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New Pd (II) and Pt (II) Schiff Base Complexes for Catalytic Applications in C-H Bond Activation and Oxygenation of Hydrocarbons

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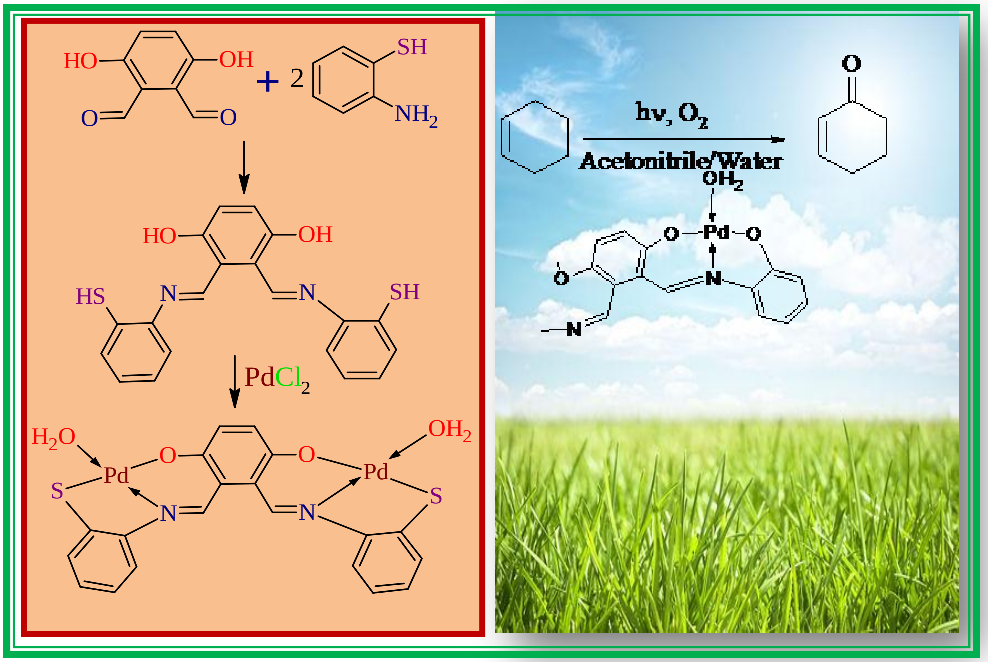
ABSTRACT

Two new Schiff base ligands have been prepared by condensing 3,6-dihydroxybenzene-1,2-dicarbaldehyde with 2-aminophenol or 2-aminothiophenol and characterized by spectroscopic methods like mass, IR, ^1H *and* ^{13}C *NMR. The new Schiff bases react with* $PdCl_2$ *and* $PtCl_2$ *to form complexes of formula* $[M_2L(H_2O)_2]$*. The IR and NMR spectral investigations reveal the coordinating atoms of the ligands as azomethine N, phenolic O and thiophenolic S atoms. The complexes are diamagnetic and electronic spectra of the complexes establish the square planar geometry around the metal centre. The complexes exhibit photocatalytic activity in the oxidation by C-H bond activation of allylic C atoms in actonitrile-water mixture. The metal complexes catalyze the formation of* $HO^{\bullet}$ *radicals from water in presence of dissolved oxygen. Pd(II) complexes exhibit better catalytic properties compared to Pt(II) complexes, probably due to less stability of the Pd(IV) state formed in the catalytic cycle and also due to the phosphorescence effect of platinum complexes that absorb 30-40% of incident light and thus decreasing photocatalytic formation of* $HO^{\bullet}$ *radicals. Aqueous acetonitrile was found to be a better solvent system compared to aqueous-DMSO or DMF, because of higher solubility of* O_2 *in acetonitrile.*

Graphical Abstract



Keywords: Schiff base ligands, Platinum group metal complexes, C-H bond activation, Allylic oxidation, Photo catalytic reactions.

INTRODUCTION

The coordination compounds of transition metals gained prominence because of their applications in areas like biology, industry, pharmaceutical, catalysis and material chemistry [1-3]. The building of C-C bonds and activation of C-H bonds are extremely important processes in synthetic organic chemistry and chemists have been working on developing suitable catalysts to achieve the same [4-7]. The activation of C-H bond and development of C-O bond is the simplest and immensely studied reaction as the C-H bond in saturated hydrocarbons is strong and unreactive on one hand and the reaction should be limited to one C-H bond only in the molecules that generally contain more than one. If this is not taken care, the reaction ends in the most stable, fully oxidized C, i.e., CO_2. Therefore, search continues for effective catalysts for C-H bond activation either by oxygenation [8] or by dehydrogenation [9]. A heteroatom or an organic coordinating group, like olefin, facilitates activation of C-H bond. Delcamp and White [10] have reported sequential C-H bond transformations with alkenes, where an allylic C-H oxidation is followed by a vinylic C-H arylation. Palladium catalyzed Sonogashira reaction for coupling of alkynes with various reagents has been considered to be cornerstone in organic synthesis and thoroughly reviewed [11]. Sanford and co-workers [12,13] have reported the use of nitrogen atoms for coordination to Pd in the arene reagents and the regioselective C-H activation in benzoquinolones. Among the different N donors, the Schiff bases constitute a special class of ligands [14]. The aromatic Schiff bases and their metal complexes catalyze reactions of oxygenation [15], hydrolysis [16] and electrochemical reduction [17] reactions. The transformations of alkenes to the resultant α,β-unsaturated enones or 1,4-enediones are predominantly vital in the synthesis of natural products and synthetic drug precursors [18]. Nishinaga et. al., have shown that four coordinated Co(II)-Schiff base complexes show catalytic activity in oxygenation of alkenes [19]. Platinum group metal complexes have been drawing the attention of academic and industrial researchers as they are proved to act as catalysts in a variety of chemical transformations. Recently, Topczewski and Sanford have reviewed the C-H bond functionalization reactions proceeding *via* $Pd^{II/IV}$ catalytic cycles that have operational simplicity, wide scope, excellent functional group tolerance and opportunities to access both C-C and C-heteroatom bond construction [19b]. Further, the interest of 21st century chemists has been the development of catalytic reactions that are environmentally benign maintaining atom economy leading to clean chemistry [20].

