



ISSN Print: 2664-6552
 ISSN Online: 2664-6560
 Impact Factor: RJIF 5.5
 IJCRD 2023; 5(2): 04-10
<https://www.chemicaljournal.in/>
 Received: 05-05-2023
 Accepted: 11-06-2023

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Cyclopalladates of 1-(2'-hydroxynaphthylazo) naphthalene complexes: Oxygen insertion into the Palladium-Carbon (Naphthyl) bond

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DOI: <https://doi.org/10.33545/26646552.2023.v5.i2a.48>

Abstract

High yield regioselective metaloxylation (M-C → M-OC) of the Pd-C (Naphthyl) bond of palladium (II) complexes [Pd(L)(D)], 1a and 2a, (D = 4-picoline and PPh₃ respectively), of the ligand H₂L [1-(2'-hydroxynaphthylazo)naphthalene] by *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature in dichloromethane medium have been described. The metaloxylated palladium (II) complexes (1c and 2c) have been characterized by spectroscopic techniques. The catalytic oxygen insertion into the Pd-C (naphthyl) bond of the cyclopalladates has also been achieved at room temperature in presence of iron (III) porphyrin catalyst, F₂₀TPPFe (III) Cl [F₂₀TPP: *meso*-5,10,15,20-tetrakis (Pentafluorophenyl) porphyrinato dianion] using mild hydrogen peroxide (H₂O₂) as terminal oxidant. Solvent effects in the catalytic metaloxylation reactions have also been examined and reported.

Keywords: Palladium, cyclometallation, metaloxylation, oxygen insertion

1. Introduction

Selective oxygen insertion into inert C-H bonds, particularly of aromatic hydrocarbons, is one of the most challenging goals in basic and industrial chemistry^[1-4]. Although significant progress has been made in this regard, majority of the systems for aromatic hydroxylation (Ar-H → Ar-OH) often rely on the application of high temperature, pressure, stoichiometric oxidants *etc.* and suffer from non-selectivity and production of toxic waste^[5-8]. Thus, development of rapid, scalable and inexpensive catalytic systems capable of activating target C-H bond under eco-friendly mild condition constitutes one of the most attractive areas of contemporary chemical research.

Reactions *via* C-H bond activation especially activation of aromatic C-H bonds following cyclometallation route are of great importance to achieve selective oxygenation at the metallated carbon. This is a potentially useful tool for functionalization of organic substrates. The transformation of a C-H to a C-M bond, selective oxidation of a C-M to a C-OM bond and then reductive demetallation of this O-M bond finally leads to the functionalization of the C-H to a C-OH bond.

The C-H bond activation reactions promoted by palladium (II) salts enjoy a special status for their wide application potential in metaloxylation reactions^[9-13]. The insertion of oxygen into metal-carbon bond of cyclopalladates may lead to a preparative process of desired selectivity^[14-17]. Several research groups have explored the metallation-oxygenation-demetallation sequence of steps (C-H → C-M → C-O-M → C-OH) for selective oxyfunctionalization of C-H bonds, especially aromatic C-H bonds^[15-19]. The study of metaloxylation reactions has mainly been confined to the domain of C (phenyl)-H bond activation. Reports on selective methods for metaloxylation of naphthyl group so far remained almost unexplored^[20-23]. Van Koten *et al.* reported that metaloxylation of the C(naphthyl)-Pd bond of a series of heteroleptic diarylpalladium compounds with *tert*-butylhydroperoxide catalyzed by vanadium catalyst resulted metaloxylation along with quinone formation^[24-25].

Herein we describe the C (naphthyl)-H activation by palladium (II) and subsequent metaloxylation of Pd-C (naphthyl) bond of the cyclopalladates [Pd(L)(D)] (D = 4-picoline or PPh₃). Oxygen insertion into the Pd-C (naphthyl) bond of the isolated orthopalladates has been studied by *m*-CPBA in dichloromethane medium at room temperature.

