

Short Note

## ***Trans*-dichloro-2,3-naphthalenediamine bis[(2-methoxyethyl)-(diphenyl)phosphine]ruthenium(II) Complex**

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**Abstract:** *Trans*-dichloro-2,3-naphthalenediamine bis[(2-methoxyethyl)(diphenyl)phosphine]ruthenium(II) complex  $\text{Cl}_2\text{Ru}(\eta^1\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3)_2(\text{C}_{10}\text{H}_{10}\text{N}_2)$  has been obtained by reaction of equimolar amounts of  $\text{Cl}_2\text{Ru}(\text{P}^{\wedge}\text{O})_2$  complex **2** with one equivalent of 2,3-naphthalenediamine as co-ligand in very good yield. The structure of this new complex **3** was confirmed by elemental analysis, IR,  $^{31}\text{P}$ -NMR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, UV-visible spectroscopy and FAB-MS.

**Keywords:** ruthenium(II) complexes; Hemilabile ether-phosphine; diamine ligand

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### **1. Introduction**

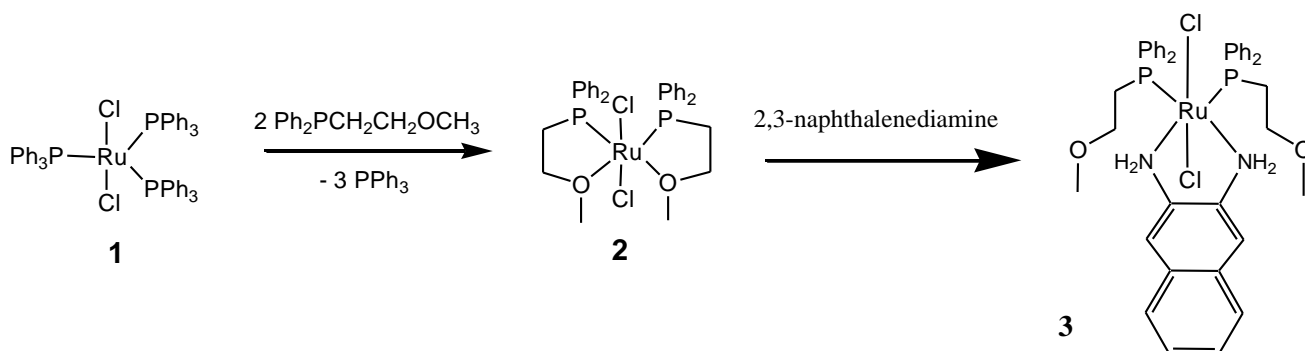
Bifunctional ether-phosphines (O,P) have significantly affected the isolation of coordinatively unsaturated species [1-7]. These ligands are provided with oxygen atoms incorporated in open-chain ether moieties which form a weak metal-oxygen contact while the phosphorus atom is strongly coordinated to the metal [3-9]. In these “hemilabile“ ligands, the ether moiety is regarded as an intramolecular solvent molecule stabilizing the vacant coordination site by chelation. 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) [1-10].

### **2. Result and Discussion**

The  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$  ligand and complex **2** were synthesized according to literature [2]. Treating complex **2** with an equivalent amount of 2,3-naphthalenediamine as co-ligand in dichloromethane at

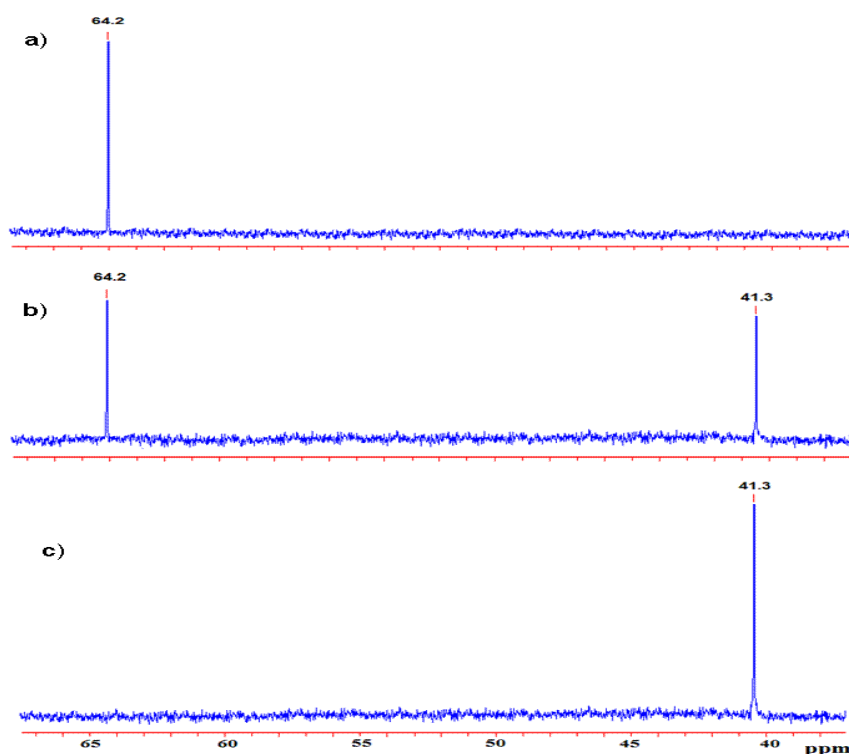
room temperature resulted in the formation of complex **3** without any side products as shown in Scheme 1.

