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Synthesis, Characterization and Catalytic Applications of 2,2-Dimethylpropane-1,3-Diaminopalladium(II) Complex in Mizoroki-Heck Reaction

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New tetradentate Schiff base ligand (L_{SB}) and its palladium(II) complex, *i.e.*, complexation of N,N'-*bis*(4-methoxysalicylidene)-2,2-dimethylpropane-1,3-diaminopalladium(II) (PdL_{SB}) has been successfully synthesized through condensation reaction between primary amine 2,2-dimethyl-1,3-propanediamine with 2-hydroxy-4-methoxybenzaldehyde. The palladium complex was then prepared by refluxing the corresponding L_{SB} with an equimolar amount of palladium(II) acetate to give $C_{21}H_{24}N_2O_4Pd$. The complex was characterized by using several techniques, such as the elemental chemical analysis CHN, FTIR, NMR spectroscopy and single crystal X-ray crystallography. This air/moisture stable complex was investigated to be a high class of homogeneous catalyst for Mizoroki-Heck reaction. The reaction was monitored by GC-FID at 12 h reaction period. The percentage conversion of 4-bromoacetophenone was 70 % indicated that PdL_{SB} can act as an ideal potential catalyst in the Mizoroki-Heck reaction.

Keywords: Tetradentate Schiff base, Homogeneous catalysis, Mizoroki-Heck.

INTRODUCTION

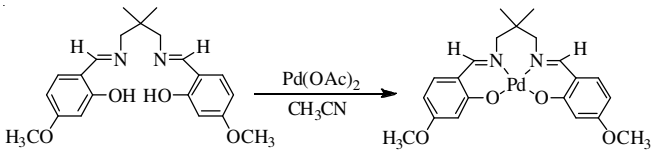
The Mizoroki-Heck reaction is the palladium catalyzed carbon-carbon bond formation between aryl halides and olefins is known to employ significant roles in modern synthetic chemistry [1,2] and are used extensively for agrochemical industry, pharmaceutical intermediates, conducting polymers, pesticides and liquid crystals application [3-5]. Basically, Mizoroki-Heck reaction is carried out in an organic solvent, such as amine, benzene, toluene, *N,N*-dimethylacetamide, *N,N*-dimethylformamide or tetrahydrofuran, which could give excellent performance and conversion to the catalytic product due to the solubility of most organic compound in *N,N*-dimethyl acetamide [6,7]. Traditionally, Mizoroki-Heck reactions are extensively catalyzed by phosphine palladium complexes. However, the cost, air and moisture sensitive as well as less stable of phosphine have led to the search for low-cost and easy accessible ligands as synthons for a new palladium Mizoroki-Heck coupling catalysts [8]. Therefore, the catalysis under phosphine-free condition represents a challenge of high importantance. To date, most of the efforts are emphasized in the search of more promising, simple, mild, efficient and economical friendly catalysts. Tetradentate ligands derived from Schiff base are widely used in coordination chemistry and can coordinate with a large number of transition metals. They can participate as catalysts in various reactions, since they have N,N,O,O donor set which possesses more benefits, such as facile approach, relative tolerance, readily adjusted ancillary ligands and tunable steric and electronic coordination environments on the metal center [9,10]. Indeed, the unique properties of tetradentate Schiff base derivatives in numerous reported applications and their tendency to form metal complexation with many metals inspired researchers to design and synthesize 2,2-dimethylpropane-1,3-diaminopalladium(II) complex. Thus, the performance of synthesized complex was further investigated as a homogeneous catalyst in the catalytic studies of Mizoroki-Heck reaction.

EXPERIMENTAL

All the chemical reagents were purchased commercially and used without further purification. Infrared spectra were carried out on the Perkin Elmer Spectrum One FTIR Spectrometer in the range of 4000-400 cm^{-1} by using KBR disks. CHN elemental analyses were recorded using a Thermo Finnigan CE 125 CHN analyzer. ^1H and ^{13}C NMR were recorded on a Bruker Avance 400 MHz spectrometer with $CDCl_3$ as a solvent. A single X-ray Crystallography was performed by using a Bruker APEX DUO CCD area detector diffractometer. The gas chromatography analyses were carried out on a GC-Hewlett-Packard 5890 series II gas chromatograph equipped with a nominal capillary column and flame ionization detector (FID).

