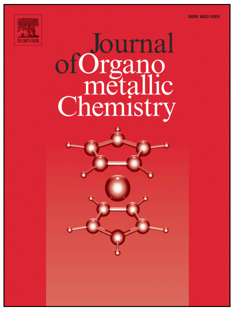

Synthesis of a novel six membered CNS palladacycle; TD-DFT study and catalytic activity towards microwave-assisted selective oxidation of terminal olefin to aldehyde

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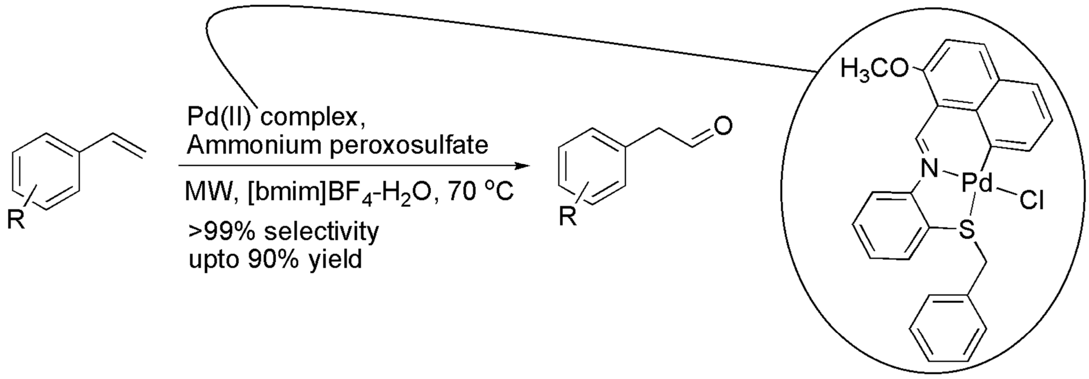
Pd(II) complex,
Ammonium peroxosulfate
MW, [bmim]BF4-H2O, 70 °C
>99% selectivity
upto 90% yield
R
R
O
H3CO
N
Pd
Cl
S

Synthesis of a novel six membered CNS palladacycle; TD-DFT study and catalytic activity towards microwave-assisted selective oxidation of terminal olefin to aldehyde

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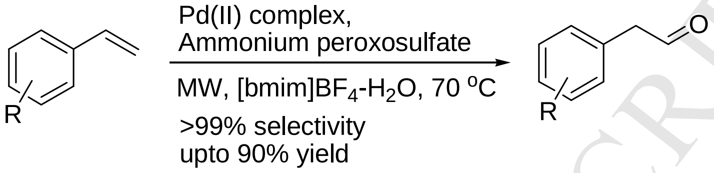
Abstract: This article documented synthesis of a Schiff base, E-2-(benzylthio)-N-{(2-methoxynaphthalene-1-yl)methylene}benzenamine (HL) by the treatment of 2-meyhoxynaphthaldehyde and 2-(benzylthio)aniline. Reaction of this synthesized Schiff base with Na_2PdCl_4 has been investigated, which gave a novel six membered Pd(II) complex (PdLCl) through C,N,S-donor atom of Schiff base. These two newly synthesized compounds were characterized by ^{1}H-NMR, FTIR and UV-Vis spectra and structure of the Pd(II) complex was confirmed by X-ray crystallography. The catalyst (PdLCl) displayed considerable reactivity (up to 99% selectivity and 90% yield) in the selective oxidation of terminal C=C bond in aryl substituted olefin to aldehyde. The method shows good functional groups compatibility, no ketone byproducts and is operationally simple. Time dependent density functional study (TD-DFT) of representative cyclopalladated complex has been undertaken. The simulated optical spectrum of the complex is in good agreement with the experimentally observed spectrum.

1. Introduction

The Schiff base derived C,N,S-palladacycles are one of the interesting classes of palladacycles due to their relevance as precatalyst in C-C and C-heteroatom bond forming reactions [1]. Besides, palladacycles are also utile in optical resolution [2] and design of advanced metallomesogenes [3]. The vast majority of these complexes possess anionic four-electron (bidentate) or six-electron (tridentate) donor ligands, with five-membered nitrogen-containing rings being the most common due to their thermodynamic stability [4]. The studies on cyclopalladation reported till date, reveals that majority of palladacyclic species are five-membered [5]. A scant literature is accessible on the synthetic details of C,N,S-palladacycles that possess a six membered ring.

The Pd(II)/Cu(I) lead oxidation of alkenes to ketone or aldehyde is a continuation of the traditional Wacker method, also known as Tsuji-Wacker method [6]. The Pd(II) catalyst have been substantially used till date on oxidation of alkenes and usually they give ketone as the prime product [7]. Formation of aldehyde is overturned by ketone, yet in some cases aldehydes are the major products [8]. Nonetheless, higher selectivity and yield always have been a matter of concern. Original Wacker method entails a transition metal catalyzed oxidation of ethylene to acetaldehyde in a solvent system of H_2O cum HCl. However, aromatic and high carbon number alkenes show poor solubility in water and in presence of HCl, carry out many side reactions [9]. Thus, in current scenario, microwave-assisted organic synthesis (MAOS) has received a considerable recognition with its ability to lessen possible side reactions and improves the yield of its outcome. It also minimizes chemical reaction time from hours to minutes. MAOS are more effective in ionic liquids [10], as ionic liquids interact very efficiently in microwaves through ionic conduction mechanism [11]. Moreover, ionic liquids are excellent substitute to various possible “green” solvents in catalytic and other possible reactions.

