated since Noyori's work using his well-known bulky XylBinap as chiral ligand in ruthenium system [14], numbers of other groups have demonstrated the use of other diphosphines and diamines that give rise to high activities and selectivities when used in this catalyst system [2, 5, 14, 18, 24, 25]. As a future step we will engage these complexes in the hydrogenation field.

In this paper, I describe the synthesis and characterization of three new ruthenium(II) complexes containing C_2-symmetric ligands possessing mixed phosphine and diamine donor sites. The spectroscopic properties, and fluxional behavior of phosphine ruthenium(I1) complexes have been investigated by $^{31}P\{^1H\}$ NMR spectroscopy.

EXPERIMENTAL

General remarks, materials and instrumentations:

All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum and Schlenk-line techniques unless otherwise noted. Prior to use dichloromethane, *n*-hexane, and diethyl ether were distilled from CaH_2, $LiAlH_4$, and from sodium/ benzophenone, respectively.

The ether-phosphine ligand ($Ph_2PCH_2CH_2OCH_3$), 1,3-bis(diphenyl-phosphino)propane (dppp), $[RuCl_2(PPh_3)_3]$, $[RuCl_2(Ph_2PCH_2CH_2OCH_3)_2]$ and $[RuCl_2(dppp)_2]$ were prepared according to literature methods [26, 6, 12]. 1,3-diamino-2-propanol was Fluka and used without further purification. PPh_3 and $RuCl_3{\cdot}3H_2O$ were available from Merck and Chempur respectively, and were used without further purification. Elemental analysis was carried out on an Elementar Varrio EL analyzer. High-resolution 1H, $^{13}C\{^1H\}$, DEPT 135, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows: ^1H NMR 250.12 MHz, $^{13}C\{^1H\}$ NMR 62.9 MHz, and $^{31}P\{^1H\}$ NMR 101.25 MHz. Chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta_p = 0$). IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Mass spectra: EI-MS; Finnigan TSQ70 (200 ^oC). FAB-MS; Finnigan 711A (8 kV), modified by AMD and reported as mass/charge *(m/z).*

General procedure for the preparation of the complexes 2, 4 and 6 (see Scheme 1)

The 1,3-diamino-2-propanol ligand (10 % excess) was dissolved in 25 ml of dichloromethane and the solution was added dropwise to a stirred solution of the corresponding complex **1**, **3** and **5** in 25 ml of dichloromethane individually. After the reaction mixture was stirred approximately for 30 min at room temperature, the volume of the solution was concentrated to about 5 ml under reduced pressure. Addition of 30 ml of *n*-hexane caused the precipitation of a solid which was filtered (P4), then dissolved again in 20 ml of dichloromethane and concentrated under vacuum to a volume of 5 ml. Addition of 50 ml of n-hexane caused the precipitation of a solid which was filtered (P4) and washed three times with 25 ml of diethyl ether each and dried under vacuum.

Preparation of Complex 2:

1 (200 mg, 0.208 mmol) was treated with 1,3-diamino-2-propanol (20.40 mg, 0.229 mmol) to give 132.25 mg of **2**. ^1H NMR (CD_2Cl_2): δ (ppm) 2.88 (m, 4H, NCH_2), 3.04 (m, br, 5H, NCH_2, CH<u>*OH*</u>), 3.92 (m, 1H, C<u>*H*</u>OH), 7.10-7.70 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 46.54 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 45.22 (s, NCH_2), 70.94 (s, CHOH), 129.34 (m, *o*-C_6H_5), 130.31 (s, *p*-C_6H_5), 134.01 (m, *m*-C_6H_5), 135.07 (m, *i*-C_6H_5).

