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SYNTHESIS, CHARACTERIZATION AND NMR STUDIES OF NOVEL1 HEMILABILE NEUTRAL AND DICATIONIC PALLADIUM(II) COMPLEXES: $Pd(\eta^2\text{-}PH_2PCH_2CH_2OCH_3)_2$ AND $Pd(\eta^1\text{-}PH_2PCH_2CH_2OCH_3)_2$DIAMINE BY USING ETHER-PHOSPHINE LIGAND

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تم تحضير مجموعة من معقدات البلاديوم(II) المتعادل وثنائي الشحنة باستخدام ايثر-الفوسفين والدايامين كمتصلات مخلبية. بمعالجة كل من $PdCl_2(NCCH_3)_2$ و $PdCl_2(NCPh)_2$ بالكمية المناسبة من متصلة الايثر-فوسفين تم تحضير معقد ٢ وحين عولج هذا المعقد بكمية اضافية من $AgBF_4$ حضر معقد ٣ وذلك من خلال الاغلاق الاني لذرة الاوكسجين في متصلة الفوسفين للفراغ المتروك على أيون البلاديوم المركزية بفعل ازالة ايوني الكلوريد. كما حضر كل من **$4L_1$-$4L_4$** بواسطة معالجة معقد ٣ باربع دايامينات مختلفة الانواع كل على حدى.

جميع هذة المعقدات تم تحليلها ودراستها بواسطة التحليل الاول، قياس طيف الكتلة والاشعة تحت الحمراء بالاضافة لقياس طيف الرنين المغناطيسي لذرة الهيدروجين والكربون والفوسفور.

لقد احتوت هذه الدراسة على قياس وملاحقة لتفاعلي الإغلاق والفتح على أيون البلاديوم(II) بواسطة $^{31}P\{^1H\}$ NMR spectroscopy عند درجة حرارة الغرفة.

The novel (ether-phosphine)palladium(II) complexes such as $Cl_2Pd(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$ **2**, $[Pd(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2]^{+2}2BF_4^-$ **3** and $[Pd(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2\text{diamine}]^{+2}2BF_4^-$ **$4L_1$-$4L_4$** (Scheme1) have been obtained by reaction of $[PdCl_2(NCCH_3)_2$ or $PdCl_2(NCPh)_2]$ with two equimolar amounts of $Ph_2PCH_2CH_2OCH_3$ to produce complex **2**. The dicationic complex **3** was produced by treating complex **2** with slightly excess amount of two equivalent of $AgBF_4$ in CH_2Cl_2. Due to the hemilabile character, the (ether)oxygen atom of the ether-phosphine ligand immediately occupied the vacant coordination sites which created by chloride abstracted agent ($AgBF_4$) and avoided complex decomposition. Several diamines were served as an incoming ligands, the (ether)oxygen atom can easily be displaced by these diamines to prepare complexes **$4L_1$-$4L_4$** in very good yields. These complexes were characterized by NMR, IR, and mass spectroscopy as well as by elemental analyses. Because of the ring contribution of the chemical shift the dissociation and association (open and close mechanism) of the weak donor can be studied by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature.

INTRODUCTION

The design and synthesis of new functionalized ligands, capable of improving certain properties in transition metal complexes, has become a central topic in the development of inorganic and organometallic chemistry. In recent years there has been considerable interest in the design and use of what so-called hemilabile ligands [1-3]. The most widely studied hemilabile ligands have been ether-phosphine which can bind to metals in a bidentate, tridentate, or tetradentate fashion [4]. In these examples, the ether is the substitutionally labile group and the phosphine is the substitutionally inert group [5,6]. Due to this feature, the (ether)oxygen atom can easily be displaced by an incoming substrate [6-11]. The substitutionally labile groups in hemilabile ligands

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can be viewed as internal solvent molecules that stabilize a transition metal but in the presence of substrate can be easily displaced [6-10,12,13]. Thus, ether-phosphines are capable of making available and protecting vacant coordination sites which lead to an improvement in both stability and catalytic activity of the organometallic species. [5,11].

The strength of the metal-oxygen bond in ether-phosphine-metal complexes depends on the O nucleophilicity, the ring size of the cyclic ether, the number and position of the oxygen atoms in the ring, and the basicity at the metal center controlled by the donor ability of the surrounding ligands [5].

$^{31}P\{^{1}H\}$ NMR spectroscopy has proven to be an invaluable experimental technique to gain information about the structure of phosphorus-containing molecules [14,15]. Important parameters in these studies are the chemical shift δ (^{31}P), the coupling constant J_{PX} to an isotope active in NMR, and relaxation rate data.

