

**PHOSPHORUS-31 NMR AND FAB-MASS SPECTROSCOPES TO CONFIRM SYNTHESIS OF DIAMINE(DIPHOSPHINE)RUTHENIUM(II) COMPLEXES STARTING FROM DIAMINE(ETHER PHOSPHINE)RUTHENIUM(II) COMPLEXES VIA PHOSPHINE LIGANDS EXCHANGED**

**Ismail Warad<sup>1\*</sup> and Saud I. Al-Resayes<sup>2</sup>**

<sup>1</sup>Department of Chemistry, Girls College at Hawtat Sudayr, Saudi Arabia

<sup>2</sup>Department of Chemistry, College of Science King Saud University,

P.O. Box 2455, Riyadh-11451, Saudi Arabia

(Received 1<sup>st</sup> May 2005; Accepted 15<sup>th</sup> Jan. 2006)

( )

The ligands exchange of the ether-phosphine ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ ) on the diamine(ether-phosphine)ruthenium(II) with 1,3-bis(diphenylphosphino)propane as a bidentate chelate ligand successfully occurs to produce diamine[1,3-bis(diphenylphosphino)propane]ruthenium(II) complexes in a good yields under vigorous stirring for one week in an inert atmosphere using dichloromethane as solvent. Several ether-phosphine-RuCl<sub>2</sub> complexes with different types of diamine have been tested to confirm the substitution method. In order to collect more information about the system <sup>31</sup>P{<sup>1</sup>H} NMR and <sup>13</sup>C{<sup>1</sup>H} NMR as well as FAB- Mass spectroscopy have been investigated in parallel way to control and support the ligands exchange reaction processes.

**Keywords:** Ruthenium(II) complexes; Ether-phosphines; Diphosphine ; Diamines; NMR.

## INTRODUCTION

Phosphines and diphosphines are important ligands in transition-metal catalyzed reactions and the electronic and steric effects of the phosphine have a pronounced influence on the organic transformation that take place at the transition metal center [1-4]. The search for new phosphine or diphosphine ligands that will enhance the rate, yield, or specificity of organic transformations remains an active field of research. Although a wide range of stereoselective reducing agents are available, each reagent has a limited scope due to

the inherent chemical property as well as the difficulty in structural modification [2-10]. Development of stereoselective hydrogenation catalyzed by transition metal-based molecular complexes is ardently desired because of the higher structural permeability of the catalyst, in addition to a series of practical benefits [5,6,8,10]. This problem was partially dissolved since the discovery that: ruthenium(II) complexes system containing diphosphine and 1,2-diamine ligands which, in the presence of a base and 2-propanol, proved to be an excellent catalysts for the hydrogenation of ketones under mild conditions

\* To whom all correspondence should be addressed; Tel.: 00966(0)501485303; Fax 00966(0)64450095; email: (ismeilkw@hotmail.com).

[6-21]. For the same target several complexes of these types have been prepared and tested as asymmetrical hydrogenation complexes [4-21]. The source of the transferred hydrogen atom was attributed to a metal-centered hydride. Generally, the most widely accepted theory is that at least one NH and a RuH unit is intimately involved in the hydride transfer process [5,6,9].

Recently we reported on a versatile synthetic route to a set of neutral and cationic diamine-(ether-phosphine)ruthenium(II) and neutral diamine(diphos)ruthenium(II) complexes and their complete structural characterization [14-21]. We introduced to the literature a facile and fast synthetic method of a series of diamine-(diphos)-ruthenium(II) complexes, within a few minutes one of the diphosphine ligands was quantitatively exchanged from  $\text{Cl}_2\text{Ru}(\text{diphos})_2$  by the corresponding diamine [16,21].

$^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy has proven to be an invaluable experimental technique to gain information about the structure of phosphorus-containing molecules and reaction processes [22,23]. Important parameters in this study are the chemical shift  $\delta$  ( $^{31}\text{P}$ ) as well as the multiplicity. In order to gain further more information on the structural changes of Ru(II) complexes during the phosphine ligands exchange processes and parallel to the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, FAB- mass spectroscopy was investigated to this study.

