J. King Saud Univ., Vol. 20, *Science* (1), pp. 1-11, Riyadh (2008/1429H.)

Oxidation Decomposition of Selected Diamine(Ether-Phosphine)-Ruthenium(II) Complexes and Comparative Solid State Structural Studies Using EXAFS Investigations and X-ray Diffraction Method

Ismail Warad*

Department of Chemistry, College of Science,
King Saud University, P.O.Box 2455, Riyadh, Saudi Arabia

(Received 24/8/1427H.; accepted for publication 19/12/1427H.)

Abstract. Diamine-bis(ether-phosphine)ruthenium(II) **A-D** have been re-synthesized starting from complex 1. These complexes revealed high degree of stability in solid state, while in solution they are oxidized depending on the complexes types and oxidation reagents. Oxidation decomposition reactions of these complexes using hydrogen peroxide and oxygen as oxidation reagents have been investigated individually in this work. (2-methoxyethyl)-(oxo)diphenylphosphorane and other oily unstable ruthenium phosphorus free complexes are formed as π products of the oxidation processes. The chemical behavior of the ether-phosphine ligand in complex 1 toward the oxidation reagents as model example was manipulated by $^{31}P\{^{1}H\}$ NMR spectroscopy at room temperature. In solid state, the X-ray crystallography collected-structural details of a selective diamine-bis(ether-phosphine)ruthenium(II) A-D complexes were compared with structural EXAF analysis date.

Keywords: Ruthenium(II) complexes, Ether-phosphine, Diphosphine, Diamines, NMR.

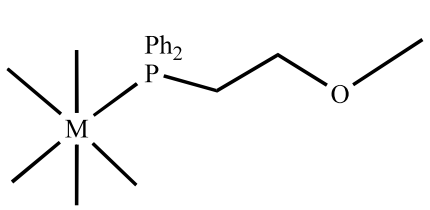
Introduction

The synthesis and chemistry of ruthenium(II) complexes possessing a chelating and hybrid phosphine ligands (P, P and P, O) remain a topic of our interest, the main impetus being the potential of such complexes as hydrogenation catalysts [1-7]. For further stabilization, we recently introduced the bifunctional (P,O) [(2-methoxyethyl)(diphenyl)-phosphine] as hemilabile ether-phosphine ligand. Such of these ligands are setup with oxygen donors incorporated in cyclic or linear ether moieties providing a weak metal-oxygen bond and a phosphorus atom closely coordinated to the central atom as in Chart 1, to act as monodentate (P~O) or bidentate (P^O) ligands, respectively [7-9].

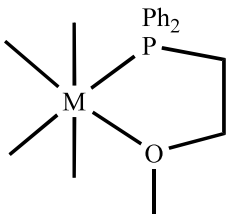
Due to the hemilabile character, the ether moieties incorporated into the phosphine ligands play a significant role, because they are able to protect vacant

*Corresponding author. Tel.: 00966501485303.
(warad@ksu.edu.sa).

coordination sites at the metal centers and hence the stability of these complexes is increased [7-9].



Monodentate linear ether-phosphine metal complex



Bidentate cyclic ether-phosphine metal complex

Chart 1. Mono and bidentate model complexation.

As part of ongoing efforts to study the hemilability phenomena of such of these ligands, recently, we have introduced to the literature a facile and a versatile synthetic route of a set of neutral and cationic diamine(ether-phosphine)ruthenium(II) and palladium complexes and their complete structural characterization as well as catalytic hydrogenation of carbonyl compounds activity [1-9]. For the same target, several complexes of these types have been prepared and tested as asymmetrical hydrogenation complexes [10-14].

One of the most powerful methods to obtain the total structure information of crystalline and non-crystalline materials is X-ray crystallographic method and EXAFS (Extended X-ray Absorption Fine Structure), respectively. The X-ray crystallographic analysis of such complexes provides a complete structural data. On the other hand, EXAFS spectrum revealed information about the bond distance, the coordination number, the Debye-Waller factor and the nature of the scattering atoms surrounding an excited atom [15].