In view of the continued interest and importance of platinum group metals in organic synthesis as reagents and catalysts and in continuation of our sustained efforts to develop novel polydentate O,N donor ligands and their metal complexes for applications in organic synthesis and catalysis [21] in consonance with the Green Chemistry principles, we report herein synthesis of two new Schiff base ligands, their Pd(II) and Pt(II) complexes and their application in oxygenation by C-H bond activation. The Schiff base ligands developed are: (i) 2,3-bis((E)-((2-hydroxyphenyl)imino)methyl)benzene-1,4-diol (HPIMB) and (ii) 2,3-bis((E)-((2-mercaptophenyl) imino)methyl)benzene-1,4-diol (MPIMB).

MATERIALS AND METHODS

General: All the chemicals, the metal chlorides and solvents used were purchased from E-Merck India Ltd. The chemicals and solvents were of AR grade and were purified before use wherever required by standard methods. The platinum content in the complexes was determined by using atomic absorption spectrometry as per the procedure described by Beamish *et. al.*, [22]. Palladium was estimated using modified complexometric titration method reported by Karthikeyan *et. al*., [23].

Instrumental: Carbon, hydrogen and nitrogen were determined using Perkin-Elmer-2401 CHN analyzer. Molar conductance measurements were made in DMF using Digisun Digital DI-909 instrument. IR spectra were recorded on Perkin-Elmer BX series spectrometer using KBr pellets in the range of 4000-600 cm^{-1} and as Nujol mulls between CsI plates in the far-IR region. The electronic spectra were recorded on Shimadzu UV-2401PC Spectrophotometer with UV probe software. ^{1}H and ^{13}C NMR spectra were recorded on JEOL 400/100 MHz spectrometer or Bruker 300/75 MHz FT NMR spectrometer, IICT, Hyderabad. Mass spectra (FAB) were recorded on a Jeol JMS D-300 spectrometer. TGA Thermograms of the complexes were obtained in the temperature range of 50º–800 ºC with a heating rate of 10 ºC min^{-1} in nitrogen atmosphere using Mettler TGA 851 instrument. The products in the catalytic application reactions were separated using Puri Flash PF800 Flash chromatograph.

Synthesis of ligands: The Schiff base ligands used in the present study are obtained by condensing 3,6-dihydroxybenzene-1,2-dicarbaldehyde with diamines. 3,6-dihydroxybenzene-1,2-dicarbal-dehyde (**4**) is prepared first as per the procedure described below:

Preparation of 2-(5,5-dimethyl-1,3-dioxan-2-yl)benzene-1,4-diol (3): To a mixture of 2,5-dihydroxy benzaldehyde (**1**) (100 mmol, 13.8 g) and 2,2-dimethylpropane-1,3-diol (**2**) (120 mmol, 12.49 g) in a 100 mL RB flask in dry toluene (60 mL) was added 4-methylbenzenesulfonic acid (5 mmol, 0.86 g). The reaction mixture was heated to reflux under inert atmosphere for 16 h, while monitoring by TLC (hexane/EtOAc 4:1). After 16 hours, TLC showed new spot with R_f 0.49. The reaction mixture was cooled to room temperature and the toluene was removed by rotary evaporation. The residue was treated with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed by rotary evaporation. The product was purified by flash chromatography on silica gel using 40:60 ethyl acetate–hexane as eluent to get 2-(5,5-dimethyl-1,3-dioxan-2-yl)benzene-1,4-diol (**3**).

Preparation of 3, 6-dihydroxybenzene-1,2-dicarbaldehyde (4): The procedure for the preparation of (**4**) (step-2) is modified Duff reaction [24]. 50 mmol (11.21 g) of **3**, trifluoro-acetic acid (50 mL) and hexamethylenetetramine (HMTA, 100 mmol, 14.62 g), were taken in a 500 mL three-necked round-bottom flask fitted with a mechanical stirrer. The homogeneous mixture was heated to 130 ^{o}C for 60 min. Then the mixture was cooled to 75 ^{o}C and 30 mL of 33% (w/w) aqueous H_2SO_4 was added. The reaction mass was heated at reflux (105-110 ^{o}C) for 60 min with continuous stirring. Then it was allowed to stand undisturbed for 30 min at this temperature, while the lower aqueous layer separated. The organic layer was transferred to a round bottom flask connected to vacuum line and dried carefully under vacuum.. The crude product was rrecrystalized from methanol to get the desired pure compound (**4**) as a free-flowing yellow solid.
Analytical data: ^{1}H-NMR: 9.93 (s, 2H), 7.82 (s, 2H) and 6.24 (s, 2H); ^{13}C-NMR: 198.34, 156.45, 132.69 and 128.19 ppm; HRMS data: 167 [M+H]$^+$, Analysis(%): Calculated for $C_8H_6O_4$: C - 57.84, H - 3.64; Found: C - 57.58, H - 3.59.