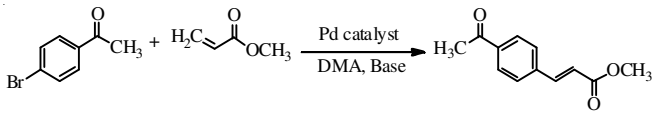
Synthesis of N,N'-*bis*(4-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine (L_{SB}): A solution of 2,2-dimethyl-1,3-propanediamine (5 mmol) in 10 mL absolute ethanol was added to a solution of 2-hydroxy-4-methoxybenzaldehyde (10 mmol) in a three-necked round bottom flask. The resultant yellow solution was refluxed under nitrogen for 5 h. The ligand obtained as yellow microcrystals were filtered off, washed with cold ethanol and dried in a vacuum desiccator over blue silica gel [11]. Yield: 89 %. m.p: 126-127 ºC.

Synthesis of N,N'-*bis*-(4-methoxysalicylidene)-2,2-dimethylpropane-1,3-diaminopalladium(II) complex (PdL_{SB}): The corresponding palladium(II) complex was synthesized by mixing a solution of L_{SB} (0.21 g; 0.62 mmol) in acetonitrile (10 mL) with a solution of palladium(II) acetate in acetonitrile (10 mL) in three necked round bottom flask. The resulting solution was refluxed with stirring for 5 h under nitrogen atmosphere (**Scheme-I**). The solid product of PdL_{SB} was then recrystallized from a mixture of dichloromethane/methanol (1:1 v/v). Slow evaporation of the solvent at room temperature over several days gave yellow crystals. Yield: 78 %. m.p: 323-324 ºC.



Scheme-I: Preparation of palladium(II) tetradentate Schiff base complex (PdL_{SB})

General procedure for homogeneous catalytic testing in Mizoroki-Heck cross-coupling reaction: In a Radleys carousel tube equipped with a magnetic stir bar, 4-bromoacetophenone (1 mmol), methyl acrylate (3 mmol), base (2.4 mmol), respective palladium(II) catalyst PdL_{SB} (1 mmol%) and N,N-dimethylacetamide (5 mL) were added whilst purged with nitrogen and heated at 120 ºC for 12 h. The conversion of the product was monitored by GC-FID. The synthetic approach for the Mizoroki-Heck reaction is illustrated in **Scheme-II**.



Scheme-II: Mizoroki-Heck reaction of 4-bromoacetophenone with methyl acrylate

RESULTS AND DISCUSSION

The FTIR spectrum for L_{SB} (Table-1) showed a strong band at 3436 cm^{-1} which can be ascribed to the stretching of phenolic ν(O-H) group. This band disappeared in the spectrum of the complex, indicating the coordination of phenolic -OH with palladium ion *via* deprotonation of phenolic hydrogen. The IR spectrum of PdL_{SB} exhibited a strong band at 1604 cm^{-1} which corresponded to the stretching frequency of imine ν(C=N) group. The contribution of C=N stretching mode was reduced as the electron pair on the nitrogen atom is involved in bond formation with metal ion [12].

In ^1H NMR spectrum of ligand, methoxy proton (O-CH_3) was observed at δ 3.83 ppm. The azomethine proton (-HC=N) signal in L_{SB} appeared as a singlet peak at δ 8.17 ppm. The signal was shifted up in the spectrum of PdL_{SB} (δ 7.35 ppm), suggesting that the shielding of the azomethine group due to the π-back bonding from Pd(II). The absence of sharp singlet resonance of the phenolic proton (δ 14.11 ppm) further approved that (-OH) group had participated in chelation through deprotonation. Meanwhile, ^{13}C NMR showed the displacement of (C=N) carbon to the lower field in PdL_{SB} supported the coordination of azomethine nitrogen and phenolic oxygen to Pd metal [13]. Table-2 shows the summary data for ^1H and ^{13}C NMR for L_{SB} and PdL_{SB}.

TABLE-1
FTIR DATA FOR LIGANDS (L_{SB}) AND PALLADIUM(II) COMPLEX (PdL_{SB})

Compd.	ν(O-H)	ν(C=N)	ν(C=C aromatic)	ν(C-O)	ν(C-N)
L_{SB}	3436	1629	1446	1118	1337
PdL_{SB}	–	1604	1440	1221	1305