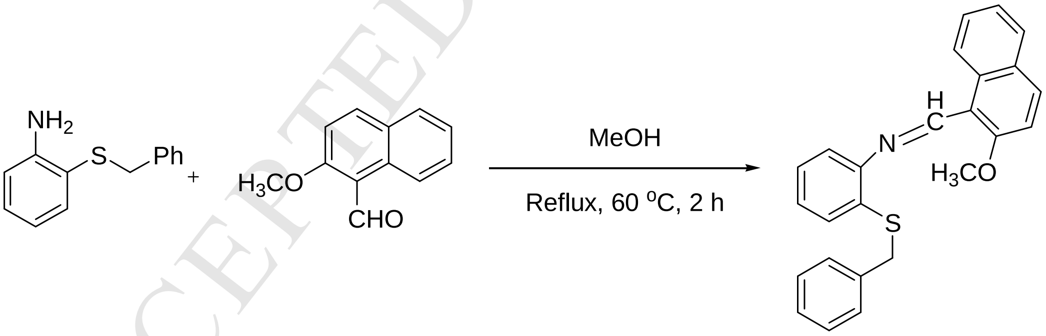
In this study, details on synthesis of a Schiff base (HL) from 2-methoxynaphthaldehyde and 2-(benzylthio)aniline and its cyclopalladated complex (PdLCl) from Pd(II) ions has been reported. The overall study reveals formation of a less common six membered cyclopalladated complex. This complex was used as a catalyst in microwave-promoted selective oxidation of substituted styrenes to aldehydes. The reactions were performed in [bmim]BF_4-H_2O medium and ammonium peroxosulfate was used as an oxidant, which avoids the use of Cu(I). The reaction offers excellent yield, and useful in terms of selectivity towards aldehyde, up to 99% **(Scheme 1)**.



Scheme 1: Oxidation of terminal alkene

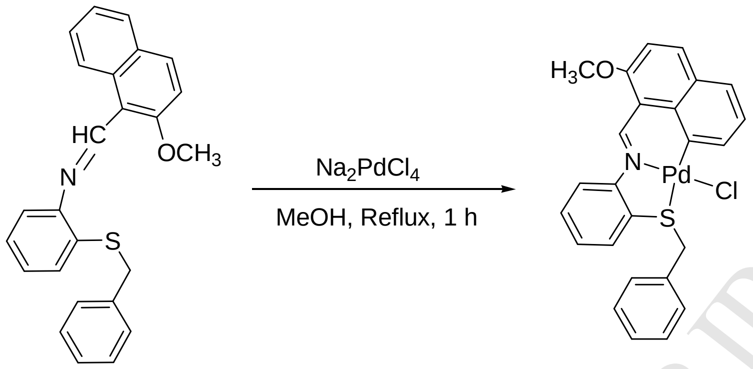
2. Results and Discussion

The synthesis of ligand, HL involves the condensation of 2-(Benzylthio)aniline and 2-meyhoxynaphthaldehyde in absolute methanol as reported in the **Scheme 2**. The ligand, HL is a yellow solid, stable in air and soluble in most organic solvents.



Scheme 2. Synthesis of ligand, HL

The reported Pd(II) complex was achieved from the synthesized ligand by reaction between Na_2PdCl_4 and HL in a 1:1 molar ratio (**Scheme 3**), obtained as an orange crystal. Both these synthesized compounds were characterized by UV-Vis, FT-IR, ^{1}H-NMR, and elemental analysis. Molecular structure of the Pd(II) complex was established by the single crystal X-ray diffraction technique.



Scheme 3. Synthesis of Pd(II) complex, PdLCl

The FT-IR spectrum for this ligand shows a peak at a frequency of 1618 cm^{-1} and it confirms the formation of an azomethine group (>C=N-). The strong peaks at 1462 cm^{-1} and 749 cm^{-1} are attributed to C=C and C-S respectively. The spectrum of the complex however, exhibits a band at 1601 cm^{-1} for ʋ(C=N) and shifted by 17 cm^{-1} compared to corresponding band of the ligand, indicating the co-ordination via nitrogen atom of azomethine moiety. Moreover, C-S band is also shifted from 741 cm^{-1} compared to the ligand and gives evidence of its coordination via sulfur atoms [12].

The ^{1}H-NMR spectra of the ligand and complex discloses the formation of Pd-N, Pd-S and Pd-C bonds. The ligand exhibits a singlet peak at δ 9.24 ppm for the imine proton (N=CH). The aromatic (Ar–H) protons appear at δ 7.2–7.9 ppm, the benzylic protons (PhCH$_2$) appear as a singlet at δ 4.19 ppm and methoxy protons (O-CH$_3$) give a singlet at δ 4.0 ppm. However, the ^{1}H-NMR spectra of Pd(II) complex shows an up field shift of the singlet peak for the imine proton. The shift occurs due to the N-coordination of palladium (Pd-N) and appears at δ 8.6 ppm. Besides, one doublet peak near δ 7.6 ppm, correspond to aromatic (Ar–H) protons is missing and a slightly downfield shift of benzylic protons (PhCH$_2$) at δ 4.2 ppm reveals the coordination of palladium through C (Pd-C) and S (Pd-S) [13].

The electronic spectra of the ligand and the complex were investigated in acetonitrile solution at 10^{-5} M concentration. The spectral observation of the ligand, HL shows bands at 254, 320, 345, and 376 nm. We ascribe these bands as the π–π* transitions in phenyl ring and n–π* transitions of the imine moiety. The Pd(II) complex shows peaks at 230, 280, 321, 367, 451, and 473 nm. For the complex, the bands that appear in the region 230–376 nm are attributed to a π–π* and n–π* transition within the ligand, and the other bands appeared in 451-473 nm are due to the fusion of LMCT and ILCT transition [14].

