Research Article

Structural Prediction of Bis{(di-*p*-anisole)-1,4-azabutadiene}-bis[triphenylphosphine]ruthenium(II) Using ^{31}P NMR Spectroscopy

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The present paper reports the use of ^{31}P NMR spectroscopy to predict the isomer structures of [bis{4-methoxy-phenyl-[3-(4-methoxy-phenyl)-allylidene]-amino}]bis[triphenylphosphine]ruthenium(II), also known as bis{(di-*p*-anisole)-1,4-azabutadiene}-bis[triphenylphosphine]ruthenium(II), complexes. The complexation reaction was carried out under refluxing condition of (di-*p*-anisole)-1,4-azabutadiene (compound 1), triphenylphosphine (PPh_3), and ruthenium chloride in the ratio of 2 : 2 : 1 for five hours. In addition, ruthenium(II) complexes were also characterized using FTIR and UV-Vis spectroscopy to support the formation of ruthenium(II) complexes. ^{31}P NMR spectroscopic study on ruthenium(II) complexes suggested that there are three isomers present after the complexation reaction and all the ruthenium complexes demonstrate octahedral geometry.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an essential instrument in chemistry as it can determine the structure of a molecule, the presence of impurities in a sample and the rate of formation as well as degradation of a compound. Even in 1970s, NMR has already been used to determine the cancer formation which offered a simple, fast, and low cost method to identify cancer formation [1–3]. For inorganic chemist, the use of ^{31}P NMR to identify the structure of a complex containing phosphine ligands is very common [4, 5]. One of the well-known examples is the use of ^{31}P NMR spectroscopy to determine the Wilkinson hydrogenation mechanism by identifying the coupling patterns among phosphine ligands and also the coupling constants between phosphine ligands as well as rhodium(I) metal centre [6].

In our long term research interest in ruthenium(II) complexes synthesis, we used (di-*p*-anisole)-1,4-azabutadiene (1) and triphenylphosphine (PPh_3) as the ligands to react with ruthenium trichloride under reflux condition. The products formed were checked by using ^{31}P NMR spectroscopy and the

results found in the spectra are worth to be discussed in the present communication.

2. Methodology

The ruthenium complexes were characterized using UV/Vis, FTIR, and ^{31}P NMR spectroscopy. The IR spectra were recorded using a Thermo Scientific Nicolet iS10 in KBr disc. ^1H NMR spectrum for compound 1 and ^{31}P NMR spectrum for ruthenium(II) complexes were recorded using JEOL JNM-ECA 500 spectrometer with TMS as an internal standard. The absorption spectra were recorded with Jasco V-630 spectrophotometer.

2.1. Preparation of (4-Methoxy-phenyl)-[3-(4-methoxy-phenyl)-allylidene]-amine or (di-*p*-Anisole)-1,4-azabutadiene (1). 4-Methoxycinnamaldehyde (1.62 g, 10.00 mmol) was dissolved in 10 mL of ethanol and followed by 4-methoxyaniline (1.23 g, 10.00 mmol) which was then added to the solution. The reaction mixture was stirred for 4 hours and resulted

FIGURE 1: ^{31}P NMR spectrum for ruthenium(II) complexes.

in green-yellow solid. The solid was filtered, washed with 5 mL of ethanol, and dried *in vacuo*. The solid was purified by dissolving in DCM and layered with hexane *via* slow diffusion: yield: 2.368 g (88.7%); IR (KBr, cm^{-1}): ν : 3036 (C-H stretching), 1627 (C=N- stretching), 1601 (C=C stretching, aliphatic), 1575 and 1468 (C=C stretching, aromatic), and 1110 (OCH_3 stretching); ^1H NMR (500 MHz, CDCl_3): δ : 8.25 (d, 1H, $J = 8$ Hz, -CH=N-), 7.47 (d, 2H, $J = 8$ Hz, H_{arom}), 7.18 (d, 2H, $J = 8$ Hz, H_{arom}), 7.05 (t, 1H, $J = 16$ Hz, H-C $_{\alpha}$), 6.99 (m, 1H, H-C $_{\beta}$), 6.90 (d, 4H, $J = 7$ Hz, H_{arom}), 3.83 (s, 3H, OCH_3), and 3.81 (s, 3H, OCH_3); UV-Vis (DCM, $\lambda_{\text{max}}/\text{nm}$): 273, 373; Anal. Calc. for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$ (%): C, 76.38; H, 6.41; N, 5.24; found (%): C, 76.75; H, 6.31; N, 5.05.

2.2. Preparation of [Bis{4-methoxy-phenyl-[3-(4-methoxy-phenyl)-allylidene]-amino}]-bis-[triphenylphosphate]ruthenium(II) or Bis{(di-*p*-anisole)-1,4-azabutadiene}-bis[triphenylphosphine]ruthenium(II) Complexes. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (2.070 g, 1.0 mmol) and PPh_3 (0.525 g, 2.0 mmol) were added to a round bottom flask containing 10 mL ethanol and the mixture was then refluxed for 5 h. Compound **1** (0.316 g, 2.0 mmol) was then added to the round bottom flask and refluxed for another 5 h. Pale maroon solids were formed, filtered, and washed with hexane. The precipitate was dried *in vacuo*: IR (KBr, cm^{-1}): ν : 3034 (C-H stretching), 1661 (C=N), 1576 (merge IR band of C=C stretching from aliphatic and aromatic), 1469 (C=C stretching of aromatic ring), and 654 (Ru-C), 577 (Ru-N); ^{31}P NMR (202.5 MHz, CDCl_3): δ : 49.7 (d, 1P, $J_{\text{P-P}} = 38$ Hz), 47.4 (d, 1P, $J_{\text{P-P}} = 38$ Hz), 41.7 (d, 1P, $J_{\text{P-P}} = 21$ Hz), 39.7 (d, 1P, $J_{\text{P-P}} = 21$ Hz), 35.1 (s, $\text{Ph}_3\text{P=O}$), and 29.9 (s, 1P); UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 321 and 382.

