Full Length Research Paper

Hemilability of ether-phosphine in ruthenium(II) complexes: ^{31}P{^{1}H}-nuclear magnetic resonance (NMR), fast atom bombardment-mass spectroscopy (FAB-MS) and extended X-ray absorption fine structure spectroscopy (EXAF) to confirm the open-closed behavior

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The hemilability of the ether-phosphine ligand [Ph$_2$PCH$_2$CH$_2$OMe] was recorded during complexes 1 and 2 synthesis. The structures of both 1 and 2 have been deduced from elemental analysis, IR, EXAF, FAB-mass spectrometry, ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. One of the chloride atoms in 1 was abstracted using AgOTf reagent to prepare the mono-cationic O-Ru-P closed 2. By treatment complex 2 with excess amount of NH$_4$Cl in 2-propanol complex 1 was re-prepared. FAB-MS, EXAF and ^{31}P{^{1}H}-NMR served to monitor the hemilability of the ether-phosphine in 1 and 2 at RT.

Key words: Ru(II) complexes, ether-phosphine, single crystal, hemilability.

INTRODUCTION

The term "hemilabile ligand" introduced by Jeffrey and Rauchfuss (1979), was attributable to polydentate chelate ligands containing two types of bonding groups (one labile and one inert). It should be emphasized that hemilability is not an intrinsic property of the sole ligand and it implies the metal-ligand couple (Jeffrey and Rauchfuss, 1979; Braunstein and Naud, 2001; Bader and lindner, 1991). These ligands significantly contained different chemical functions: hard and soft donors (often called hybrid ligands) find increasing use in chemistry because of the selectivity introduced in the metal-ligand interactions and their possible dynamic behaviour (Braunstein and Naud, 2001; Bader and lindner, 1991).

Complexes containing hemilabile phosphine-ether ligands can be regarded as species containing an intramolecular coordinated solvent (Bader and Lindner, 1991). However, limited information is available about the real catalytic properties of metal complexes containing ether-phosphine. Thus, complexes of these ligands have been investigated as models for very reactive intermediates of catalytic reactions, where coordinated solvents are believed to be involved (Warad et al., 2006, 2004; Warad, 2007; Lindner et al., 2003, 2005; Lu et al., 2003). Phosphorus-oxygen hemilabile ligands like 2-(diphenylphosphino) ethyl methyl ether (P~O), reacts with various metals of catalytic relevance due to their ability to act as both a chelate ligand, stabilizing the metal complex and a monodentate ligand providing a free coordination site for an incoming substrate (through the labilization of the weakly bonded oxygen atom). Thus, ether-phosphines are capable of making available and protecting

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vacant coordination sites which lead to an improvement in both stability and catalytic activity of the organometallic species (Lindner et al., 2003; Warad et al., 2010; Warad, 2010).

$^{31}P\{^1H\}$ nuclear magnetic resonance (NMR) spectroscopy has proven to be an invaluable experimental technique to gain information about such structures of phosphorus-containing complexes (Warad, 2009, 2011).

We have currently introduced ruthenium(II) complexes which contains hemilabile phosphine-ether ligand successfully in hydrogenation of functionalized carbonyl compounds (Lindner et al., 2003). Preferential reduction of a C=O function over a coexisting C=C linkage is observed under mild conditions (Jakob et al., 2010; Xi et al., 2009; Das et al., 2002; Hsu et al., 2009; Lindner et al., 2003).

In this work, three ruthenium(II) complexes were made available by using ether-phosphine and rac-1,2-diphenyl-1,2-ethanediamine ligands. One of the chloride atoms was abstracted using AgOTf agent to prepare mono-cationic complex 2. The closed-open mechanism of the hemilable ligand in these complexes was monitored by fast atom bombardment-mass spectroscopy (FAB-MS), extended X-ray absorption fine structure spectroscopy (EXAF) and $^{31}P\{^1H\}$-NMR spectroscopy.

MATERIALS AND METHODS

General

All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum and Schlenk-line techniques, unless otherwise noted. Ph$_2$PCH$_2$CH$_2$OMe ligand and Cl$_2$Ru(P⌒O)$_2$ were prepared according to literature methods (lindner et al., 2003), rac-1,2-diphenyl-1,2-ethanediamine and AgOTf were purchased from Across and used as purchased. Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution liquid ^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 tetramethylsilane (TMS). ^{31}P-NMR chemical shifts were measured relative to 85% H$_3$PO$_4$. Infrared (IR) data were obtained on a Bruker IFS 48 FT-IR spectrometer. Mass spectra: FAB-MS, Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (m/z).