2.1. X-ray crystallography

The crystal of Pd(II) complex was collected by using diffusion recrystallization technique through slow diffusion of hexane into DCM solution. Prospective view of the molecular structure of the complex is shown in **Figure 1.**

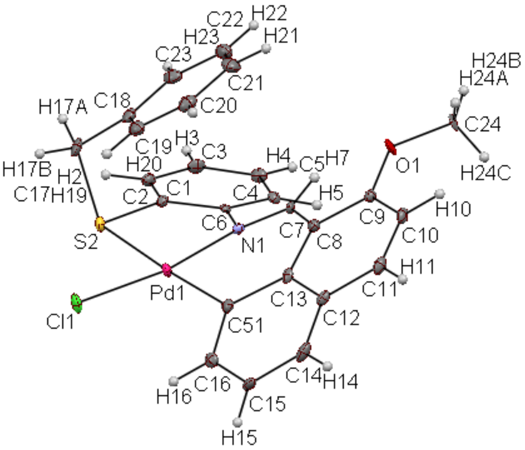


Figure 1. Molecular structure of the Pd(II) complex, shown with 30% probability ellipsoids

The Pd(II) complex crystallizes in the orthorhombic space group P2(1)2(1)2(1) and it contains one molecule in the asymmetric unit. The crystallographic evidence substantiate the spectroscopic results. It reveals that, the compound is consisted of a Pd(II) metal ion arranged in a distorted square-planar environment. The metal atom is surrounded by N, S, and C atom from the Schiff base ligand (HL) and one -Cl atom. Compared to our earlier reported Pd(II) complex [12], the 2-position of the naphthalene ring is blocked by one methoxy group, leading to the coordination of Pd metal center via C-H activation at 8th position. As a result, the complex formed is a six member palladacycle, which is rare in case of N containing ligand. In general, the metallated CY-type palladacycles (anionic four-electron donor) are preferably stable five member rings. Reports on other six-member palladacycles from the Schiff bases are very few, and in most cases, the metallated carbon is sp^3, in a CH_2 group. Only two previous cases verify the presence of a metallated aromatic (sp^2) carbon atom, included in a polyaromatic systems, such as perylene [15] as well as, an endocyclic six-membered cyclopalladated imine derived from anthracene [16]. The formation of a six member ring via tail of the ligand is usual where the ligand has electronegative atoms like phosphorus, oxygen etc. But, formation of a six membered ring by C-H activation at peri position of a naphthalene ring including C=N within the ring is not explored. Presence of a softer sulfur in the co-ordination sphere may strengthen the binding of the ligand to the palladium center, resulting in the formation of a stable six membered ring. All important bond lengths and bond angles of the complex are given in **Table 1**. The Pd—S, Pd—N, and Pd—C bond lengths are 2.013(4), 2.3893(13), and 2.3444(12). The bite angles C(51)—Pd(1)—N(1), C(51)—Pd(1)—Cl(1), N(1)—Pd(1)—S(2) and Cl(1)—Pd(1)—S(2) are 90.89(19), 94.36(15), 85.24(11) and 89.49(5) respectively. The Pd, N, S, and C (coordinated) atoms lie in same plane. Again, angles for N(1)—Pd(1)—Cl(1) and C(51)—Pd(1)—S(2) are 171.51(12) and 176.5(13) confirms that geometry is slightly distorted square planner. It should, however, be noted that the benzyl moiety of the ligand lies perpendicular to the plane.

Table 1. Selected bond lengths (Å) and bond angles (˚) for Pd(II) complex, PdLCl

Bond lengths	Expt	Calc	Bond angles	Expt	Calc
Pd(1)—N(1)	2.013(4)	2.05	C(51)—Pd(1)—N(1)	90.89(19)	92.18

Pd(1)—S(2)	2.3893(13)	2.47	C(51)—Pd(1)—Cl(1)	94.36(15)	95.17
Pd(1)—Cl(1)	2.3444(12)	2.38	N(1)—Pd(1)—Cl(1)	171.51(12)	169.01
Pd(1)—C(51)	2.000(5)	2.01	C(51)—Pd(1)—S(2)	176.13(16)	175.49
S(2)—C(1)	1.766(5)	1.79	N(1)—Pd(1)—S(2)	85.24(11)	84.00
S(2)—C(17)	1.841(5)	1.87	Cl(1)—Pd(1)—S(2)	89.49(5)	88.94
O(1)—C(9)	1.357(6)	1.36	C(1)—S(2)—C(17)	101.0(2)	104.38
O(1)—C(24)	1.444(6)	1.42	C(17)—S(2)—Pd(1)	104.40(18)	107.17
N(1)—C(7)	1.302(6)	1.30			
N(1)—C(6)	1.439(6)	1.42			
C(6)—C(1)	1.399(7)	1.41			
C(7)—C(8)	1.426(7)	1.43			
C(13)—C(8)	1.432(7)	1.44			
C(13)—C(51)	1.447(7)	1.42			

2.2. Computational Study

The molecular geometry of the palladium complex is fully optimized in the gas phase employing DFT based B3LYP method along with the 6-31G** basis set for lighter atoms (H, C, N, O, S and Cl) and LanL2DZ for heavier atom (i.e. Pd). The calculated bond distances and bond angles along with the corresponding experimental data are listed in **Table 1** and the optimized structure of the complex is shown in **Figure 2.** The theoretically calculated structural parameters of the Pd(II) complex are very similar to those found in crystal, indicating a substantial stability of the complex even inside the crystal lattice. The TD-DFT method is used to calculate the electronic absorption spectra of the complex under the same basis set. The charge distribution analysis is carried out by Natural Bond Orbital, (NBO) analysis.

