



Synthesis and Characterization of A New *Ortho* Palladed Complex Via C-H Activation of Redox Non-Innocent 2-(Arylazo)-N-Phenyl Aniline

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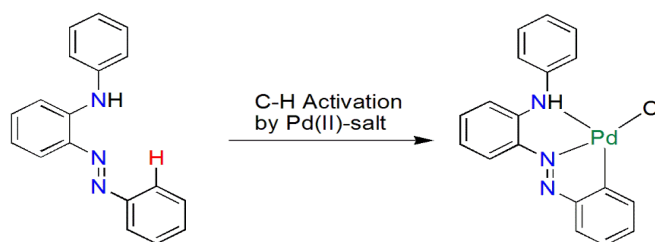
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ABSTRACT

The new redox active 2-(arylazo)-N-phenyl aniline ligand **LH** has been prepared by the reaction between N-phenyl-ortho-phenylenediamine and nitrobenzene in the presence of NaOH. The room temperature reaction of equimolar amounts of **LH** and $[PdCl_2(CH_3CN)_2]$ in methanol in the presence of triethylamine afforded ortho palladed complex $[Pd^{II}(L)Cl]$ (**I**) in 63% yield, where the ligand is bound to the Pd(II) metal in tridentate (C,N,N) coordination. The complex **I** was characterized from spectroscopic data and its structure was confirmed by X-ray crystallographic analysis. The redox chemical behaviors of **LH** and complex **I** were studied.

Graphical abstract



Keywords: Cyclopalladation; C-H Activation; Azobenzene; Redox-active.

INTRODUCTION

Transition metal mediated C-H bond activation represents a valuable tool for the synthetic chemistry [1-3]. The term “activation” suggests usually the formation of M-C bond, although in fact it is already “functionalization” just well-known metallation and genuine activation is the electrone-orbital interaction of C-H bond with metal center in the primary formed sigma complex [4-5]. The metal of choice for simple hydrocarbons is platinum which capable of cleavage the strongest C-H bonds in

intermolecular reactions. The Pd is poor activator for such reactions. In the case of functionally complex molecules a solution of the problem of Pd low activity observed in intermolecular C-H bond activation is use of coordinating heteroatoms (N and others) in such molecules that makes the process intramolecular one. It solves also the selectivity problem. Organic molecule becomes bound to the metal atom reducing the enthalpic and entropic costs for subsequent interaction between the metal and C-H bond due to chelation. This reaction results in the formation of metallacycle and is called cyclometallation. Five or six membered chelates are often formed as a result of the formation of a stable M-C bond, assisted by coordination of one or more donor group [6]. Palladium is one of the most popular metal for intramolecular C-H bond activation and cyclopalladation is studied in greatest details [7]. Synthesis of new cyclopalladed complexes represents big interest as a model for intermolecular C-H bond activation and due to potential application of these compounds in organic synthesis and catalysis, photochemistry, for design optical devices, metallomesogenes and antitumor drugs [8]. Palladocycles are encountered as intermediates in many reactions promoted by palladium. Cyclometallation allows to get an insight into different aspects of metal-mediated C-H bond activation. Another basic interest of cyclopalladed complexes is connected with stabilization of usually very reactive Pd-C intermediate [9]. Intramolecular C-H activation is much easier in comparison with intermolecular process and this, together with its importance in basic and applied science, explains the enormous progress achieved in the intramolecular C-H bond activation in the recent decades.

The present research interest focuses on the C-H bond activation in substituted azobenzenes. Azobenzenes are important class of compounds widely used in many fields including organic dyes and pigments, food additives, photoluminophores and photoconductors, liquid crystal etc, [10]. Organometallic Pd(II) complexes incorporating azo group are active towards Suzuki and Heck and other coupling reactions and alkene epoxidation [11].

The bi and tri-dentate azo ligands have been demonstrated to form orthopalladed complexes (Fig.1). In similar reactions in the case of tridentate and tetradentate azo ligands the bidentate N_{azo} , N_{azo} or N_{azo} , N_{imino} and the tridentate N_{azo} , N_{imino} , N_{oxo} coordinations were also used [12].

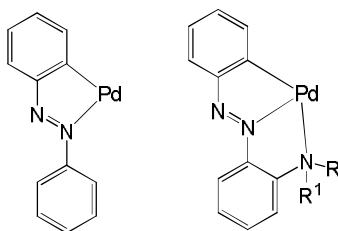


Figure 1. Bi- and tri-dentate coordination of azo ligands.