Here, it will be reported the chemical behavior of the ether-phosphine ligand in the ruthenium(II) complexes toward several oxidation reagents (H_2O_2 and oxygen) and to compare for the first time the structural analysis data of selective diamine(ether-phosphine)ruthenium(II) complexes which has been collected from X-ray crystallography and EXAF investigations in solid state.

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 the use of dichloromethane, *n*-hexane and Et_2O were distilled from CaH_2, $LiAlH_4$ and from sodium/benzophenone, respectively. The diamines were purchased from Acros, Fluka

and Merck and had to be purified by distillation and recrystallization, respectively. The ether-phosphine ligand $Ph_2PCH_2CH_2OCH_3$ and other starting material complexes were prepared according to literature methods [5]. $^{31}P\{^1H\}$ 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. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta = 0$). IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. FAB-MS; Finnigan 711A (8 kV), modified by AMD and reported as mass/charge *(m/z).*

EXAFS measurements

The EXAFS measurements of these complexes were performed at the Ru K-edge at 21.57-25.03 KeV of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY, Hamburg, under ambient conditions at the positron energy of 4.45 GeV and beam current of about 120 mA. For harmonic rejection, the second crystal of the Si(311) double crystal monochromator was tilted to 30%. Data were collected in transmission mode using ion chambers filled with argon. The energy was calibrated with a ruthenium metal foil of 20 μm thickness. The data were analyzed with a program package specially developed for the investigation of amorphous solids [15]. The program AUTOBK of the University of Washington was used for background removal and the EXCURV92 module of the program package CERIUS that was used for the data evaluation [16]. Data analysis in *k*-space was performed using Curved Wave theory with XALPHA potentials and phase shifts and the resulting EXAFS function was weighted with k^3. The mean free path of the scattered electrons were calculated from the imaginary part of the potential (VPI set to –4.00), the amplitude reduction factor AFAC was fixed at 0.8 and an overall energy shift ΔE_0 was introduced to give a best fit to the data.

X-ray measurements

Crystals suitable for X-ray structural analysis have been obtained for Ru(II) by the layer-diffusion of diethylether into dichloromethane solutions of the complex. Selected crystals were mounted on a P4 Siemens diffractometer by using a perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) was used for the measurement of intensity data in the ω-scan mode. The data were corrected for polarization and Lorentz effects. The structures were solved by direct methods with SHELXS [17]. Refinement was carried out with full-matrix least-squares methods based on F^2 in SHELXL [18].

General oxidation procedures of Ru(II) complexes

Oxidation using H_2O_2 reagent

One small drop of the hydrogen peroxide was added to the 0.005 mmol of Ru(II) complex in 2 ml of dichloromethane in the special NMR tube under Argon atmosphere. The reaction mixture was sealed and shacked for 10 seconds at room temperature and the color changed to green, which is parallel to the $^{31}P\{^1H\}$ NMR measurement indicated the full complex oxidation-decomposition.