General procedure for the preparation of 1 from Cl$_2$Ru(P⌒O)$_2$

Rac-1,2-diphenyl-1,2-ethanediamine co-ligand was dissolved in 10 ml of dichloromethane and the solution was added drop-wise to a stirred solution of Cl$_2$Ru(P⌒O)$_2$ in 10 ml of dichloromethane. The reaction mixture was stirred approximately for 20 min at room temperature and the color changed from red 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 60 ml of diethyl ether caused the precipitation of a solid which was filtered (P4), then dissolved again in 40 ml of dichloromethane and was 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 and washed three times with 25 ml of *n*-hexane each and dried under vacuum.

Cl$_2$Ru(P⌒O)$_2$ (300 mg, 0.454 mmol) was treated with 1,2-diphenyl-1,2-ethanediamine (0.105 g, 0.50 mmol) to give 1. Yield of 348 mg (88%) of a yellow powder, m.p. 220°C, ^1H NMR (CDCl$_3$): δ (ppm) 2.2 to 4.2 (m, 14H, PCH$_2$, OCH$_2$, NH$_2$CH), 2.93 (s, 6H, OCH$_3$) and 6.7 to 7.7 (m, 30H, C$_6$H$_5$). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ (ppm) 38.3 (s). $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ (ppm) 24.5 (m, PCH$_2$), 56.8 (s, OCH$_3$), 62.5 (s, NCH), 67.9 (s, CH$_2$O), 125.8 (s, o-C$_6$H$_5$), 126.8 (s, p-C$_6$H$_5$), 126.9 (m, m-C$_6$H$_5$), 127.6 (s, m-C$_6$H$_5$), 127.9, 128.1 (2s, p-C$_6$H$_5$), 131.1, 131.9 (2m, o-C$_6$H$_5$) and 133.2 (2m, i-C$_6$H$_5$), 138.8 (s, i-C$_6$H$_5$). FAB-MS: (m/z) 872.2 (M$^+$). Analytical calculation for C$_{44}$H$_{50}$Cl$_2$N$_2$O$_2$P$_2$Ru: C, 60.55; H, 5.77; Cl, 8.12; N, 3.21. Found: C, 60.31, H, 5.50; Cl, 7.97; N, 2.90%.

General procedure for the preparation of the 2 from 1

Excess (2%) of AgOTf was dissolved in 20 ml of dry 2-propanol, then added to the neutral 1 dissolved in 10 ml of fresh distilled dichloromethane in a 100 ml Schlenk tube. The reaction mixture was stirred around 10 min (during that, samples were taken and subjected to $^{31}P\{^1H\}$ NMR). After filtration through silica, the solution was concentrated to about 2 ml under reduced pressure. The corresponding cationic complex was precipitated by addition of 30 ml of diethyl ether, filtered off (P3), washed three times with 25 ml portions of diethyl ether and dried under vacuum.

1 (300 mg, 0.344 mmol) was treated with AgOTf (89 mg, 0.346 mmol) to give complex 2. Yield of 320 mg (96%) of a brown powder, 180°C, ^1H NMR (CD$_2$Cl$_2$): 0.7 to 4.6 (m, 14H, CH$_2$P, OCH$_2$, H$_2$NCH), 2.88, 2.97, 4.2, 4.4 (4s, 6H, OCH$_3$), 6.5 to 7.8 (m, 30H, C$_6$H$_5$). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): 2d (ppm) 54.6, 54.3 (d, $^2J_{PP}$ = 37.2 Hz), 48.2, 47.9 (d, $^2J_{PP}$ 37.2 Hz); $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$): 24.2 to 32.8 (m, PCH$_2$), 58.7 to 69.2 (8s, H$_2$NCH, OCH$_3$), 68.62, 69.26, 74.30, 74.58 (4m, CH$_2$O), 127.6 to 131.4 (C$_6$H$_5$). FAB-MS: (m=z) 837.2 (M) (OTf). Analytical calculation for C$_{45}$H$_{50}$ClF$_3$N$_2$O$_5$SP$_2$Ru: C, 55.11; H, 5.02; Cl, 3.53; N, 2.42. Found: C, 54.70; H, 5.30; Cl, 3.67; N, 2.32%.

