

## Synthesis, Identification and NMR of New *Trans*-dichloro-piperazine *bis*(ether-phosphine)ruthenium(II) Complex

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### Abstract

*Trans*-dichloro-piperazine-*bis*(ether-phosphine)ruthenium(II) complex of general formula  $\text{Cl}_2\text{Ru}(\eta^1\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2(\text{C}_4\text{H}_{10}\text{N}_2)$  **2** was made available in good yield through treating equimolar amounts of  $\text{Cl}_2\text{Ru}(\text{P}^{\text{O}})_2$  complex **1** with piperazine as co-ligand. The hemilability ring open reaction of ether-phosphine in complex **1** to prepare complex **2** was monitored by  $^{31}\text{P}$ -NMR. The structure of complex **2** was confirmed by elemental analysis, IR,  $^{31}\text{P}$ -NMR  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, FAB-MS and UV-visible spectroscopy.

**Keywords:** Ruthenium(II) complexes; Hemilabile ether-phosphine; piperazine ligand.

### 1. Introduction

Hemilabile ligand was introduced to the literature in 1979 by Jeffrey and Rauchfuss [1], attributable to polydentate chelate ligands containing two types of bonding groups (soft and hard) [1–5]. In general, hemilabile phosphines ligands display interesting properties such as selective binding to various types of metal, dynamic behavior *via* reversible dissociation of the weaker metal–ligand bonds, and stereo-electronic control about the metal centers [8–11]. Ether-phosphine P~O ligands are designed to act as monodentate (P~O) as well as bidentate (P∩O) donor ligands. Due to the hemilabile character of the ether-phosphine ligand, the oxygen donor is regarded as an intramolecular solvent impeding decomposition of the complex by protection of vacant coordination sites [8]. The weak ruthenium-oxygen bonds in *bis*(chelate)ruthenium(II) complexes of the type  $\text{Cl}_2\text{Ru}(\text{P}\cap\text{O})_2$  are easily cleaved during the reaction with other incoming ligands such as diamine [4-11]. 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 [5-10].

As a part of our ongoing studies on the synthesis of new ligands and their complexes for their structural coordination and applications studies [2-11], we wish here to report the synthesis of  $\text{Cl}_2\text{Ru}(\eta^1\text{-}$

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2(\text{C}_4\text{H}_{10}\text{N}_2)$  **2** from  $\text{Cl}_2\text{Ru}(\text{P}^\wedge\text{O})_2$  **1** using piperazine as co-ligand The hemilability ring open reaction of ether-phosphine in complex **1** was monitored by  $^{31}\text{P}$ -NMR.

## 2. Materials and methods

### 2.1. Experimental section

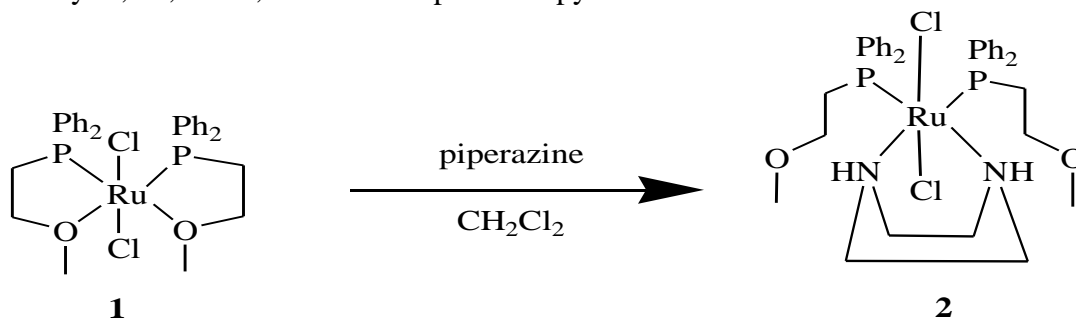
Piperazine (0.3 mmol) was dissolved in 3 mL of dichloromethane and the solution was added dropwise to a stirred solution of  $\text{Cl}_2\text{Ru}(\text{P}^\wedge\text{O})_2$  (0.3 mmol) in 10 ml of dichloromethane. After the reaction mixture was stirred approximately for 10 min. at room temperature, the volume of the solution was concentrated to  $\sim 1$  mL under reduced pressure. Addition of 30 mL of *n*-hexane caused the precipitation of a solid which was filtered (P4), washed well with 25 ml of *n*-hexane and dried under vacuum.