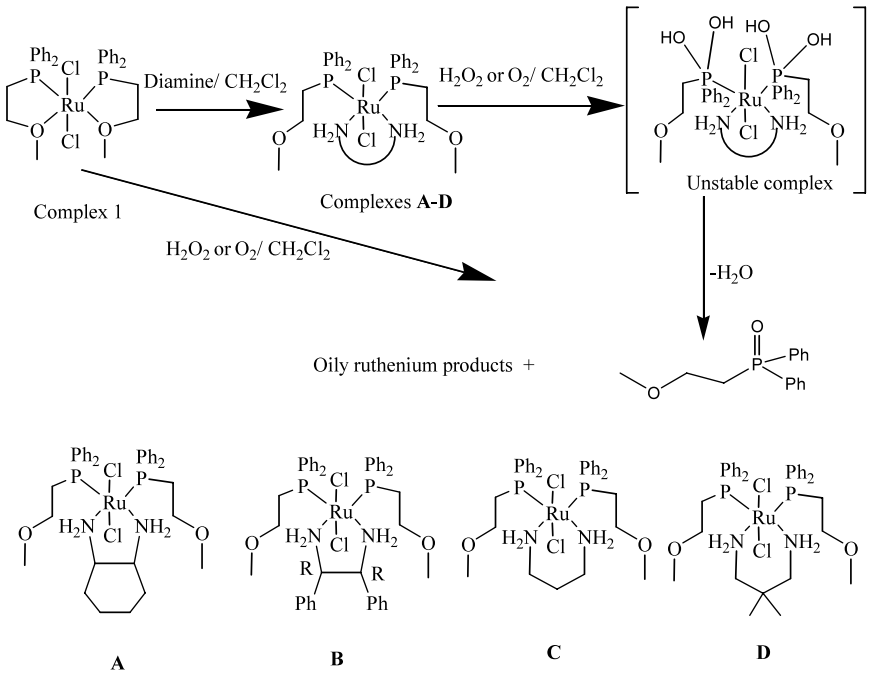
Oxidation using O_2 in dichloromethane

0.005 mmol amount of the corresponding Ru(II) complex was dissolved in 50 ml of dichloromethane. At room temperature and air open atmosphere, the reaction mixture was stirred vigorously. Samples were taken during the reactions and measured by ^{31}P NMR to control and ensure the complete oxidation-decomposition.

Results and Discussion

Ruthenium(II) complexes

Four diamine-bis(diphosphine)ruthenium(II) complexes **A-D** as in Scheme 1, which are provided with different diamines types that were made available. Because of the x-ray crystal structure identifications of these complexes, it has been selected to re-synthesize in this investigation [1].



Scheme 1. Synthesis of the Ru(II) complexes.

Previous studies of ether-phosphine complexing properties toward Ru(II) have shown their ability to act as mono (*P*) or bidentate (*O, P*) ligands consistent with their hemilabile character. In contrast to previously studied ligands, complex 1 contained two oxygen atoms which can be simultaneously coordinated to the metal atom so as bidentate (*O, P*) ligand. New ruthenium-ether-phosphine-diamine complexes were

synthesized when several diamine individuals were mixed with complex 1. On the other hand, complexes **A-D** and complex 1 were oxidative-decomposed when it was treated with H_2O_2 or oxygen caused Ru-O bond repulsion. The oxidation decomposition of these complexes led to oxo-ether-phosphine formation, in addition to oily green unstable phosphorous free ruthenium complexes. Several spots with no phosphorus peaks were detected when these green matrix ruthenium complexes were subjected to spot analysis [19] and ^{31}P $\{^1H\}$ NMR, which confirmed the multi-ruthenium cluster complexes formation as in Scheme 1. The study of these reactions was limited to NMR spectroscopy on the account of the nature of these complexes. The ^{31}P $\{^1H\}$ NMR spectra of these investigations display each single peak, as follows: a signal at -21.4 ppm assigned to free ether-phosphine ligand, *trans*-dichloro-*cis*-bis(ether phosphine)ruthenium(II) complex (1) showed a single resonance at 64.4 ppm. Because of the ring contribution Δ_R, this resonance was shifted to lower NMR field, while diamine-bis(diphosphine)ruthenium(II) complexes **A-D** revealed resonances at around 40 ppm. The decomposed products of complex 1 and complexes **A-D** ruthenium complexes by H_2O_2 or oxygen gave a single resonance at 30.2 ppm attributed to free new oxo-ether-phosphine [(2-methoxyethyl)(oxo)diphenylphosphorane] ligand formation, while the oily green complexes revealed no ^{31}P $\{^1H\}$ NMR peaks after column chromatography separation (see Fig. 1).

Both complex 1 and complexes **A-D** are very stable in solid state, while in a solution state it is using dichloromethane such complexes decomposed very slowly under argon atmosphere. At an open oxygen system, it is decomposed within one to several days depending on the complexes structures as summarized in Table 1. The reactions decomposition was accompanied by a color change, the green color appearances strongly indicate the oxidation decomposition reaction lunching. This fact is confirmed by ^{31}P $\{^1H\}$ NMR. Oxidation of these complexes by H_2O_2 were very fast comparing by oxygen. When one small drop of H_2O_2 is added to the solution of complex 1 in the NMR tube at ambient temperature, the reaction mixture became green spontaneously. The decomposition rate of complex 1 by oxygen was found to be around 10 times faster than complexes **A-D** which showed a degree of stability at the same oxidation reaction conditions as in Table 1.