Recently we reported on a synthetic route to a set of neutral and cationic diamine(ether-phosphine)ruthenium(II) complexes and their complete structural characterization [7,8]. The weak ruthenium-oxygen bonds in bis(chelate)ruthenium(II) complexes of the type $Cl_2Ru(P\hat{}O)_2$ were easily cleaved during the reaction with diamines [6,8,9]. Compounds of this type can easily be supported in polysiloxane matrices and are potential candidates for the application of parallel methods [16-19].

Here we wish to report on the synthesis and characterization of neutral and dicationic (ether-phosphine)$_2$palladium(II) and novel dicationic diamine(ether-phosphine)$_2$palladium(II) complexes using different aliphatic diamines as well as the NMR studies of reactions processing.

EXPERIMENTAL

General remarks, materials, and instrumenttations:

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 CH_2Cl_2, *n*-hexane, and Et_2O were distilled from CaH_2, $LiAlH_4$, and from sodium / benzophenone, respectively.

The ether-phosphine ligand $Ph_2PCH_2CH_2OCH_3$ was prepared according to literature methods [20]. The diamines were purchased from Acros, and Merck and were purified. Ph_3P, BuLi, $CH_3OCH_2CH_2Cl$, $AgBF_4$, from Fluka, and used without purification. $PdCl_2(NCCH_3)_2$ or $PdCl_2(NCPh)_2$] were prepared according to the literature. Elemental analyses were carried out on 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. Frequencies are as follows: ^{1}H NMR 250.12 MHz, $^{13}C\{^{1}H\}$ NMR 62.9 MHz, and $^{31}P\{^{1}H\}$ NMR 101.25 MHz. Chemical shifts in the ^{1}H and $^{13}C\{^{1}H\}$ 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 (δ = 0). IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Mass spectra: EI-MS; Finnigan TSQ70 (200 ^{o}C). 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:

Two equimolar amounts of the ether-phosphine ligand was dissolved in 30 ml of dichloromethane and the solution was added dropwise to a stirred solution of **1** [$PdCl_2(NCCH_3)_2$ and $PdCl_2(NCPh)_2$] individually in 30 ml of dichloromethane. The reaction mixture was stirred approximately for 20 min. at room temperature the color changed from brown to yellow. After removal of any turbidity by filtration (P4), the volume of the solution was concentrated to about 2 ml under reduced pressure. Addition of 80 ml of diethyl ether caused the precipitation of a solid which was filtered (P4) and washed three times with 25 ml of *n*-hexane each and dried under vacuum.

Complex **1** [$PdCl_2(NCCH_3)_2$ or $PdCl_2(NCPh)_2$] (400 mg, 1.554 mmol and 400 mg, 1.447 mmol) respectively were treated with 10% excess two equivalent ether - phosphine (0.753 ml, 3.102 mmol) to give complex **2**. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.85 (m,4H,PCH_2), 3.23 (s,6H, OCH_3), 3.64 (m,4H,CH_2O), 7.20-7.60 (m,20H, C_6H_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ (ppm) 13.13. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ (ppm) 26.20 (m,PCH_2),

58.78 (s, OCH_3), 68.35 (s, CH_2O), 128.69 (m, *m*-C_6H_5), 131.97 (s, *p*-C_6H_5), 134.03 (m, *o*-C_6H_5), 135.21 (m, *i*-C_6H_5). FAB - MS: *(m/z)* 664.2 (M^+).

General procedure for the preparation of the complexes 3

A solution of $AgBF_4$ (10% excess) in 20 ml of dichloromethane was added to a solution of the neutral complexes **2** in 20 ml of dichloromethane. The reaction was employed and reaction mixture was stirred at room temperature in a sealed Schlenk tube for 60 min under exclusion of light and the precipitated AgCl was removed by centrifugation. After filtration through silica the solution was concentrated to a small volume (2 ml). The addition of 60 ml of hexane caused the precipitation of a solid, which was filtered off (P3), washed three times with 25 ml portions of diethyl ether, and dried under vacuum.

Complex **2** (400 mg, 0.603 mmol) was treated with $AgBF_4$ (0.100 mg, 1.210 mmol) to give complex **3**. ^1H NMR ($CDCl_3$): δ (ppm) 3.30 (m, 4H, PCH_2), 3.72, 3.82 (2m, 4H, CH_2O), 4.01 (s, 6H, OCH_3), 7.20-7.60 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 55.00. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 30.52 (m, PCH_2), 66.82 (s, OCH_3), 72.42, (s, CH_2O), 130.34 (m, *m*-C_6H_5), 132.82 (s, *p*-C_6H_5), 134.89 (m, *o*–C_6H_5), 134.91 (m, *i*-C_6H_5). FAB - MS: *(m/z)* 594.2 (M^{+2}-2 BF_4).