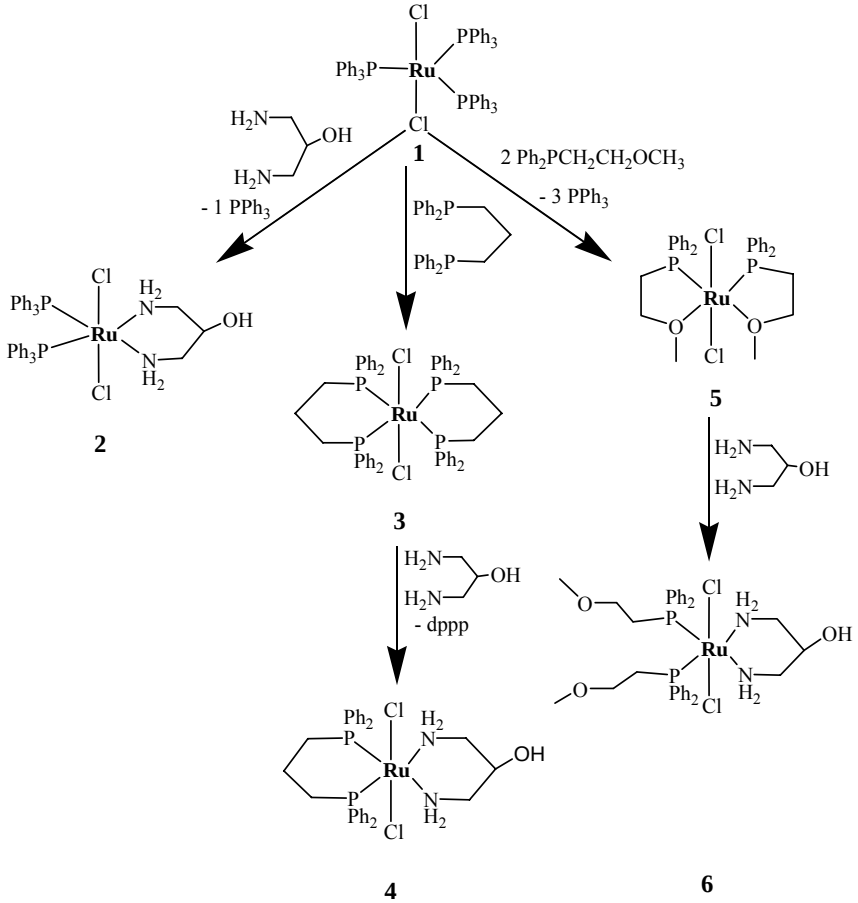
Preparation of Complex 4: 3 (200 mg, 0.201 mmol) was treated with 1,3-diamino-2-propanol (19.67 mg, 0.221 mmol) to give 119.04 mg of **4**. ^{1}H NMR (CD_2Cl_2): δ (ppm) 1.26 (m, 2H, $PCH_2C\underline{H_2}$), 1.93 (m, 4H, $PC\underline{H_2}CH_2$), 2.76 (m, br, 4H, NCH_2), 2.98 (m, br, 5H, NCH_2, $CH\underline{OH}$), 3.84 (br, 1H, $\underline{CH}OH$), 7.10-7.60 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) 41.43 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 19.42 (s, $PCH_2\underline{C}H_2$), 26.51 (t, $^{1}J_{pc}$ = 12.36 Hz, $P\underline{C}H_2CH_2$), 44.50 (s, NCH_2), 68.78 (s, CHOH), 128.33 (m, *o*-C_6H_5), 129.50, 129.60 (2s, *p*-C_6H_5), 134.12 (br, *m*–C_6H_5), 135.25 (m, *i*-C_6H_5).

Preparation of Complex 6: 5 (200 mg, 0.302 mmol) was treated with 1,3-diamino-2-propanol (29.56 mg, 0.332 mmol) to give 208.82 mg of **6**. ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.29 (m, 4H, PCH_2), 2.80 (m, 4H, NCH_2), 2.88 (s, 6H, OCH_3), 2.99 (m, br, 5H, NH_2, $CH\underline{OH}$), 3.15 (br, OCH_2), 3.83 (br, 1H, $C\underline{H}OH$), 7.20 - 7.60 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) 40.49 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 25.71 (t, $^{1}J_{pc}$ = 12.68 Hz, PCH_2), 44.10 (s, CH_2N), 58.02 (s, OCH_3), 68.06 (s, CHOH), 69.28 (s, CH_2O), 128.47 (m, *o*-C_6H_5), 129.59, 129.65 (2s, *p*-C_6H_5), 133.33 (m, m-C_6H_5) 134.84 (m, *i*-C_6H_5).

RESULTS AND DISCUSSION

Synthetic studies:

[*trans*-dichloro(bis(triphenylphosphine)(1,3-diamine)ruthenium(II)] (**2**), [*trans*-dichloro(1,3-bis(diphenylphosphino)propane)(1,3-diamine)-ruthenium(II)] (**4**) and [*trans*-dichloro(bis(etherphosphine)(1,3-diamine)ruthenium(II)] (**6**) (Scheme 1).