3. Results and Discussion

The appearance of two pairs of doublets and one singlet in the ^{31}P NMR spectrum for ruthenium complexes (Figure 1) indicates that there are three isomers present in the complexation reaction with the ratio of 1:1:1.

The singlet at 29.88 ppm reveals that the two PPh_3 are magnetically equivalent in ruthenium(II) complex. In this case, the two PPh_3 are either located at axial position, which is *trans* to each other (Figure 2(a)) [7], or located at equatorial plane, which is only *trans* to either C atom from C=C or N atom from N=C (Figure 2(b)). Apparently, the one shown in Figure 2(a) is a *trans*-isomer, whereas the two isomers in Figures 2(b) and 2(c) are *cis*-isomer. Unfortunately, we cannot identify which one is the correct structure represented by the singlet at 29.88 ppm at this stage.

Meanwhile, a pair of doublets at 41.84 and 39.74 ppm with $J_{\text{P-P}}$ coupling constant of 21 Hz is assigned to a *cis*-isomer of ruthenium(II) complex as shown in Figure 3(a). Lastly, another pair of doublets at 49.80 and 47.36 ppm with $J_{\text{P-P}}$ coupling constant of 38 Hz is assigned to a *trans*-ruthenium(II) complex (Figure 3(b)). The difference in $J_{\text{P-P}}$ coupling between ruthenium(II) complexes in Figures 3(a) and 3(b) is due to the positions of PPh_3 ligands. The smaller coupling constant, namely, 21 Hz, is assigned to the *cis*-isomer because both PPh_3 ligands are in the equatorial plane. The presence of doublets for the PPh_3 ligands in the complex is shown in Figure 3(a) because both PPh_3 ligands are *trans* to different atoms, that is, nitrogen and carbon atoms. For ruthenium(II) complex as shown in Figure 3(b), the two PPh_3 ligands are located at axial position and *trans* to each other. Unlike the *trans* complex in Figure 2(a), the magnetic field of these two PPh_3 in Figure 3(b) is different because the two ligands of (di-*p*-anisole)-1,4-azabutadiene are *trans* to each other at the equatorial plane (Figure 3(b)). Lastly, the single peak observed at 35.14 ppm is attributed to the presence of the triphenylphosphine oxide [8].

On the other hand, the binding of compound **1** to ruthenium(II) metal centre can be confirmed using FTIR and UV-Vis spectroscopy. Comparing the IR spectra between compound **1** and ruthenium complexes (Figure 4), the vibrations of C=N and C=C stretching bands have been shifted after binding to ruthenium(II) metal centre. For C=N stretching band, it shifted from 1627 cm^{-1} in compound **1** to 1661 cm^{-1} in ruthenium complex [9, 10], whereas for C=C stretching, the IR band appears at 1601 cm^{-1} in compound **1** but it is not clearly shown in the complex because the IR bands of C=C bands for aliphatic and aromatic were merging into one broad IR band centred at 1576 cm^{-1} . Nevertheless, two additional IR peaks are present in the finger print region at 577 and 654 cm^{-1} indicating the formation of respective Ru-N and Ru-C bonds [11].

The complexation of compound **1** to ruthenium(II) metal centre can be further supported by the UV-Vis data as shown in Figure 5. For compound **1**, two absorption bands were observed at 273 and 372 nm which are assigned to $\pi \rightarrow \pi^*$ transition of the benzene ring and $n \rightarrow \pi^*$ transition of the imine group [12], respectively. After the complexation,

FIGURE 2: Postulated structure of (a) *trans*- and ((b) and (c)) *cis*-[bis{(di-*p*-anisole)-1,4-azabutadiene}]-bis[triphenylphosphine]ruthenium(II).

FIGURE 3: Postulated structure of (a) *cis*- and (b) *trans*-[bis{(di-*p*-anisole)-1,4-azabutadiene}]-bis[triphenylphosphine]ruthenium(II).

both absorption bands shifted to 321 and 382 nm, respectively. Significant shifts of these two absorption bands have proven compound **1** was successfully bound to ruthenium(II) metal centre *via* the nitrogen atom from C=N group and carbon atom from C=C aliphatic group in C=C-C=N moiety. The bathochromic shift of these two absorption bands was due to the backbonding of π electrons from Ru to the antibonding orbitals of C=C-C=N moiety in compound **1**. This, in turn, has weakened the bond in C=C-C=N [13].

4. Conclusion

The evidence from ^{31}P NMR spectrum has shown the presence of three isomers of bis{(di-*p*-anisole)-1,4-azabutadiene}-bis[triphenylphosphine]ruthenium(II) complex in the ratio

of 1:1:1. In addition, the data from IR and UV-Vis revealed that compound **1** has bound to ruthenium(II) metal centre.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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FIGURE 4: IR spectra of compound 1 (a) and ruthenium(II) complexes (b).

FIGURE 5: UV-Vis spectra of compound 1 (a) and ruthenium(II) complex (b).

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