2,3-bis((E)-((2-hydroxyphenyl)imino)methyl)benzene-1,4-diol (HPIMB): 25 mmol (4.15 g) of **4** was dissolved in 70 mL toluene and piperidine (5 mmol, 0.42 g) was added at room temperature. To this a solution of 50 mmol (5.45 g) of 2-aminophenol in 30 mL toluene was slowly added. The mixture was refluxed for 16 h. The reaction mixture was cooled and toluene was removed by distillation under low pressure to get the product. The compound was filtered and washed with cold ethanol and dried. The crude product was recrystalized from acetone/ethanol (3:7) mixture to get light yellow colored pure Schiff base, **HPIMB**.

Analytical data: Yield (5.38 g) 62%; M. P. 180 ^{o}C; Mass (m/z) 349 [M+H] $^+$; Calcd. for (%): $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.08; Found: C 68.89, H 4.59, N 7.96. IR (cm^{-1}) 3072$_{br}$ υ (O-H), 1602 υ(C=N), 1230 υ(C-O). ^{1}H NMR (δ, ppm in DMSO-d_6): 8.38$_s$ (*H*C=N), 7.28-6.38 (*H*-Ar), 5.78 (-*H*O). ^{13}C NMR (δ, ppm in DMSO-d_6): 161.42 (*C*=N), 142.08 (Ar*C*-N), 154.86, 153.32 (*C*-OH), 129.14-118.51 (Ar-*C*s).

2,3-bis((E)-((2-mercaptophenyl)imino)methyl)benzene-1,4-diol (MPIMB): 25 mmol (4.15 g) of 3,6-dihydroxybenzene-1,2-dicarboxaldehyde was dissolved in 100 mL toluene and to this a solution of 2-aminobenzenethiol (50 mmol, 6.26 g) in toluene and 5 mmol (0.42 g) of piperidine was added. The resulting mixture was heated on an oil bath at reflux for 16 h. The reaction mixture was cooled and the toluene was removed under reduced pressure to give the crude product which was washed with cold ethanol and recrystalized from acetone-ethanol mixture (3:7) to get pure ligand, **MPIMB**.

Analytical data: Yield: 6.73 g, 74%, M. P. 168 ^{o}C, Mass (m/z) 381 [M+H]$^{+}$. Calcd. for$C_{20}H_{16}N_2O_2S_2$ (%): C 63.13, H 4.24, N 7.36, S 16.85; Found: C 63.08, H 4.29, N 7.26, S 16.56. IR (cm^{-1}): 3072$_{br}$ υ(O-H), 2656 υ(S-H), 1608 υ(C=N), 1230 υ(O-H), 710 υ(C-S). ^{1}H NMR (δ ppm, DMSO-*d*$_6$): 8.72$_s$ (*H*C=N), 7.48-6.82$_m$ (*H*-Ar), 5.92$_s$ (*H*O-), 3.62 (*H*S-). ^{13}C NMR (δ ppm, DMSO-*d*$_6$): 162.34 (*C*=N), 155.98 (*C*-N), 151.74 (*C*-OH), 143.25 (*C*-S), 141.11-115.23 (*C*-Ar).

General procedure for the preparation of Pd(II) and Pt(II) complexes of the Schiff bases: To one mmol, (0.348 g) of HPIMB or (0.380 g) of MPIMB, in 20 mL methanol was added two mmole of $PdCl_2$ (0.3546 g) or $PtCl_2$ (0.5319 g) in 20 mL methanol under nitrogen atmosphere. The colour changed immediately to dark brown, and the reaction mixture was refluxed for three hours. The solid complex precipitated out was filtered and collected on a fine frit. Washed with cold methanol and then with cold acetone and finally with ether. The solid complexes were dried under vacuum and stored over fused $CaCl_2$.

[Pd_2(HPIMB)(H_2O)$_2$]: Yield: 0.83 g, 84%, Decomposition temp. (DT) 306 ^{o} C, Mass m/z 593.19, Calcd. for $C_{20}H_{16}N_2O_6Pd_2$ (%): C 40.51, H 2.72. N 4.72, Pd 35.88; Found: C 40.38, H 2.64, N 4.64, Pd 36.03. Λ_M (ohm^{-1}cm^{2}mole^{-1}) 9.6. IR (cm^{-1}): 3675-2850, 1570, 1512, 1479, 1384, 1210, 1051, 754, 536, 488, 404. ^{1}H NMR (δ, ppm in DMSO-*d*$_6$): 8.1$_s$ (*H*-C=N), 7.1-6.1$_m$ (Ar-*H*'s), 3.8 (*H*$_2$O). Electronic spect. (cm^{-1}): 23256, 31746, 38167.

[Pd_2(MPIMB)(H_2O)$_2$]: Yield: 1.03 g, 82%, Decomposition temp. (DT) 293 ^{o}C, Mass m/z 625.32, Calcd. for $C_{20}H_{16}N_2O_4Pd_2S_2$ (%): C 38.41, H 2.58. N 4.48, Pd 34.04, S 10.26; Found: C 38.28, H 2.52, N 4.42, Pd 34.26, S 10.19. Λ_M (ohm^{-1}cm^{2}mole^{-1}) 11.3. IR (cm^{-1}): 3790-2805, 2630, 1600, 1508, 1484, 1196,1101, 1026, 967, 887, 821, 696, 620, 476, 442, 416. ^{1}H NMR (δ, ppm in DMSO-*d*$_6$): 8.32$_s$ (*H*-C=N), 7.1-6.22$_m$ (Ar-*H*'s), 3.36 (*H*$_2$O). Electronic spect. (cm^{-1}): 24390, 31250.