General procedure for the preparation of the complexes $4L_1$-$4L_4$ (see Scheme 1)

The corresponding diamine ligand (10 % excess of L_1-L_4) was dissolved in 25 ml of dichloromethane and the solution was added dropwise to a stirred solution of **3** in 25 ml of dichloromethane. After the reaction mixture was stirred approximately for 10-20 min at room temperature the color changed from brown to yellow. After removal of any turbidity 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 the precipitation of a solid which was filtered (P4), then dissolved again in 40 ml of dichloromethane and concentrated under vacuum to a volume of 5 ml. Addition of 80 ml of n-hexane caused the precipitation of a solid which was filtered (P4) and washed three times with 25 ml of *n*-hexane each and dried under vacuum.

$4L_1$: Complex **3** (400 mg, 0.673 mmol) was treated with L_1 (0.044 ml, 0.733 mmol) to give complex **$4L_1$**. ^1H NMR (CD_2Cl_2): δ (ppm), 2.62 (m, 4H, NCH_2), 2.76 (m, 2H, PCH_2), 2.88 (br, s, 10H, NH_2, OCH_3), 2.97 (s, 4H, CH_2O), 7.20 - 7.70 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 18.97 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 26.37 (m, PCH_2), 45.21 (s, CH_2N), 58.79 (s, OCH_3), 69.93 (s, CH_2O), 128.32 (m, *m*-C_6H_5), 129.42 (s, *p*-C_6H_5), 132.98 (m, *i*-C_6H_5) 133.42 (m, *o*-C_6H_5). FAB-MS: *(m/z)* 654.2 (M^+).

$4L_2$: (with *trans*-L_2): Complex **3** (400 mg, 0.673 mmol) was treated with L_2 (0.083 ml, 0.734 mmol) to give complex **$4L_2$**. ^1H NMR ($CDCl_3$): δ (ppm) 1.05 - 3.50 (m, 22H, CH_2CH_2, PCH_2, NCH, NH_2, OCH_2), 3.00 (s, 6H, OCH_3), 7.20-7.70 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 20.43 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 24.91 (s, NCH*C*H_2), 25.47 (m, PCH_2), 30.2 (s, NCHCH_2*C*H_2), 56.65 (s, NCH), 58.45 (s, OCH_3), 69.57 (s, CH_2O), 127.98 (m, *m*-C_6H_5), 130.12 (s, *p*-C_6H_5), 133.29 (m, *o*-C_6H_5), 133.94 (m, *i*-C_6H_5). FAB-MS: *(m/z)* 700.1 (M^+).

$4L_3$: Complex **3** (400 mg, 0.763 mmol) was treated with L_3 (0.055 ml, 0.740 mmol) to give complex **$4L_3$**. ^1H NMR (CD_2Cl_2): δ (ppm), 1.86 (m, 2H, NCH_2CH_2), 2.78 (m, 2H, PCH_2), 2.90 (br, 10H, NH_2, OCH_3), 3.20 (br, 8H, CH_2O, NCH_2), 7.20-7.80 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 22.04 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 26.22 (m, PCH_2), 36.42 (s, CH_2CH_2N), 40.71 (s, CH_2N), 58.87 (s, OCH_3), 68.92 (s, CH_2O), 126.55 (m, *m*-C_6H_5), 128.80 (s, *p*-C_6H_5), 131.76 (m, *i*-C_6H_5), 132.12 (*t*, *o*-C_6H_5). FAB-MS: *(m/z)* 669.1 (M^+).