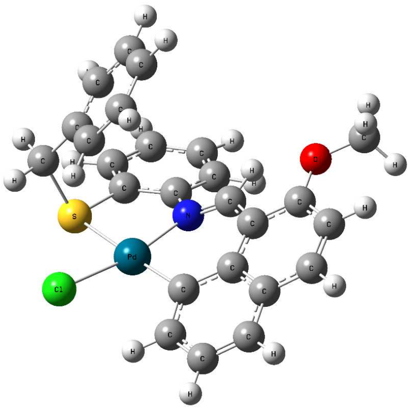


Figure 2. Optimized structure of the Pd(II) complex, PdLCl

2.3. Charge distribution

The charge distribution analysis is an important tool to elucidate the pattern of electron delocalization from ligand to complex. In the ligand HL, the charges on N and S are obtained as -0.454 e and 0.241 e respectively. However, on complex formation, the negative charge on N reduces to -0.449 e and the positive charge on S increases to 0.429 e. The charge on Pd is found to be 0.212 e which is much lower than its formal charge of +2. All these results confirm that, the ligand transfers its negative charge to the Pd metal on complex formation. In free Pd(II) state, the population of $4d_{xy}$, $4d_{xz}$, $4d_{yz}$, $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals are 1.999, 1.999, 1.999, 1.4986 and 0.499 e respectively. But on complex formation, the population on $4d_{xy}$, $4d_{xz}$, $4d_{yz}$, $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals changes and attains a value of 1.976, 1.955, 1.906, 1.268 and 1.941 e respectively. It is clearly visible that the population is slightly reduced in $4d_{x^2-y^2}$ orbital and it has increased in $4d_{z^2}$ orbital upon complex formation. The population of the remaining three orbitals are less affected on interacting with the metal (Pd).

2.4. Absorption spectra and Frontier Molecular Orbital

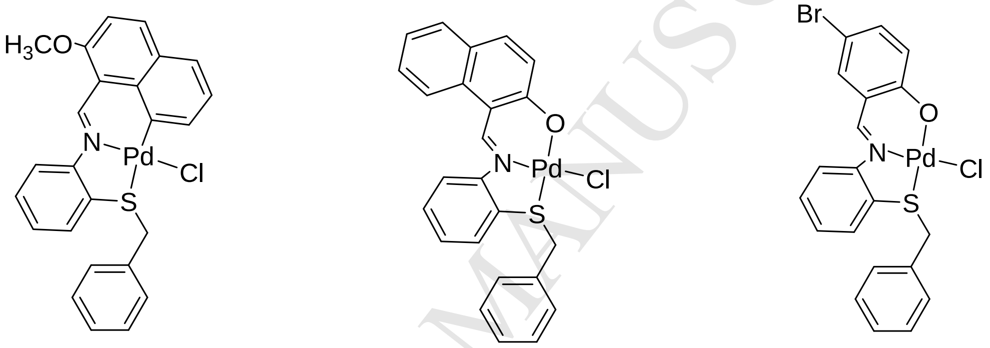
The electronic absorption spectrum was calculated using the TD-DFT method in acetonitrile solvent employing the PCM model as implemented in the Gaussian 09W programs. The calculated and the experimental absorption data, HOMO-LUMO energy gaps, and the character of electronic transitions are listed in **Table 2**. The HOMO→LUMO transition for the complex is found to possess ILCT character. Two MLCT transitions at around 412 and 374 nm has been observed which corresponds to dπ(Pd)→π*(L) transfer. A few LLCT transitions for PdLCl complex at around 360 and 358 nm can be assigned to the Pπ(Cl)→π*(L) transition. This is however in good agreement with the experimental data. The high energy absorptions of the complex that occur in a range between 228-279 nm correspond to the ILCT character, i.e. π→π* transitions. The UV-Vis spectra based on TD-DFT calculations is seen to be in good agreement with the experimental graph (Figure 14 in SI**).**

Table 2. Electronic transitions calculated by the TD-DFT/B3LYP method and experimental absorption bands of Pd(II) complex, PdLCl

The most important orbital excitations	λ(nm)	E (eV)	f	Character	Experimental λ (nm)
HOMO→LUMO	461.11	3.02	0.1912	Ligand→Ligand(ILCT)	473,451
HOMO-1→LUMO	412.45	3.13	0.0112	Pd/Cl→Ligand(MLCT/LLCT)	
HOMO-1→LUMO+1	374.03	4.55	0.0191	Pd/Cl→Ligand(MLCT/LLCT)	
HOMO-3→LUMO	360.35	3.60	0.0276	Cl→Ligand (LLCT)	367
HOMO-2→LUMO	358.31	3.60	0.0819	Cl→Ligand (LLCT)	
HOMO-6→LUMO	320.86	4.37	0.0265	Ligand→Ligand(ILCT)	321
HOMO→LUMO+2	315.98	4.33	0.0258	Ligand→Ligand(ILCT)	
HOMO-10→LUMO	284.85	4.94	0.0017	Pd/Ligand→Ligand(MLCT/ILCT)	280
HOMO-1→LUMO+2	283.26	4.73	0.0036	Pd/Lligand→Ligand(MLCT/ILCT)	
HOMO→LUMO+3	279.37	4.73	0.0203	Ligand→Ligand(ILCT)	
HOMO-14→LUMO	230.31	5.72	0.0132	Ligand→Ligand(ILCT)	230
HOMO-5→LUMO+3	228.04	5.83	0.0930	Ligand→Ligand(ILCT)	

The HOMO-LUMO energy gap is known to be a good measure for the chemical reactivity and kinetic stability of a molecule. Molecule with a lower HOMO-LUMO gap can be excited easily and thereby enhances the reactivity of the molecule. The higher energy gap leads to kinetic stability but less reactivity. The present work reports the comparison of our synthesized complex PdLCl with the earlier reported Pd complexes, **2** and **3** (**Figure 3**). Thus, we would like to compare its kinetic stability and chemical reactivity in terms of HOMO-LUMO energy gap and to further compare their composition of molecular orbitals. The structure of complex **2** and **3** is almost similar; hence we compare PdLCl with the complex **2**. The HOMO-LUMO energy gap for PdLCl and complex **2** are found to be 3.02 and 3.23 eV respectively

(**Figure 4**). It is evident that the energy gap is slightly less for PdLCl complex indicating its enhanced reactivity over the complex **2**. From the % contribution of molecular orbital analysis as shown in Table 1 of Supplementary Information, it is clearly visible that for complex **2** and PdLCl, most percentage of HOMO as well as LUMO is located on the ligand itself. But for HOMO-1 level in PdLCl, the maximum percentage (about 41%) of molecular orbital is located on the metal, whereas similar pattern has not been encountered for the complex **2**.