[Pt_2(HPIMB)(H_2O)$_2$]: Yield: 0.71 g, 46%, Decomposition temp. (DT) 338 ^{o}C, Mass m/z 770.5, Calcd. for $C_{20}H_{16}N_2O_6Pt_2$ (%): C 31.18, H 2.09. N 3.64, Pt 50.64; Found: C 30.87, H 1.98, N 3.49, Pd 50.16. Λ_M (ohm^{-1}cm^{2}mole^{-1}) 9.3. IR (cm^{-1}): 3800-2865, 1568, 1478, 1384, 1210, 1051, 754, 510, 462. ^{1}H NMR (δ, ppm in DMSO-*d*$_6$): 8.05$_s$ (*H*-C=N), 7.8-5.9$_m$ (Ar-*H*'s), 3.3 (*H*$_2$O). Electronic spect. (cm^{-1}): 26178, 32786.

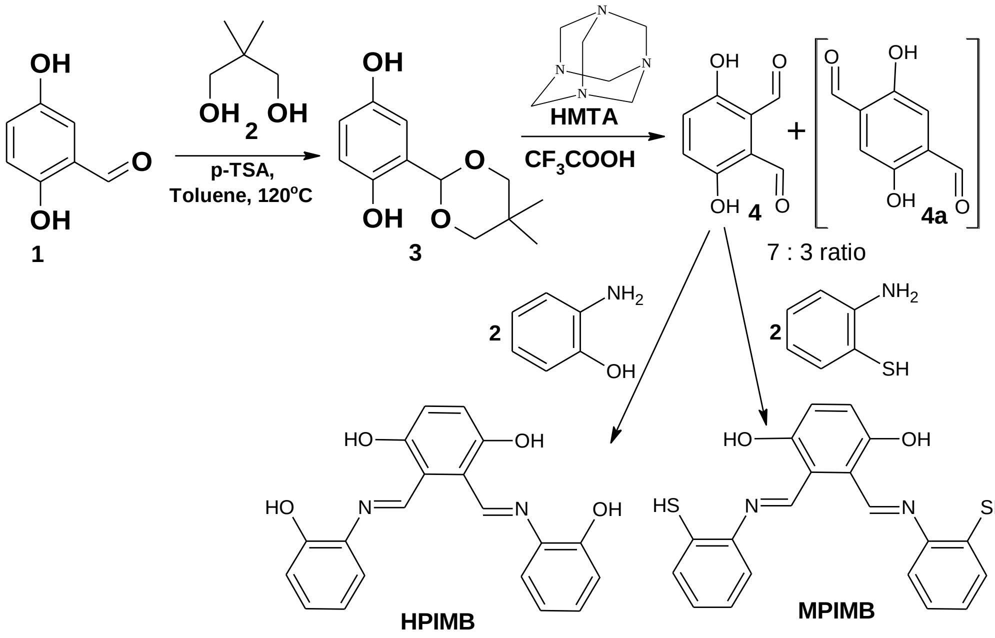
[Pt_2(HPIMB)(H_2O)$_2$]: Yield: 0.70 g, 44%, Decomposition temp. (DT) 319 ^{o}C, Mass m/z 802.65, Calcd. for $C_{20}H_{16}N_2O_4Pt_2S_2$ (%): C 29.93, H 2.01. N 3.49, Pt 48.61, S 7.99; Found: C 29.36, H 1.84, N 3.28, Pd 48.18, S 7.62. Λ_M (ohm^{-1}cm^{2}mole^{-1}) 8.5. IR (cm^{-1}): 3650-2960, 1564, 1446, 1384, 1186, 1049, 949, 898, 862,759, 640, 514, 442, 382. ^{1}H NMR (δ, ppm in DMSO-*d*$_6$): 8.62$_s$ (*H*-C=N), 7.48-6.59$_m$ (Ar-*H*'s), 3.63 (*H*$_2$O). Electronic spect. (cm^{-1}): 25380, 33783.

Procedure for catalytic reactions: The catalytic activity of all the complexes evaluated by carrying out the reactions in a Visible Annular Type Photoreactor, model HVAR1234 (Haber Scientific, India) under visible light irradiation using 300 W tungsten lamp as light source (380nm $\leq \lambda \leq$ 840nm). In a typical experiment, to 10 mL of acetone: water mixture (1:1) in a cylindrical-shaped glass reactor fitted with a serum cap, 10 mmol (0.82 g) of cyclohexene was added. After the reaction mixture reached the experimental temperature, 0.1 mmol of catalyst solution, [Pd_2(HPIMB)(H_2O)$_2$] (0.059 g) or [Pt_2(HPIMB)(H_2O)$_2$] (0.077 g), in 2 mL of acetonitrile was added through a syringe over a period of 3 minutes. Then the reaction mixture was stirred at ambient temperature under 300/500 watt tungsten lamp for a period of 2 h. The reaction mixture was monitored by TLC at 20 min intervals. At the end of the reaction time, the glass reactor was removed from the instrument and solvent was removed under reduced pressure. The residue was extracted and purified by flash column chromatography with hexane/ethyl acetate (9:1 v/v) mixture as eluent to get the pure product in a previously weighed bottle. The experiments were first repeated under different experimental conditions to optimize the catalytic reactions. Then the catalytic reactions were performed with all the selected substrates and catalysts at optimized conditions.

Analysis of the reaction mixtures: Qualitative analysis was accomplished by NMR; the data were compared with those of authentic samples purchased from commercial suppliers. Quantitative evaluation of product was carried out using standard methods that allowed reproducibility within ±1%.