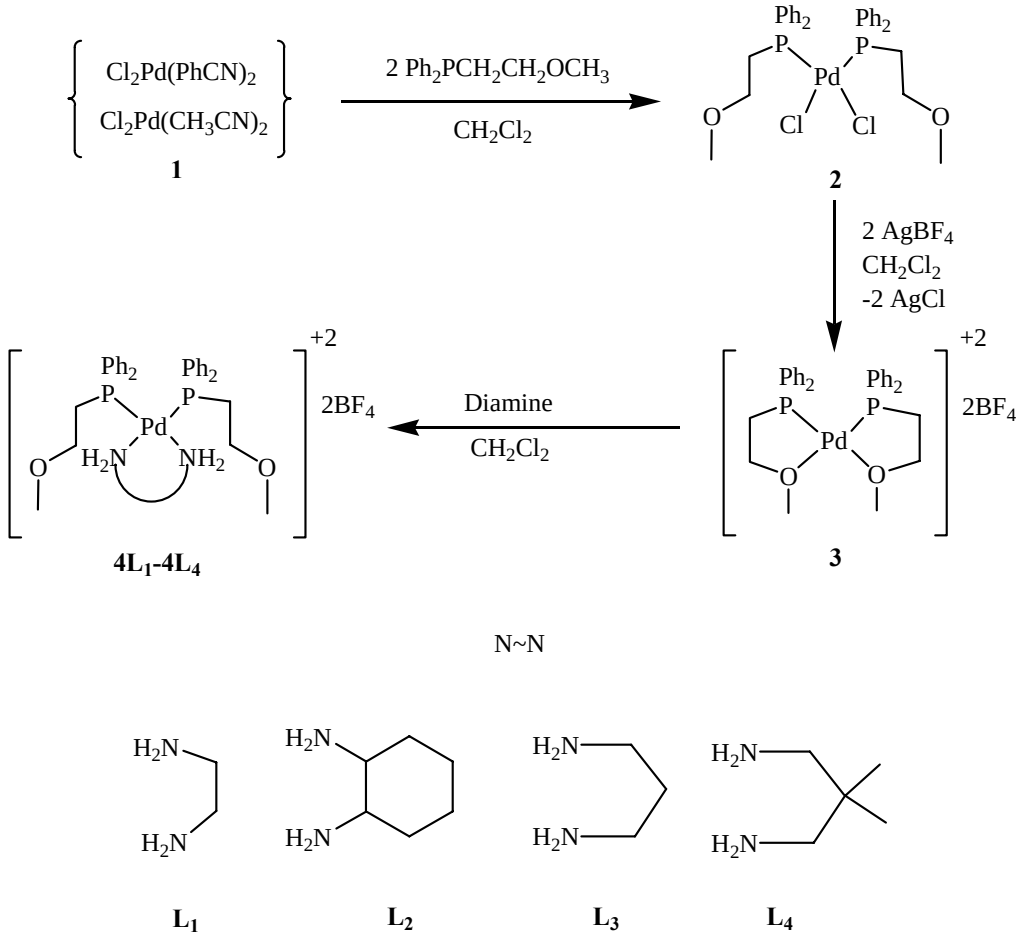
$4L_4$: Complex **3** (400 mg, 0.673 mmol) was treated with L_4 (0.074 ml, 0.734 mmol) to give complex **$4L_4$**. ^1H NMR (CD_2Cl_2): δ (ppm) 0.89 (s, 6H, $C(CH_3)_2$), 2.31 (m, 4H, NCH_2), 2.72 (m, 2H, PCH_2), 2.95 (br, s, 10H, NH_2, OCH_3), 3.18 (s, 4H, CH_2O), 7.30-7.90 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 22.33 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 25.12 (s, $C(CH_3)_2$), 25.52 (m, PCH_2), 32.53 (s, $C(CH_3)_2$), 50.11 (s, CH_2N), 59.95 (s, OCH_3), 70.32 (s, CH_2O), 128.40 (t, *Jpc* = 8.80 Hz, *m*-C_6H_5), 129.50 (s, *p*-C_6H_5), 132.87 (m, *i*-C_6H_5), 133.24 (*t*, *Jpc* = 7.42 Hz, *o*-C_6H_5). FAB-MS: *(m/z)* 697.1 (M^+).

RESULTS AND DISCUSSION

Synthesis of neutral and dicationic bis(ether–phosphine)$_2$palladium(II) 2 and 3 complexes

The neutral Palladium(II) complex **2** was obtained in quantitative yield, as yellow powder by treatment of complex **1** [$PdCl_2(NCCH_3)_2$ or $PdCl_2(NCPh)_2$] with the ether-phosphine ligand ($Ph_2PCH_2CH_2OCH_3$), at room temperature in dichloromethane, leads to the formation of complex **2** in very good yields as in Scheme 1 and Table 1. They are soluble in chlorinated organic solvents and insoluble in ethers and aliphatic hydrocarbons. Their molecular composition was corroborated by FAB mass spectra.

If the neutral dichloro(ether–phosphine)$_2$-palladium(II) complexes **2** is treated with two equivalent of $AgBF_4$ in dichloromethane two chloride atoms are abstracted within one hour (see Scheme 1). The vacant coordination site in this complex is occupied by an ether–oxygen atom resulting in the formation of the dicationic complex **3**. The hemilabile ether-oxygen reaction behavior to produce complex **3** from complex **2** by cyclization (ring closed) reaction can be followed by $^{31}P\{^1H\}$NMR spectroscopy (as in Figure 1). No side reactions were observed during the stirring duration of the reaction.



Scheme 1: Synthesis of the complexes 2, 3 and 4L$_1$-4L$_4$.