The oxidation-decomposition rate of complex 1 using oxygen followed by ^{31}P $\{^1H\}$ NMR as in Fig. 2. The stability and chemical behavior of these complexes toward oxygen have been understood through this study.

EXAFS and X-ray analysis

In the analysis of the experimental k^3 weighed $\chi(k)$ function, a three-shell model can be fitted for the complexes **A-D**. The first shell has two nitrogen backscatterers, the second shell contains two phosphorus backscatterers, and the third shell has two chlorine backscatterers. In the fitting theoretical procedure, the coordination numbers were fixed to the known values for the ligands around the ruthenium atom and the other parameters, which include the interatomic distances, Debye-Waller factors and energy zero value that were determined by iterations.

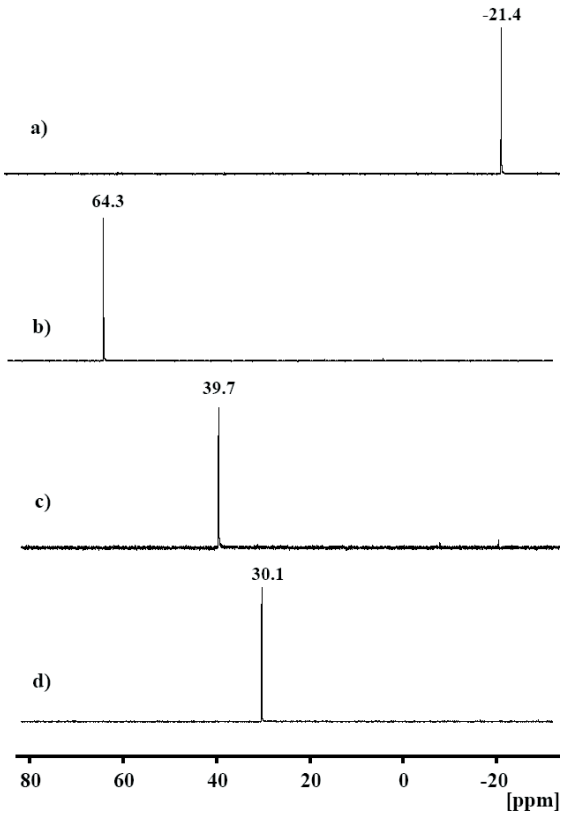


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectroscopic in CH_2Cl_2 of free ether-phosphine, complex 1, complex B, and oxo-ether-phosphine a), b), c) and d) respectively.

Table 1. Characterization and properties of some Ru(II) complexes

Complex	Formula and M. Wt.	^{31}P NMR chemical shift [ppm]	Δδ |δ of ligand in complex - δ of free ligand|	CH_2Cl_2 solution color	Decomposition time by atmospheric oxygen
1	$C_{30}H_{34}Cl_2O_2P_2Ru$ 660.51	64.4	85.8	Red	4 hours
A	$C_{36}H_{48}Cl_2N_2O_2P_2Ru$ 774.70	38.8	60.2	Brown	2 days
B	$C_{44}H_{50}Cl_2N_2O_2P_2Ru$ 872.80	39.7	60.4	Yellow	more than 2 weeks
C	$C_{33}H_{44}Cl_2N_2O_2P_2Ru$ 734.64	42.5	63.9	Light- orange	2 days
D	$C_{35}H_{48}Cl_2N_2O_2P_2Ru$ 762.69	40.7	62.1	Brown-yellow	3 days

