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Synthesis and Characterization of Palladium (II) Complex with Azobenzene-4, 4'-dicarbonyl Chloride

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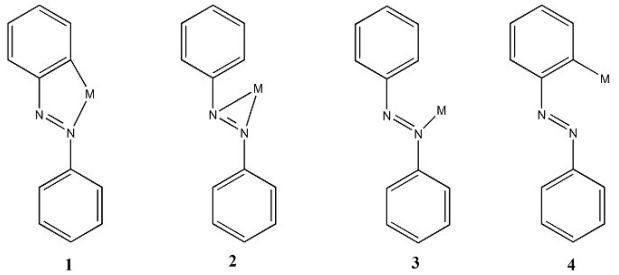
Abstract

A palladium(II) complex has been synthesized by reaction of dichloro-bis(benzonitrile) palladium(II) with azobenzene-4, 4'-dicarbonyl chloride. Elemental analyses technique has been used for characterization of the complexe. The complex does not exhibit photoisomerization. This is most probably due to the fact that the trans-conformation of the palladium complex is fixed by coordination to the palladium(II) in the bidentate mode.

***Key words**: Azo-compounds, transition metals, photoisomerization, bidentate, dichloromethane*

Introduction

The design and synthesis of transition metal complexes of azobenzene and its derivatives have attracted much interest in recent years owing to their fascinating molecular structures and potential applications in catalysis[1], nonlinear optics[2] or liquid crystalline materials[3]. Diversified coordination modes (monodentate, chelating, and/or bridging) of azobenzene and its derivatives with transition metals allow access to a wide variety of structures[4,5].



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In recent years, the photochromic properties of azobenzenes have attracted great interest owing to the isomerization of N=N bonds that occurs readily in the presence of a light source[6-8].Several transition metal complexes containing azobenzenes have been investigated as photosensitizes for organic and inorganic reactions[9,10] .The present work involves synthesis and characterization of palladium complex with azobenzene-4,4'-dicarbonyl chloride for its potential application as a photoactive material.

Experimental Methods

All reagents and solvents were commercially available and used as received. The carbon, nitrogen, and hydrogen contents of the compounds were determined by Carbo-Erba elemental analyzer 1108. The

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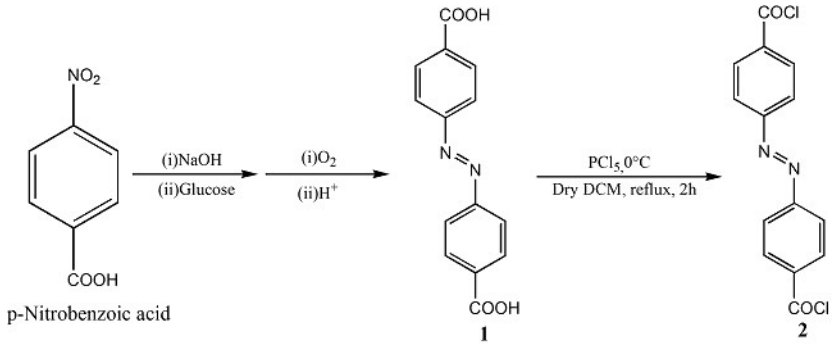
infrared spectra of the compounds were recorded on a Varian 3100 FT-IR spectrometer (4000−400cm^{-1}) using KBr disks.

^{1}H and ^{13}C NMR spectra of compounds were recorded using JEOL AL 300 MHz spectrometer. The starting compound azobenzene-4, 4′-dicarboxylic acid **1** and azobenzene-4, 4'-dicarbonyl chloride **2** were synthesized following reported methods used[11].

Synthesis of azobenzene-4, 4'-dicarboxylic acid **1**: For the synthesis of H_2ADA, *p*-Nitrobenzoic acid (15 g, 67.5 mmol) and NaOH (50 g, 1.25 mmol) were mixed in water (225 mL), and the solution was heated on a water bath until the solid dissolved; hot aqueous glucose (100 g in 150 mL of water) was then added slowly into the above mixture at 50 °C whereupon a yellow precipitate was obtained, which immediately changed to a brown solution upon further addition of glucose. This reaction was highly exothermic. Then, a stream of air was passed into the mixture for 3 h and a light brown precipitate was obtained. This was filtered, dissolved in water, and acidified with acetic acid (25 mL) whereupon a light pink precipitate was obtained. This was filtered, washed with plenty of water (300 mL), and dried in a desiccator to obtain H_2ADA as a brownish orange powder. The analytical data of the compound **1** are as follows: Brownish orange solid, yield 80%, m.p. 335 °C, IR (KBr) ν cm^{-1}: 1683(C=O), 1600(N=N); ^{1}H NMR($CDCl_3$) δ: 13.3 (2H, s, COOH), 8.16 (4H, *J*= 8.4 Hz, d, Ar), 8.01 (4H, *J*= 8.1 Hz, d, Ar); ^{13}C NMR ($CDCl_3$) δ: 166(COOH), 154(Ar), 133(Ar), 130(Ar), 122(Ar); analysis for $C_{14}H_{10}N_2O_4$: 58.53 (58.34), 4.06 (4.53), 11.38 (11.04).