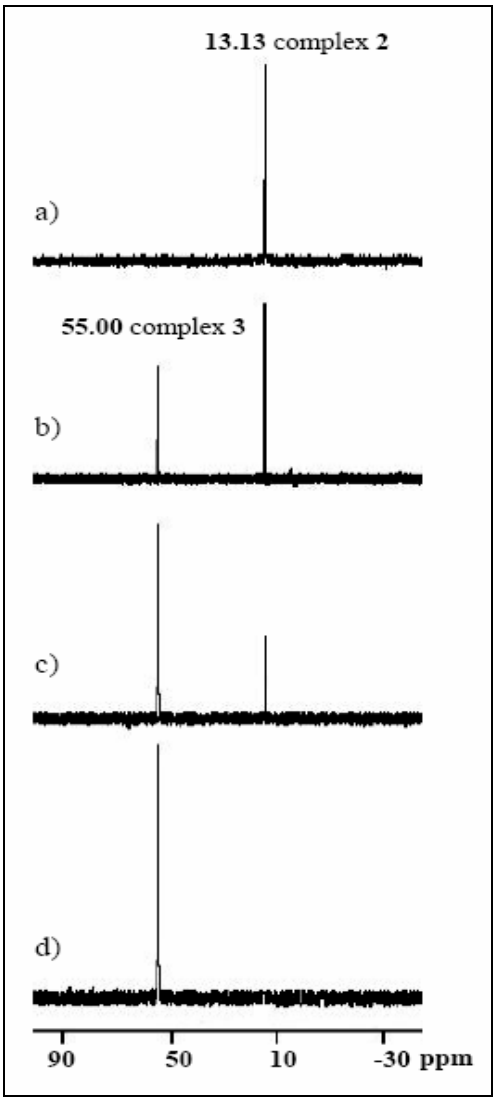


Fig. 1: Time-dependent $^{31}P\{1H\}$ NMR spectroscopic of the reaction between complex 2 and $AgBF_4$ in CH_2Cl_2 to produce Complex 3 [a) 1 min after addition of $AgBF_4$; (no change); b) 20 min after addition of $AgBF_4$; c) 40 min after addition of $AgBF_4$; d) 60 min after addition of $AgBF_4$].

Synthesis of dicationic diamine-bis(ether–phosphine)$_2$palladium(II) complexes $4L_1$-$4L_4$

The dicationic bis(ether-phosphine)$_2$-palladium(II) complex **3** has two weak palladium-oxygen bond interactions which are easily cleaved by the stronger nitrogen donors of bidentate diamine ligands. Thus treating complex **3** with a slight excess of diamines L_1-L_4 in dichloromethane gives the somewhat air-sensitive mixed dicationic diamine-bis(ether-phosphine)$_2$-palladium(II) complexes $4L_1$-$4L_4$ are formed in a very good yields (Scheme 1). They are soluble in chlorinated organic solvents and insoluble in ethers and aliphatic hydrocarbons. $^{31}P\{^1H\}$NMR spectroscopy shows that ring opening reaction of Pd-O bond to produce Pd-N bond is around 60 time faster that ring closing reaction to produce a closed Pd-O compound. The reacting of complex **3** with L_1 to prepare complex $4L_1$ was followed by ^{31}P $\{^1H\}$ NMR, while the reaction was completed in 5 min as in Figure 2.