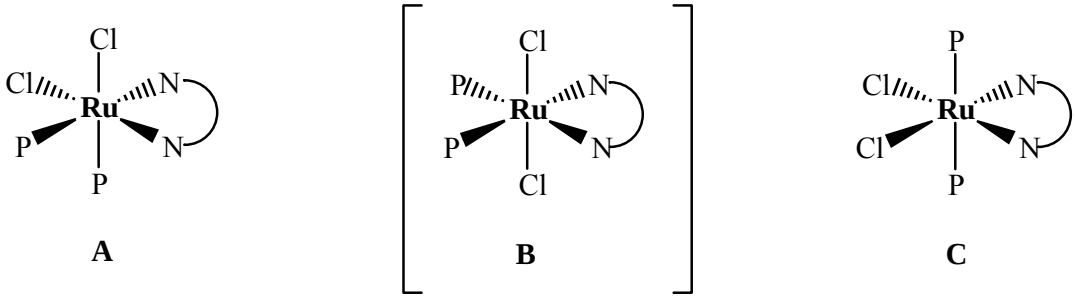
Scheme 1: Synthesis of the ruthenium(II) complexes.

The neutral Ru(II), chelating phosphine or diphosphine with 1,3-diamine of the type $RuCl_2(P)(N)$, are readily synthesized starting from $[Cl_2Ru(PPh_3)_3]$ at room temperature using degassed dichloromethane as solvent. **1**, **3**, and **5** were synthesized using previous reported procedures [25, 12, 6], while **2**, **4** and **6** were synthesized for the first time. The direct equivalent reaction of 1,3-diamino-2-propanol with $[Cl_2Ru(PPh_3)_3]$ led to the isolation of **2** in very good yield. Treating *trans*-$Cl_2Ru(dppp)_2$ with 1,3-diamino-2-propanol following procedure [12] revealed the somewhat air-insensitive **4** formation. To prepare **6** bis(ether-phosphine)ruthenium(II) complex was treated with the 1,3-diamino-2-propanol in an inert atmosphere (as in Scheme 1).

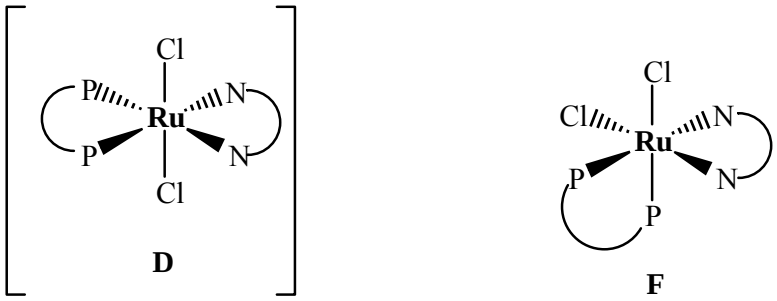
All these complexes were fully characterized by combination of ^{1}H NMR, $^{31}P\{^1H\}$ NMR and ^{13}C NMR, infrared spectrophotometric, mass spectroscopy (FAB) and also elemental analysis.

Complexes with general formula $RuCl_2(P)(N)$, where N-donor is bidentate and P-donor is monodentate ligands can show three possible geometries Scheme 2a, when the P-donor is exchanged by bidentate ligands, this number of geometries is reduced to two Scheme 2b.

(**a**)



(**b**)



Scheme 2: The possible geometries of: (a): $RuCl_2(P)_2(NN)$ and (b) $RuCl_2(PP)(NN)$, where NN-donor is bidentate diamine ligand, P-donor is monodentate phosphine ligand (PPh_3 or $Ph_2PCH_2CH_2OCH_3$) and PP-donor is bidentate diphosphine ligand (dppp).

From our previous study with such of these complexes it was well defined that isomer of type **B** and **D** *trans*-$RuCl_2$ with nitrogen atoms are *trans* to phosphorus atoms are structurally favored isomers and exhibit $^{31}P\{^1H\}$ NMR singlets in the range 30-50 ppm.

The kinetic favored products (**B** and **D**) are the *trans*-chloro-isomers, while in some case heating the *trans*-chloro-isomers to reflux in dichloromethane or benzene results in isomerization to the thermodynamically favored full- *cis*-isomers [26].

In this study the real structure formations of synthesized complexes have been monitored by $^{31}P\{^1H\}$ NMR in CD_2Cl_2 at room temperature. The singlets of **2**, **4** and **6** complexes in the $^{31}P\{^1H\}$ NMR spectra indicated that the two phosphine groups are chemically equivalent in solution which is compatible with the C_{2v} symmetry of the $RuCl_2(phosphine)_2diamine$ complexes. $^{31}P\{^1H\}$ NMR spectra of **2**, **4** and **6** were characterized by δ_p at 46.53, 41.43, 40.49 ppm, respectively, which confirmed the expected *trans*-$RuCl_2$ **B** and **D** isomers formations as in Figure 1.