General procedure for the preparation of 1 from 2

2 g of NH$_4$Cl was dissolved in 10 ml of 2-propanol in a 100 ml Schlenk tube, the non-soluble NH$_4$Cl was removed by filtration, 2 ml of this solution was added to stirred solution of 100 mg of complex 2 dissolved 20 ml of dichloromethane. Several samples were taken by time and subjected to $^{31}P\{^1H\}$-NMR, 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), which was washed three times with 25 ml of *n*-hexane each and dried under vacuum.

RESULTS AND DISCUSSION

Ruthenium(II) 1 and 2 synthetic investigation and structural behavior

Treatment of Cl$_2$Ru(P⌒O)$_2$ with an equivalent amount of raceme 1,2-diphenyl-1,2-ethanediamine ligand in dichloromethane resulted in the formation of 1, the stepwise formation of 2 from 1 is detected by $^{31}P\{^1H\}$-NMR spectroscopy, the singlet of Cl$_2$Ru(P⌒O)$_2$ at δ$_p$ = 64.4 ppm was displaced by another singlet at δ$_p$ = 38.6 ppm belonging to 1, confirming the hemilabile ring open cleavage of 2Ru-O in Cl$_2$Ru(P⌒O)$_2$ to form the 2Ru-N of
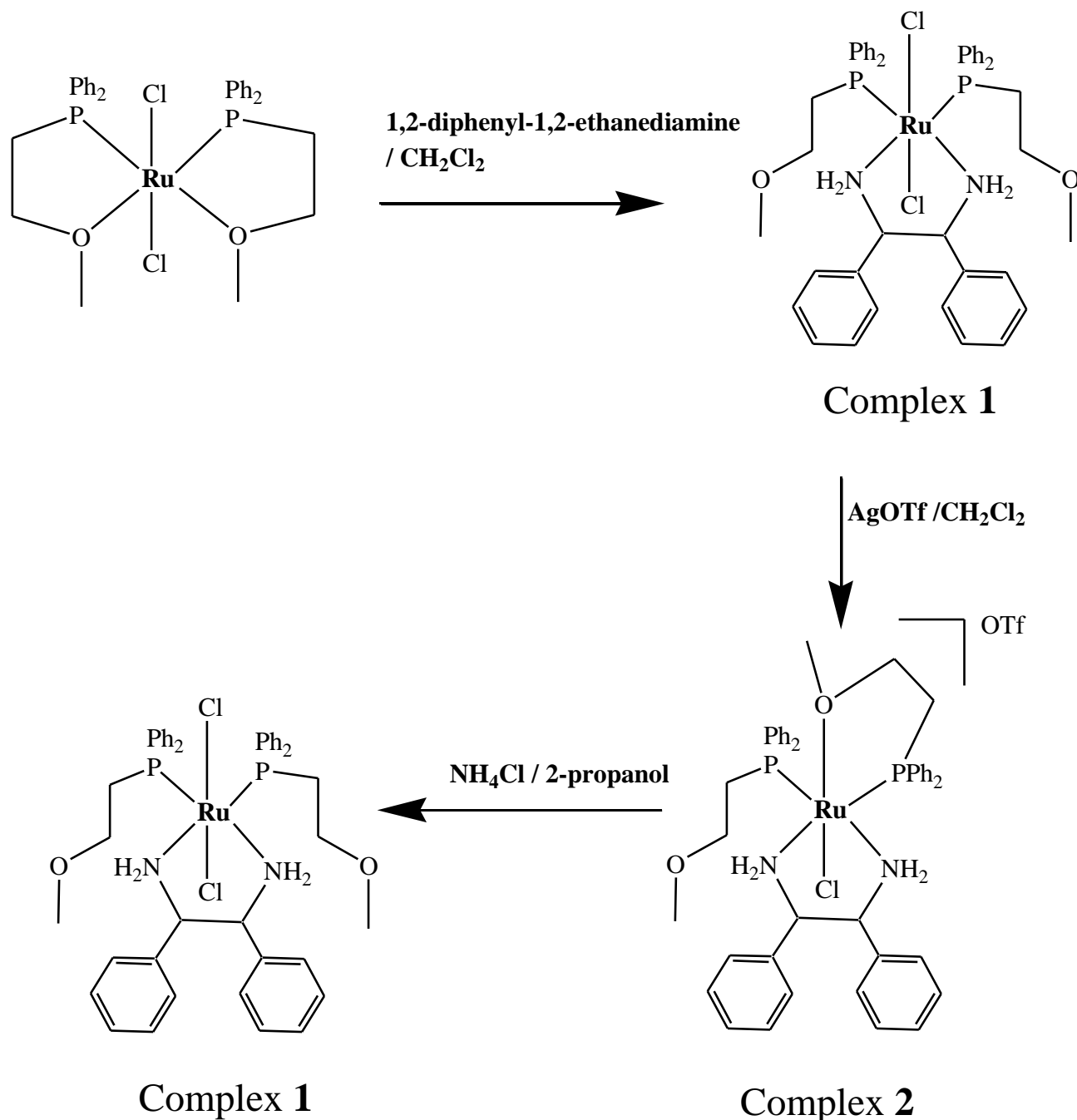
Figure 1. The synthetic route to prepare Ruthenium(II) complexes.