**Scheme 1.** The synthetic route to complex **3**.



The stepwise formation of the desired complex **3** is monitored by  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy, in an NMR tube experiment, where addition of 2,3-naphthalenediamine 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  $\delta_{\text{p}} = 64.2$  ppm and the appearance of the singlet at  $\delta_{\text{p}} = 41.3$  ppm due to the formation of complex **3** with a *trans*- $\text{Cl}_2\text{Ru}(\text{P}\sim\text{O})(\text{N}^{\wedge}\text{N})$  formula as shown in Figure 1.

**Figure 1.** Time-dependent  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy of complex **2** at  $\delta_{\text{p}} = 64.2$  ppm mixed with 1 equivalent of 2,3-naphthalenediamine co-ligand in  $\text{CD}_2\text{Cl}_2$  in the NMR tube to produce complex **3** at  $\delta_{\text{p}} = 41.3$  ppm a) before co-ligand addition, b) the first shot  $\sim 40$  second and c) the second shot  $\sim 1$  min. after the co-ligand addition.



Liquid  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra using  $\text{CD}_2\text{Cl}_2$  show that complex **3** formed as *trans*- $\text{Cl}_2\text{Ru}(\text{P}\sim\text{O})(\text{N}\wedge\text{N})$ , since only a singlet at  $\delta_{\text{p}} = 41.3$  ppm is detected without any other singlets. If *cis*- $\text{Cl}_2\text{Ru}(\text{P}\sim\text{O})(\text{N}\wedge\text{N})$  isomer was formed, an AB  $^{31}\text{P}\{^1\text{H}\}$ -NMR pattern with a  $J_{\text{PP}}$  coupling constant of ~40 to 100 Hz would be detected due to the formation of inequivalent phosphorus atoms.

### 3. Experimental

2,3-Naphthalenediamine (0.04 g, 0.25 mmol) was dissolved in 10 mL of dichloromethane and the solution was added dropwise to a stirred solution of  $\text{Cl}_2\text{Ru}(\text{P}\wedge\text{O})_2$  (0.17 g, 0.25 mmol) in 15 mL of dichloromethane. After the reaction mixture was stirred for approximately 20 min at room temperature, the solution was concentrated to a volume of ~1 mL under reduced pressure. Addition of 30 mL of diethyl ether caused the precipitation of a solid which was filtered (P4), washed well with 25 mL of *n*-hexane and dried under vacuum.

Melting point: 280 °C

Yield: 89% (0.18 g) of a violet powder.

MS (FAB):  $m/z = 818.2$  ( $\text{M}^+$ ).

IR (KBr,  $\text{cm}^{-1}$ ): 3340 ( $\nu_{\text{NH}}$ ), 3180 ( $\nu_{\text{PhH}}$ ) and 2970 ( $\nu_{\text{CH}}$ ). 1540 ( $\nu_{\text{C}=\text{C}}$ ).

UV-visible absorption:  $\lambda_{\text{max}} = 270$  nm and 503 nm.

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 41.3.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 2.4 (m, 4H,  $\text{PCH}_2$ ), 2.9 (s, 6H,  $\text{OCH}_3$ ), 3.0 (m, 4H,  $\text{OCH}_2$ ), 4.4 (b, 4H,  $\text{NH}_2$ ), 6.6–7.7 (4m, 26H, Ph).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 24.7 (m, 2C,  $\text{PCH}_2$ ), 57.6 (s, 2C,  $\text{OCH}_3$ ), 68.6 (s, 2C,  $\text{OCH}_2$ ), 126.8–132.4 (9s, 34C, Phs).

Elemental analysis: Calcd for  $\text{C}_{40}\text{H}_{44}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Ru}$ . C, 58.68; H, 5.42; Cl, 8.66; N, 3.42%. Found: C, 58.23; H, 5.77; Cl, 8.28; N, 3.32%.

### Acknowledgements

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