Of interest, complex **6** formed trace (less 2%) of full *cis*-$RuCl_2(P\sim O)_2(NN)$ **A** isomer (thermodynamic product) with inequivelant P atoms was observed by $^{31}P\{^1H\}$ NMR in CD_2Cl_2 at room temperature forming duplet of duplet AX pattern (δ_A = 50.68 ppm and δ_X = 41.57 ppm). The coupling constant of P-P atoms ($^2J_{AX}$ = 38.38 Hz) strongly confirmed **A** isomer formation as in Scheme 2 and Figure 1.

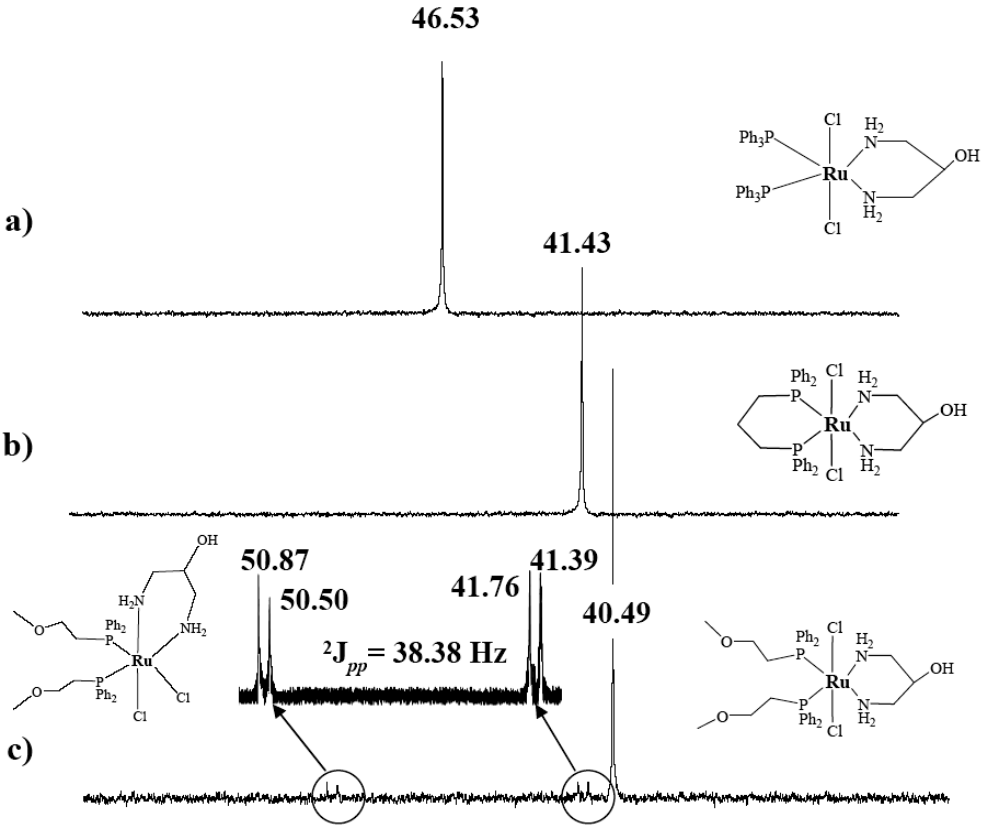


Figure 1: $^{31}P\{^1H\}$ NMR spectroscopic in ppm of the complexes 2, 4 and 6 in CD_2Cl_2 (a), (b) and (c), respectively.

NMR spectroscopic investigations:

In the ^{1}H NMR spectra of the diamine-(phosphine)ruthenium(II) complexes **2**, **4** and **6** characteristic sets of signals in the aliphatic and aromatic regions are observed, which are attributed to the diamine ligand (**2**) and both diamine and phosphine ligands (**4** and **6**). Their assignment was supported by two-dimensional H,H-COSY experiments which establish the connectivity between (NH_2 and CH_2) as well as (CHOH and CH_2) functions in the diamine ligand (**2**), and additionally between (CH_2 and CH_2P) groups in the dppp fragment (**4**) as well as between (CH_2O and CH_2P) groups in the ether-phosphine fragment (**6**). The integration of the ^{1}H resonances confirms that the phosphines to diamine ratio which are in agreement with the structural compositions of the desired complexes as in Figure 2.