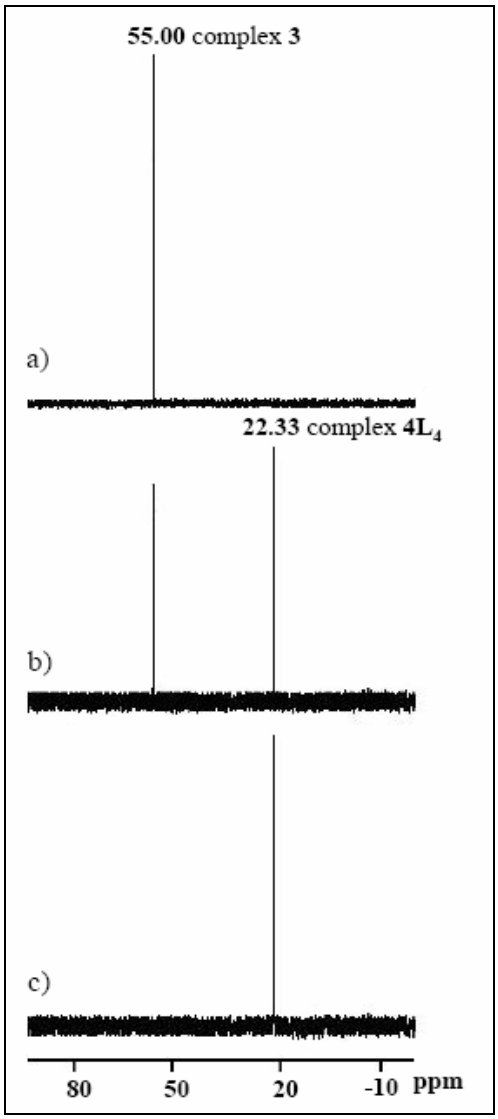


Fig. 2: Time-dependent $^{31}P\{1H\}$ NMR spectroscopic of the reaction between complex 3 and diamine L_4 in CD_2Cl_2 to produce Complex $4L_4$ [a) before addition of L_4; b) 2 min after addition of L_4; c) 5 min after addition of L_4 (the reaction was carried out in the NMR tube and measured direct after the diamine L_4 addition).

NMR investigations

The ^1H NMR spectra of the free ether-phosphine and in neutral dichloro(ether–phosphine)$_2$palladium(II) complexes **2** in addition to dicationic (ether–phosphine)$_2$palladium(II) complexes **3** were compared as Figure 3.

The chemical shift for three types of the aliphatic protons in the ether-phosphine (PCH_2 CH_2 and OCH_3) as changed dramatically by coordinated to palladium(II) complex **2** and more upfield as total complex charge increased as in

case of complex **3**. The chemical shifts of ether-phosphine fragments were listed in Table 2.

Coordination and positive charge are the major factors which could affect the chemical shift of the ligands in complexes, it is expected theoretically that the chemical shifts of PCH_2 CH_2 and OCH_3 for the ether-phosphine obey the following order:

$\{[Pd(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2]^{+2}2BF_4^-\}$ > $\{Cl_2Pd(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2\}$ > $Ph_2PCH_2CH_2OCH_3$

The experimental results which listed in Table 2 for the chemical shifts of the free ligand, neutral and dicationic palladium(II) complexes are in agree with this order.

In the ^{1}H NMR spectra of the dicationic diamine-bis(ether-phosphine)palladium(II) complexes **$4L_1$-$4L_4$** characteristic sets of signals are observed, which are attributed to the phosphine as well as to the diamine ligands. Their assignment was supported by two-dimensional H,H-COSY experiments which establish the connectivity between NH_2 and CH_2 functions in the diamine ligand, and between CH_2O and CH_2P groups in the phosphine ligand.