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The catalytic metaloxylation reaction of the orthopalladates has also been undertaken by mild H₂O₂ as terminal oxidant in the presence of catalytic amount of iron (III) porphyrin catalyst. Solvent effects in catalytic oxygen insertion process have also been investigated.

2. Experimental

2.1 Materials

Palladium dichloride was purchased from Arora Matthey (Kolkata, India). Disodium tetrachloropalladate was prepared following a reported method [26]. All reagents were obtained from commercial sources and used without purification. The active oxygen content of *m*-CPBA and H₂O₂ (as ~30% solution in water) were determined iodometrically prior to use. Solvents used for the metaloxylation reactions were purified according to standard procedures prior to use [27]. The ligands 1-(2'-hydroxynaphthylazo) naphthalene (H₂L) [28] and 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene (H₂OL) [29] were prepared according to a published procedure.

2.2 Physical measurements

Elemental microanalyses (C, H and N) were done by either Perkin-Elmer (Model 240C) or Heraeus Carlo Erba 1108 elemental analyzer. The IR spectra were recorded on JASCO 5300 FT-IR spectrophotometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V530 spectrophotometer equipped with thermostated cell holder. ¹H NMR spectra were measured in CDCl₃ with a Bruker DPX 300 NMR Spectrometer with SiMe₄ as an internal standard.

2.3 Syntheses of the cyclopalladates

The cyclopalladates were prepared according to the reported method [30].

2.3.1 [Pd(L)(Pic)] (1a): Yield: 23%. Anal. Calc.: C, 62.98; H, 3.86; N, 8.47. Found: C, 62.75; H, 3.62; N, 7.98. IR (KBr): ν 1437 cm⁻¹ (-N=N-). ¹H NMR (300 MHz, CDCl₃): 2.39 (s, 3H, 5'-Me), 6.56 (d, 1H, J=8.22 Hz), 6.69 (d, 1H, J=9.11 Hz), 7.21-7.36 (m, 7H), 7.43-7.57 (m, 4H), 7.64 (d, 1H, J=8.23), 8.44 (d, 1H, J=8.49), 9.17 (d, 1H, J=8.34 Hz).

2.3.2 [Pd(L)(PPh₃)] (2a): Yield: 28%. Anal. Calc.: C, 68.63; H, 4.09; N, 4.21. Found: C, 68.71; H, 4.15; N, 4.09. IR (KBr): ν 1435 cm⁻¹ (-N=N-), 1090 cm⁻¹ (PPh₃). ¹H NMR (300 MHz, CDCl₃): δ 6.17 (s, 1H), 6.55 (d, 2H, J=9.1 Hz), 6.84 (d, 1H, J=8.0 Hz), 7.25-7.67 (m, PPh₃ and other naphthyl ring protons), 8.48 (d, 1H, J=7.8 Hz), 9.18 (d, 1H, J=8.0 Hz).

2.4 Metaloxylation reaction: General procedure

2.4.1 Stoichiometric oxygen insertion by *m*-CPBA

To a dichloromethane solution (5 mL) of the orthopalladate (0.02 mmol) was added dropwise a solution of *m*-CPBA (0.024 mmol) in dichloromethane (5 mL) with constant stirring. The colour of the solution changed from blue to pink. The solid residue was collected after the removal of

solvent followed by washing with water and ethanol. The residue was dissolved in dichloromethane and chromatographed on silica gel using dichloromethane as eluant. The unreacted blue band of the cyclopalladate separated first followed by a pink band of the oxygenated product. Evaporation of the solvent afforded the pink product. Yield: 75-80%.

2.4.2 Catalytic oxygen insertion by H₂O₂

In a vial, a solution of the cyclopalladate, 1a (1.85-2.22 mM) in dichloromethane or in 2:1 (v/v) mixture of dichloromethane/methanol (1.2 mL) was taken. A dichloromethane solution of the catalyst was added to it such that the final concentration of the catalyst was 5-15 μ M. H₂O₂ (4-6 mM) was then added to this mixture. The mixture was stirred for 1 h. The reaction mixture was evaporated to dryness, dissolved in a minimum volume of dichloromethane and chromatographed on a thin layer of silica gel using dichloromethane as the eluant. Evaporation of the solvent afforded the metaloxylated product. Yield: 45-60%.