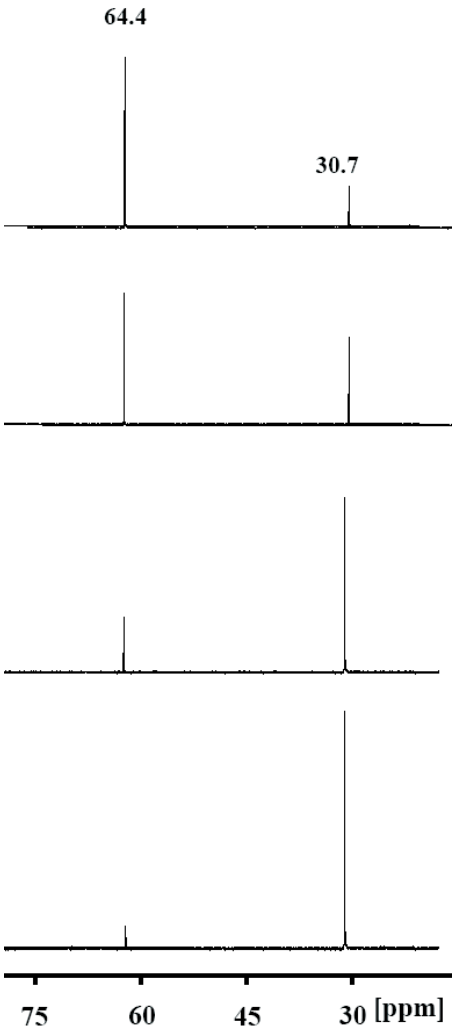


Fig. 2. Time-dependent $^{31}P\{^{1}H\}$ NMR spectroscopic of the oxidation-decomposition reaction of complex 1 at 40.2 ppm with oxygen in dichloromethane to produce oxo-ether-phosphine at 30.7 ppm [a) 0.5h under vigorous stirring; b) the same reaction mixture after 1h; c) after 3h; d) after 3.5h].

The experimental data and the fitted functions of complexes **A-D** are, respectively, shown in k^3 space as well as by Fourier transformations in real space (Fig. 3).