RESULTS AND DISCUSSION

Characterization of Ligands: The intermediate (**4**) required for the preparation of Schiff base ligands used in the present investigation is prepared from (**1**) as shown in the reaction Scheme 1. The first step is protection of aldehyde group followed by modified Duff reaction [24] (second step) to get, **4**. Two isomers (**4** and **4a**) are formed in 7:3 ratio (TLC) which were separated by column chromatography. The dicarbaldehyde is finally treated with 2 moles of 2-aminophenol or 2-aminothiophenol to get the desired Schiff base, HPIMB/MPIMB in more than 60% yield.



Scheme 1. Reaction scheme for the preparation of Schiff base ligands

The disappearance of υ(C=O) in the IR spectra of the ligands at 1637 cm^{-1} and appearance of a new absorption at 1602 cm^{-1} in HPIMB and 1608 cm^{-1} in MPIMB assignable to υ(C=N) indicate the formation imine group. Similarly in the ^1H NMR spectra of the ligands, the signal at 9.937 ppm assignable to aldehyde proton (*H*C=O) of **4** disappeared and a signal at 8.38 (HPIMB) and 8.72 (MPIMB) ppm appeared that may be assigned to the azomethine group proton (*H*C=N) of the ligands. In the ^{13}C NMR spectrum of the ligands no signal in the downfield side around 180 ppm confirms the conversion of >C=O group to >C=N group that exhibits its corresponding signal at 161.42 (HPIMB)/162.34 (MPIMB). The Mass spectra of the ligands HPIMB and MPIMB show peaks (m/z) at 349.2 and 381.3 respectively, corresponding to $[M+H]]^+$. The spectral analyses confirm the formation of the new Schiff bases, HPIMB and MPIMB.

Characterization of catalysts

Elemental analysis and mass spectra: The ligands, HPIMB and MPIMB react with the metal salts, $PdCl_2$ and $PtCl_2$ in 1:2 ratios resulting in the respective metal complexes. The analytical and physicochemical data of the complexes are presented in the experimental section. The mass spectra (FAB) of the complexes exhibit m/z peak corresponding to $[M\text{-}2H_2O]^+$ [25] with the adequate isotopic pattern. In addition to this all the spectra of the complexes show a peak corresponding to the $[L+H]^+$ ion, indicating the formation of 1:2 (ligand: metal) complexes. The analytical data for C, H, N and metal and S in the case of MPIMB complexes are in good agreement with the calculated values for the formula $[M_2L(H_2O)_2]$. [L = ligand - $4H^+$ ion, M = Pd/Pt].

Thermogravimetric analysis: Thermograms of the complexes recorded between 50^o and 800 ^oC, show two stage decomposition. Thermal data are presented in table 1. The first stage decomposition between 110-220 ^oC is found to be 4.72-5.83% for all the complexes and this is in close agreement with the loss of two water molecules and the temperature range indicates that the water molecules are coordinated [26]. The final stage of decomposition starts around 370 ^oC and the thermogram becomes parallel to the temperature axis around 800 ^oC. The final residue left corresponds to the percentage of metal oxide [27]. The data supports the proposed molecular formula of the complexes based on mass spectra and elemental analyses.

Table 1. Thermal decomposition data of the Schiff base complexes of Pd(II) and Pt(II)

S. No.	Compound	1st Stage Decompn. ^oC	%loss		2nd Stage Decompn. ^oC	Residue left (%)	
			Found	Cal.		Found	Cal.
1	$[Pd_2L1(H_2O)_2]$	110 – 220	5.83	6.20	370 - 860	40.74	41.20
2	$[Pd_2L3(H_2O)_2]$	115 - 180	5.87	5.75	550 - 810	38.92	39.15
3	$[Pt_2L1(H_2O)_2]$	110 - 185	4.88	4.67	495 - 800	55.05	54.79
4	$[Pt_2L3(H_2O)_2]$	120 - 160	4.72	4.48	530 - 790	53.08	52.59

Infrared Spectra: The IR spectra of the complexes are recorded in KBr pellets and CsI plates in the far-IR region. In all the spectra, there is a broad absorption in the range of 3800-2800 cm^{-1} that may be assigned to the υ(O-H) of coordinated water molecules [26b,c,28]. The υ(C=N) stretching frequency observed in the ligands at 1602 cm^{-1} (HPIMB) and 1608 cm^{-1} (MPIMB) shifted low frequency side by 25 cm^{-1} indicating the coordination of the azomethine-N atom to the metal ions [29]. Further, the (C-O) stretching frequency in complexes of both the ligands and (C-S) stretching frequency in the case of complexes of MPIMB, have shown low frequency shifts by 20-30 cm^{-1} confirming involvement of phenolic O and thiophenolic S atoms in bonding [26b,c]. In addition to these changes in the IR spectra of the complexes, conspicuous absorptions that confirm the metal-ligand bonding are observed in the far-IR spectra of the complexes. υ(M-O) and υ(M-N) absorptions are observed at 488-514 cm^{-1} and 396-456 cm^{-1} respectively in all the four complexes [29]. In the case of $[Pd_2(MPIMB)(H_2O)_2]$ and $[Pt_2(MPIMB)(H_2O)_2]$, another absorption is found at 416 cm^{-1} and 382 cm^{-1} respectively assignable to υ(M-S) [30].