2.5 Syntheses of authentic palladium complexes

The authentic Pd(ONO) complexes were synthesized following the procedure for orthopalladates [30]. Here, 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene (H₂OL) ligand was used instead of 1-(2'-hydroxynaphthylazo) naphthalene (H₂L).

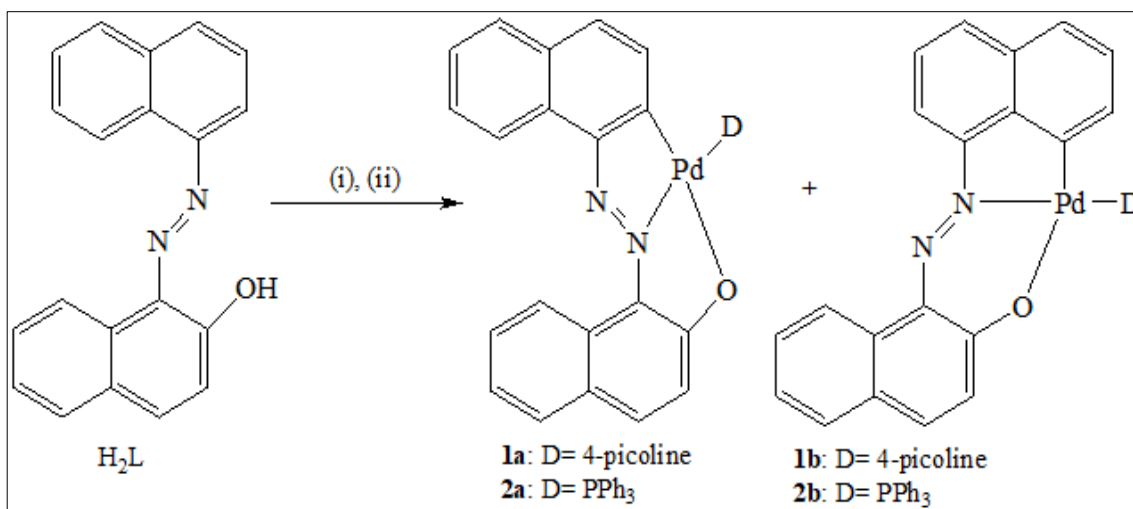
2.5.1 [PdOL (Pic)] (1c): Yield: 46%. Anal. Calc.: C, 61.01; H, 3.74; N, 8.21. Found: C, 60.75; H, 3.62; N, 7.98. IR (KBr): ν 1435 cm⁻¹ (-N=N-). ¹H NMR (300 MHz, CDCl₃): δ 2.51 (s, 3H, 5'-Me), 7.34-7.44 (m, 6H), 7.52 (d, 1H, J=8.0 Hz), 7.67-7.82 (m, 6H), 7.86 (d, 1H, J=8.0 Hz), 8.96 (d, 1H, J=8.0 Hz), 9.87 (d, 1H, J=8.0 Hz).

2.5.2 [PdOL (PPh₃)] (2c): Yield: 53%. Anal. Calc.: C, 67.02; H, 4.00; N, 4.11. Found: C, 66.71; H, 3.85; N, 4.09. IR (KBr): ν 1431 cm⁻¹ (-N=N-), 1096 cm⁻¹ (PPh₃). ¹H NMR (300 MHz, CDCl₃): δ 6.43 (d, 1H, J= 9.0 Hz), 6.99 (d, 1H, J= 8.0 Hz), 7.42-7.86 (m, PPh₃ and other naphthyl ring protons), 8.38 (d, 1H, J= 8.0 Hz), 9.04 (d, 1H, J= 8.0 Hz), 9.95 (d, 1H, J= 8.0 Hz).