Here we wish to report a new method of Ru(II) complexes synthesis, which describes a procedure for the preparation of Ru(II) complexes with diphosphine and diamine ligands  $2\text{L}_1-2\text{L}_4$  starting from other readily available materials diamine(ether-phosphine)ruthenium(II)  $1\text{L}_1-1\text{L}_4$  complexes [14,19], by exchanging of two ether-phosphine molecules with one molecule of diphosphine ligand under mild condition. As a diphos ligand 1,3-bis(diphenylphosphino)propane (dppp) was selected, for two reasons, because in a subsequent investigation it can be attached to a spacer unit at the symmetric carbon atom 2 of the ligand backbone then transferring the system into interphase chemistry can be done [16,18], additionally, it supposed to form the more stable bidentate six-membered ring cyclometallated complexes.

## 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  $\text{CH}_2\text{Cl}_2$ , n-hexane, and  $\text{Et}_2\text{O}$  were distilled from  $\text{CaH}_2$ ,  $\text{LiAlH}_4$ , and from sodium / benzophenone, respectively. The ether phosphine ligand  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$  was prepared according to literature methods [14]. 1,3-Bis(diphenylphosphino)propane (dppp) was prepared according to literature methods [16]. The diamines were purchased from Acros, Fluka, and Merck and had to be purified by distillation and recrystallization.  $\text{Ph}_3\text{P}$ , n-BuLi, and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  were available from Merck and ChemPur, respectively, and were used without further purification. Elemental analyses were carried out on an Elementar Varrio EL analyzer. High-resolution  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , DEPT 135, and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows:  $^1\text{H}$  NMR 250.12 MHz,  $^{13}\text{C}\{^1\text{H}\}$  NMR 62.9 MHz, and  $^{31}\text{P}\{^1\text{H}\}$  NMR 101.25 MHz. Chemical shifts in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS.  $^{31}\text{P}$  chemical shifts were measured relative to 85%  $\text{H}_3\text{PO}_4$ . IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Mass spectra: FAB-MS, Finnigan 711 A (8 kV), modified by AMD and reported as mass/charge ( $m/z$ ).

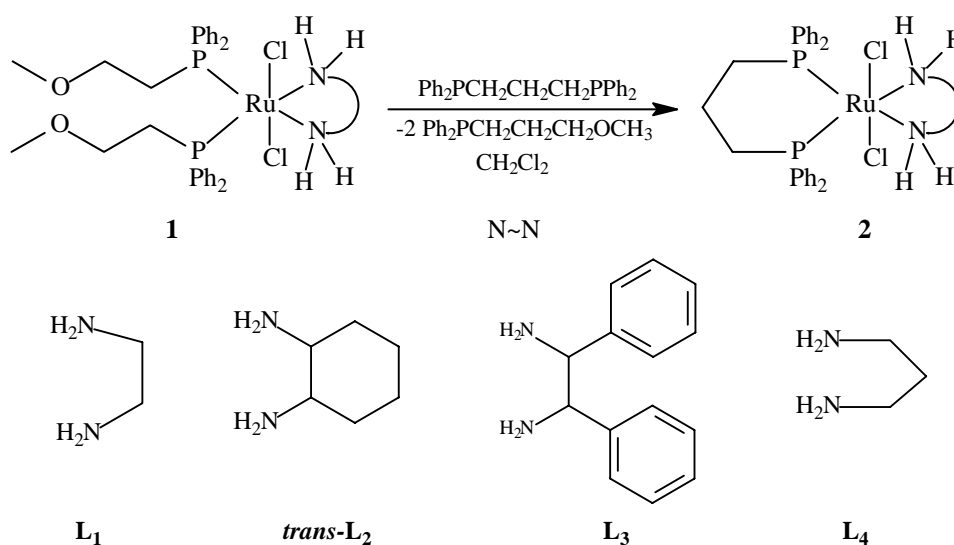
### General procedure for the preparation of the $2\text{L}_1-2\text{L}_4$ complexes from $1\text{L}_1-1\text{L}_4$ complexes:

In 200 ml volume Schlenk tube an excess equimolar amount of 1,3-Bis(diphenylphosphino)propane ligand (0.5 g, 1.22 mmole) was dissolved in 20 ml of dichloromethane then the solution was added to a stirred solution of the corresponding diamine(ether-phosphine)ruthenium(II) complex  $1\text{L}_1-1\text{L}_4$  (0.76-0.95 g, 1.20 mmole) which was already dissolved in 80 ml of dichloromethane. Subsequently the Schlenk tube was filled with argon and the mixture was vigorously stirred at

room temperature for eight days. During the reaction process samples were taken from the reaction mixture by a special glass syringe to control and check the reaction process by  $^{31}\text{P}\{^1\text{H}\}$  NMR and FAB-MS. When the reaction is completely finished the turbidity was removed of by filtration (P4), the volume of the solution was concentrated to about 5 ml under reduced pressure. Addition of 40 ml of diethyl ether caused precipitation of a solid, which was filtered (P4). After recrystallization from dichloromethane /n-hexane, the precipitation of a solid which was filtered (P4) and washed three times with 25 ml of n-hexane (to remove all free phosphine ligands). The corresponding complexes  $2\text{L}_1-2\text{L}_4$  was obtained in analytically pure form.