Electronic spectra: The Pd (II) and Pt(II) complexes of Schiff bases prepared in the present investigation are found to be diamagnetic as expected for these d^8 metal ions and from this a square planar environment around the metal ions may be expected. The electronic spectra of the complexes exhibit two absorptions. These absorptions may be assigned to the transitions ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_{1g}$ respectively of square planar d^8 metal complexes. In the case of HPIMB complex of Pd (II), one more absorption is found at high energy side. 38,167 cm^{-1}, which is ascribed to the charge transfer transition. The electronic spectra of the Pd (II) and Pt(II) complexes are similar to the spectra of the complexes reported in literature [29,31].

^{1}H NMR spectra: The ^{1}H NMR spectra of the diamagnetic complexes are recorded in DMSO-d_6. The signals of the protons in the vicinity of coordinate covalent bond to the metal ions have shown a marked up-field shift confirming the coordination of the ligands [29,30b, 32]. The azomethine-H signal shifted from 8.38 (HPIMB) and 8.71 (MPIMB) to 8.10-8.32 ppm in Pd(II) and Pt(II) complexes indicating that the azomethine-N atom is coordinated to the metal ions. Further, the acidic protons' (-OH, -COOH and -SH) signals have disappeared in the NMR spectra of the complexes confirming the de-protonation followed by coordination of O and S atoms to the metal ions. All the complexes show a new signal between 3.3 and 3.8 ppm, which may be ascribed to the coordinated water molecules [32,33].

The analytical and spectral data confirm the formation of the complexes and also gives an idea about the plausible geometry around the metal ions in the complexes. However, our attempts to obtain crystals suitable for single crystal X-ray structure determination were not successful. Based on the analytical and spectral data and interpretation as presented in the discussion, the tentative structures proposed for the complexes are shown in figure 1.

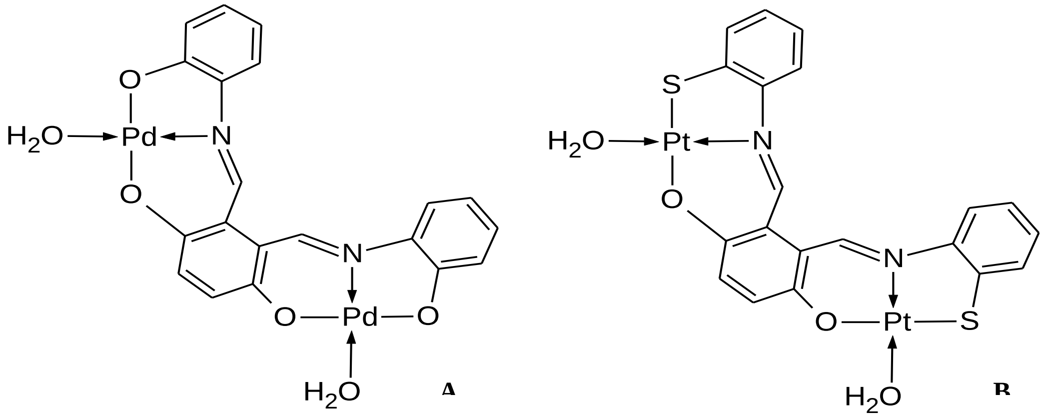


Fig.1. Tentative structures of complexes; (A) [$Pd_2(HPIMB)(H_2O)_2$], (B) [$Pt_2(MPIMB)(H_2O)_2$]

Catalytic activity towards the activation of C-H bond: In view of the application of Pd complexes in C-H bond activation with varying degree of success [7-9,21f,34] and existence of great potential for improving the reaction conditions, yields, stereo and regioselectivity and atom efficiency, the complexes prepared are tested for their catalytic activity. The catalytic reactions described here are within the scope of our current interest in developing catalytic reactions and are akin to the Green Chemistry principles [35]. The experimental conditions used are environmentally benign and atom economical. The oxygen added to the substrate molecules is derived from water molecules and the amount of catalyst used is in millimole scale. A detailed catalytic study towards the activation of C-H bond and oxygenation using the Pd(II) and Pt(II) complexes was carried out under visible light and water as source of oxygen by carrying out runs to optimize reaction conditions. The table 2 gives the data of the reactions carried out. Pd(II) complexes were more effective than Pt(II) complexes. Further, in view of the lower yields of the Pt(II) complexes and the cost of Pt compounds, it is thought of exploring the catalytic properties Pd(II) complexes than Pt(II) complexes.

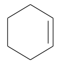
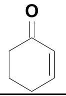
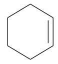
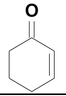
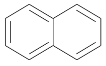
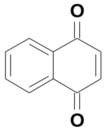
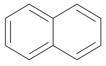
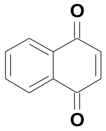
The experiments to optimize the conditions for the catalytic reactions were first carried out till there is no change in the TLC plates developed with the reaction mixture drawn at selected intervals of time. The subsequent reactions with different substrates were carried out till completion, and then the TLC was assayed. In the reactions carried out on oxygenation of cyclohexene and naphthalene using Pd(II) and Pt(II) catalysts, the Pt(II) catalyzed reactions took more than an hour time than the Pd(II) catalyzed reactions and the yields were also less by approximately 30%. To the best of our knowledge, there is no comparative evaluation of the catalytic activity of Pt(II) and Pd(II) complexes in C-H bond activation reactions, though several reports appeared on the catalytic activity of Pd(II) and Pt(II) complexes separately. The reason for this difference may be ascribed to the fact that +4 state for Pt is more stable than for Pd. It is well established that in reactions of C-H bond activation, the oxidation state of metal in the oxidative addition step increases from +2 to +4. The support for this comes from the point that Ni(II) complexes generally do not catalyze C-H bond activation, as the +4 state is not accessible. Since, the Pd(IV) state is less stable it facilitates the next step more easily on thermodynamic and kinetic considerations compared to Pt(II) complexes. Further, Pt(II) complexes are reported to exhibit phosphorescence, and thus absorb a good part of light used in the photocatalytic reactions [36]. The Pt(II) complexes are found to absorb 30 to 40% of visible light making less intense radiation available for the photochemical reactions as compared to Pd(II) complexes. The observations in the present investigations *i.e.*, slow reaction rates and lower yields in the case of Pt(II) complexes support the same.

