

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}P -NMR, ^1H -NMR, ^{13}C -NMR, UV-visible spectroscopy and FAB-MS.

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

1. Introduction

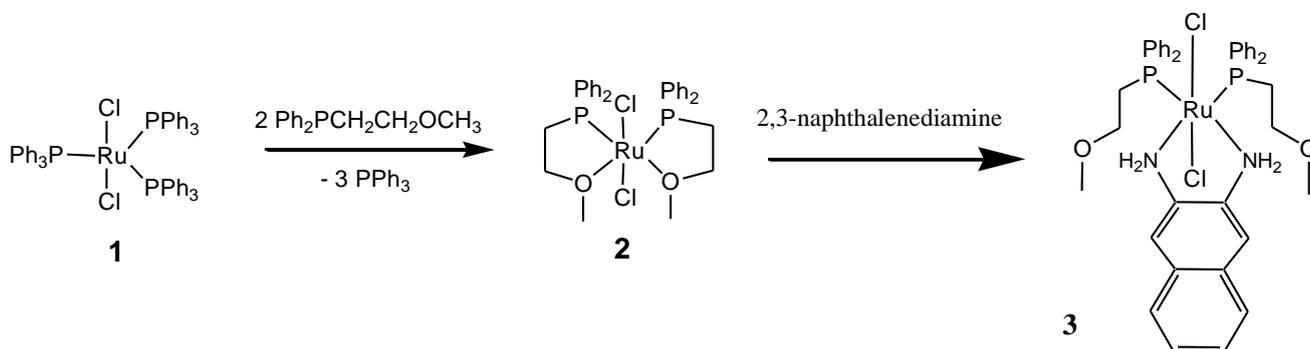
Bifunctional ether-phosphines (O,P) have significantly affected the isolation of coordinatively unsaturated species [1-7]. These ligands are provided with oxygen atoms incorporated in open-chain ether moieties which form a weak metal-oxygen contact while the phosphorus atom is strongly coordinated to 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

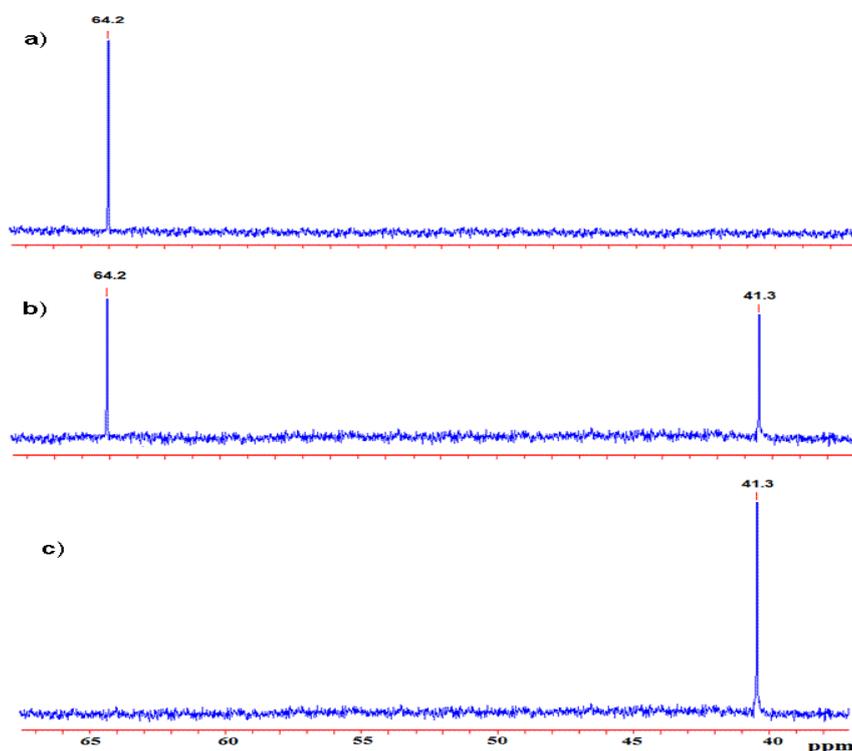
room temperature resulted in the formation of complex **3** without any side products as shown in Scheme 1.

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 CD_2Cl_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 CD_2Cl_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 ~ 40 second and c) the second shot ~ 1 min. after the co-ligand addition.



Liquid $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra using CD_2Cl_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_{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): $m/z = 818.2$ (M^+).

IR (KBr, cm^{-1}): 3340 (ν_{NH}), 3180 (ν_{PhH}) and 2970 (ν_{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 (CDCl_3): δ (ppm) 41.3.

^1H NMR (CDCl_3): δ (ppm) 2.4 (m, 4H, PCH_2), 2.9 (s, 6H, OCH_3), 3.0 (m, 4H, OCH_2), 4.4 (b, 4H, NH_2), 6.6–7.7 (4m, 26H, Ph).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 24.7 (m, 2C, PCH_2), 57.6 (s, 2C, OCH_3), 68.6 (s, 2C, 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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