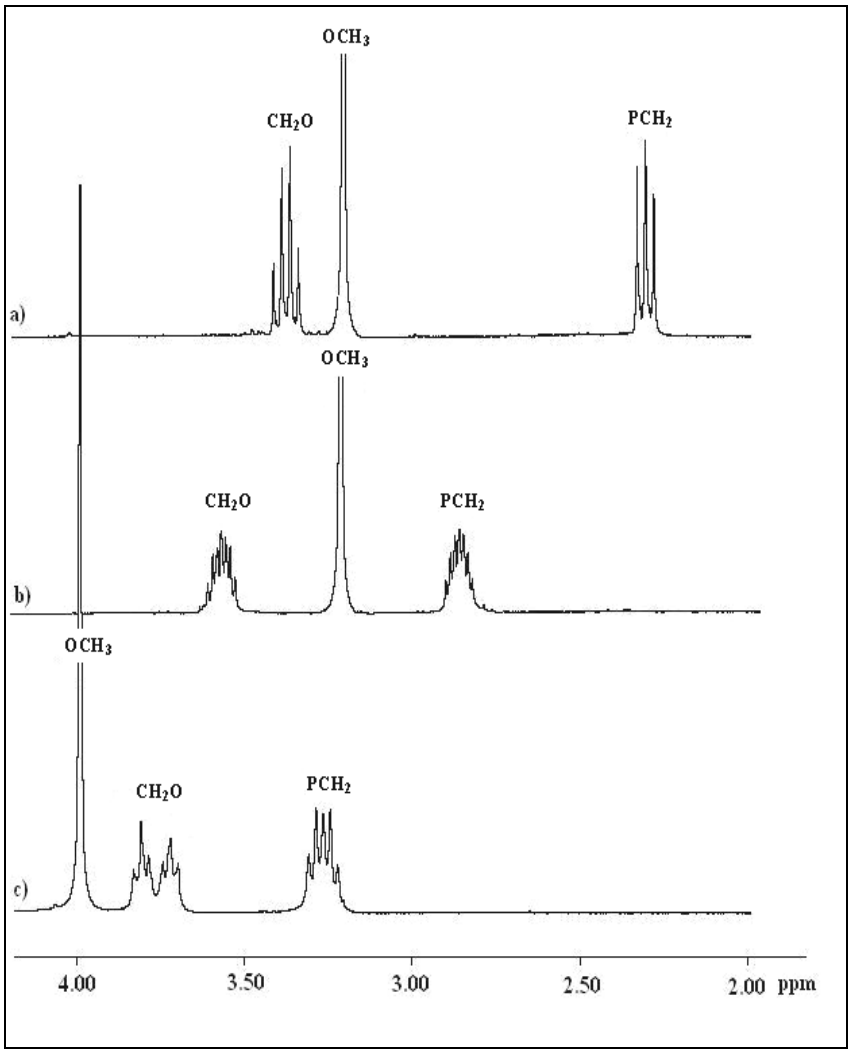


Fig. 3: The ^{1}H NMR spectra of the free $Ph_2PCH_2CH_2OCH_3$ a) compared by it self in complex 2 b) and complex 3 c).

In the $^{31}P\{^{1}H\}$ NMR spectra of complex **2,** complex **3** and complexes **4L$_1$-4L$_4$,** the singlets indicate that the phosphine groups are chemically equivalent in solution which is compatible with the C_{2v} symmetry of the square planer coordination palladium(II) complexes. The phosphorus chemical shifts constants suggest that the ether-phosphines η^1-P~O are coordinated *cis* to each other and *trans* to the diamine chelate ligand.

The $^{13}C\{^{1}H\}$ NMR spectra also corroborate the structures given in Scheme 1. Characteristic ^{13}C signals are due to the η^1-P~O and the η^2-P~O binding modes in case of complex **2** and complex **3** respectively, as well as due to the both η^1-P~O and diamines ligands in case of complexes **4L$_1$-4L$_4$**.

Table 2: The upfield chemical shifts ^{1}H NMR result of the free ether-phosphine and in neutral and dicationic palladium(II) complexes.

Groups	Fee ether-phosphine	Neutral Complex 2	Dicationic Complex 3	Δδ δ of ligand in complex 2 - δ of free ligand	Δδ δ of ligand in complex 3 - δ of free ligand
PCH_2	2.31	2.85	3.30	0.54	0.99
CH_2O	3.43	3.63	3.72 and 3.82	0.20	0.29 and 0.39
OCH_3	3.22	3.26	4.01	0.04	0.99

The Dept $^{13}C\{^{1}H\}$ NMR spectra of complex **4L$_4$** which represented in Figure 4 as an example to differentiate the C, CH_2 and CH_3 carbons, the chemical shifts of the corresponding fragments are in agree with the free ligands studies.

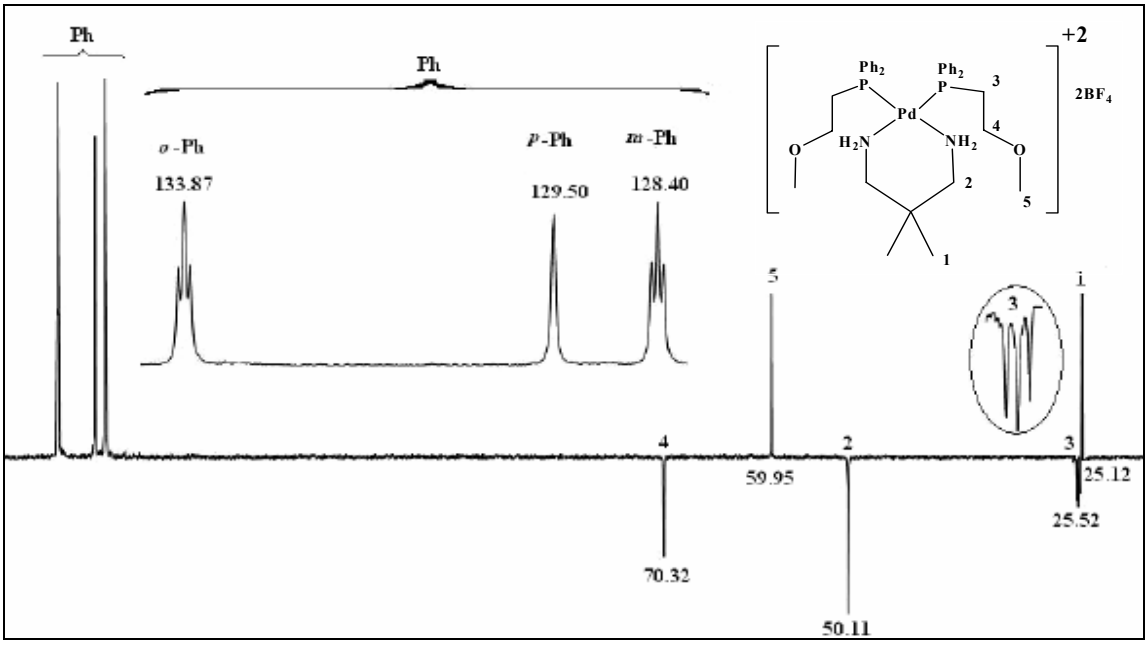


Fig. 4: The Dept $^{13}C\{^{1}H\}$ NMR spectra corroborates the structure of complex 4L$_4$

