

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

Author Details

Abstract¹

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) complex were also characterized using FTIR and UV-Vis spectroscopic 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. All the ruthenium complex demonstrate octahedral geometry.

Keywords: ^{31}P NMR spectroscopy; FTIR spectroscopy; UV-Vis spectroscopy; Ru complex; Isomers; Structure prediction

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¹ NMR, nuclear magnetic resonance; FTIR, Fourier transform infrared; UV-Vis, ultraviolet-visible

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1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an essential instrument in the chemistry as it can determine the structure of a molecule, identify 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]. In our long term research interest in ruthenium(II) complexes synthesis, we used the (di-*p*-anisole)-1,4-azabutadiene (1) and triphenylphosphine (PPh₃) as the ligands to react with ruthenium trichloride under reflux condition. Products were formed, were checked by using ³¹P NMR spectroscopy and the results found in the spectra are worth to be discussed in the present communication. For inorganic chemist, using of ³¹P NMR to identify the structure of a complex containing phosphine ligands is very common [4, 5]. The well-known examples is the use of ³¹P 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].

2. Methodology

The ruthenium complexes were characterized using UV/Vis, FTIR, and ³¹P NMR spectroscopy. The IR spectra were recorded using a Thermo Scientific Nicolet iS10 in KBr disc. ¹H NMR spectrum for compound 1 and ³¹P NMR spectrum for ruthenium(II) complexes were recorded using JEOL JNM-ECA 500 spectrometer with TMS as an internal standard. The absorption spectra was 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 solution. Reaction mixture was stirred for 4 hours and resulted 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): 3036 (C-H stretching), 1627 (C=N stretching), 1601 (C=C stretching, aliphatic), 1575 and 1468 (C=C stretching, aromatic), and 1110 (OCH₃ stretching); ¹H NMR (500 MHz, CDCl₃) δ: 8.25 (d, 1H, Hz, -CH=N-), 7.47 (d, 2H, Hz,), 7.18 (d, 2H, Hz,), 7.05 (t, 1H, Hz, H-C_a), 6.99 (m, 1H, H-C_β), 6.90 (d, 4H, Hz,), 3.83 (s, 3H, OCH₃), and 3.81 (s, 3H, OCH₃); UV-Vis (DCM, /nm): 273, 373; Anal. Calc. for C₁₇H₁₇O₂N (%): 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

RuCl₃·xH₂O (2.070 g, 1.0 mmol) and PPh₃ (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 another 5 h. Pale maroon solids were formed, filtered and washed with hexane. Precipitate was dried in vacuo: IR (KBr, cm⁻¹): 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); ³¹P NMR (202.5 MHz, CDCl₃) δ: 49.7 (d, 1P, Hz), 47.4 (d, 1P, Hz), 41.7 (d, 1P, Hz), 39.7 (d, 1P, Hz), 35.1 (s, Ph₃P=O), and 29.9 (s, 1P); UV-Vis (DCM) (λ): 321 and 382.

3. Results and Discussion

Characterization of the ruthenium complexes was done using UV/Vis, FTIR, and ³¹P NMR spectroscopy. The IR spectra was found by Thermo Scientific Nicolet iS10 in KBr disc. ¹H NMR spectrum for compound 1 and ³¹P NMR spectrum for ruthenium(II) complexes obtained through JEOL JNM-ECA 500 spectrometer with TMS as an internal standard. The absorption spectra recorded with Jasco V-630 spectrophotometer.

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

The singlet at 29.88 ppm reveals that the two PPh₃ are magnetically equivalent in ruthenium(II) complex. In this case, the two PPh₃ are either located at axial position, which is trans to each other (Figure 2(a)) [7], or

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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.

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

Meanwhile, a pair of doublets at 41.84 and 39.74 ppm with 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 coupling constant of 38 Hz is assigned to a trans-ruthenium(II) complex (Figure 3(b)). The difference in coupling between ruthenium(II) complexes in Figures 3(a) and 3(b) is due to the positions of PPh₃ ligands. The smaller coupling constant, namely, 21 Hz, was assigned to the cis-isomer because both PPh₃ ligands are in the equatorial plane. The presence of doublets for the PPh₃ ligands in the complex is shown in Figure 3(a) because both PPh₃ ligands are trans to different atoms, that is, nitrogen and carbon atoms. For ruthenium(II) complex as shown in Figure 3(b), the two PPh₃ 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 PPh₃ 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].

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

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].

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

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 transition of the benzene ring and transition of the imine group [12], respectively. After the complexation, both absorption bands shifts 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 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].

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

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

4. Conclusion

The evidence from ³¹P 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.

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HIGHLIGHTS

- Three isomers were detected for a phosphine-bearing Ru complex using ³¹P NMR.
- Formation of Ru-N and Ru-C bonds were confirmed by FTIR spectroscopy.
- At least one cis isomer and one trans isomer of the complex were formed.

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