1, as shown in Figure 1.

If 1 is treated with one equivalent of AgOTf in dichloromethane, only one chloride is abstracted. The vacant coordination site in the complex is occupied by the oxygen atom of 2-(diphenylphosphino)ethyl methyl ether ether-oxygen ligand resulting in the formation of the mono-cationic O-Ru-P five membered ring 2, as shown in Figure 1. In contrast to the reaction with AgBF$_4$, which needs several hours, that with AgOTf proceeds within a few minutes (Lindner et al., 2003). The brown mono-cationic complexes are sensitive to aerial oxygen, dissolve readily in chlorinated organic solvents, and are insoluble in ethers and aliphatic hydrocarbons. The molecular composition of 1 and 2 has been deduced from elemental analysis, infrared spectroscopy, FAB-mass spectrometry, ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy.

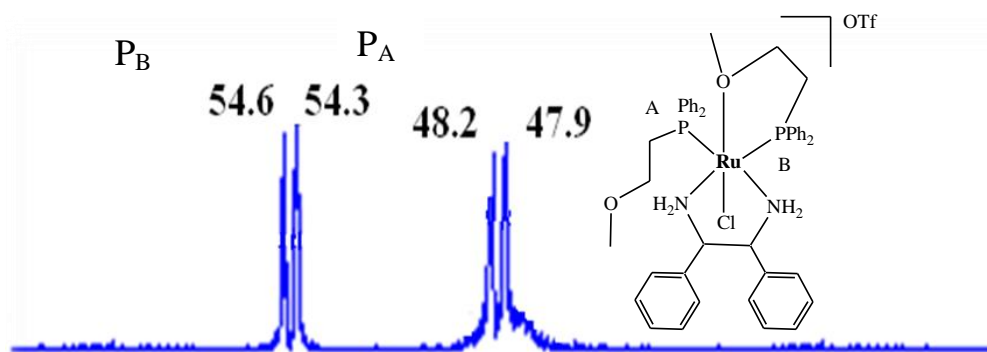In the ^{31}P{^{1}H} NMR spectra, the two doublet which are observed for 2 with typical coupling constants between

Figure 2. $^{31}P\{^1H\}$ NMR (ppm) spectrum of 2 direct dissolved in CD_2Cl_2 at room temperature.

36.2 Hz agree with the cis arrangement of the phosphine ligands (Figure 2).

Treatment of the mono-cationic 2 with chlorinated agent, such as NH_4Cl in 2-propanol leads to the formation of the neutral 1 as in Figure 1.

Due to the hemilabile character, the oxygen donor in the ether-phosphine ligand is regarded as an intramolecular solvent impeding decomposition of such complexes by protecting the vacant coordination sites, which accelerates and stabilizes the synthesis of 1 without any side products. The weak ruthenium-oxygen bonds in mono-cationic 2 are easily cleaved by an incoming molecule, such as Cl^- in NH_4Cl in 2-propanol to form the neutral 1 again as shown in Figure 1.

The stepwise reformation of 1 from 2 using excess NH_4Cl/2-propanol is monitored by $^{31}P\{^1H\}$-NMR spectroscopy. All the $^{31}P\{^1H\}$-NMR signals belonging to the mono-cationic 2 as shown in Figure 3 was replaced by one singlet belonging to the neutral 1, signals of 2 start to disappear parallel to the appearing of the singlet at δ_p = 38.6 ppm, this reaction confirm the hemilabile ring open through cleavage of Ru-O in mono-cationic 2 by NH_4Cl in 2-propanol to form the Ru-Cl in neutral 1 within 10 min, as shown in Figure 3.