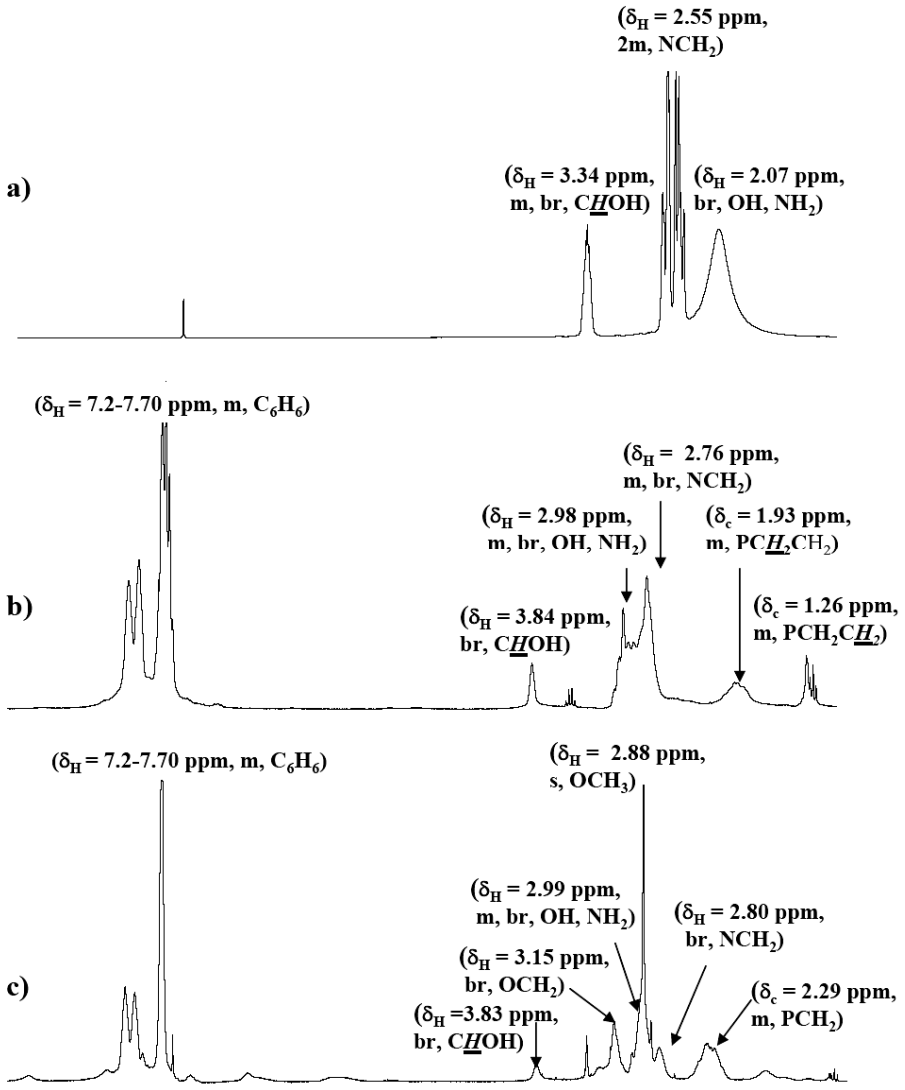


Figure 2: The ^{1}H NMR comparison spectra of the free 1,3-diamino-2-propanol ligand, 4 and 6 complexes, (a), (b) and (c), respectively.

In the $^{31}P\{^{1}H\}$ NMR spectra and due to C_2-symmetry of the diamine co-ligand, singlets were observed confirming that the phosphine groups are chemically equivalent in solution which is compatible with the C_{2v} symmetry of the $RuCl_2(phosphine)_2$diamine complexes. Phosphorus chemical shifts depend directly on the electron density environment around the phosphorous atom of free ligands (PPh_3 > dppp > ether-phosphine upfield). The coordination chemical shift, ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) of complexes **2**, **4** and **6** were changed after binding and found to be 50.83, 57.67 and 61.91 ppm downfield, respectively (see Fig. 1).

The $^{13}C\{^{1}H\}$ NMR spectra also corroborate the structures given in Scheme 1. Together the carbon chemical shifts and carbon-phosphorus coupling constants in these complexes fragments supported and confirmed the proposed structural isomer (**B** and **D**) formation. Characteristic ^{13}C and 135 DEPT ^{13}C signals in the aliphatic and aromatic regions are due to the phosphines and diamine binding mode ligands where cited.

To compare the chemical shift of C-fragments in free ether-phosphine, **5** and **6**, $^{13}C\{^{1}H\}$ and 135 DEPT $^{13}C\{^{1}H\}$ have been carried out and presented in Figure 3.