3. Results and Discussion

3.1 Synthesis

Disodium tetrachloropalladate (II), Na₂[PdCl₄] smoothly activates C (naphthyl)-H bond of 1-(2'-hydroxynaphthylazo) naphthalene (H₂L) in ethanol medium at room temperature and produces isomeric mixtures of monomeric cyclopalladates [Pd(L)(D)] in presence of neutral Lewis base, D [D = 4-picoline or PPh₃]. Here, the activation of C2 (naphthyl)-H bond and C8 (naphthyl)-H bond result in the formation of 1a/2a (blue) and 1b/2b (pink) respectively (Scheme 1). The separation of the two types of isomers has been done by thin layer chromatography. The resulting complexes have been thoroughly characterized [30].



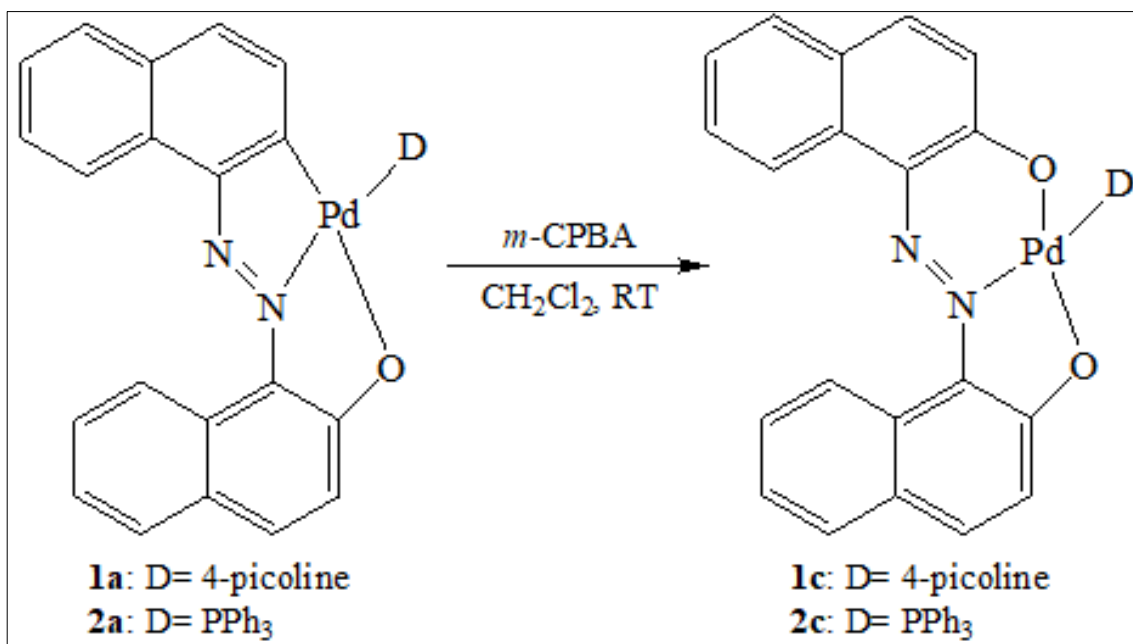
Scheme 1: (i) Na₂[PdCl₄], EtOH, room temperature, 8 h; (ii) 4-picoline or PPh₃, room temperature, 2h.

3.2 Metaloxylation reaction

3.2.1 Stoichiometric oxygenation of Pd-C (naphthyl) bond

The orthopalladates [Pd(L)(D)] (1a and 2a) was reacted with *m*-CPBA in dichloromethane medium at room

temperature and transformed into the metaloxylated product [PdO(L)(D)] (1c and 2c) as shown in Scheme 2. For optimum yield, slightly larger than the stoichiometric amount of *m*-CPBA is usually used.



Scheme 2: Oxygenation reaction by *m*-CPBA.

Upon addition of *m*-CPBA to the solution of 1a in dichloromethane, the colour changes from blue to pink. The course of reaction has been monitored by UV-visible spectroscopy. Gradual addition of *m*-CPBA to the dichloromethane solution of 1a resulted in the generation of a new band at 554 nm at the expense of the bands at 725 nm, 664 nm and 400 nm (Fig. 1).