1 2 3

Figure 3. Structure of three Pd catalyst, **1** (PdLCl), **2** (Ref.12) and **3** (Ref.17)

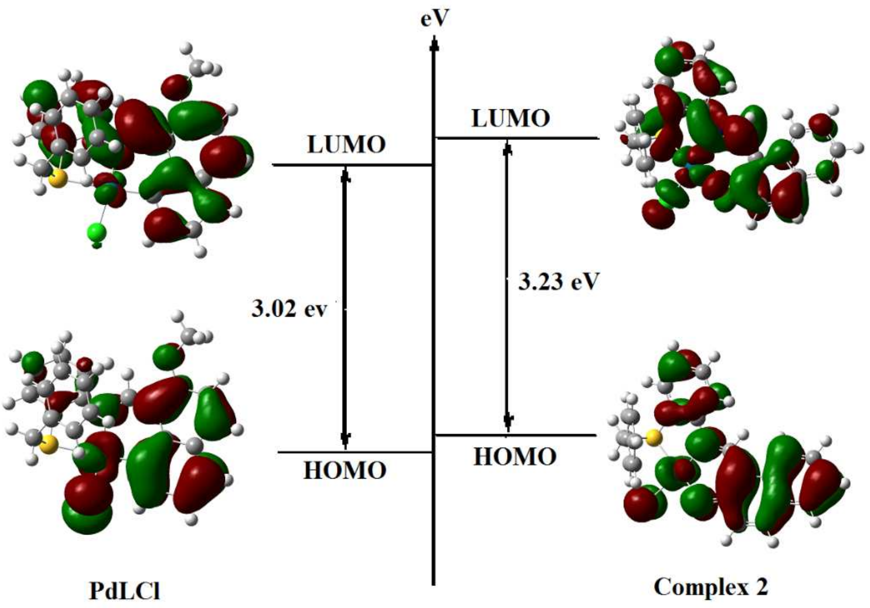
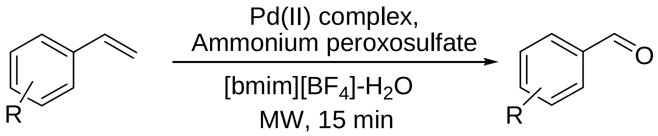


Figure 4. HOMO-LUMO energy gap comparison of PdLCl and complex **2**

2.5. Catalytic Activity study

The PdLCl complex mediated transformation of terminal olefin to aldehyde is performed on various substituted styrene in microwave (**Table 3).** The reaction condition is standardized by performing a series of experiments with various solvents, oxidant and catalysts. The optimized reaction conditions and the results for oxidation of styrene are shown in **Table 4**. The **Table 5** however monitors the optimum microwave parameter for the reaction.

Table 3. Oxidation of terminal olefin to aldehyde catalyzed by Pd(II) complex in [bmim]BF_4-H_2O-$(NH4)_2S_2O_8$ system



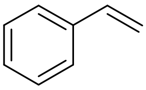
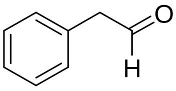
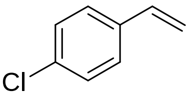
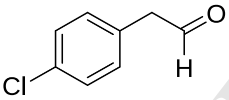
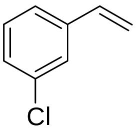
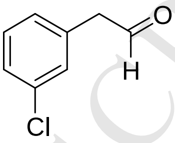
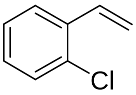
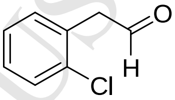
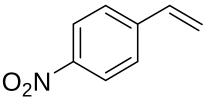
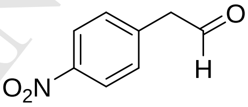
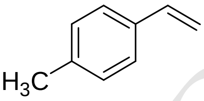
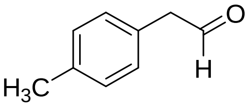
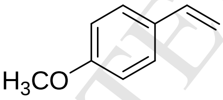
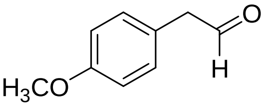
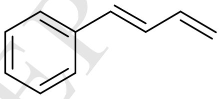
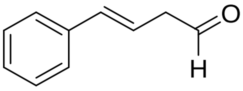
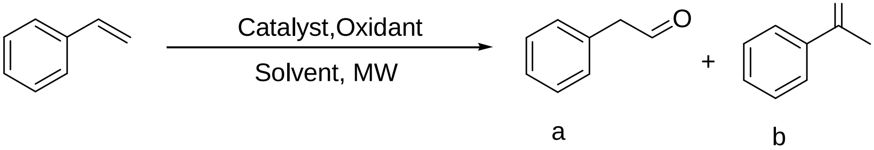
Entry	Substrate	Product	Yield
1			90
2			86
3			86
4			82
5			82
6			91
7			85
8			86

Table 4. Optimized reaction condition for conversion of styrene to 2-phenyl acetaldehyde



Sl. No.	Catalyst	Oxidant	Solvent	Yield (%) a	Yield (%) b
1	PdLCl	$(NH_4)_2S_2O_8$	DMF	35	10
2	PdLCl	$(NH_4)_2S_2O_8$	CH_3CN	38	25
3	PdLCl	$(NH_4)_2S_2O_8$	NMP	48	40
4	PdLCl	$(NH_4)_2S_2O_8$	DMSO	55	32
5	**PdLCl**	**$(NH_4)_2S_2O_8$**	**[bmim]BF_4-H_2O**	**90**	**Trace**
6	2	$(NH_4)_2S_2O_8$	[bmim]BF_4-H_2O	83	10
7	3	$(NH_4)_2S_2O_8$	[bmim]BF_4-H_2O	81	12`
8	PdLCl	$(NH_4)_2S_2O_8$	[bmim]BF_4	70	25
9	PdLCl	$(NH_4)_2S_2O_8$	[bmim]Br	58	32
10	None	$(NH_4)_2S_2O_8$	[bmim]BF_4-H_2O	-	-
11	$PdCl_2$	$(NH_4)_2S_2O_8$	[bmim]BF_4-H_2O	50	30
12	Pd complex	Benzoquinone	[bmim]BF_4-H_2O	40	56
13	Pd complex	H_2O_2	[bmim]BF_4-H_2O	35	31