## RESULTS AND DISCUSSION

It was found that the known complexes of trans-diamine(diphos)ruthenium(II)  $2\text{L}_1-2\text{L}_4$  are prepared in high yields with rapid stirring of trans-diamine(ether-phosphine)ruthenium(II)  $1\text{L}_1-1\text{L}_4$ , in dichloromethane in the presence of 1,3-Bis(diphenylphosphino)propane ligand solution at room temperature as in Scheme 1. These complexes obtained after purification in good to very good yields, the yields and other conformation data were listed in Table 1. Such of these complexes were collected in shorter times as we described in the literature [16, 21], and were used as standards for this study.



Scheme 1: Synthesis of the complexes  $2\text{L}_1-2\text{L}_4$  from  $1\text{L}_1-1\text{L}_4$

Table 1: Characterization and some reactions data of  $2\text{L}_1-2\text{L}_4$  complexes.

Complex	Yield %	$^{31}\text{P}$ ppm	Reaction Time (day)	Calculated Exact Mass*	Measured FAB-MS
$2\text{L}_1$	83	41.2	7	644.19	644.10
$2\text{L}_2$	77	41.6	7	698.20	698.10
$2\text{L}_3$	81	41.5	8	796.13	796.10
$2\text{L}_4$	72	42.7	8	658.18	658.10

\*were calculated using ChemTool software.

By heating up the reaction mixture up to 100°C or Fixing to another solvents reaction like ethanol, THF, and chloroform, no change in the rate of the ligands exchange reaction was observed. The ligand substitution of the ether-phosphine on the diamine(ether-phosphine)-ruthenium(II) **1L<sub>1</sub>-1L<sub>4</sub>** complexes with dppp ligand successfully occurred to yield a yellow diamine(diphos)ruthenium(II) **2L<sub>1</sub>-2L<sub>4</sub>** complexes in dichloromethane only by vigorous stirring in an inert atmosphere for around eight days period time.

The presence of aliphatic ether part in the backbone of the monodentate ether-phosphine (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>) ligand facilitate the exchanging of it by the bidentate (dppp) ligand on Ru(II)-phosphine-diamine complexes, which never be occurred in case of using an other monodentate-phosphine ligands such as triphenyl-phosphine (PPh<sub>3</sub>).

In the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **2L<sub>1</sub>-2L<sub>4</sub>** are very simple, they exhibit a singlets which reveal that the phosphine groups are chemically equivalent in solution, due to the C<sub>Zv</sub> symmetry of the RuCl<sub>2</sub>(dppp)diamine complexes. The phosphorus chemical shifts of RuCl<sub>2</sub>(dppp)diamine complexes are differ by 1-5 ppm compared with the corresponding diamine(ether-phosphine)-ruthenium(II), which is quite enough to be recorded.

The <sup>31</sup>P{<sup>1</sup>H} NMR of **2L<sub>1</sub>** in dichloromethane exhibit a singlet at 41.2 ppm which start to increase after dppp ligand addition, instead of a singlet at 38.8 ppm belongs to **1L<sub>1</sub>** which decreased parallel to **2L<sub>1</sub>** increasing. The appearing of the free monodentate ether-phosphine ligand at -21.3 ppm as well as the consuming of the free bidentate diphosphine (dppp) ligand at -16.5 ppm clearly confirm that two ether-phosphine ligands on **1L<sub>1</sub>** were replaced by one dppp ligand to reveal the trans-configured dichloro-RuCl<sub>2</sub> complex (**2L<sub>1</sub>**) as shown in Figure 1.