After 15 min, the pink product was isolated in high yield based on orthopalladate by preparative TLC on silica gel using dichloromethane as the eluant. The metaloxylated product obtained after evaporation of the solvent has been thoroughly characterized by elemental analysis and spectroscopic techniques.

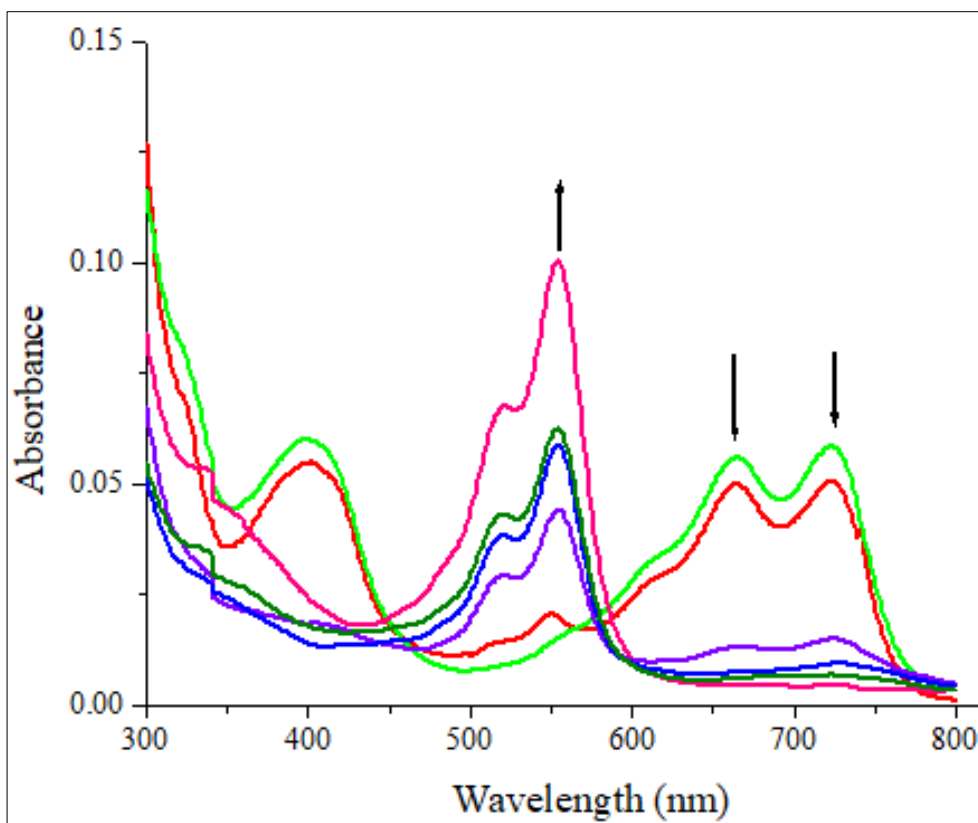


Fig 1: Graphical changes in UV-vis spectra during oxygenation of 1a by gradual addition of *m*-CPBA. The arrows indicate increase and decrease of band intensities as reaction proceeds.

In case of orthopalladate containing PPh_3 as Lewis base (2a), the characteristic absorption band at 402 nm, 672 nm and 733 nm disappears and new absorption band develops at

558 nm after treatment with *m*-CPBA in dichloromethane at room temperature. The overlay spectra of 2a with its oxygenated product 2c have been shown in the Fig. 2.