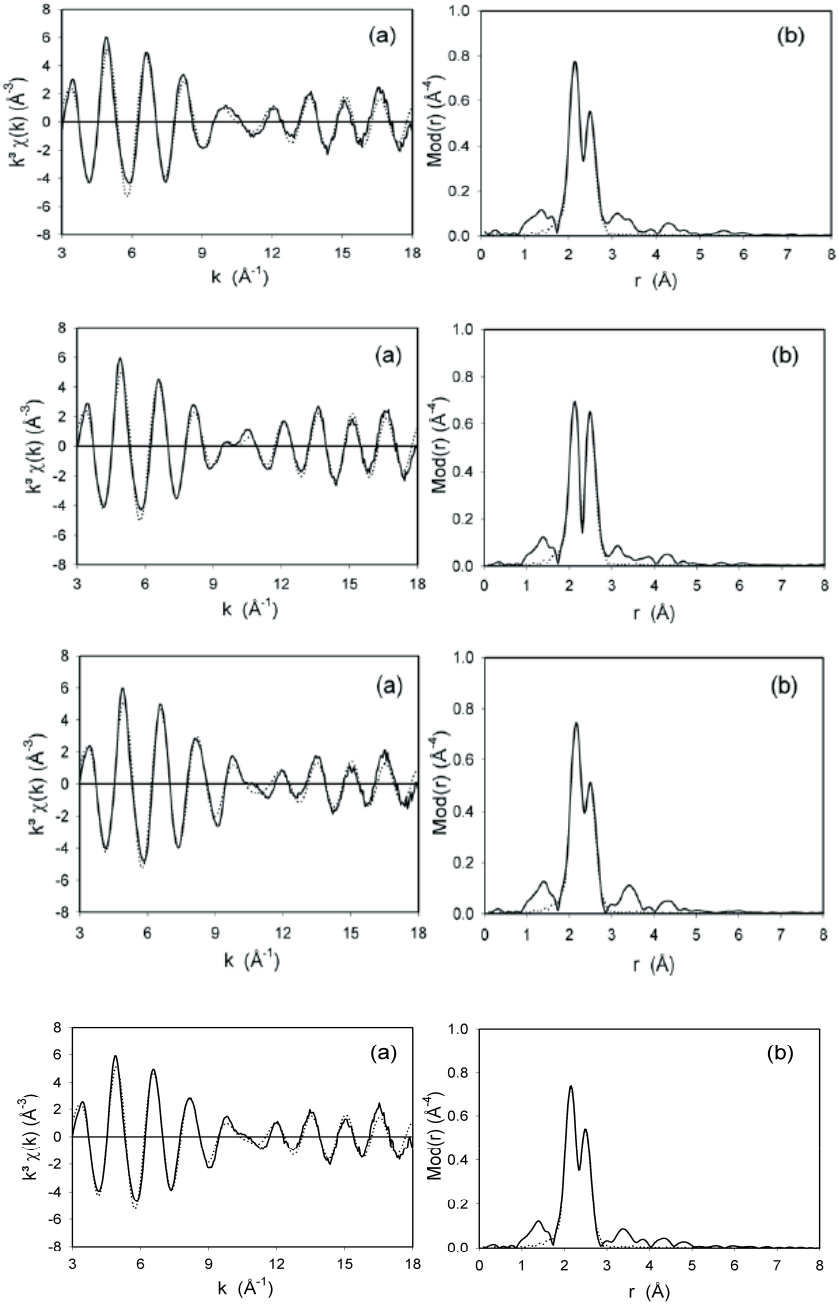


Fig. 3. Experimental (solid line) and calculated (dotted line) k^3 χ (k) functions (a) and their Fourier transforms (b) for complexes A-D, Fig 3a-3d respectively, in the *k*–range 3.0-18.0 Å^{-1}.

The structural parameters of the complexes obtained from EXAFS and X-ray diffraction [3, 4, 7] are compared in Table 2.

Table 2. Structural parameters for the complexes A-D obtained from X-ray diffraction and EXAFS

Complex	Bond type	r[Å], X-ray data	r[Å], EXAFS data	Debye-Waller factor σ [Å]	R factor and E_0 value [Kev]
A	Ru–N	2.18 ± 0.02	2.18 ± 0.02	0.050 ± 0.005	25.03 22.07
	Ru–P	2.28± 0.02	2.28± 0.02	0.062 ± 0.006	
	Ru–Cl	2.41± 0.02	2.41± 0.02	0.058 ± 0.006	
B	Ru–N	2.17 ± 0.02	2.17 ± 0.02	0.050 ± 0.005	22.06 22.26
	Ru–P	2.27± 0.02	2.27± 0.02	0.067 ± 0.007	
	Ru–Cl	2.41± 0.02	2.42± 0.02	0.054 ± 0.005	
C	Ru–N	2.19 ± 0.02	2.18 ± 0.02	0.050 ± 0.005	23.28 21.71
	Ru–P	2.29± 0.02	2.29± 0.02	0.068 ± 0.007	
	Ru–Cl	2.42± 0.02	2.41± 0.02	0.063 ± 0.006	
D	Ru–N	2.19 ± 0.02	2.18 ± 0.02	0.050 ± 0.005	21.88 21.57
	Ru–P	2.29± 0.02	2.29± 0.02	0.069 ± 0.007	
	Ru–Cl	2.42± 0.02	2.42± 0.02	0.061 ± 0.006	

The bond distances obtained from X-ray diffraction and EXAFS are in very good agreement with each other.

Conclusion

In this work, a set of four diamine-(ether-phosphine)ruthenium(II) **A-D** complexes were made available which are provided with different types of diamine. These complexes revealed high degree of stability in solid state, while in solution they are oxidized depending on complexes and oxidation reagents types. Oxidation-decomposition reactions of complex 1 which contains no diamine was very fast compared with complexes **A-B** under the same reaction conditions using oxygen as oxidation reagent. The chemical behavior of the ether-phosphine ligand in these complexes toward the oxidation were manipulated by $^{31}P\{^{1}H\}$ NMR spectroscopy at room temperature parallel to the appearances of the green ruthenium(II) complexes. Oxygen should be excluded during the reactions of these complexes to avoid any decomposition. In solid state, the bond distances of diamine-bis(ether-phosphine)ruthenium(II) **(A-D)** complexes obtained from X-ray diffraction and EXAFS are in very good agreement with each other. Such of these complexes are recommended to be used as standard in order to calibrate the EXAFS machine before any run take please.