Trace of RuCl<sub>2</sub>(dppp)<sub>2</sub> was detected as a special case (side product) by <sup>31</sup>P{<sup>1</sup>H} NMR as shown in Figure 2, when ether-phosphine-RuCl<sub>2</sub> with 1,3-diaminopropane (**1L<sub>4</sub>**) as diamine ligand was investigated, which indicated that a little amount of 1,3-diaminopropane was exchanged also by ligand dppp and ruthenium six-membered ring formed by 1,3-diamine is less stable compared to ruthenium five-membered ring formed by 1,2-diamine. In all the other cases the ligands exchange reactions are very clean and clear processes, with no side reactions are detected.

<sup>1</sup>H NMR spectra of the diamine(dppp)-ruthenium(II) complexes **2L<sub>1</sub>-2L<sub>4</sub>** characteristic sets of signals were observed, which are attributed to the phosphine and diamine ligands, the result are in agree with the literature [16].

Characteristic sets of resonances between 20-30 and 30-50 ppm are found in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2L<sub>1</sub>-2L<sub>4</sub>**, which are attributed to the aliphatic part of the phosphine and diamine ligands, respectively. AXX' splitting patterns were observed for the aliphatic and aromatic carbon atoms directly attached to phosphorus. The Dept <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **2L<sub>3</sub>** complex as an example to corroborate this structural synthetic method are represented in Figure 3.

For farther more improvements, FAB mass spectra was introduced to the study, as an example reaction, **1L<sub>3</sub>** complex to produce **2L<sub>3</sub>** complex before and during as well as after the reaction processing, were recorded in positive mode show strong peaks corresponding to the parent ion M<sup>+</sup>, the [M-Cl]<sup>+</sup> and the [M-Cl<sub>2</sub>]<sup>+</sup> ion along with additional fragment ions as illustrated in Figure 4 and Table 2.

The IR spectra of the complexes **2L<sub>1</sub>-2L<sub>4</sub>** in particular show four main sets of characteristic absorptions in the ranges 3454-3287, 3254-3216, 3182-3158, and 270-250 cm<sup>-1</sup>, which can be assigned to NH<sub>2</sub>, amine-CH, phosphine-CH, and RuCl stretching vibrations, respectively.