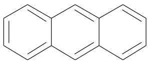
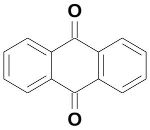
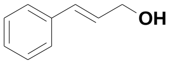
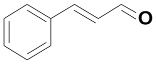
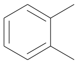
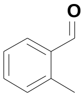
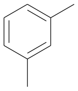
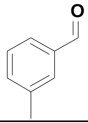
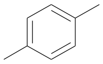
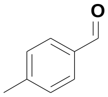
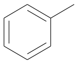
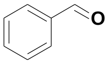
Oxygenation reactions of the substrates, cyclohexene, naphthalene, anthracene, 1,2-xylene, 1,3-xylene, 1,4-xylene and oxidation of 3-phenylprop-1-en-1-ol are carried out using Pd(II) complexes of HPIMB and MPIMB. The reactions took 1.5 h to 5.5 h with the yields ranging between 54 and 96% indicating that the catalytic activity of the Pd(II) Schiff base complexes reported here is comparable or better than that of the catalysts reported earlier [7,21f,31,32,34].

An attempt was made to study the effect of the catalyst concentration in the oxygenation of cyclohexene by changing the amount of catalyst, [Pd_2(HPIMB)(H_2O)$_2$], from 0.1 mmol to 0.025, 0.05, 0.2, 0.4 and 0.6 mmols under the similar experimental conditions and time. In a series of 10 (5 x 2) experiments carried out, an increase by only 2% (96-98%) was observed in two experiments with 0.6 mmol. While in the case of catalytic reactions by using 0.025 and 0.05 mmol of the catalyst, the product yield was found to be less than 50%. These results indicate that there is no effect of the concentration of the catalyst beyond the optimum amount, 0.1 mmol.

We have also carried out the cyclohexene oxygenation reactions in other solvents like, DMSO, DMF and toluene in addition to acetonitrile. In all these solvents, the reactions proceeded slowly resulting in lower yields compared to that in solvent acetonitrile. Thus acetonitrile is found to be better solvent in these catalytic reactions. The properties that make it a good solvent are obviously that acetonitrile is a better organic-aqueous tunable solvent for homogenously catalyzed reactions [35] and higher solubility of oxygen. Oxygen has a better solubility in acetonitrile (8.1 mM) than in most other normally used organic solvents [37], such as DMF (4.5 mM) and DMSO (2.1 mM). Oxygen plays a crucial role in this type of reactions under visible light [38] as shown in Scheme 2.

Table 2. The Allylic C-H bond activation reactions catalyzed by Pd(II) and Pt(II) Schiff base complexes

Sl. No.	Substrate	Product	Complex	Time (h)	Yield (%)
1			[Pt_2(HPIMB)(H_2O)$_2$] [Pt_2(MPIMB)(H_2O)$_2$]	3.00 2.45	52 57
2			[Pd_2(HPIMB)(H_2O)$_2$] [Pd_2(MPIMB)(H_2O)$_2$]	1.45 1.30	81 96
3			[Pt_2(HPIMB)(H_2O)$_2$] [Pt_2(MPIMB)(H_2O)$_2$]	2.45 2.35	45 59
4			[Pd_2(HPIMB)(H_2O)$_2$] [Pd_2(MPIMB)(H_2O)$_2$]	2.00 2.00	74 88

5			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	2.45 2.45	72 85
6			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	2.30 2.15	80 95
7			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	5.30 5.00	54 78
8			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	5.30 5.30	58 80
9			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	5.30 5.30	61 83
10			$[Pd_2(HPIMB)(H_2O)_2]$ $[Pd_2(MPIMB)(H_2O)_2]$	4.00 3.30	68 90

The oxygenation/oxidation reactions on hydrocarbons studied in the present investigations are carried out in presence of Pd(II) and Pt(II) catalyst using visible light in aqueous acetonitrile. The generation of $HO^{\bullet}$ is found to be an important step. The formation of $HO^{\bullet}$ radicals in the reactions is shown in Scheme 2. The incident light energy is larger or equivalent to the band gap energy of the Pd(II)/Pt(II) Schiff base complexes. This facilitates the transfer of electrons from the valence band to the conduction band, and creates a hole in the valence band. The excited electrons and the holes move onto the complex molecules and interact with the oxygen atoms and water molecules producing $HO^{\bullet}$ and $O_2^{\bullet-}$ radicals respectively. Further, the formation of $HO^{\bullet}$ continues as H^+ ions react quickly with $O_2^{\bullet-}$ radicals resulting in $HO_2^{\bullet}$ radicals that react with one another forming H_2O_2, the oxidizing agent *in situ*. The H_2O_2 molecules decompose forming $HO^{\bullet}$ radicals that react with the allylic carbon atoms resulting in oxygenation reaction ultimately giving rise to ketones or aldehydes. Although the authors do not speculate on the mechanism, it is believed that the reaction likely proceeds via a high oxidation state Pd (IV) intermediate analogous to earlier reports [19b].