[a,b]Isolated yield. Reaction condition: 1 mmol styrene, 0.5 mol% Pd(II) complex, 10 ml [bmim]BF_4-H_2O, 1.5 mmol ammonium persulfate, 80 W,70°C, 15 min. The significance of bold values shows the optimized reaction conditions for styrene.

Table 5. Optimized microwave parameter for conversion of styrene to 2-phenyl acetaldehyde

Entry	MW (W)	T (℃)	Time (min)	Yield (%)[b]
1	80	70	5	45
2	80	70	10	67
3	**80**	**70**	**15**	**90**
4	80	100	15	82
5	80	50	15	75
6	100	70	15	89
7	-	70	24 h	73[c]

[b]Isolated yield. [c]Conventional heating (open vessel reflux condition).

The reported reaction was performed depending on higher loss factors [11] for some common organic solvents that follows the trend [bmim]BF_4> DMSO> NMP> DMF> CH_3CN. The solvent screening showed that, DMF and acetonitrile leads to an incomplete conversion of olefin and the outcome obtained is a mixture of aldehyde and ketone. When treated in NMP solvent, the styrene showed good conversion but it offers the aldehyde and ketone in almost 1:1 ratio. DMSO however gives approx. 3:2 ratio of aldehyde and ketone. Then we performed the same reaction with ionic liquid, [bmim]BF_4 and we observed that a pure [bmim]BF_4 solvent increases the selectivity towards aldehyde with a minimum amount of ketone. However, increasing the water content in the solvent, at a ratio of 6:1 subsequently led to higher selectivity towards aldehyde formation. The maximum selectivity observed is ~99% when [bmim]BF_4-H_2O ratio is 2:1.

The miscibility of ionic liquid with water is strongly dependent upon the nature of counter anion. [bmim]BF_4 was selected for this study since it has an excellent miscibility with H_2O. The method avoids the use of any acid as an additive contrary to the classical Wacker process. This may be due to the hydrolysis of BF_4^- liberating HF during the reaction, which may act as the acid source [9]. The chemical structure of [bmim]BF_4 is presented in **Figure 5.**

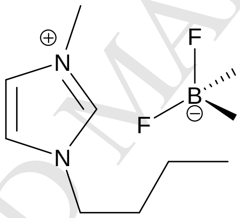


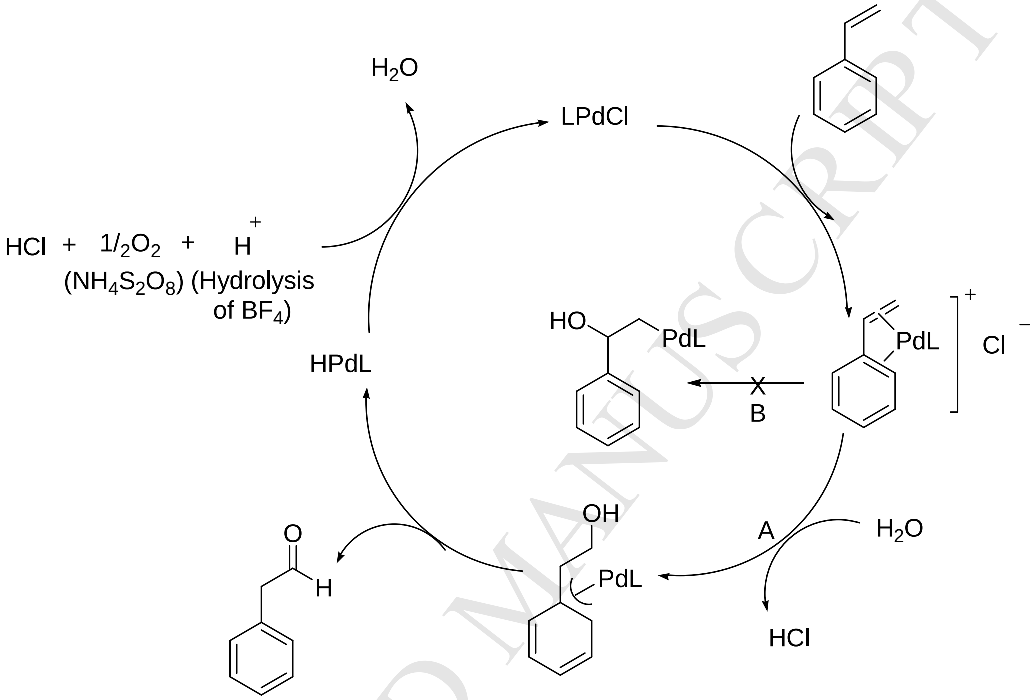
Figure 5. Structure of [bmim]BF_4

The optimization of a suitable oxidant in this reaction shows that, ammonium persulfate in presence of a transition metal is a very good oxygen source. Presence of ammonium persulfate led to avoid the use of Cu(I) necessitate to complete the catalytic cycle. The reaction remained incomplete when performed with H_2O_2. However, benzoquinone showed a very good conversion of styrene although discarded due to equivalent mixture of aldehyde and ketone.