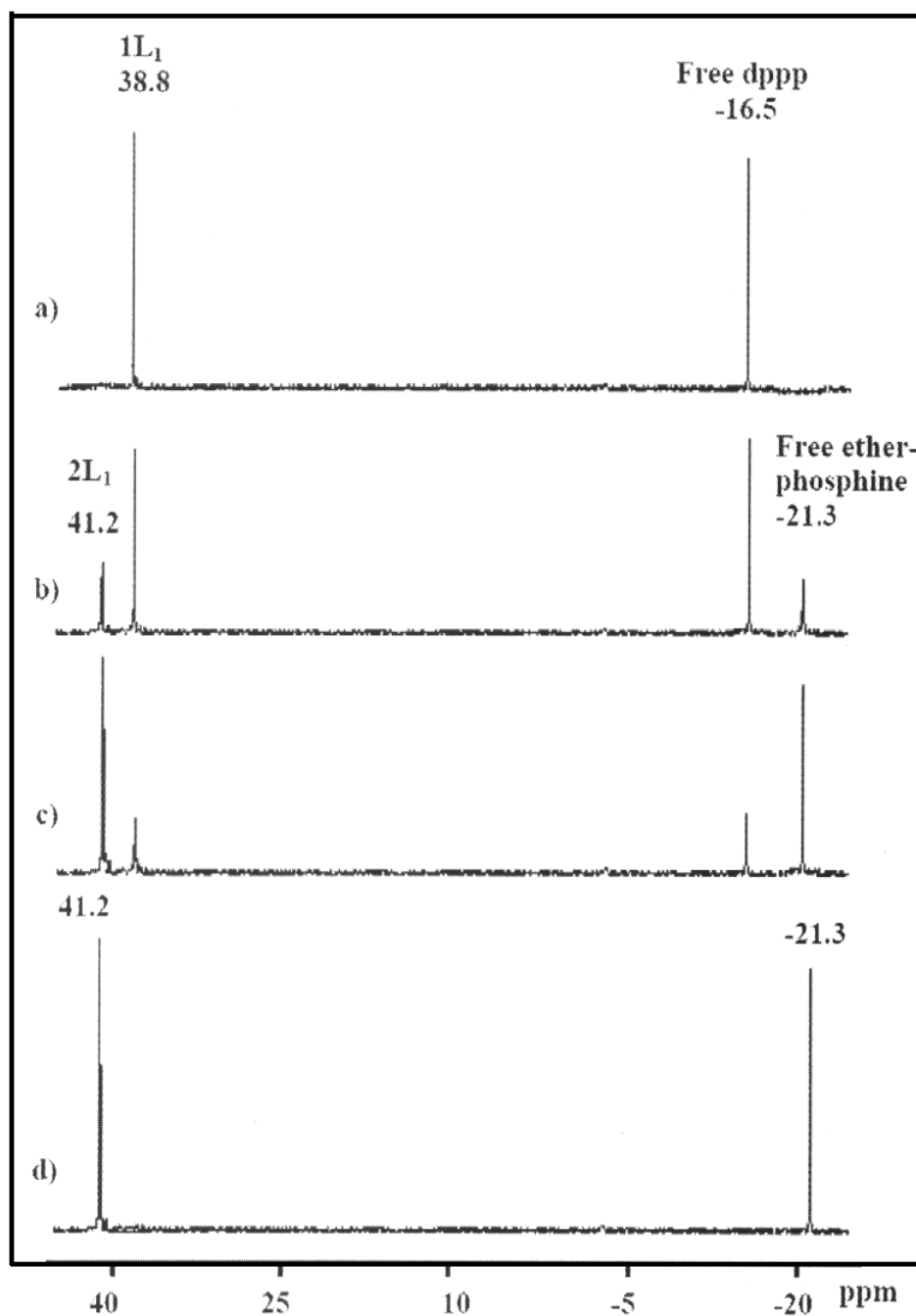


Figure 1: Time-dependent  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic of the reaction between  $1\text{L}_1$  complex and dppp ligand under vigorous stirring in  $\text{CH}_2\text{Cl}_2$  to produce  $2\text{L}_1$  complex; a) 2 hour from the dppp addition (no change); b) the same reaction mixture but after 1 day; c) after 4 day; d) after 7 day.

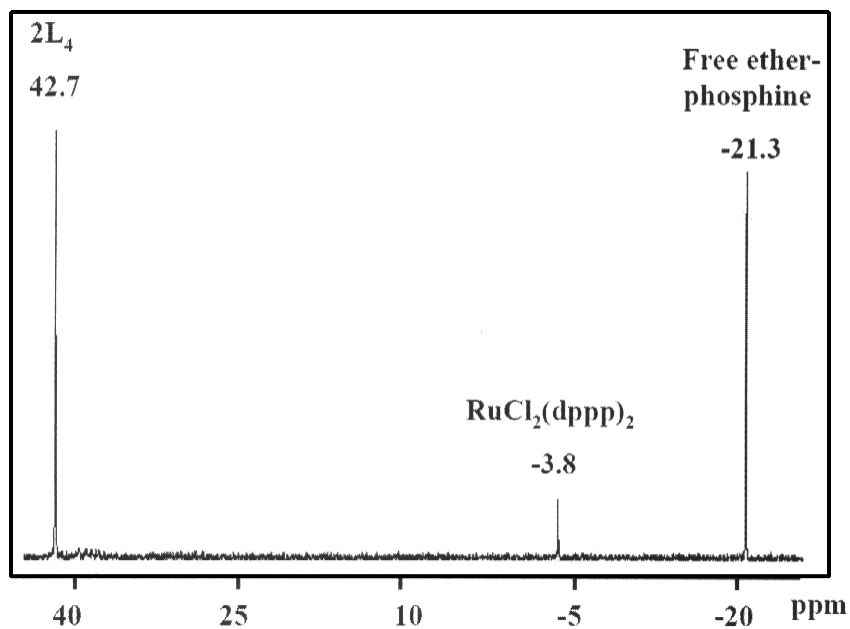


Figure 2:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic of  $2\text{L}_4$  complex and free ether-phosphine ligand products (produced from  $1\text{L}_4$  and dppp) as well as the  $\text{RuCl}_2(\text{dppp})_2$  complex as side product.

