



# Diverse reactivity of (N, N, N) tridentate bis-2,2'-(N-benzylamino) azobenzene, ligands with $\text{Na}_2\text{PdCl}_4$ and $\text{K}_2\text{PtCl}_4$

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## Abstract:

The newly designed tridentate ligand, bis-2,2'-(N-benzylamino)azobenzene (**2**), has been prepared by the reaction between 2,2'-diaminoazobenzene (**1**) and benzyl chloride in the presence of  $\text{K}_2\text{CO}_3$ . The reaction of these ligands with  $\text{Na}_2\text{PdCl}_4$  and  $\text{K}_2\text{PtCl}_4$  separately in a 1:1 ratio in methanol afforded two structurally diverse Pd(II) and Pt(II) complexes (**3** & **4**). The reaction of the N-benzylated azo ligand (**2**) gives a new cyclopalladated Pd(II) amido azo complex (**3**). However, when this ligand reacts with platinum salt, it affords an unprecedented ortho-platinated azo-imine complex (**4**). All three complexes were characterized by  $^1\text{H}$  NMR, UV-vis, FT-IR spectroscopy, and elemental analysis. Furthermore, the solid-state structures of azo-amido Pd(II) (**3**) and ortho-platinated azo-imine complex (**4**) were determined using single crystal X-ray diffraction analysis, and it revealed that the bis-2,2'-(N-benzylamino)azobenzene ligand binds with the Pd(II) ion center in a monoanionic tridentate (N, N, N) fashion, offering a distorted square planar geometry where the fourth coordination site is satisfied by one chloride ligand. In contrast, ligand (**2**) binds to Pt(II) in a bi-anionic tetra-anionic tetra-dentate (C, N, N, N) fashion, resulting in distorted square planar geometry. Furthermore, the air/moisture stable Pd(II) complex (**3**), with N-benzyl substituted azobenzene ligand, acts as an efficient catalyst for the Suzuki and Heck reactions under mild conditions. The electrochemical behaviors of the new ortho-platinated complex (**4**) were also examined.

**Keywords:** Pd(II) & Pt(II) azo-amido complexes, ortho-platinated complex, Crystal structures, Catalytic activity, Redox property.

## 1. INTRODUCTION

Palladium and platinum are noble transition metals and have abundant chemistry. Metals are undoubtedly ubiquitous metals and have gained importance in organometallic chemistry. In a few decades, palladium complexes were used as a very powerful, popular, and versatile catalyst in various cross-coupling reactions for the selective construction of C-C, C-S, C-O, and C-N bonds, which are useful in industrial fine chemical synthesis [1-7]. Transition metal complexes with azo ligands have been extensively investigated after the synthesis of ortho-metallated palladium and platinum azo complexes by A. C. Cope and his coworkers in 1965 [8]. A small number of palladium complexes incorporating tri and tetradentate azo-imine ligands have been utilized for photochromism, oxidative addition, structural isomerization, metal-assisted transformation, and catalytic and biological activity [9-16]. Besides, platinum chelates embedded in suitable azo ligands show versatile structures, C-H bond activation, fluorescence, chemotherapeutic agents, and antitumor activity [17-23]. Cycloplatinated complexes incorporating N-donor ligands have grown interesting because of their versatile application in the functionalization of organic molecules [24], luminescence/phosphorescence [25-26], mesogenic materials [27], and antitumor agents [28]. In addition, cyclo-metallated-organo Pt(II) complexes have been used in bioimaging materials, optoelectronics, and sensors [29-31]. Changing the steric and electronic properties of some azo ligands has dramatically changed the coordination mode, reactivity, and catalytic activity [32-34].

Herein, we report the synthesis of two different complexes of palladium and platinum with bis-2,2'-(N-benzylamino)azobenzene ligands. The ligand and complexes were characterized by UV-vis, IR, and  $^1\text{H}$  NMR spectroscopy. The structures of ligand (**1**) and complexes (**3**) and (**4**) were determined by X-ray crystallography. The new complex (**3**) has been successfully applied to the Suzuki cross-coupling and Heck reactions in the presence of air and moisture. The electroanalytical properties of the Pt(II) complex (**4**) were also examined in cyclovoltammetry.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by general procedures [35]. Sodium tetrachloropalladate and 2,2'-diaminoazobenzene were prepared following reported procedures [36,37].