The Pd center has a notable effect on this catalytic conversion as the reaction stops in its absence. The use of the salt, $PdCl_2$ enhances the reaction significantly, accompanying mixture of keto derivatives. However, the Pd metal complex is seemed to be extremely selective. The synthesized Pd complex, PdLCl trigger the progress of the reaction unlike $PdCl_2$. The accumulation of electrons surrounding the Pd-centre from S, N atom of the ligand increases the efficiency of the complex as a catalyst. The high reactivity and selective nature of this complex leads to the significant yield of aldehyde in almost 90%. To understand, whether this selective nature is solely the property of our synthesized complex, PdLCl, or all pd-complexes follow the same behavior, we performed the reaction with our previously reported Pd Complexes, **2** [12] and **3** [17] (**Figure 3**) maintaining others parameters as constant. The observation showed that, other two complexes are also effective towards terminal oxidation, though leads to a significantly lower yield along with ketone as minimum by-product. The anomaly in reactivity of these complexes has been established by FMO, HOMO-LUMO energy gap. One of those structurally variant complexes was taken as a model and computational investigation was compared with our newly reported complex, PdLCl. The lower energy gap of complex PdLCl leads to lower kinetic stability enhancing its reactivity. Moreover, Pd centre of the complex, PdLCl accumulates more electron cloud (41%) in HOMO-1 level compared to the other one (11%) which is another reason of higher reactivity.

Table 3 explains that the reaction is tolerant to a range of substituent from donating to highly withdrawing (-NO_2) group. However, there is a little effect of substituent towards isolated yield, except highly withdrawing -NO_2 substituent lowers the yield substantially. Oxidation of 1-phenyl-1,3-butadiene was also performed to examine the selectivity of the catalyst toward oxidation of terminal double bonds.

The plausible mechanism (**Scheme 4**) involves PdLCl as a catalyst. The η^4 nature of styrene acts as a pseudo-diene to form the η^3-palladium intermediate followed by nucleophilic attack of H_2O [18]. This η^4-interaction between the palladium and substrate apparently contributes to the anti-Markovnikov behavior. The η^3-palladium intermediate offer desired aldehyde and releases HPdL to the solution. The high selectivity towards aldehyde formation is probably due to the favorable path A. The catalytic cycle of Pd is completed in presence of oxygen from ammonium persulfate, H^+ from hydrolysis of BF_4^-, and HCl from the solution.



Scheme 4. Plausible reaction mechanism

Thus, we have seen that our synthesized palladacycle, PdLCl is more selective compared to readily available Pd-complexes. Many synthetic processes accompany limitations of moderate aldehyde selectivity, requirement of hetero polyacid or stoichiometric palladium [18a]. In some cases, they are restricted to activated olefins, that is, olefins containing a chelating group located at an appropriate position, such as a heteroatom or unsaturation, in order to result in the regioselectivity [7c]. The advantage of our method is, it minimizes these limitations under a greener approach which avoids use of any acid. However, use of catalytic amount of Pd (0.5 mol%) limits toxic metal wastes with enhanced regioselectivity towards aldehyde.

3. Conclusions

Here, we have reported a new cyclometalated complex by activating the inert C-H bond, and presented a combined experimental and theoretical study. We have validated the DFT results of Pd complex through crystallographic confirmation of structural calculations. The complex formed is a new six membered palladacycle, having slightly distorted square planar geometry. TD-DFT calculation is used to elaborate the electronic structure and to provide band assignments in UV-Vis spectra of the complex. The Pd(II) complex shows effective catalytic behavior towards selective oxidation of terminal alkenes to aldehyde by a microwave assisted Wacker oxidation method. The reaction is efficient in terms non-hazardous solvent selection, high yield and selective conversion to aldehyde almost up to 99%.

4. Experimental Section

4.1. Experimental Details

4.1.1. Materials

All chemicals were used without further purification. 2-Methoxynaphthaldehyde and Sodium tetrachloropalladate were purchased from Alfa Aesar. 2-(Benzylthio)aniline were prepared by reported method [19]. Solvent used were extra pure grade purchased from Merck India and were dried according to the reported procedure [20].

4.1.2. Methods

The infrared spectra of the ligand and complexes were recorded with FT-IR-3000 Hyperion Microscope (Bruker, Germany). Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument. ^{1}H NMR spectra of the ligand, Pd(II) complex and substituted 2-phenylacetaldehyde were performed on Mercury-400 and JNM-ECS400 spectrometer using $CDCl_3$ as solvent. The electronic spectra of the compounds were carried out with Cary 100 Bio UV-visible spectrometer in acetonitrile solvent.

4.2. Synthesis of Ligand, HL

2-(Benzylthio)aniline (0.215 g, 1 mmol) and 2-meyhoxynaphthaldehyde (0.186 g, 1 mmol) was dissolved in methanol separately. Then to the methanolic solution of 2-(Benzylthio)aniline, solution of 2-meyhoxynaphthaldehyde was added drop wise with continuous stirring. The resulting solution was stirred under reflux (60 °C) condition for 2 h. Color of the solution changed to dark yellow. Progress of the reaction was monitored by TLC. The solution was kept in 0 °C; after 2-3 days a yellow crystalline product was formed. Filtered off the product and washed with 25% methanol and dried in vacuum (10^{-2} torr). Yield was almost quantitative. M. P: 190 °C. Elemental analysis calculated for ($C_{25}H_{21}NOS$): %C 78.3, %H 5.52, %N 3.65, %S 8.36, %O 4.17; found: %C 77.98, %H 5.81, %N 3.72, %S 8.44, %O 4.30. FT-IR (KBr, cm^{-1}): 1618, 1531, 1432, 1315, 1158, 1062, 749. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 9.24 (1H, s, CH=N), 7.07-7.96 (15H, m, Ar-H), 4.189 (2H, s, -SCH_2-), 4.00 (3H, s, -OCH_3). UV-Vis [CH_3CN, λ_{max}, nm (ε_{max}, $Lmol^{-1}cm^{-1}$)]: 254 (36231), 320 (18720), 345 (16450), 376 (21320) nm.