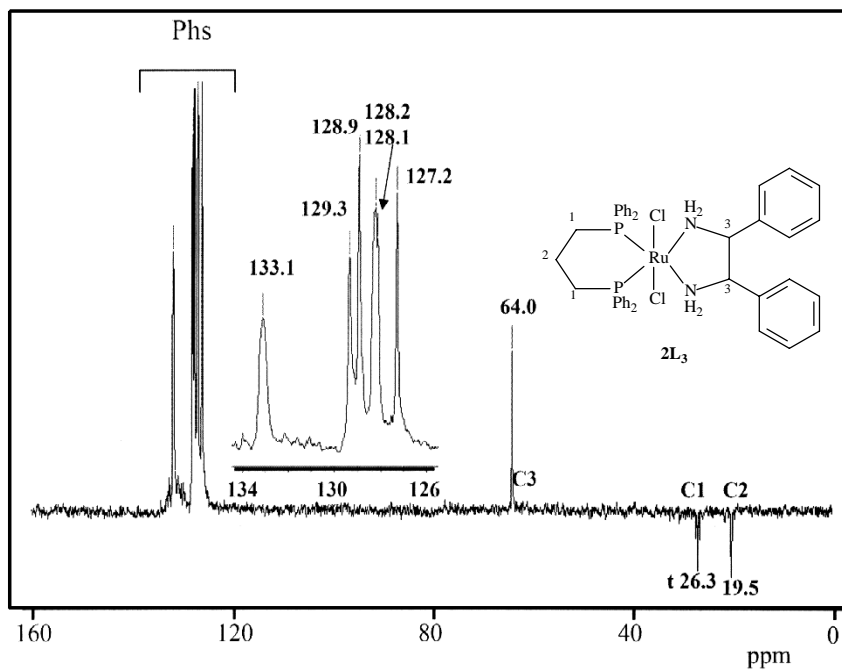


Figure 3: The Dept  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra corroborated the structure of complex  $2\text{L}_3$