IR investigations

The IR spectra of the complexes **2** and **3** in particular show three main sets of characteristic absorptions in the ranges 3272-3205 and 3178-3165 cm^{-1}, which can be attributed to stretching vibrations of the main function group, PCH_2, Ph-H, OCH_2, OCH_3 of the phosphine ligand.

In the IR spectra of the complexes **$4L_1$-$4L_4$** an addition functions group were characterized in the ranges 3386-3300 cm^{-1}, which can be assigned to NH_2. The IR spectra of complex **$4L_1$** as an example were illustrated in Figure 5.

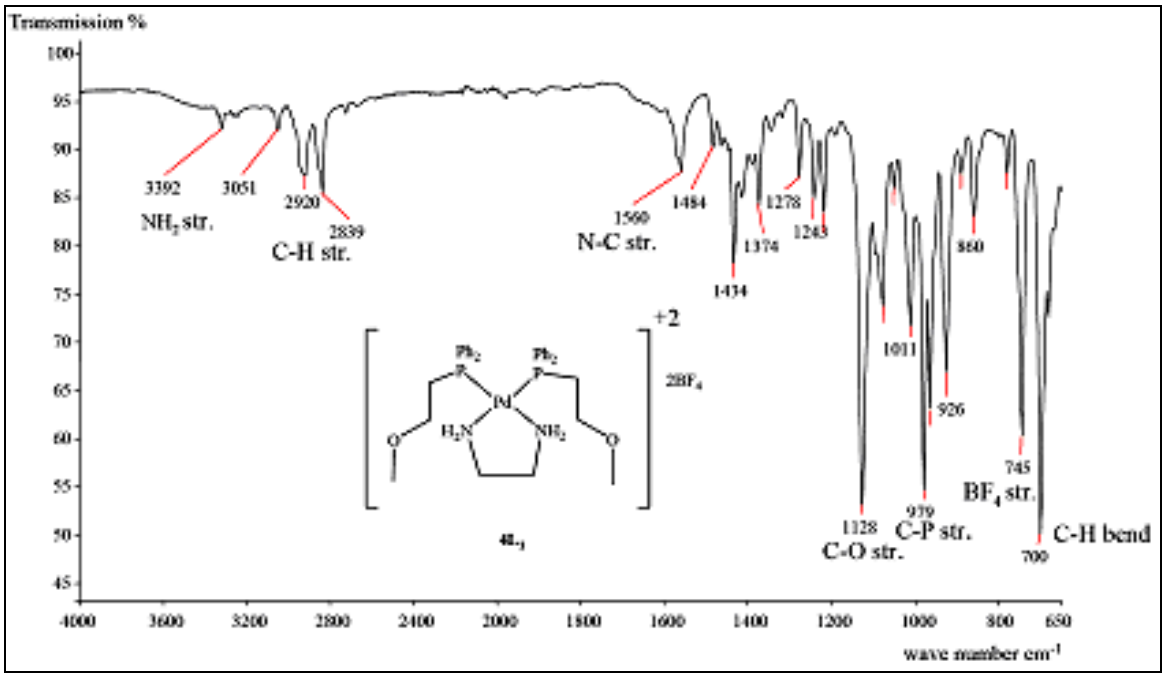


Fig. 5: Infra-red spectrum of complex $4L_1$.

Conclusion:

Neutral $Cl_2Pd(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$ complexes **2**, was made available starting from $[PdCl_2(NCCH_3)_2$ and $PdCl_2(NCPh)_2]$ complexes individually, dicationic $[Pd(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2]^{+2}2BF_4^-$ complex **3** and $[Pd(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$diamine$]^{+2}2BF_4^-$ complexes **$4L_1$-$4L_4$** were made available in a very good yield. The ^1H NMR spectra of the free ether-phosphine was compared by the neutral dichloro-(ether–phosphine)$_2$palladium(II) complexes **2** and dicationic (ether-phosphine)$_2$palladium(II) complexes **3.** The hemilability behavior of the bidentate ether-phosphine ligand in palladium(II) complex towered closing reaction to form two Pd-O bonds as in complex **3** and cleavage (opening) it by diamine to form two Pd-N bonds as in complexes **$4L_1$-$4L_4$** were followed by liquid $^{31}P\{^1H\}$ NMR.

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