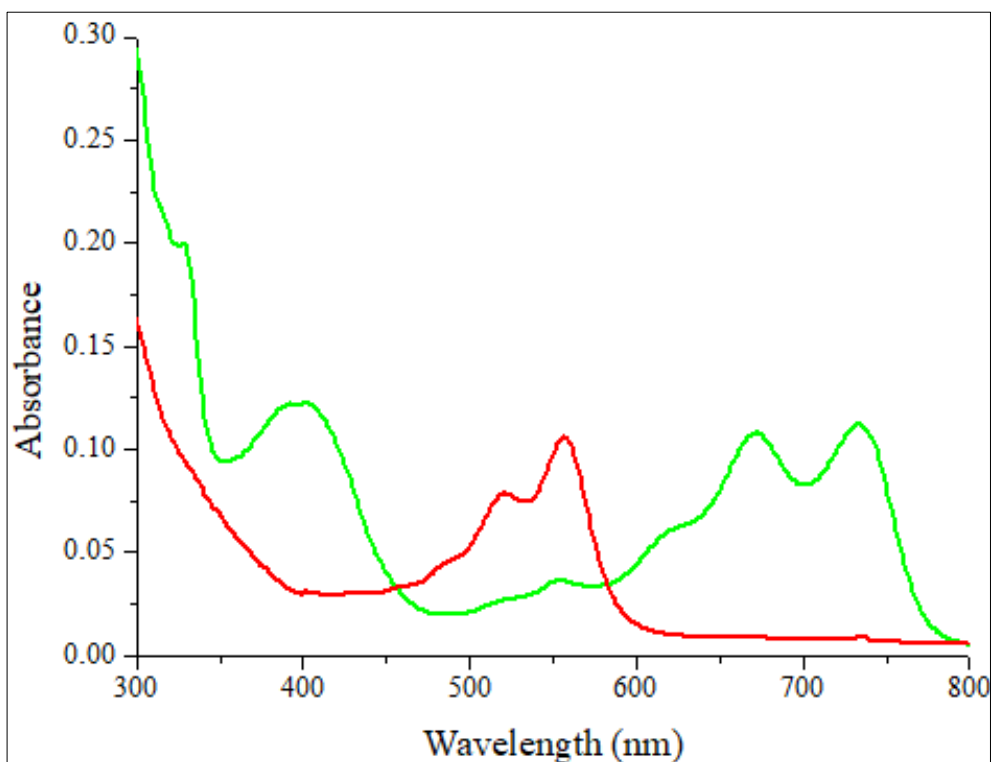


Fig 2: UV-vis spectra of 2a (green) and its oxygenated product 2c (red).

3.2.2 Catalytic oxygenation of Pd-C (naphthyl) bond

Stoichiometric regioselective metaloxylation of Pd-C(naphthyl) bond by *m*-CPBA prompted us to develop more

efficient and mild oxygenation system as the process has major drawbacks from the environmental as well as economical point of view. Thus, attempts have been made to

achieve Pd-C (naphthyl) bond oxygenation using green and inexpensive oxidant H_2O_2 , as H_2O_2 generates only water as a side product and contains the largest amount of active oxygen species among the known oxidants. The well-known iron(III) porphyrin complex, $\text{F}_{20}\text{TPPFe(III)Cl}$ [F_{20}TPP : meso-5, 10, 15, 20-tetrakis (pentafluorophenyl) porphinato dianion] widely used in model systems is employed as catalyst in selective oxygenation of Pd-C(naphthyl) bond using environment-friendly H_2O_2 as terminal oxidant at

room temperature in dichloromethane or in a mixture of dichloromethane/methanol(2:1, v/v). However, H_2O_2 itself does not show any appreciable reactivity towards the metaloxylation reaction.

The solvent plays an important role in the catalytic metaloxylation reaction. Among the various solvent systems studied, mixture of dichloromethane/methanol (2:1, v/v) has been found to deliver the best results (Table 1).

Table 1: $\text{F}_{20}\text{TPPFe(III)Cl}$ catalyzed oxygenation of orthopalladate 1a by H_2O_2 .

Entry	Substrate, 1a (mM)	Catalyst (μM)	H_2O_2 (mM)	Solvent	Yield (%) ^a
1	2.22	10	4	CH_2Cl_2	46
2	2.22	10	6	CH_2Cl_2	48
3	2.22	15	6	CH_2Cl_2	54
4	1.85	5	4	2:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	35
5	1.85	10	4	2:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	60
6	1.85	10	6	2:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	59
7	1.85	10	6	2:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$	63

^aYields are measured spectrophotometrically and based on 1a.