Cyclopalladation of azobenzene was one of the first cyclometallation reactions [13]. The reaction is usually fulfilling in methanolic solutions, while in DMF double C-H bond activation takes place [14]. Parent azobenzene employed in C-H activation by using the azo functionality as monodentate directing group. In 2-amino azobenzenes the formation of ortho Pd-C bond can occur upon substitution of the ortho aryl proton from azobenzene fragment as a result of prior binding with two nitrogen donors of the ligand, N_{azo} and N_{am} . It is evident that bidentate coordination more favorable than monodentate one for the next chelation. There are only a few examples where the tridentate azoamine ligands were used for intramolecular C-H bond activation. It was noted¹⁵ that the C-H activation in 2-(arylo) aniline, one of the simplest azoamine ligands, did not occur due to the preferable formation of a six membered azoimine chelate upon dissociation of the amino proton. The first cyclopalladated 2-alkylamino and 2-benzylamino azobenzenes were prepared and characterized in 2005 and in 2016 [12d, 16]. While Pd (II) assisted C-H activation in 2-alkylamino and 2-benzylamino azobenzenes is well documented, there is no information on the corresponding reactivity of 2-phenylamino azobenzene. At the same time, conjugation of azo chromophore with phenyl ring

may appear as an attractive way for synthesis of new interesting azo compounds for photochemistry. These researches also widen the scope of catalysts for the coupling and other types of useful organic reactions. Palladocycles offer broad variety of catalytic applications [7c]. Syntheses of new organometallic compounds of azo ligands with enhanced performance are still required.

MATERIALS AND METHODS

Materials: Reagents and solvents were of at least 99% purity and used as received without any further purification. N-phenyl-1,2-phenylenediamine was purchased from Sigma Aldrich. PdCl₂ salt was purchased from Arora Matthey Limited, India. PdCl₂(CH₃CN)₂ was prepared by stirring PdCl₂ salt in CH₃CN at room temp and the resulting yellow precipitate was filtered off and dried. All other reagents and solvents were purchased from Spectrochem, India and Fisher Scientific. Dichloromethane and acetonitrile were dried by distillation from CaH₂.

Instrumentation: NMR spectra were obtained using a Bruker Avance 400/500 MHz spectrometer, respectively, and SiMe₄ was used as the internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded on a Micromass Q-TOF mass spectrometer (Model No. YA263). Cyclic voltammetry potentials were measured under a nitrogen atmosphere using a Ag/AgCl reference electrode, with a Pt-disk working electrode and a Pt-wire auxiliary electrode, in acetonitrile containing 0.1 M [Bu₄N]ClO₄. The E_{1/2} value for the ferrocenium-ferrocene couple under our experimental conditions was 0.40 V.

Synthesis of NPhAzo ligand (LH): N-Phenyl-ortho-phenylenediamine (1.84 g, 0.01 mol) was mixed with nitrobenzene (1.23 g, 0.01 mol) in a clean 100 mL beaker and to it, finely divided NaOH pellets (0.04 g, 0.01 mol) were added. The mixture was gently heated to 70 °C with constant scratching and stirring with a glass rod for about 20 min. The mixture became dark reddish and sticky. It was cooled to room temp and dissolved in minimum volume of CH₂Cl₂. The solution was then passed through a silica column using a mixture of hexane:toluene (9:1) as an eluent. The red band thus separated was collected and the pure ligand was obtained as a reddish liquid. Yield: 1.56 g (57%). ESI-MS: 272.0673. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.069 (s, 1H), 7.9065 (d, 1H, J = 7.5 Hz), 7.8525 (d, 2H, J = 7.5 Hz), 7.5 (t, 2H), 7.426 (t, 1H), 7.371 (t, 2H), 7.317-7.242 (m, 4H), 7.109 (t, 1H), 6.907 (t, 1H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 152.81, 140.72, 140.46, 137.61, 132.44, 130.35, 129.61, 129.29, 128.73, 123.77, 122.38, 118.44, 114.60.