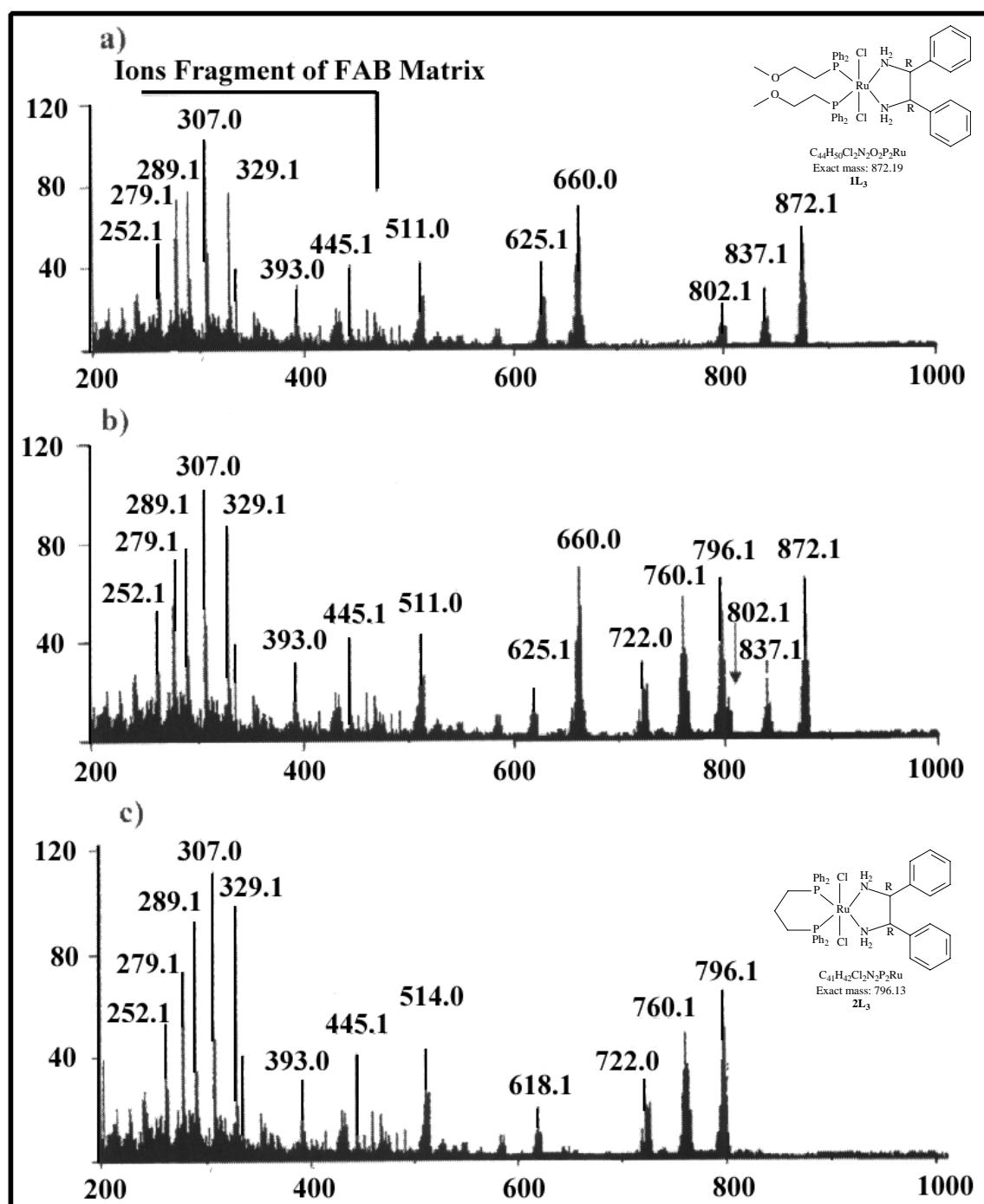


Figure 4: FAB-MS of the reaction between 1L<sub>3</sub> complex and dppp ligand in CH<sub>2</sub>Cl<sub>2</sub> to produce 2L<sub>3</sub> complex [a] 1 hour after addition of dppp and under vigorous stirring (1L<sub>3</sub> fragments); b) the same reaction mixture but after 3 day (1L<sub>3</sub> + 2L<sub>3</sub> fragments); c) after 8 day (2L<sub>3</sub> fragments), both the free phosphine ligands can't be detected by FAB-MS.

**Table 2: The main ions fragment and their chemical shifts of  $1L_3$  and  $2L_3$  complexes.**

Complex	Ion Fragment	Chemical Shift
$1L_3$	$M^+$	872.1
	$M^+-Cl$	837.1
	$M^+-2Cl$	802.1
	$M^+-diamine$	660.0
	$M^+-diamine-Cl$	625.1
$2L_3$	$M^+$	796.1
	$M^+-HCl$	760.1
	$M^+-2HCl$	722.0

**Conclusion:**

In this work a set of four (diphosphine)-ruthenium(II) complexes  $2L_1-2L_4$  were made available which are provided with different aliphatic and cycloaliphatic diamines via ligands exchange technique, the bidentate dppp ligand was able to exchange two of the monodentate etherphosphine ligand on the diamine(etherphosphine)ruthenium(II)  $1L_1-1L_4$  to prepare the corresponding  $2L_1-2L_4$  complexes. We believe that aliphatic ether part in the backbone of the  $Ph_2PCH_2CH_2OCH_3$  ligand enhanced this exchange. However, it is noteworthy that in all the cases the rate of reaction can't be increased by heating or using other solvents like (ethanol, THF, chloroform). The reaction was performed only under vigorous stirring for eight days using dichloromethane as solvent. Here we described a procedure for the preparation of Ru(II) complexes with diphosphine and diamine ligands from other readily available materials. Different types of diphosphine ligands to prepare such of these kinds of Ru(II) complexes can be tested by using this procedure in future work.

**Acknowledgments:**

We are grateful to the Graduiertenkolleg "Chemie in Interphasen" Tuebingen University, Germany.

**REFERENCES**

- [1] D.C. Gilheany and C.M. Mitchell, In The chemistry of organophosphorus compounds, F.R. Hartley, Ed.; J. Wiley and Sons: New York, Vol. 1, pp 151-190 (1990).
- [2] B. Cornils and A.W. Herrmann, Aqueous-phase organometallic catalysis, Wiley-VCH: Weinheim, Chapter 3.2 (1998).
- [3] R. Noyori, Asymmetric catalysis in organic synthesis, J. Wiley and Sons, New York (1994).
- [4] C.A. Tolman, "Steric effects of phosphorus ligand in organometallic chemistry and homogeneous catalysis". Chem. Rev., **77**, 313-348 (1977).
- [5] H. Takaya, T. Ohno and R. Noyori, In "Catalytic asymmetric synthesis", L. Ojima, Ed.; VCH: New York, Chapter 1 (1993).
- [6] T. Ohkuma, M. Koizumi, K. Muniz, G. Hilt, C. Kabuta and R. Noyori, "Trans-RuH( $\eta^1$ -BH<sub>4</sub>)(binap)(1,2-diamine): A Catalyst for asymmetric hydrogenation of simple ketones under base-free conditions". J. Am. Chem. Soc., **124**, 6508-6509 (2002) and reference therein.
- [7] S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya and R. Noyori, "Kinetic resolution of racemic secondary alcohols by Ru(II)-catalysed hydrogen transfer". Angew. Chem. Int. Ed. Engl., **36**, 288-290 (1997).