$$\text{Catalyst} + h\nu \longrightarrow e_{cb}^{-} + h_{vb}^{+}$$

$$H_2O + h_{vb}^{+} \longrightarrow HO^{\bullet} + H^{+}$$

$$O_2 + e_{cb}^{-} \longrightarrow O_2^{\bullet-}$$

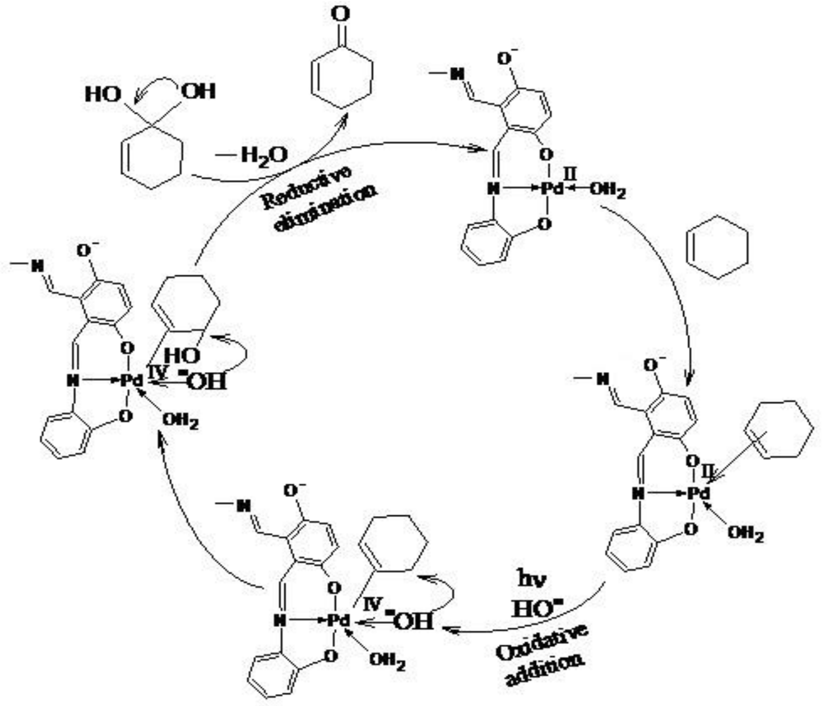
$$O_2^{\bullet-} + H^{+} \longrightarrow HO_2^{\bullet}$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \longrightarrow 2HO^{\bullet}$$

$$\text{Substrate} + HO^{\bullet} \longrightarrow \text{Oxygenated product}$$

Scheme 2. Scheme showing the involvement of O_2 and generation of $HO^{\bullet}$ in the catalytic process (e_{cb}^{-} is electron in the conduction band and h_{vb}^{+} is hole in the valence band)



Scheme 3. Proposed mechanism for the oxygenation of allylic carbon by H_2O in presence of catalyst and hv

The results and observations in the present investigation are similar to those reported earlier in the case of different catalytic reactions using transition metal Schiff base complexes [21f, 39].

APPLICATIONS

The prepared complexes are found to be exhibiting a good catalytic activity with slightly more than 50% yield by Pt (II) complexes and 60-95% yield by the Pd(II) complexes. The greater stability of Pt (IV) intermediate complex formed in the reaction cycle is predicted for the slower reactions in the case of platinum complexes. The reactions were carried out under visible light in acetone-water mixture, which is proved to be a better solvent system for these reactions in view of the greater solubility of O_2 that is involved in the generation of $HO^\bullet$ free radicals that attack the allylic C atom of the substrates in presence of metal complexes. As the reactions are carried out in 1:1 water-acetonitrile mixture in presence of visible light without using any chemical oxidant, the reaction protocol falls under Green Chemistry and thus proved to have better prospects for further investigations.

CONCLUSIONS

Two new Schiff base ligands were prepared by condensation of 2-aminophenol and 2-aminothiophenol with 3,6-dihydroxybenzene-1,2-dicarbaldhyde. The ligands, 2,3-bis((E)-((2-hydroxyphenyl)imino) methyl) benzene-1,4-diol (HPIMB) and 2,3-bis((E)-((2-mercaptophenyl)-imino)methyl)benzene-1,4-diol (MPIMB) were characterized using different spectral measurements and analyses. These two ligands readily interact with $PdCl_2$ and $PtCl_2$ resulting in stable complexes. The complexes of formula, $[ML(H_2O)_2]$, are found to be diamagnetic and are coordinated through azomethine N and phenolic O and S (MPIMB) atoms of the ligands and square planar geometry has been assigned based on the magnetic and electronic spectra. The complexes are tested for their catalytic activity in C-H bond activation followed by oxygenation of allylic

C atoms. The complexes are found to be exhibiting a good catalytic activity with slightly more than 50% yield by Pt (II) complexes and 60-95% yield by the Pd(II) complexes. The greater stability of Pt (IV) intermediate complex formed in the reaction cycle is predicted for the slower reactions in the case of platinum complexes. The reactions were carried out under visible light in acetone-water mixture, which is proved to be a better solvent system for these reactions in view of the greater solubility of O_2 that is involved in the generation of $HO^{\bullet}$ free radicals that attack the allylic C atom of the substrates in presence of metal complexes. As the reactions are carried out in 1:1 water-acetonitrile mixture in presence of visible light without using any chemical oxidant, the reaction protocol falls under Green Chemistry and thus proved to have better prospects for further investigations. We are continuing the work to improve the reaction conditions, making them more environmental friendly by avoiding organic solvents on one hand and developing a few more complexes with new ligands that exhibit better properties as catalysts for C-H bond activation for oxidation and alkylation reactions and also to characterize and propose the structure of the intermediate complexes in the catalytic cycle.

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