Synthesis of [Pd^{II}(L)Cl] (complex 1): One equivalent of NPhAzo ligand (LH) (1.36 mg, 0.5 mmol) was dissolved in CH₃OH in a 50 ml RB flask. To it, one equivalent of [PdCl₂(CH₃CN)₂] salt (1.3 mg, 0.5 mmol) was added under stirring at room temp followed by addition of 2-3 drops of triethylamine. The colour of the reaction mixture was immediately changed from orange reddish to purple. The reaction was stirred for about 30 min and the solvent was evaporated. The crude solid thus obtained was dissolved in minimum amount of CH₂Cl₂ and isolated as crystalline complex **1** by slow evaporation of the CH₂Cl₂ solution. Yield: 1.31 mg (63%). ESI-MS (m/z): exp. 377.7693; calc. 378.0234 ([Pd(L)]⁺). Elemental analysis calculated for C₁₈H₁₄N₃ClPd: (%) C 52.2, H 3.41, N 10.14; found (%) C 54.01, H 3.29, N 10.03.

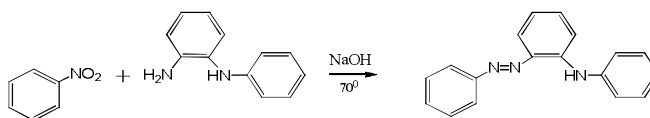
X-ray Crystallography of complex 1: Suitable X-ray quality crystals of complex **1** were obtained by the slow diffusion of a CH₂Cl₂ solution of the complex into hexane. All data were collected on a Bruker SMART APEX-II diffractometer, equipped with graphite-monochromated Mo K α radiation (λ = 0.71073 Å), and were corrected for Lorentz polarization effects. Data for **1**: a total of 10954 reflections were collected, of which 1744 were unique (Rint = 0.050), satisfying the I > 2 σ (I) criterion, and were used in subsequent analysis. Data for **2**: A total of 20125 reflections were collected, of which 3031 were unique (Rint = 0.164). The structures were solved by employing the SHELXS-97 program package⁵⁰ and were refined by full-matrix least-squares based on F² (SHELXL-97).⁵¹ All hydrogen atoms were added in calculated positions. Selected crystallographic data for complex **1** are listed in table 1 and table 2.

Table 1. Crystallographic data table for complex **1**.

Empirical formula	C ₃₆ H ₂₈ N ₆ Cl ₂ Pd ₂
Formula weight	828.41
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 10.815(2) Å
	b = 26.258(5) Å
	c = 12.434(2) Å
	α = 90°
	β = 108.618(5)°
	γ = 90°
Volume	3346.2(10) Å ³
Z	4
Density (calculated)	1.630 Mg m ⁻³
Absorption coefficient	1.270 mm ⁻¹
F(000)	1648.0
Crystal size	0.18 X 0.16 X 0.14 mm ³
Theta range for data collection	2.31 to 22.57°
Index ranges	-13<=h<=13, -32<=k<=32, -13<=l<=15
Reflections collected	42480
Independent reflections	7048
Completeness	99.6% (to theta = 25.937)
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	6512/0/415
Goodness-of-fit on F ²	0.904
Final R indices [I>2σ(I)]	R1 = 0.0401, wR2 = 0.1126
R indices (all data)	R1 = 0.072, wR2 = 0.1410
Largest diff. peak and hole	0.484 and -0.607 e.Å ⁻³

RESULTS AND DISCUSSION

Synthesis: The red colored 2-aryazo-1*N*-phenyl aniline ligand(**LH**) was prepared by condensation reaction of equimolar amounts of *N*-Phenyl-*ortho*-phenylenediamine with nitrobenzene in the presence of NaOH at 70°C and purified by column chromatography (Scheme 1) following literature method for 2-(phenylazo)aniline [17].

**Scheme 1.** Synthesis of the ligand **LH**

The Pd(II) complex [Pd^{II}(L)Cl](complex **1**) was prepared in 63% yield by reacting equimolar amounts of **LH** and [PdCl₂(CH₃CN)₂] in methanol under stirring at room temperature in the presence of 2-3 drops of triethylamine. The coordination of L⁻ in N,N,C mode was supported by X-ray analysis, ESI-MS and ¹H NMR. The composition and structure of the ligand **LH** was checked by ESI-MS, ¹H NMR and ¹³C NMR. The ESI-MS spectrum of **1** in CH₂Cl₂ solution (positive mode) is shown in Fig. 2a. The spectrum is consistent with the composition and molecular mass of **1**. The major envelop (Fig. 2c) could be simulated satisfactorily (Fig. 2b) on the basis of formula [Pd(L)]⁺.

The ¹H NMR spectrum shows that PhNH proton of **1** shifts up field (δ 9.12) relative to the ligand **LH** (δ 10.07) supporting ligand coordination. This shift (-0.98) is compared to that of BzNH proton (-0.8) [16].