- [8] K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, "The catalyst precursor, catalyst, and intermediate in the Ru-II-promoted asymmetric hydrogen transfer between alcohols and ketones". *Angew. Chem, Int. Ed. Engl.*, **36**, 285-288 (1997).
- [9] J.-X. Gao, T. Ikariya and R. Noyori, "A ruthenium(II) complex with a C<sub>2</sub>-Symmetric diphosphine/diamine tetradentate ligand for asymmetric transfer hydrogenation of aromatic ketones". *Organometallics*, **15**, 1087-1089 (1996).
- [10] K. Abdur-Rashid, M. Faatz, A.J. Lough and H.R. Morris, "Catalytic cycle for the asymmetric hydrogenation of prochiral ketones to chiral alcohols: direct hydride and proton transfer from chiral catalysts trans-Ru(H)<sub>2</sub>(diphosphine)(diamine) to ketones and direct addition of dihydrogen to the resulting hydridoamido complexes". *J. Am. Chem. Soc.*, **123**, 7473-7474 (2001).
- [11] Y. Jiang, Q. Jiang and X. Zhang, "A new chiral Bis(oxazolinylmethyl)amine ligand for Ru-catalyzed asymmetric transfer hydrogenation of ketones". *J. Am. Chem. Soc.*, **120**, 3817-3818 (1998).
- [12] P. Gamez, F. Fache and M. Lemaire, "Asymmetric catalytic reduction of carbonyl compounds using C<sub>2</sub> symmetric diamines as chiral ligands". *Tetrahedron Asymmetry*, **6**, 705-718 (1995).
- [13] G.-Z. Wang and J.-E. Backvall, "Ruthenium-catalyzed transfer hydrogenation of imines by propan-2-ol". *J. Chem. Soc., Chem. Commun.*, 980-982 (1992).
- [14] E. Lindner, I. Warad, K. Eichele and H.A. Mayer, "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**, 49-56 (2003).
- [15] T. Ohkuma, H. Ikehira, T. Ikariya and R. Noyori, "Asymmetric Hydrogenation of cyclic alpha, beta-unsaturated ketones to chiral allylic alcohols". *Synlett.*, 467-469 (1997).
- [16] E. Lindner, I. Warad, K. Eichele and H.A. Mayer, "Supported organometallic complexes Part 35: Synthesis, characterization, and catalytic application of a new family of diamine(diphosphine)ruthenium(II) complexes", *J. Organomet. Chem.*, **665**, 176-185 (2003).
- [17] Z.-L. Lu, K. Eichele, I. Warad, H.A. Mayer, E. Lindner, Z. Jiang and V. Schurig, "Supported organometallic complexes: bis(methoxyethyl dimethylphosphine)-ruthenium(II) complexes as transfer hydrogenation catalysts". *Z. Anorg. Allg. Chem.*, **629**, 1308-1315 (2003).
- [18] E. Lindner, S. Al-Gharabli, I. Warad, H.A. Mayer, S. Steinbrecher, E. Plies, M. Seiler and H. Bertagnolli, "Supported organometallic complexes: Diaminediphosphine-ruthenium(II) interphase catalysts for the hydrogenation of  $\alpha,\beta$ -unsaturated ketones". *Z. Anorg. Allg. Chem.*, **629**, 161-171 (2003).
- [19] I. Warad, E. Lindner, K. Eichele and H.A. Mayer, "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**, 1847-1853 (2004).
- [20] C. Nachtigal, S. Al-Gharabli K. Eichele, E. Lindner and H.A. Mayer, "Structural studies of an array of mixed diamine phosphine Ruthenium(II) complexes". *Organometallics*, **21**, 105-112 (2002).
- [21] I. Warad, Diamine(phosphine)ruthenium(II) complexes and their application in the catalytic hydrogenation of  $\alpha,\beta$ -unsaturated ketones in homogeneous and heterogeneous phase, University of Teubingen, Germany (2003).
- [22] J.G. Vekade and L.D. Quin, *Phosphorus-31 NMR spectroscopy in stereochemical analysis: organic compounds and metal complexes*, VCH publishers, New York, (1987).
- [23] L.D. Quin and J.G. Vekade, *Phosphorus-31 NMR spectral properties in compound characterization and structural analysis*, VCH publishers, New York, (1994).