### 2.2 Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S/O series II elemental analyzer. Infrared spectra were recorded on a Perkin Elmer BX-1 FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded

on a Shimadzu UV-1800 PC spectrophotometer.  $^1\text{H}$  NMR spectra were obtained on Bruker 300 and Bruker 400 NMR spectrometers in  $\text{CDCl}_3$  using TMS as the internal standard.

### 3. SYNTHESSES

#### 3.1 Synthesis of the ligand (2)

A mixture of 2,2'-diaminoazobenzene (0.5 g, 2.36 mmol), benzyl chloride (0.6 g, 4.72 mmol), 4 g of  $\text{K}_2\text{CO}_3$  in 30 mL dry ethanol was refluxed for 5h. The orange solid mass that was obtained after evaporation of the solvent, afforded the ligand (2), which was isolated by column chromatography on silica gel (60–120 mesh) using the eluent petroleum ether–toluene (75/25 v/v). Upon evaporation of the solvent after chromatography, the orange-red solid of pure (2) was obtained [34]. Yield: 62%. Anal. Calc. for  $\text{C}_{26}\text{H}_{24}\text{N}_4$ : C, 79.56; H, 6.16; N, 14.27. Found: C, 79.24; H, 6.10; N, 14.12%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{N}=\text{N})$ .  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ): 4.46 ( $\text{CH}_2$ , s, 2H), 4.70 ( $\text{NH}_2$ , s, 1H), 5.50 ( $\text{NH}_2$ , s, 1H), 6.70–6.78 (ArH, m, 4H), 7.11–7.13

#### 3.2 Synthesis of the palladium complex (3)

A solution of ligand (2) (0.135 g, 0.34 mmol) in 10 mL methanol was added to a solution of  $\text{Na}_2\text{PdCl}_4$  (0.1 g, 0.34 mmol) in 10 mL methanol. The mixture was stirred for 4 h. The dark solid precipitate was separated by filtration and purified by column chromatography using silicagel (60–120 mesh). The eluent was toluene-acetonitrile (85/15 v/v) mixed solvent. Upon evaporation of the solvent, a blue solid of pure (3) was obtained [38]. Yield: 70%. Anal. Calc. for  $\text{C}_{26}\text{H}_{23}\text{N}_4\text{ClPd}$ : C, 58.55; H, 4.35; N, 10.50. Found: C, 58.36; H, 4.45; N, 10.14%. IR (KBr,  $\text{cm}^{-1}$ ): 1736  $\text{m}(\text{C}=\text{N})$ , 1401  $\text{m}(\text{N}=\text{N})$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) d, ppm: 4.12 ( $\text{CH}_2$ , d, 2H), 4.39 ( $\text{CH}_2$ , d, 2H), 5.57 (NH, d, 1H), 6.42–6.38 (ArH, m, 1H), 7.09–7.06 (ArH, t, 3H), 7.20–7.14 (ArH, m, 3H), 7.31–7.22 (ArH, m, 4H), 7.38 (ArH, d, 3H), 7.54(ArH, d, 1H), 7.64(ArH, d, 1H).