Melting point: 320-322 °C. Yield: 82 % of a yellow powder. MS (FAB):  $\text{M}^+$  ( $m/z$ ) 746.13. IR (KBr,  $\text{cm}^{-1}$ ): 3320 ( $\nu_{\text{NH}}$ ), 3140 ( $\nu_{\text{PhH}}$ ) and 2960 ( $\nu_{\text{CH}}$ ). 1540 ( $\nu_{\text{C=C}}$ ). UV-visible absorption:  $\lambda_{\text{max}} = 280$  nm and 480 nm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 38.0.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 2.5 (m, 8H,  $\text{CH}_2$ -piperazine), 2.8 (m, 4H,  $\text{PCH}_2$ ), 3.2 (s, 6H,  $\text{OCH}_3$ ), 3.6 (m, 4H,  $\text{OCH}_2$ ), 4.8 (b, 2H, NH), 6.6 - 7.7 (4m, 26H, Phs).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 24.7 (m, 2C,  $\text{PCH}_2$ ), 45 (s, 4C-piperazine), 57.6 (s, 2C,  $\text{OCH}_3$ ), 68.6 (s, 2C,  $\text{CH}_2$ ), 126.8-132.4 (9s, 34C, Phs). Elemental analysis: Calculated for  $\text{C}_{34}\text{H}_{44}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Ru}$ . C, 54.69; H, 5.94; Cl, 9.50; N, 3.75% Found: C, 54.23; H, 5.87; Cl, 9.28; N, 3.62%.

## 3. Results and Discussions

### 3.1. Synthesis of complex (2)

Treatment of complex  $\text{Cl}_2\text{Ru}(\text{P}^\wedge\text{O})_2$  with equivalent amount of piperazine co-ligand empowered the formation of  $\text{Cl}_2\text{Ru}(\eta^1\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2(\text{C}_4\text{H}_{10}\text{N}_2)$  in good yield as given in Scheme 1. Yellow powders with high melting points were obtained in good yields. These complexes are soluble in chlorinated solvents such as chloroform, dichloromethane and insoluble in polar or non-polar solvents like water, methanol, diethyl ether and *n*-hexane.. The structure of complex **2** was confirmed by elemental analysis, IR, NMR, UV-visible spectroscopy and FAB-MS.