The procedure of the synthesis in this work which is illustrated in Figure 1 can serve as a novel method for halides exchanges in ruthenium(II) complexes containing such of this ether-phosphine ligand.

FAB mass spectra of 1 and 2

In order to make direct comparison, 1 was subjected to FAB-MS before and after AgOTf reagent addition to prepare 2. The most important fragments belonging to the molecular ion peaks M+ of 1 showed sign at m/z 872.2, and revealed the exact calculated mass (872.6) as shown in Figure 4. When 1 was treated with AgOTf to prepare 2, a new sign at m/z 837.9 [M-Cl]$^+$ replaced totally the sign of 1 as shown in Figure 5, which confirmed the chloride abstraction, the other fragments were sited to their positions.

IR investigations of 1 and 2

In particular, the mid-IR spectra of 1 and 2 showed no big difference between each complex and no water molecules was detected in both structures by IR. Several similar peaks attributed to stretching vibrations of the main function group, in the ranges of 3360 to 3270 cm^{-1} (v_{NH}), 3250 to 3040 cm^{-1} (v_{PhH}) and 3020 to 2780 cm^{-1} (v_{CH}). All other characteristic bands due to the other function groups are also present in the expected regions, typical IR spectrum of 1 was presented in Figure 6.

EXAFS measurement of 1 and 2

Extended X-ray absorption fine structure spectroscopy (EXAFS) is considered to be one of the most powerful methods to obtain interatomic distances in complexes.

1 was subjected to EXAFS before and after AgOTf addition (to prepare 2) in order to determine the number and bond lengths between the metal center and the coordinating atoms of the ligands. The k^3 weighted EXAFS function of both complexes can be described best by six different atom shells. The first intensive peak of 1 (before AgOTf addition) in the corresponding Fourier transform is mainly due to the nitrogen and phosphorus atoms which is found in the case of the most intense peak, 2Ru-P and 2Ru-N bond distances of 2.27 and 2.18 Å, respectively. The second peak was cited to the two chlorine atoms (Ru-Cl) with bond distance 2.44 Å (Figure 7).

Of interest, when 1 was *in situ* treated with equivalent amount of AgOTf in dichloromethane to prepare 2, half of the chlorine peak (Ru-Cl) was reduced as shown in Figure 7, which strongly confirmed: that only one chloride atom was abstracted from ruthenium internal sphere to the outer sphere as desired in Figure 1.