4.3. Synthesis of Pd(II) complex, PdLCl

A solution of ligand (0.191 g, 0.5 mmol) in 10 mL of methanol was slowly added in a dropwise manner to a solution of Na_2PdCl_4 (0.147 g, 0.5 mmol) in 10 mL of methanol. The resulting reaction mixture was stirred under reflux condition for 1 h, and kept at 0 °C. After a couple of days, an orange precipitate formed was filtered off and recrystallized from DCM and hexane. The orange red needle like crystals suitable for single crystal X-ray diffraction analysis was washed with 25% methanol-water solution for several times to remove impurities and dried under vacuum (10^{-2} torr) (Purity was checked by TLC). Yield 72%; MP: > 300 °C. Elemental analysis calculated for ($C_{25}H_{20}ClNOPdS$): %C 57.26, %H 3.84, %N 2.67, %S 6.11, %O 3.05; found: %C 57.36, %H 3.60, %N 2.55, %S 5.96, %O 3.14. FT-IR (KBr, cm^{-1}): 1601, 1516, 1447, 1378, 1158, 1062, 741. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.61 (1H, s, CH=N), 7.01-8.40 (14H, m, Ar-H), 4.27 (2H, s, $-SCH_2-$), 4.14 (3H, s, $-OCH_3$). UV-Vis [CH_3CN, λ_{max}, nm (ε_{max}, $Lmol^{-1}cm^{-1}$)]: 230 (38450), 280 (18750), 321 (6723), 367 (5420), 451 (7891), 473 (9750).

4.4. Crystallography

X-ray diffraction experiment was carried out with a Bruker APEX-II CCD diffractometer for the Pd(II) complex using graphite monochromated Mo-Kalpha radiation (l ¼ 0.71073_A, u-scans) at 100 K temperature. Structure was determined by using SHELXS-97 program [21]. Cell measurement and data reduction were done by Bruker SAINT [22]. Multi-scan method (SADABS) was used for absorption corrections [22]. Full matrix least-squares on F^2 were performed using the SHELXS-97 program. All non-H atom were refined in anisotropic approximation using reflector with $I>2\sigma$ (I). Crystal data and structure refinements of Pd(II) Complex are given in **Table 6.**

Table 6. Crystal structure and structure refinement details of the Pd(II) complex , (PdLCl)

Compound	Pd(II) complex
CCDC entry no.	1428239
Empirical formula	$C_{25} H_{20} Cl N O Pd S$
Formula weight	524.33
T (K)	100(2)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	
a (Å)	9.5822(3)
b (Å)	11.3805(3)
c (Å)	18.9062(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V ($Å^3$)	2061.73(10)
Z	4
D_{calc} (Mg/m^3)	1.689
μ (mm^{-1})	1.149
F (0 0 0)	1056.0
Crystal size (mm^3)	0.36 x 0.14 x 0.13
θ(°)	2.38-26.02
Index ranges	$-10 \leq h \leq 11$ $-14 \leq k \leq 14$ $-21 \leq l \leq 22$
Reflections collected	8880
Independent reflections (R_{int})	4069(0.0407)
Completeness (%)	1.72/0.98
Absorption correctio	multi-scan(SADABS)
Max and min transmission	0.8199 and 0.6825
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	4069/0/272
Goodness-of-fit on F^2	1.138
Final R indices [I>2σ(I)]	R1=0.0347, wR2=0.0826
R indices (all data)	R1=0.0402, wR2=0.1053
Largest difference in peak and hole($eÅ^{-3}$)	0.631/-1.253

4.4. Computational method

All computational studies were performed by using Gaussian 09W [23]. Full geometry optimizations of the ligand and palladium complex were carried out using the density functional theory based B3LYP method and with basis set 6-31G(d,p) for all 2nd row elements and hydrogen and LanL2DZ basis set for Pd. TD-DFT calculation for singlet-excitations in acetonitrile and the calculation of vibrational spectrum of the complex in the gas phase were performed by using the same basis set. The charge distribution analysis was carried out by Natural Bond Orbital (NBO) analysis [24]. The percentage composition of the molecular orbital analysis was done by Chemissian software package [25].

4.5. Catalytic activity studies

4.5.1. Microwave assisted palladium complex catalyzed selective oxidation of terminal olefin to aldehyde

To a homogeneous solution of Pd(II) complex (0.5 mol%) in 10 ml [bmim]BF_4-H_2O (2:1), substituted styrene (1 mmol) was added, followed by ammonium persulfate (1.5 mmol) as oxidant were taken in glass tubes, sealed and placed in the cavity of microwave apparatus. Then set parameters are as follows: microwave irradiation power 80 W, increasing time 5 min, target temperature 70 °C, standing time 15 min, standing temperature 70 °C. A maximum irradiation power of 80 W and 70 °C were applied for 15 min. After the temperature reached 70 °C, the instrument was automatically adjusted to maintain a constant temperature. After completion of the reaction (monitored through TLC), the reaction mixture was cooled to room temperature then diluted with 2x10 ml water, then extracted with ethyl acetate and dried over Na_2SO_4. The resulting solution was concentrated under vacuum. Product was further purified by chromatographic separation with a mixture of ethyl acetate:hexane (1:10).

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Keywords: Schiff Base • Six membered Palladacycle • TD-DFT Study • Olefin Oxidation • MAOS

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Highlights

- The complex formed is a new six membered palladacycle, having slightly distorted square planar geometry.
- The electronic absorption spectrum of the complex was calculated using the TD-DFT method in acetonitrile solvent employing the PCM model as implemented in the Gaussian 09W programs.
- The Pd(II) complex shows effective catalytic behavior towards selective oxidation of terminal alkenes to aldehyde by a microwave assisted Wacker oxidation method.
- The reaction is efficient in terms non-hazardous solvent selection, high yield and selective conversion to aldehyde almost up to 99%.