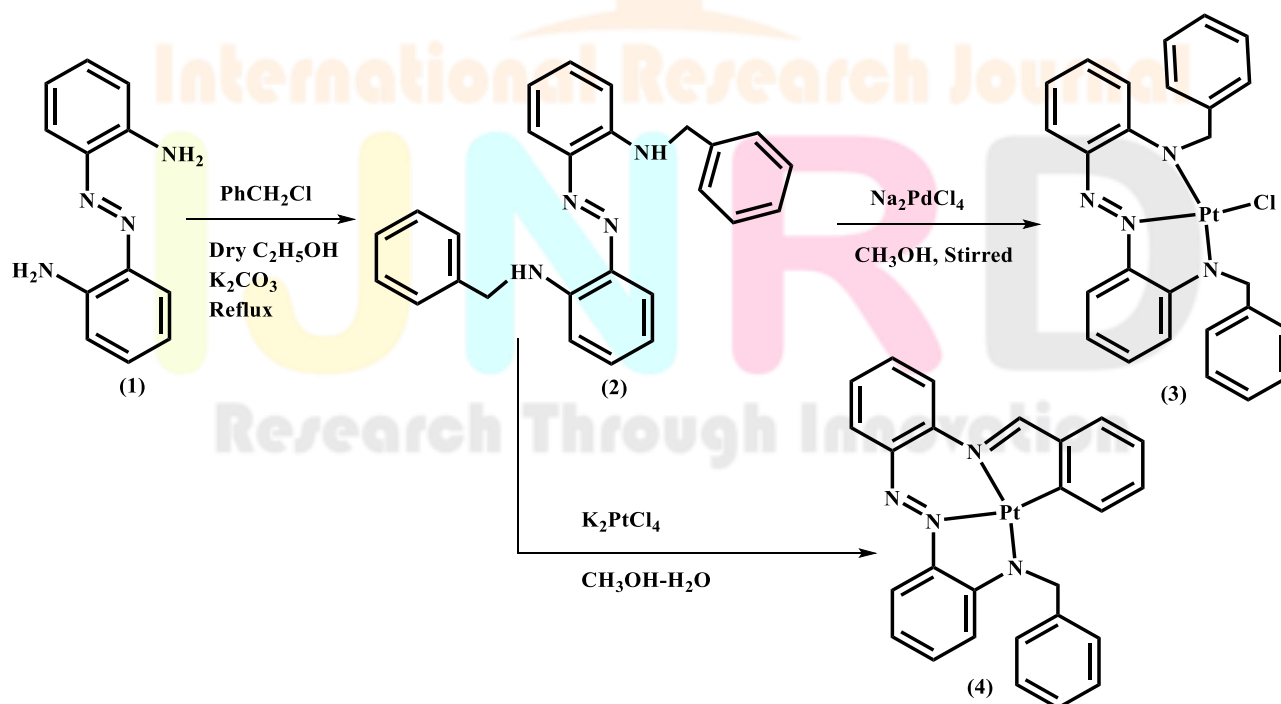
#### 3.3 Synthesis of the platinum complex (4)

A solution of HL (IV.1c) ligand (0.04 g, 0.12 mmol) in 15 mL methanol was added to a solution of  $\text{K}_2\text{PtCl}_4$  (0.05 g, 0.12 mmol) in 1 mL water. The mixture was stirred for 6 h at  $50^\circ\text{C}$ . The dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60–120 mesh). The eluent was toluene-acetonitrile (85/15 v/v) mixed solvent. Upon evaporation of the solvent, a deep blue solid of pure (4) was obtained [39]. Yield: 70%. Anal. Calc. for  $\text{C}_{26}\text{H}_{20}\text{N}_4\text{Pt}$ : C, 53.51; H, 3.45; N, 9.60%. Found: C, 53.68; H, 3.37; N, 9.53%. IR (KBr,  $\text{cm}^{-1}$ ): 1616  $\text{m}(\text{C}=\text{N})$ , 1408  $\text{m}(\text{N}=\text{N})$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) d, ppm: 7.75 (b, s, ArH, 1H), 7.50 (b, s, ArH, 2H), 7.33 (d, ArH, 2H), 7.24 (t, 4H, ArH), 7.16 (d, 4H, ArH), 7.07 (d, 2H, ArH), 6.57 (b, s, CH), 6.43 (t, 1H, ArH), 5.74(b, 1H, ArH), 5.10 (b, 1H, ArH), 4.70 (d,  $\text{CH}_2$ , 1H), 3.64 (s,  $\text{CH}_2$ , 1H).