Conclusion

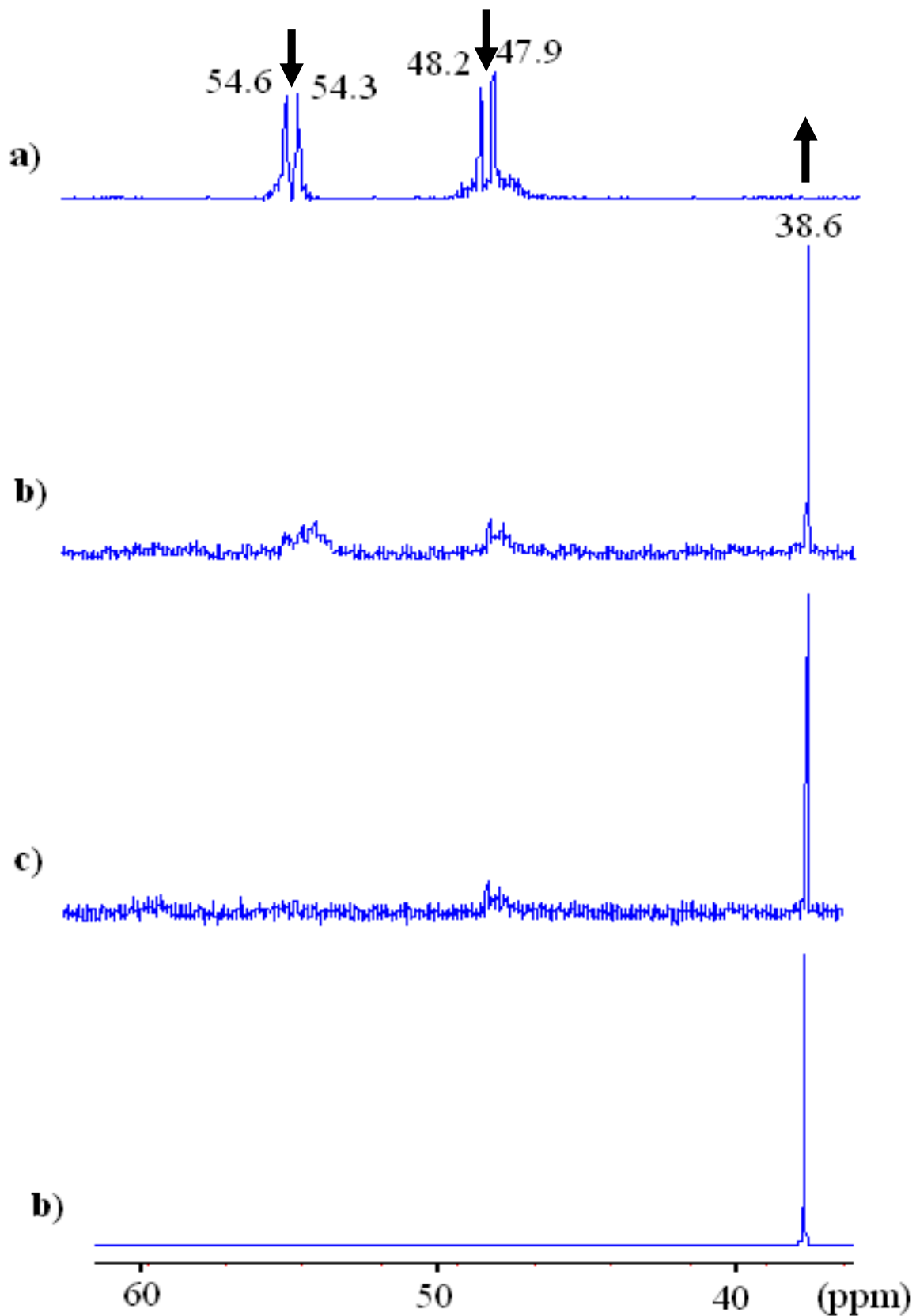The hemilability of 2-(diphenylphosphino)ethyl methyl