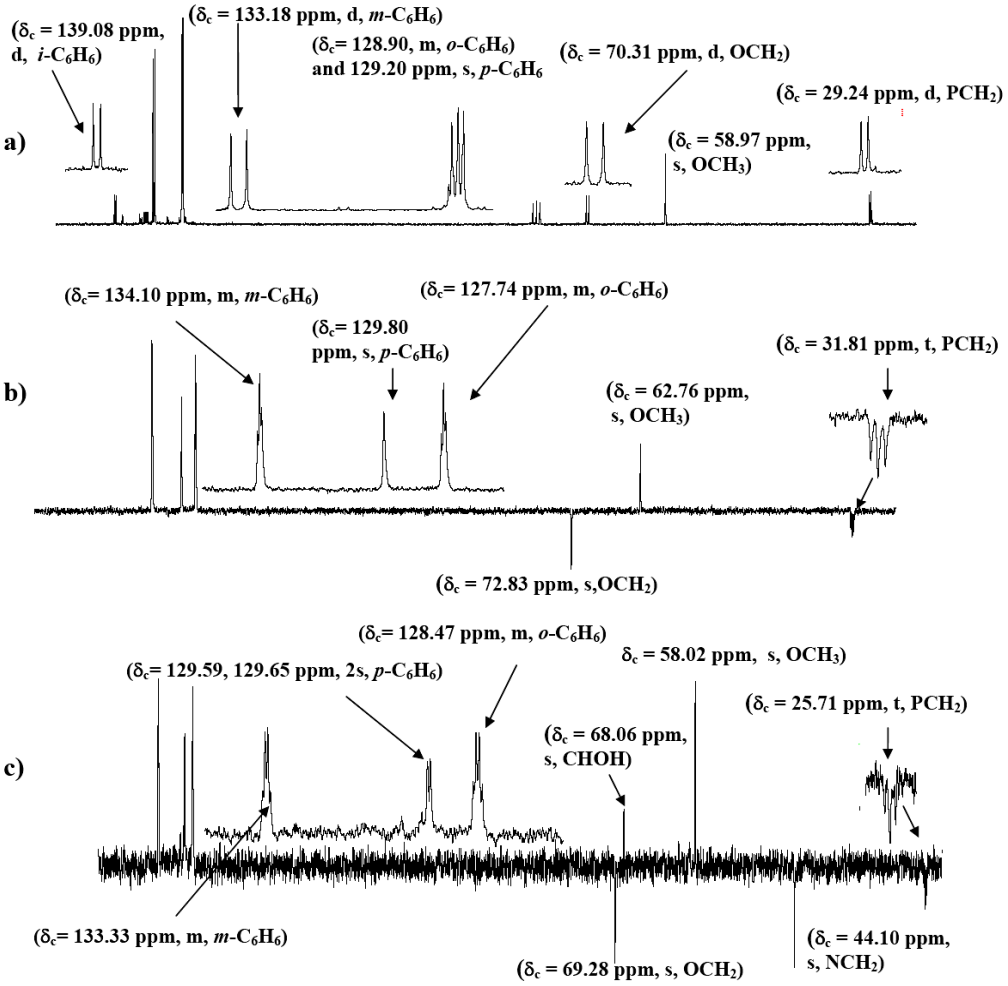


Figure 3: Normal $^{13}C\{^{1}H\}$ NMR spectrum of free $Ph_2PCH_2CH_2OCH_3$ (a) and 135 DEPT $^{13}C\{^{1}H\}$ NMR of complexes 5 and 6, (b) and (c), respectively.

IR investigations:

In order to study the binding mode of the phosphines and diamine ligands to ruthenium in the new complexes, IR spectra of the free ligands were compared with the spectra of complexes. The IR spectra of the complexes **2**, **4** and **6** in particular show several peaks which attributed to stretching vibrations of the main function group, in the ranges 3390-3300 cm^{-1} (ν_{NH}) and (ν_{OH}), 3290-3210 cm^{-1} (ν_{PhH}) and 3190-3050 cm^{-1} (ν_{CH}). All other characteristic bands due to the other function groups are also present in the expected regions.

Mass spectroscopy and elemental analysis:

For farther more structural improvements, FAB mass spectra was introduced to the study, in all the cases, positive modes were recorded in showing strong peaks corresponding to the parent ions M^+, $[M\text{-}Cl]^+$, $[M\text{-}Cl_2]^+$, along with additional fragment ions of complexes. As typical FAB-MS example spectra of **4** and **6** complexes are illustrated in Figure 4 and Table 1.