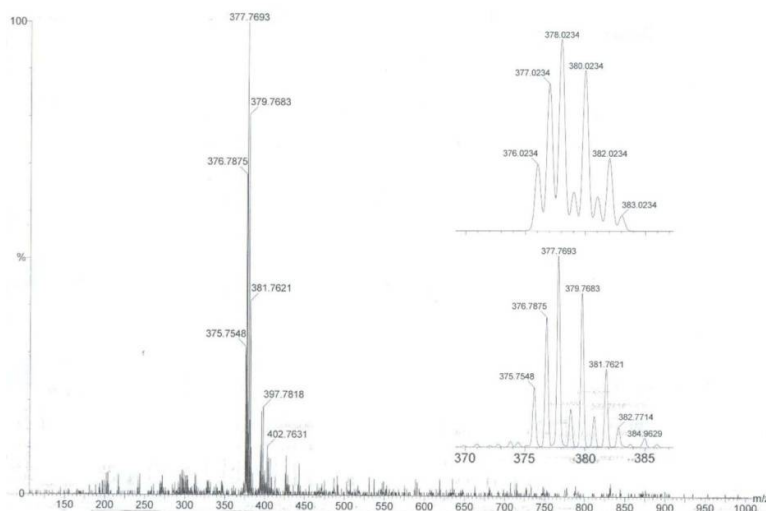


Figure 2. (a) The electrospray mass spectrum (positive mode) of **1** in CH_3CN . (b) Simulated spectrum of **1**. (c) Experimental isotopic distribution pattern.

Crystal and molecular structure: Suitable X-ray quality crystals of complex **1** were grown by the slow diffusion of a CH_2Cl_2 solution of the complex into hexane. The crystals are monoclinic and the space group is $P21/c$. A perspective view with the atom numbering scheme is given in figure 3.

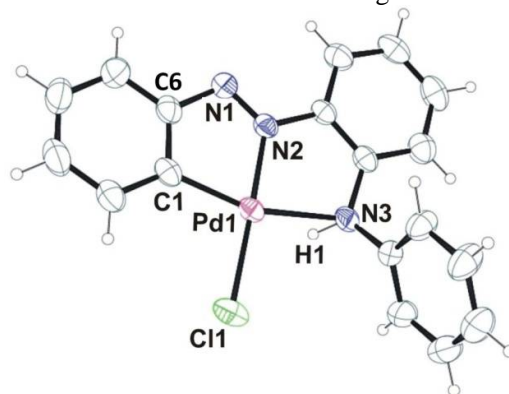


Figure 3. Molecular structure of **1** (thermal ellipsoids are drawn with 30% probability ellipsoids).

Selected bond distances and angles are collected in table 2. The asymmetric unit of **1** in the crystal lattice contains the weak bounded dimer of two equivalent molecules just as in the structure of 2-benzylamine complex of Pd(II) [16]. The molecular structure exhibits a distorted square planar geometry about the palladium, where the anionic ligand **L** binds the metal in a tridentate (N,N,C) fashion. A chloride ligand completes the tetracoordination about Pd(II). The Pd-Cl and Pd- N_{azo} distances are within the normal range [12c,d,16]. Pd-C bond length is also matches well with Pd-C bond lengths in other orthopalladated azobenzene complexes [12a,16]. The Pd- N_{am} bond length is much longer than the Pd- N_{azo} distance because of stronger trans-influence of the aryl carbon [16]. Ligand acts as monoanionic tridentate donor toward Pd(II) using one C_{ph} , one N_{azo} and one N_{am} atoms with the formation of two contiguous five-membered chelates. The pendant phenyl_{am} ring do not lie on the molecular plane and makes almost the right angle with the rest. It is worth to note that in complex **1** the coordination of the secondary phenylamine nitrogen occurs without dissociation of proton just as in the case of related alkylamine nitrogen [16], while in many other cases, the secondary amino groups bind the metals only when the amino proton gets dissociated [18]. It worth note that the C-H activation in 2-(arylamino)-1N-pyridyl aniline, the similar azoamine ligand, did not occur due to the

preferable formation of a five membered Pd-pyridyl chelate [19]. In the complex **1** the N_{azo} atom lays closer to Pd than the N_{am} atom forming a stronger bond with the metal relative to the N_{am} atom. The bond (Pd- N_{am}) of the phenylamine nitrogen with the metal atom is appreciably weaker than for the corresponding alkylamino nitrogen due to decrease of donor strength of nitrogen at the replacement the alkyl for the phenyl. Correspondingly, it is observed some increase of the Pd-C bond in complex **1** in comparison with alkylamino complexes [16].