## 4. RESULTS AND DISCUSSION

### 4.1 Synthesis

The new ligand bis-2,2'-(N-benzylamino)azobenzene (2), was prepared by substituting one of the amino proton of each amino group of 2,2'-diaminoazobenzene (1), with benzyl chloride in the presence of  $\text{K}_2\text{CO}_3$  in refluxing dry ethanol. The ligands were isolated as orange-red solids after column chromatographic purification. The reactions of ligand (2) with  $\text{Na}_2\text{PdCl}_4$  and  $\text{Na}_2\text{PtCl}_4$  separately in methanol at room temperature afforded blue-colored complexes (3 & 4) shown in (Figure No. 1).



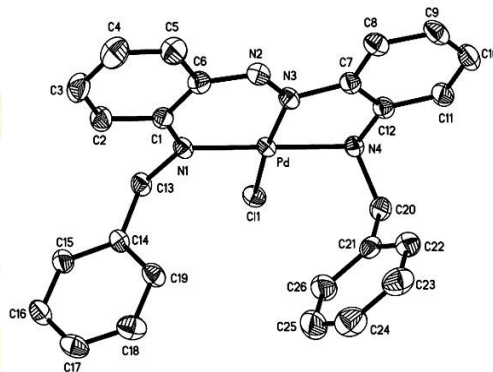
**Figure No. 1** Synthetic route of ligand (2) and complexes (3) & (4)

In Pd(II) complex (3), the ligand binds in (N, N, N) tridentate fashion through one amido nitrogen, azo nitrogen, and amino nitrogen atoms forming two fused rings- one six-membered and the other five-membered. The fourth coordination site of the palladium in the complexes is occupied by a chloride ligand. The presence of alkyl substituents at amino nitrogen of 2,2'-diaminoazobenzene is expected to stabilize the chloride complex by changing electronic and steric properties rather than the phosphine complex [37].

Whereas the reaction of ligand (2) with  $K_2PtCl_4$  in methanol-water at room temperature afforded blue-colored complex (2) and it is surprisingly found to be an unexpected tetradentate ortho-platinated complex instead of amido azo complexes (3) ortho-platination occur through oxidative dehydrogenation of one secondary amine ( $-CH_2-NH-$ ) to imine ( $-CH=N-$ ) function of ligand (2) and maintain the ring planarity.

#### 4.2 Structure characterization by X-ray crystallography

The structures of (3) and (4) have been determined by the single crystal X-ray diffraction method and crystal data. The molecular structures of (3) and (4) are shown in **Figures No. 2 & 3**. Bond lengths and bond angles are given in **Tables No. 1 & 2**. Complex (3), is monoclinic and crystallizes in the space group  $C2/c$  and  $P2_1/n$  with  $Z = 8$  and 4 respectively. The ligand is coordinated with palladium (3) in a monoanionic tridentate (N, N, N) mode, forming a six-membered chelate ring with imino-nitrogen and azo nitrogen and a five-membered ring with amino nitrogen and azo nitrogen atoms. The fourth coordination site of the palladium in the complexes is occupied by a chloride ligand. The geometry of Pd(II) is near square planar. The C(1)-N(1) and C(6)-N(2) lengths ( $\sim 1.334 \text{ \AA}$ ) are shorter than the C-N single bond C(7)-N(3) and C(12)-N(4), ( $\sim 1.44 \text{ \AA}$ ) in the same molecule is close to the imine distance [12, 37, 17]. The bond lengths within the ligand frame indicate the presence of extensive delocalization of the negative charge along the ligand backbone [12, 37, 17].