Figure 3. Time-dependent $^{31}P\{^{1}H\}$ NMR spectroscopic control of reaction between the mono-cationic 2 with excess of NH_4Cl in 2-propanol and CD_2Cl_2 at room temperature to re-prepare 1: (a) before the addition of NH_4Cl; (b) 2 min after the addition; (c) 4 min after the addition; (d) 10 min after the addition.
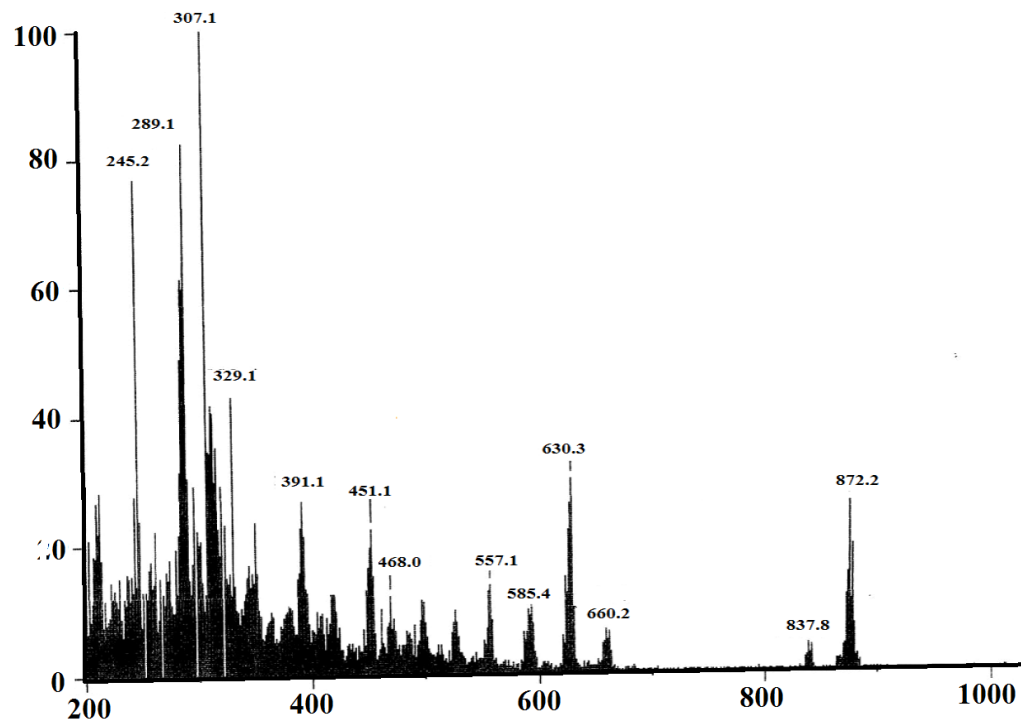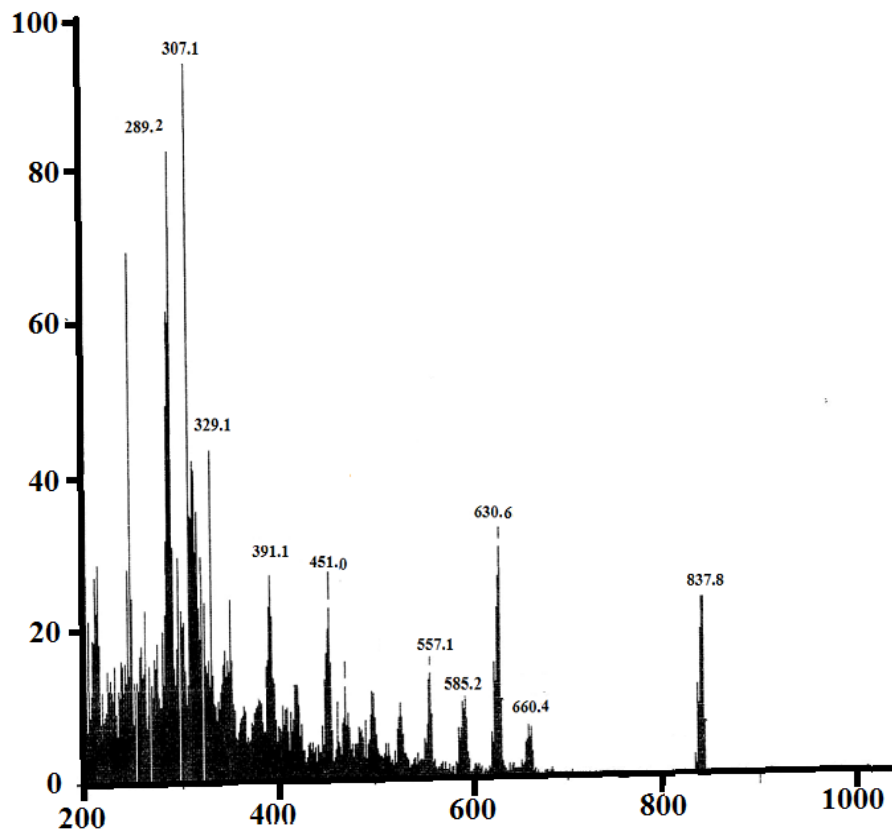
Figure 4. FAB-Mass spectrum of 1.