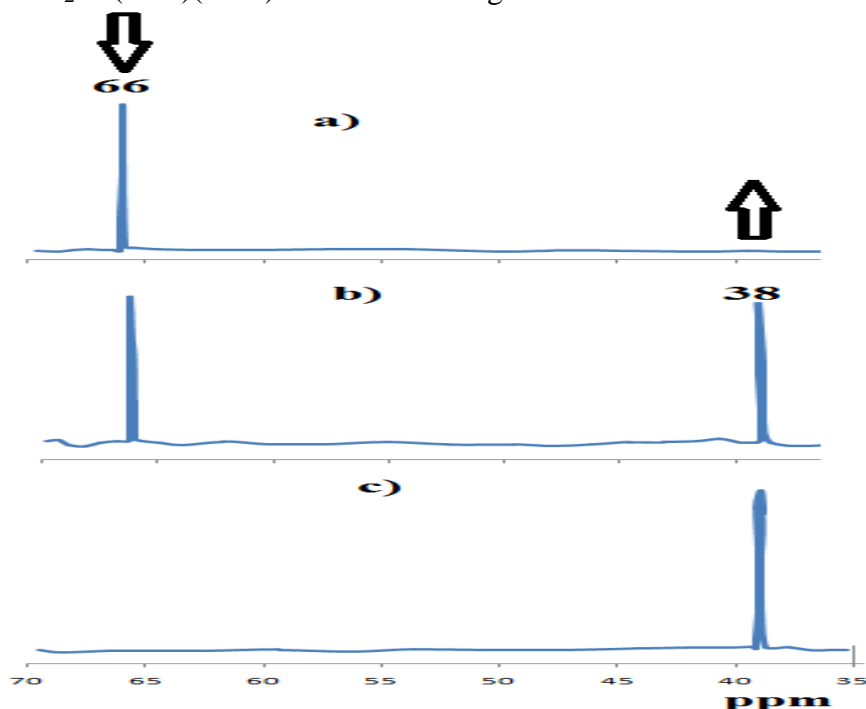


**Scheme 1.** The synthetic route to prepare complex **2**.

### 3.2. Characterisation of complex (2)

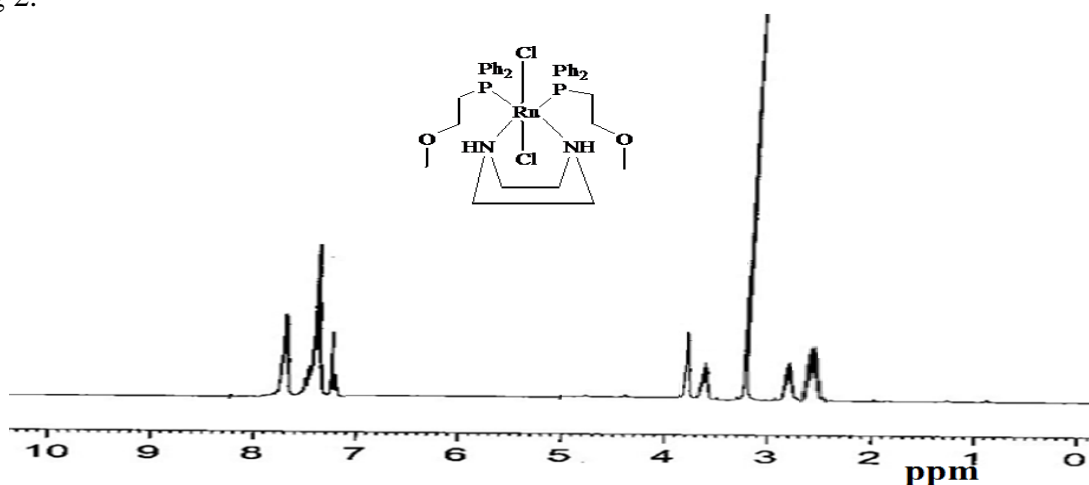
The stepwise formation of the desired complex **2** was monitored by  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy, in an NMR tube experiment, addition of piperazine to a  $\text{CD}_2\text{Cl}_2$  solution containing  $\text{Cl}_2\text{Ru}(\text{P}^\wedge\text{O})_2$  complex as starting material leads to the disappearance of the red color of the  $\text{Cl}_2\text{Ru}(\text{P}^\wedge\text{O})_2$  complex and the

singlet of this complex at  $\delta_p = 66$  ppm and the appearance of the singlet at  $\delta_p = 38$  ppm belongs to complex **2** with a *trans*-Cl<sub>2</sub>Ru(P~O)(N<sup>∩</sup>N) formula as in Fig 1.



**Figure 1.** Time-dependent  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic of complex **1** at  $\delta_p = 66$  ppm mixed with equivalent of piperazine co-ligand in  $\text{CD}_2\text{Cl}_2$  in the NMR tube to produce complex **2** at  $\delta_p = 38$  ppm a) before co-ligand addition, b) the first shot  $\sim 60$  second and c) the second shot  $\sim 120$  min. from the co-ligand addition.

Due to the expected  $C_{2v}$  symmetry in complex **2**, it is easily to identify it through  $^1\text{H}$ -NMR peaks. A sets of signals were observed, which are attributed to the ether-phosphine as well as piperazine diamine co-ligand. Their assignment was supported by the free ligands  $^1\text{H}$ -NMR study. The integration of the  $^1\text{H}$  resonances confirmed that the phosphines to amine ratios are in an agreement with the compositions of the desired complexes. As a typical example the  $^1\text{H}$ -NMR of complex **2** was figured in Fig 2.



**Figure 2.**  $^1\text{H}$ -NMR spectroscopic of complex **2** in  $\text{CD}_2\text{Cl}_2$ .

#### 4. Conclusion

*Trans*-Cl<sub>2</sub>Ru(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>) complex was made available starting from Cl<sub>2</sub>Ru(P<sup>^</sup>O)<sub>2</sub> complex in good yield, the piperazine was served as diamine co-ligand. The hemilability ring open reaction of ether-phosphine was monitored by <sup>31</sup>P-NMR at RT. The structure of the desired complex was deduced from elemental analysis, IR, NMR, FAB-MS and UV-visible spectroscopy.

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