**Figure No. 2** Molecular structure of Pd(II) complex (3)

**Table No. 1** Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for Pd(II) complex (3)

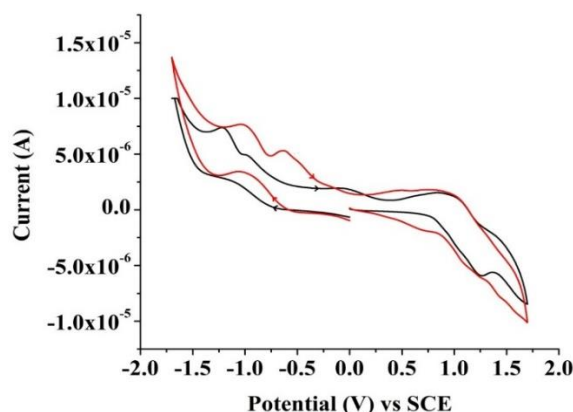
Distances			
N(1)-C(1)	1.334(3)	C(21)-C(26)	1.383(4)
N(1)-C(13)	1.478(3)	C(21)-C(22)	1.389(4)
N(2)-N(3)	1.280(3)	C(22)-C(23)	1.394(4)
N(2)-C(6)	1.355(3)	C(23)-C(24)	1.372(4)
N(3)-C(7)	1.431(3)	C(24)-C(25)	1.375(4)
Angles			
Cl(1)-Pd-N(1)	97.69(6)	N(2)-C(6)-C(1)	127.8(2)
Cl(1)-Pd-N(3)	169.53(6)	C(8)-C(7)-C(12)	120.2(2)
N(1)-Pd-N(3)	91.59(8)	N(3)-C(7)-C(8)	124.0(2)
N(1)-Pd-N(4)	174.29(8)	C(7)-C(8)-C(9)	119.0(3)
N(3)-Pd-N(4)	83.77(8)	C(8)-C(9)-C(10)	120.7(3)

On the other hand, Pt(II) complex (4), is monoclinic and crystallizes in the space group  $C12/c1$  with  $Z = 8$ . The compounds feature a four-coordinated Pt(II) center with the C, N, N, N donor set of the Schiff base ligand. The dianionic ligand is coordinated through imine nitrogen N(1), azo nitrogen N(3), amino nitrogen N(2), and pendant phenyl carbon C(1) atoms to constitute the equatorial plane with Pt(II) ion and forming two five-membered chelate ring and one six-membered ring. The tetra-coordination geometry of the platinum(II) atom is distorted square planar (mean deviation  $0.021 \text{ \AA}$ ) except benzyl fragment. The azo  $N=N$  and imine  $C=N$  bond lengths are  $1.214(8) \text{ \AA}$ , and  $1.241(9) \text{ \AA}$ , both distances are very shorter than the reported values of similar types of azo ligands [17, 37].



### 5.3 Electrochemical behavior

The electrochemical behavior of complex (4) was examined in dichloromethane acetonitrile mixed solvent (0.1 M TBAP) by cyclic voltammetry with a scan rate of  $0.1 \text{ V s}^{-1}$  vs. SCE. The platinum complex (4) exhibited two reductive responses, one irreversible and other quasi-reversible, reductive responses at negative to SCE and have assigned to the reduction of azo (-N=N-) and imine (-C=N-) group [40]. One redox response appeared on the positive side to SCE in the potential range of 1.04–1.58 V and oxidative in nature. This redox response is quasi-reversible in nature and it is also ligand centric [41]. The Cyclic Voltammogram of (4) in dichloromethane acetonitrile mixed solvent is shown in **Figure No. 4**.



**Figure No. 4** CV of Pt(II) complex (4) (red colour) in DCM +  $\text{CH}_2\text{Cl}_2$  solvent

## 6. CONCLUSION

The reaction of the new (N, N, N) tridentate ligand (2) with  $\text{K}_2\text{PdCl}_4$  and  $\text{K}_2\text{PtCl}_6$ , separately afforded amido azo (3) and ortho-platinated azo-imine complex (4). The spectral studies and solid-state X-ray crystallography confirmed the coordination mode of the ligand (2) with palladium and platinum ions. In air and moisture-stable conditions, the Pd(II) complex (3) is a highly active and efficient catalyst for promoting the Suzuki and Heck coupling reactions. The activity of the molecular complex itself The redox-non-innocent character of the Pt(II) complex (4) was examined.

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