The catalytic oxygenation of Pd-C (naphthyl) bond of the cyclopalladate containing PPh_3 as donor (2a) has also been studied. Under the similar reaction conditions, the conversion in terms of product yield diminished in the range of 28-30% even after 24 h reaction time. It is probably due to the steric hindrance imposed by the sterically demanding PPh_3 .

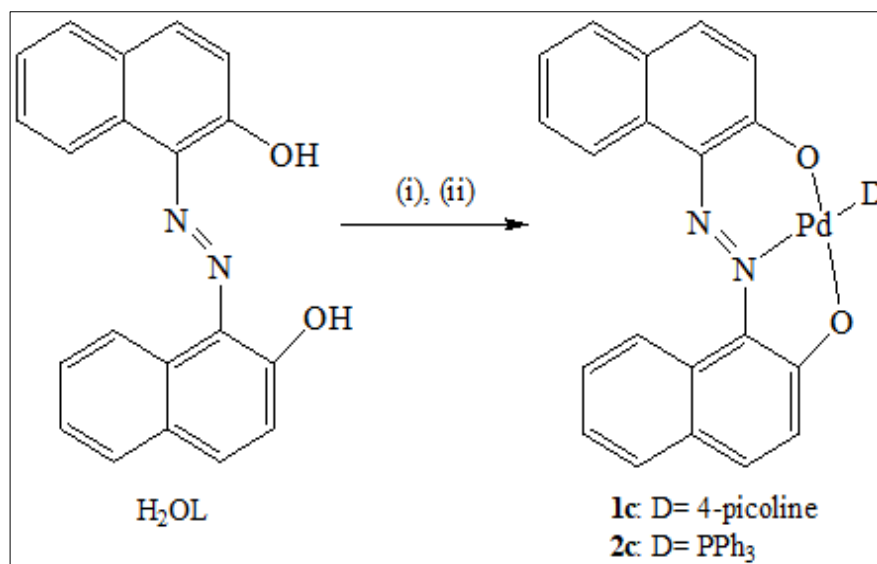
3.3 Probable mechanistic consideration

The mechanism of metaloxylation proposed by Bandyopadhyay *et al.* seems reasonable in this case^[17]. In the present oxygenation experiment, the oxoiron(IV) porphyrin cation radical is generated by the reaction of iron(III) porphyrin catalyst and H_2O_2 and, in the presence of

an excess of H_2O_2 , oxoiron(IV) porphyrin cation radical abstracts hydrogen atom from H_2O_2 and hydroperoxy radical ($\text{HOO}\cdot$) becomes the major reactive species in the present oxidizing system.

3.4 Preparation of authentic H_2OL ligand and its complexes

For unambiguous characterization of the metaloxylated products, a structurally similar palladium(II) compound with tridentate naphtholato-O, N, O ligand, 1-(2'-hydroxy-1'-naphthylazo)-2-hydroxynaphthalene (H_2OL) was independently synthesized following a non-oxidative route as shown in Scheme 3.



Scheme 3: (i) $\text{Na}_2[\text{PdCl}_4]$, EtOH, room temperature, 8 h; (ii) 4-picoline or PPh_3 , room temperature, 2h.

Characterization data, spectral features and other physical characteristics of these complexes were identical with the products obtained after metaloxylation of 1a and 2a with peroxy reagents.