Table 2. Selected bond distances (Å) and bond angles (°) for complex **1**.

Pd(1)-Cl(1)	2.309(1)
Pd(1)-N(2)	1.945(3)
Pd(1)-C(1)	1.975(5)
Pd(1)-N(3)	2.212(5)
N(1)-N(2)	1.261(6)
Cl(1)-Pd(1)-N(2)	178.4(1)
Cl(1)-Pd(1)-C(2)	99.3(1)
Cl(1)-Pd(1)-N(4)	100.2(1)
N(2)-Pd(1)-C(2)	79.1(2)
N(2)-Pd(1)-N(4)	81.4(2)
C(2)-Pd(1)-C(4)	160.5(2)
Pd(1)-N(2)-N(1)	122.4(3)
Pd(1)-N(2)-C(5)	117.4(3)

Redox properties of LH and complex 1: Azo function is well-known for its rich redox nature [20]. Owing to the presence of low-lying vacant π^* orbital it can accept one electron to form azo-anion radical and this radical species can further accept one more electron to form dianion. When coordinated to a metal the azo function behaves as a dominant electron sink and the reduction becomes more facile [20]. The ligand **LH** showed one reversible reduction at $E_{1/2} = -1.34$ V ($\Delta E = 180$ mV) corresponding single electron reduction of the azo function (Fig. 4, left). On complexation with Pd(II) ion, the reduction of the azo function underwent considerable anodic shift and showed an irreversible response at -0.86 V in complex **1** (Fig. 4, right).

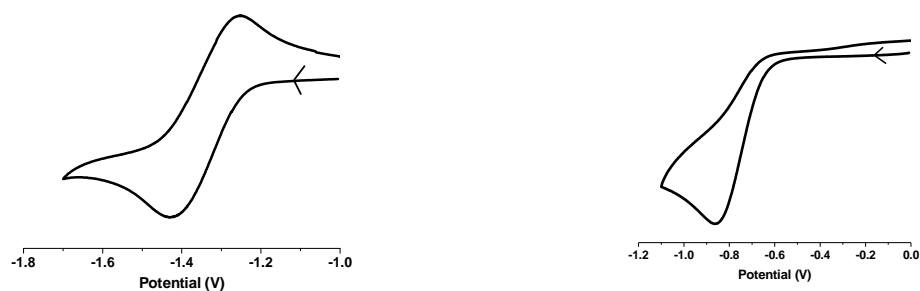


Figure 4. Cyclic voltammograms of **LH** (left) and complex **1** (right); conditions: potentials vs Ag/AgCl, CH_3CN solvent, electrolyte $[\text{Et}_4\text{N}]\text{ClO}_4$, scan rate 50 mV Sec^{-1} .

APPLICATION

The present work describes C-H activation in redox active N-phenyl-(2-phenylazo)aniline ligand by using commercially available Pd(II)-salt at room temperature and under air. Such reactions are highly relevant for formation of new C-C bonds as well as C-hetero atom (e.g. N, O, S) bonds leading to various azo derivatives. As previously mentioned, azo compounds are well known for their uses in dye industries and pharmaceutical industries and more recently in material research. The present research methodologies can be utilized for making new and relevant azo compounds based on N-phenyl-(2-phenylazo)aniline moieties via C-H activation using catalytic amount of Pd(II)-salt

CONCLUSIONS

We have reported the synthesis and structure of a new *orthopalladed* complex **1** comprising of N-phenyl-(2-phenylazo)aniline ligand and fully characterized. The complex was formed via Pd(II)-assisted C-H activation of the phenyl ring of the ligand. This leads to a square planar geometry around the metal center where the ligand provides three coordination sites (N,N,C) and the fourth coordination site is occupied by the chloride anion. The ligand exhibited one reversible response corresponding to single electron reduction while its palladium complex exhibited irreversible reduction at lower potential. Further studies on catalytic activity of complex **1** in the Suzuki and Heck coupling reactions are underway in the laboratory and will be reported in due course.

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Electronic Supplementary Information: ESI available: ^1H and ^{13}C NMR spectra, ESI-MS spectra of the ligand and ^1H NMR spectrum of complex. For ESI and crystallographic data in CIF format see CCDC no. 1578352 and DOI.

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