Acknowledgments. Dr. I. Warad is grateful to the Graduiertenkolleg ‘‘Chemie in Interphasen’’ Tuebingen University Germany, and Dr. Saud Al-Resayes from King Saud University for his continuous encouragement.

References

[1] Lindner, E.; Warad, I.; Eichele, K. and Mayer, H.A. "Supported Organometallic Complexes Part 35: Synthesis, Characterization, and Catalytic Application of a New Family of Diamine-(diphosphine)ruthenium(II) Complexes." *J. Organomet. Chem.,* 665 (2003), 176-185.

[2] Warad, I.; Al-Gharabli, S.; Al-Labadi, A. and Abu-Rayyan, A. "Synthesis, Characterization and NMR Studies of Novel1 Hemilabile Neutral and Dicationic Palladium(II) Complexes: Pd(η^2-$PH_2PCH_2CH_2OCH_3)_2$ and Pd(η^1-$PH_2PCH_2CH_2$-$OCH_3)_2$ diamine by Using Ether-phosphine Ligand." *J. Saudi Chem. Soc.,* 9 (2005), 507-518.

[3] Lindner, E.; Warad, I.; Eichele, K. and Mayer, H. A. "Supported Organometallic Complexes Part 34: Synthesis and Structures of an Array of Diamine(ether-phosphine)ruthenium(II) Complexes and Their Application in the Catalytic Hydrogenation of *Trans*-4-phenyl-3-butene-2-one." *Inorg. Chim. Acta,* 350 (2003), 49-56.

[4] Lu, Z-L.; Eichele, K.; Warad, I.; Mayer, H.A.E.; Lindner, Jiang Z. and Schurig, V. "Supported Organometallic Complexes: Bis(methoxyethyldimethylphosphine)-ruthenium(II) Complexes as Transfer Hydrogenation Catalysts." *Z. Anorg. Allg. Chem.,* 629 (2003), 1308-1315.

[5] Warad, I.; Lindner, E.; Eichele, K. and Mayer, A. H. "Supported Organometallic Complexes Part 39: Cationic Diamine(ether–phosphine)ruthenium(II) Complexes as Precursors for the Hydrogenation of *Trans*-4-phenyl-3-butene-2-one." *Inorg. Chim. Acta,* 357 (2004), 1847-1853.

[6] Lindner, E.; Al-Gharabli, S.; Warad, I.; Mayer, H. A.; Steinbrecher, S.; Plies, E.; Seiler, M. and Bertagnolli, H. "Supported Organometallic Complexes: Diaminediphosphineruthenium(II) Interphase Catalysts for the Hydrogenation of α,ß-unsaturated Ketones." *Z. Anorg. Allg. Chem.,* 629 (2003), 161-171.

[7] Warad, I. and Al-Resayes, S. " Phosphorus-31 NMR and FAB-Mass Spectroscopes to Confirm Synthesis of Diamine(diphosphine)ruthenium(II) Complexes Starting from Diamine-(wther-phosphine)ruthenium(II) Complexes via Phosphine Ligands Exchanged." *J. Saudi Chem. Soc*., 10 (2006), 285-294.

[8] Bader, A. and Lindner, E. "Coordination Chemistry and Catalysis with Hemilabile Oxygen-phosphorus Ligands." *Coor. Chem. Rev.*, 108 (1991), 27-110.

[9] Valls, E.; Suades, J. and Mathieu, R. "Synthesis of New Hemilabile Amphiphilic Phosphines. Complexing Properties toward Ruthenium(II) and Catalytic Activity for Hydrogenation of Prenal." *Organometallics*, 18 (1999), 5475-5483.

[10] Noyori, R. *Asymmetric Catalysis in Organic Synthesis*. 1st ed., New York: J. Wiley and Sons, 1994.

[11] Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuta, C. and Noyori, R. "*Trans*-RuH(η^1-BH_4)(binap)(1,2-diamine): A Catalyst for Asymmetric Hydrogenation of Simple Ketones under Base-free Conditions." *J. Am. Chem. Soc.,* 124 (2002), 6508-6509 and reference their in.