Synthesis of azobenzene-4, 4'-dicarbonyl chloride **2:** For the synthesis of ACCL, to a suspension of azobenzene-4, 4'-dicarboxylic acid (1 g, 3.7 mmol) in 20 mL of 1, 2-dichloromethane was added 2.0 g PCl_5 at 0 °C and then refluxed for 2 h. The red precipitate obtained was filtered and dried. It was recrystallized by mixture of DMF/methanol. Single crystal suitable for X-ray was obtained by layering the solution of compound in DMF with methanol. The analytical data of the compound **2** are as follows: Red solid, yield 75%, m.p. 158 °C, IR (KBr) ν cm^{-1}: 1776(C=O), 1601(N=N); ^{1}H NMR($CDCl_3$) δ: 8.30 (d, *J*=8.7 Hz, 4H, Ar), 8.05 (d, *J*=8.7 Hz, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ: 167 (C=O), 155 (C-N=N), 135 (C-C=O), 132 (Ar), 123 (Ar); analysis for $C_{14}H_8N_2O_2Cl_2$: 54.75 (54.33), 2.63 (2.54), 9.12 (9.14).

Scheme 1. Synthetic strategy of **1** & **2**



Synthesis of palladium(II) complex **3**: A solution containing 38.4 mg (0.1 mmol) of dichloro-bis(benzonitrile) palladium(II) in 5.0 mL of dichloromethane was added to a solution of azobenzene-4,4'-dicarbonyl chloride (61.4 mg, 0.2 mmol) in 5.0 mL of dichloromethane. The mixture was stirred and

filtered. The filtrate was transferred to a glass tube and layered with ether. After standing at room temperature for 3 days red crystal were obtained. Brownish red solid, yield 65%, m.p. above 200 °C, analysis for $C_{14}H_8N_2O_2Cl_3Pd$: 37.41 (37.33), 1.78 (1.98), 6.23 (6.14).

The Azobenzene-4, 4′-dicarbonyl chloride **2** exhibits typical photoisomerization from *trans* to *cis* upon irradiation with Uv light and from *cis* to *trans* upon irradiation with visible light. On the other hand, Palladium complex **3** does not exhibit photoisomerization.

Results and DiscussionS

Photoisomerization is a property of azo group containing compounds. The trans-form easily isomerizes to the *cis* isomer by irradiation with a wavelength between 320–350 nm. The reaction is reversible and the *trans* isomer is recovered when the *cis* isomer is irradiated with light of 400–450 nm. No photoisomerization in complex **3** is most probably due to the fact that the *trans*-conformation of the palladium complex is fixed by coordination to the palladium(II) in the bidentate mode and the photochromic reaction is presumably inhibited. The above experimental results suggest the following structure for the Pd(II) complexes:

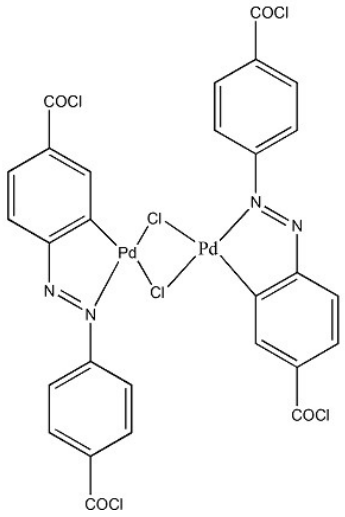


Figure.1: *Possible structures for palladium complexe* ***3.***

Conclusions

A new palladium complex was obtained by reaction of dichloro-bis(benzonitrile) palladium(II) with azobenzene-4, 4′-dicarbonyl chloride. Elemental analyses technique has been used for characterization of the complexes. It could be promising candidate for isomeric reversion of organic substances.

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