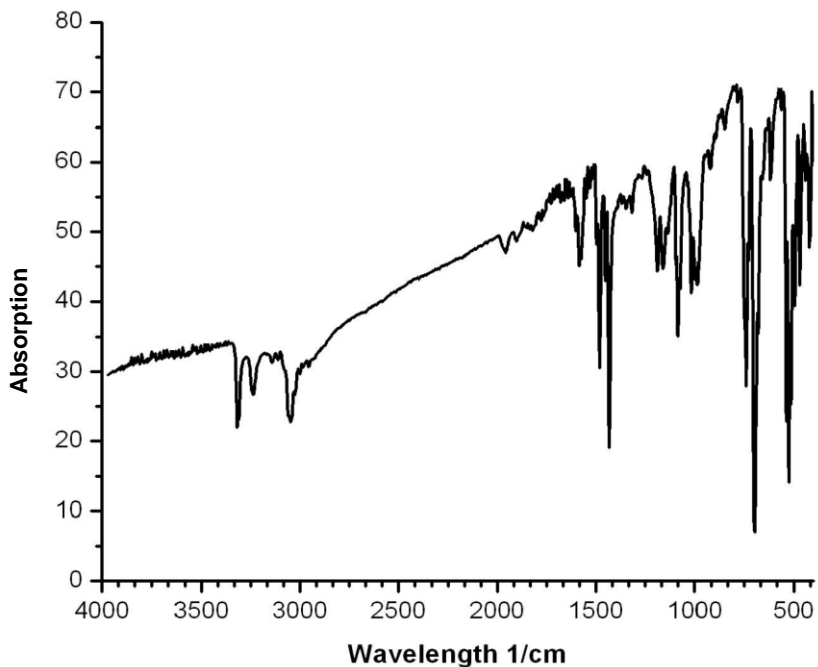**Figure 5.** FAB-Mass spectrum of 2 (after treating 1 with AgOTf).
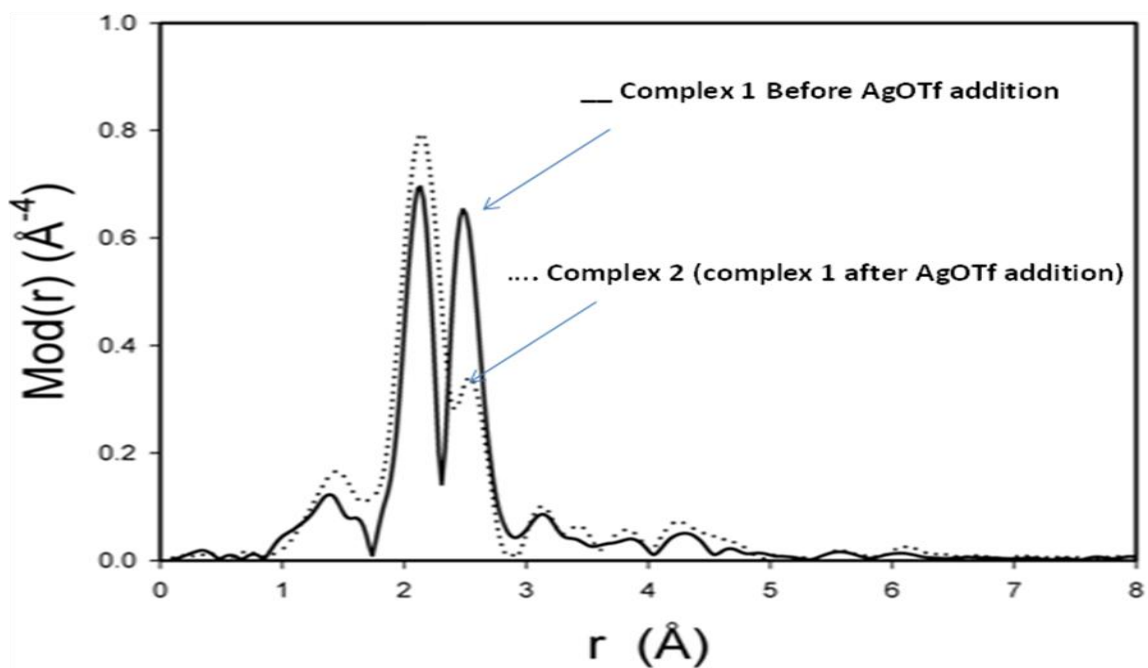
Figure 6. IR-KBr disk spectrum of 1.

Figure 7. EXAFS functions Fourier transforms of 1 before (__) and after AgOTf addition to prepare 2 (….) measured at Ru K-edge.

ether as hybrid ligand was recorded in 1 and 2. Two ruthenium (II) complexes were made available by using ether-phosphine ligand and rac-1,2-diphenyl-1,2-ethanediamine co-ligand. One of the chloride atoms in 1 was abstracted using AgOTf to prepare mono-cationic 2. The structures of the desired complexes have been deduced from elemental analysis, infrared spectroscopy, FAB-mass spectrometry, EXAF, ^{1}H-, ^{13}C{^{1}H} and ^{31}P{^{1}H}

NMR spectroscopy data. The hemilability of the ether-phosphine in 1 and 2 was investigated to closed-open mechanism using AgOTf and NH_4Cl, respectively, these reactions were monitored by $^{31}P\{^1H\}$-NMR spectroscopy, EXAF and FAB-mass spectrometry.

ACKNOWLEDGEMENT

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