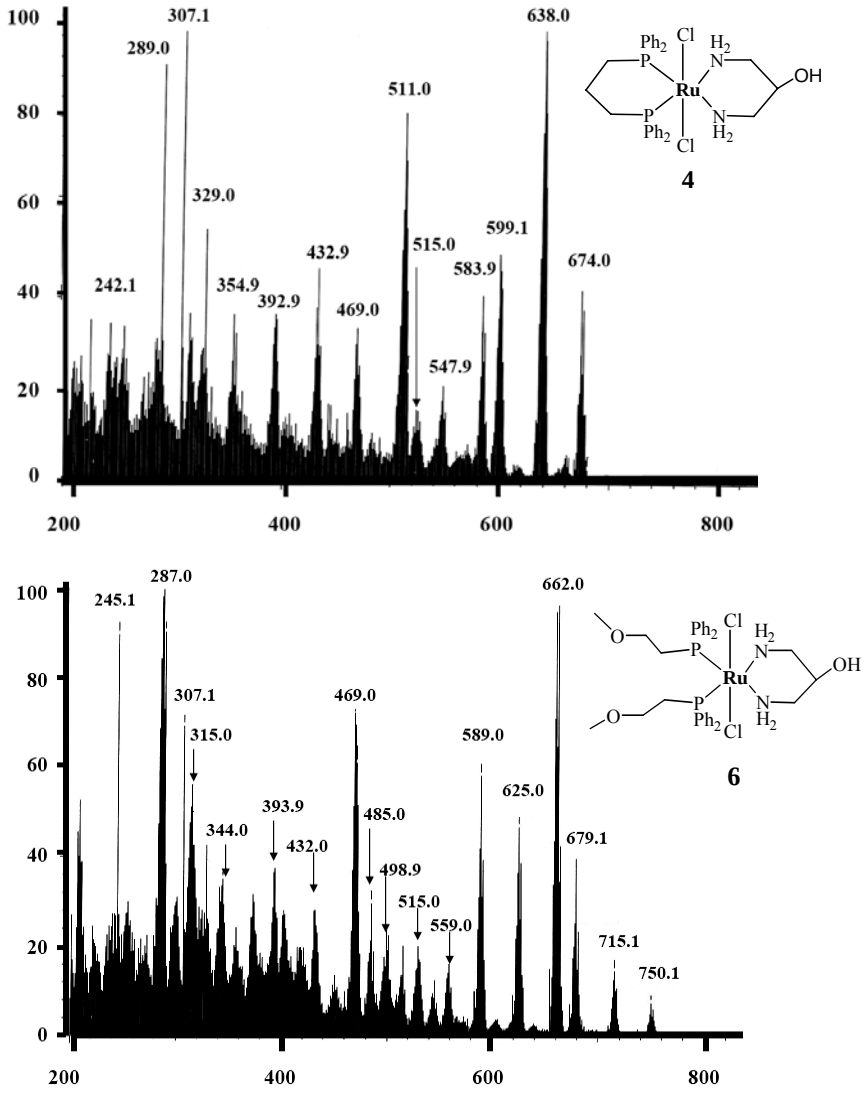


Figure 4: FAB-MS of complexes 4 and 6 using NBA matrix at 52 °C.

Elemental analysis of complexes **2**, **4** and **6**, which were carried out on an Elementar Varrio EL analyzer confirmed the desired complexes formulas formation, the result were listed in Table 2.

Conclusion:

This study has demonstrated synthetic utility of three of five-coordinate complexes of type [*trans*-dichloro(bis-phosphine)(1,3-diamine)-ruthenium(II)]. Complexes **2, 4** and **4** were made available provided with different monodentate phosphine (PPh_3 and $Ph_2PCH_2CH_2OCH_3$) and bidentate diphosphine (dppp) ligands, as well as 1,3-diamino-2-propanol as 1,3-diamine ligand. The kinetic favored **B** and **D** isomers with *trans*-$RuCl_2$ and nitrogen atoms are *trans* to phosphorus atoms are collected as structurally favored isomer over any other expected isomers. The new ruthenium(II) complexes were synthesized in very good yields and characterized by analytical and spectral techniques.

Table 1: The first six main ions fragment of complexes 4 and 6 and their chemical shifts.

4		**6**	
Ion Fragment	**Chemical Shift**	**Ion Fragment**	**Chemical Shift**
M^+	674.0	M^+	750.1
M^+-HCl	638.0	M^+-Cl	715.1
M^+-2HCl-4H	599.1	M^+-2Cl	679.1
M^+-diamine-2H	583.9	M^+-diamine	662.0
M^+-diamine-2H-HCl	547.0	M^+-diamine-HCl	625.0
M^+-diamine-2Cl	515.0	M^+-diamine-2Cl	589.0

Table 2: Characterization of ruthenium(II) complexes.