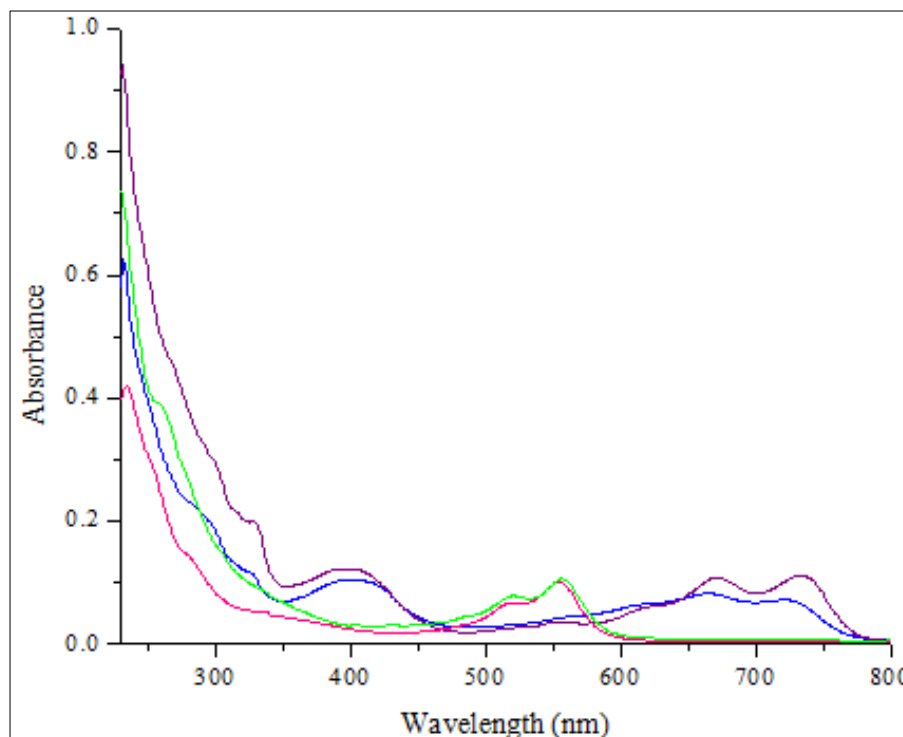
3.5 Electronic spectra

All the cyclopalladates are soluble in common organic solvents, such as dichloromethane, acetonitrile, and acetone,

producing either bluish green (Orthopalladates) or pink solutions (Metaloxylated products) in dichloromethane. Spectral data are presented in the Table 2. The electronic spectra of the palladium cyclometallates (1a and 2a) with the authentic Pd(ONO) complexes (1c and 2c) recorded in dichloromethane are shown in Fig. 3.

Table 2: Electronic spectral data of the cyclopalladates in dichloromethane.

Compound	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)
1a	272 (39,500), 400 (8,800), 664 (7,950), 725 (8,200)
2a	275 (53,000), 402 (11,300), 672 (11,050), 733 (11,500)
1c	296 (11,200), 520 (4,550), 554 (7,050)
2c	232 (57,450), 263 (24,860), 523 (7,630), 558 (10,720)

**Fig 3:** Electronic spectra of 1a ((blue), 2a (purple), 1c (pink) and 2c (green) in dichloromethane.

The cyclopalladates show several absorptions in the ultraviolet and visible region. The bands appearing in the ultraviolet region with high molar extinction coefficient are generally thought to be arisen from intraligand charge transfer transition whereas absorptions in the visible region are attributed to the metal-to-ligand charge transfer transition^[31].

4. Conclusion

Stoichiometric selective oxygen insertion into the Pd-C(naphthyl) bond of orthopalladates has been achieved by *m*-CPBA in dichloromethane medium at room temperature. The metaloxylated products have been isolated and well characterized by elemental analysis and spectroscopic techniques. Catalytic metaloxylation of organometallates, i.e., Pd-C(naphthyl) \rightarrow Pd-O-C(naphthyl) has also been achieved at room temperature using iron(III) porphyrin catalyst, F₂₀TPPFe(III)Cl. Environmentally benign and inexpensive hydrogen peroxide has been successfully employed as terminal oxidant in catalytic oxygenation process. Solvents play important role in catalytic oxygenation of C(naphthyl)-Pd bond.

5. Acknowledgements

The financial support from Department of Science & Technology and CSIR, New Delhi are gratefully acknowledged. The author is grateful to Dr. P. Bandyapadhyay for his assistance and kind cooperation. The author also expresses his sincere thanks to the Department

of Chemistry, University of North Bengal for providing instrumentation facilities.

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