[12] Hashiguchi, S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T. and Noyori, R. "Kinetic Resolution of Racemis Secondary Alcohols by Ru(II)-catalyzed Hydrogen Transfer." *Angew. Chem. Int. Ed. Engl.,* 36 (1997), 288-290.

[13] Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T. and Noyori, R. "The Catalyst Precursor, Catalyst, and Intermediate in the Ru-II-promoted Asymmetric Hydrogen Transfer between Alcohols and Ketones." *Angew. Chem, Int. Ed. Engl.,* 36 (1997), 285-288.

[14] Abdur-Rashid, K.; Faatz, M.; Lough, A. J. and Morris, H. R. "Catalytic Cycle for the Asymmetric Hydrogenation of Prochiral Ketones to Chiral Alcohols: Direct Hydride and Proton Transfer from Chiral Catalysts *Trans*-Ru$(H)_2$(diphosphine)(diamine) to Ketones and Direct Addition of Dihydrogen to the Resulting Hydridoamido Complexes." *J. Am. Chem. Soc*., 123 (2001), 7473-7474 and reference their in.

[15] Lindner, E.; Salesch, T.; Brugger, S.; Steinbrecher, S.; Plies, E.; Seiler, M.; Bertagnolli, H. and Mayer, A. M. "Accessibility Studies of Sol-Gel Processed Phosphane-substituted Iridium(I) Complexes in the Interphase." *Eur. J. Inorg. Chem.,* (2002), 1998-2006.

[16] AUTOBK. EXCURV92: Program for the EXAF Calculation, University of Washington, USA, 1992.

[17] Sheldrick, G. M. SHELXS-90: Program for Crystal Structure Solution, University of Göttingen, Germany, 1990.

[18] Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[19] Feigl, F. *Spot Tests in Organic Analysis*. New York: Elsevier Publishing Co., 1956.

الأكسدة التدميرية لبعض معقدات ثنائي أمين ايثرفوسفين روثنيوم (II) مع دراسة مقارنة لتركيبها البنائي بواسطة تقنية الامتداد التركيبي الامتصاصي للأشعة السينية (EXAF) والأشعة السينية التحليلي (X-ray)

إسماعيل خليل وراد

قسم الكيمياء، كلية العلوم، جامعة الملك سعود،

الرياض، المملكة العربية السعودية

(قدم للنشر في ١٤٢٧/٨/٢٤هـ؛ وقبل للنشر في ١٤٢٧/١٢/١٩هـ)

ملخص البحث. تم تحضر معقدات من ثنائي ايثرفوسفين روثنيوم (+٢) Complex A-D وذلك بواسطة استخدام معقد ايثرفوسفين روثنيوم (+٢) Complex 1 كمركب أولي. لقد أظهرت هذه المعقدات درجة عالية من الثبات في الحالة الصلبة، لكن في حالة وجود هذه المركبات في محلول باستخدام ثنائي كلوريد الميثان كمذيب تأكسد بدرجات مختلفة، معتمدة على نوع المعقد والعامل المؤكسد.

تم في هذه الدراسة استخدام كل من الأوكسجين وفوق أكسيد الهيدروجين في غياب الأوكسجين كعوامل مؤكسدة بهدف دراسة تفاعل الأكسدة المدمر للمعقدات المذكورة كلٌّ على حدة. لوحق السلوك الكيميائي لمتصلة ايثرفوسفين في معقدات روثنيوم (+٢) أثناء التفاعل مع العوامل المؤكسدة بواسطة طيف الرنين النووي المغناطيسي للفسفور[٣١]، بالإضافة إلى التغير الظاهر في اللون، حيث كان ظهور اللون الأخضر دليلاً كافيًا على اكتمال التأكسد المدمر لهذه المعقدات. قورنت كل من أطوال الروابط وبعض الثوابت الشكلية في المعقدات المدروسة والمذكورة أعلاه بواسطة كل من الأشعة السينية التحليلي X-ray crystallography وتقنية الامتداد التركيبي لامتصاص الأشعة السينية EXAF.