Complex	**Molecular Formula and Exact Mass**	**Yield %**	**FAB-MS (M^+)**	**Elemental Analysis**			
				% C	**% H**	**% N**	**% Cl**
				Calcd. (Found)	**Calcd. (Found)**	**Calcd. (Found)**	**Calcd. (Found)**
2	$C_{39}H_{40}Cl_2N_2OP_2Ru$ 786.10	81	786.2	59.54 (59.14)	5.13 (5.02)	3.56 (3.65)	9.01 (9.26)
4	$C_{30}H_{36}Cl_2N_2OP_2Ru$ 674.07	88	674.2	53.42 (52.93)	5.38 (5.26)	4.15 (4.47)	10.51 (10.72)
6	$C3_3H_{44}Cl_2N_2O_3P_2Ru$ 750.12	92	750.0	52.80 (52.47)	5.91 (5.85)	3.73 (3.39)	9.45 (10.02)

Acknowledgments:

The author wish to thank Prof. E. Lindner and Prof. H. A. Mayer from Tuebingen University Germany. Dr. S. Al-Resayes King Saud university for their encouragements.

REFERENCES

[1] I. Warad, S. Al-Resayes and K. Eichele, Z. Kristallogr. NCS, **221**, 1779-1782 (2006).
[2] N. Shan, H. Adams and J.A. Thomas, Inorg. Chim. Acta, **358**, 3377- 3377 (2005).
[3] E. Lindner, Z-L. Lu, H.A. Mayer, B. Speiser, C. Tittel and I. Warad, Electrochemistry Communication, **9**, 1013-1020 (2005).
[4] I. Warad, S. Al-Gharabli, A. Al-labadi, and A. Abu-rayyan, J. Saudi. Chem. Soc. **9**, 507-518 (2005).
[5] I. Warad, E. Lindner, K. Eichele and H.A. Mayer, Inorg. Chim. Acta, **357**, 1847-1853 (2004).
[6] E. Lindner, I. Warad, K. Eichele and H.A. Mayer, Inorg. Chim. Acta, **350**, 49-56 (2003).
[7] E. Lindner, A. Ghanem, I. Warad, K. Eichele, H.A. Mayer and V. Schurig, Tetraheron: Asymmetry, **14**, 1045-1053 (2003).
[8] Z. Lu, K. Eichele, I. Warad, H.A. Mayer, E. Lindner, Z. Jiang and V. Schurig, Z. Anorg. Allg. Chem., **629**, 1308-1315 (2003).
[9] E. Lindner, S. Al-Gharabli, I. Warad, H.A. Mayer S. Steinbrecher, E. Plies, M. Seiler, and H. Bertagnolli, Z. Anorg. Allg. Chem., **629**, 161-171 (2003).
[10] C.D. Gilheany, and M. C. Mitchell, In the Chemistry of Organophosphorus Compounds, Hartley, F.R., Ed.; J. Wiley and Sons: New York (1990).
[11] R. Noyori, Asymmetric catalysis in organic synthesis J. Wiley and Sons, New York (1994).
[12] E. Lindner, I. Warad, K. Eichele and H.A. Mayer, J. Organomet. Chem. **665**, 176-176 (2003).
[13] A.C. Tolman, Chem. Rev., **77**, 313-348 (1977).
[14] R. Noyori, and T. Ohkuma, Angew. Chem., Int. Ed., **40**, 40-120 (2001) and references cite therein.
[15] M. Kitamura, M. Tokunaga, T. Ohkuma, and R. Noyori, Tetrahedral Lett,, **32**, 4163-4168 (1991).
[16] T. Ohkuma, M. Koizumi, K. Muniz, G. Hilt, C. Kabuta and R. Noyori, J. Am. Chem. Soc., **124**, 6508-6509 (2002).
[17] J.-X. Gao, T. Ikariya and R. Noyori, Organometallics, **15**, 1087-1089 (1996).
[18] K. Abdur-Rashid, M. Faatz, J.A. Lough and R.H. Morris, J. Am. Chem. Soc., **123**, 7473-7474 (2001).
[19] Y. Jiang, Q. Jiang and X. Zhang, J. Am. Chem. Soc., **120**, 3817-3818 (1998).
[20] P. Gamez, F. Fache and M. Lemaire, Tetrahedron: Asymmetry, **6**, 705-718 (1995).
[21] E. Lindner, M. Gepriigs, K. Gierling, R. Fawzi, and M. Steimann, Inorg. Chem., **34**, 6106-6117 (1995).
[22] C. Nachtigal, S. Al-Gharabli, K. Eichele, E. Lindner and H.A. Mayer, Organometallics, **21**, 105-112 (2002).
[23] G.A. Grasa, A. Zanotti-Gerosa, J.A. Medlock and W.P. Hems, Org. Lett., **7**, 1449-1451 (2005).
[24] I. Warad, S. Al-Resayes, J. Saudi. Chem. Soc., **10**, 285-294 (2006).
[25] A. Batista, M. Santiago, C. Donnici, I. Moreira, P. Healy, S. Berners-Price and S. Queiroz, Polyhedron, **20**, 2123-2128 (2001).
[26] T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., **28**, 945-956 (1966).