TABLE-2
^1H AND ^{13}C NMR SPECTRAL DATA FOR L_{SB} AND PdL_{SB}

Compd.	^1H NMR δ_H (ppm)	^{13}C NMR δ_C (ppm)
L_{SB}	C-CH_3 (1.07) N-CH_2 (3.42) Ar-OCH_3 (3.83) N=CH (8.17) C-H, aromatic (6.44-7.13) C-OH (14.11)	C-CH_3 (24.19) CH_2-C-CH_2 (36.23) Ar-OCH_3 (55.34) N-CH_2 (66.58) C-H, aromatic (112.2-132.7) C-OH (163.7) C=N (164.7)
PdL_{SB}	C-CH_3 (1.06) N=CH (7.35) N-CH_2 (3.34) Ar-OCH_3 (3.79) C-H, aromatic (6.59-6.98)	C-CH_3 (23.99) CH_2-C-CH_2 (34.14) Ar-OCH_3 (55.27) N-CH_2 (71.62) C-H, aromatic (113.6-135.0) C-OH (161.6) C=N (165.6)

The elemental analysis of L_{SB} and PdL_{SB} was analyzed to determine the agreement between the theoretical and experimental values with molecular formula suggested in Table-3.

TABLE-3
ELEMENTAL ANALYSIS OF LIGAND (L_{SB}) AND COMPLEX (PdL_{SB})

Compd.	Elemental analysis (%): Found (calcd.)		
	C	H	N
L_{SB}, $C_{21}H_{26}N_2O_4$	68.20 (68.09)	7.31 (7.07)	7.53 (7.56)
PdL_{SB}, $C_{21}H_{24}N_2O_4Pd$	53.25 (53.12)	5.26 (5.09)	6.20 (5.90)

The square planar of PdL_{SB} was confirmed by single X-ray crystallography analysis and found to be in agreement with the literature [14]. As shown in Fig. 1, Pd^{2+} ion is located in the inner *cis*-N_2O_2 core of the ligand L_{SB} and adopts a perfectly square planar geometry where N(1A)-Pd(1)-N(1) and O(1A)-Pd(1)-O(1) angles are 94.20(4)º and 85.03(3)º, respectively. The dihedral angle between two benzene rings of the ligand was 79.21(4)º. The Pd(1)-O(1) and Pd(1)-N(1) distances were 1.9932(6) Å and 2.0029(7) Å, respectively and all parameters were within normal ranges (68) and comparable with the other related structures [15]. The selected bond lengths and angles are listed in Table-4.

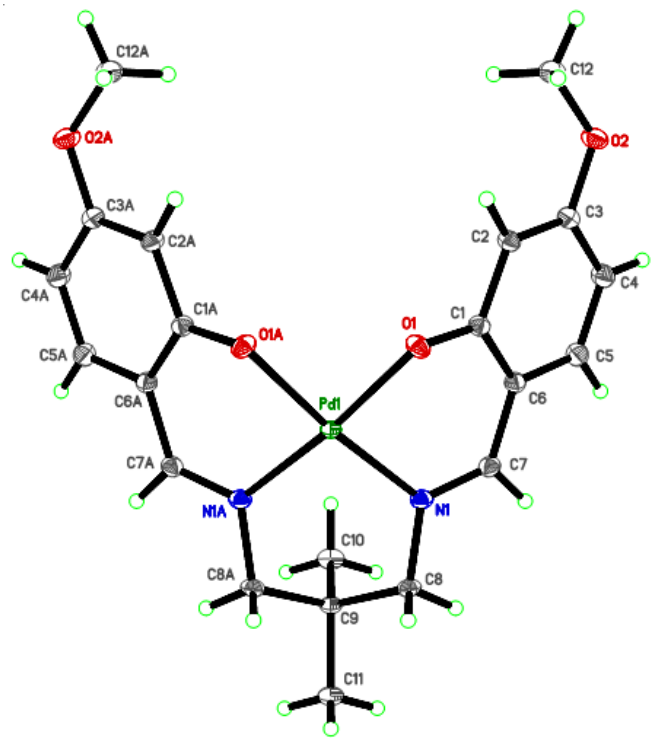


Fig. 1. Molecular structure of **PdL$_{SB}$**, showing the atom-labelling system and 50 % probability displacement ellipsoids

TABLE-4
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR **PdL$_{SB}$**

Assignment	Bond distances (Å)	Assignment	Angles (°)
Pd(1)-O(1)	1.9932(6)	O(1A)-Pd(1)-O(1)	85.03(3)
Pd(1)-O(1A)	1.9932(6)	O(1A)-Pd(1)-N(1A)	90.27(3)
Pd(1)-N(1)	2.0029(7)	O(1)-Pd(1)-N(1A)	174.10(3)
Pd(1)-N(1A)	2.0029(7)	O(1A)-Pd(1)-N(1)	174.10(3)
N(1)-C(7)	1.2951(10)	O(1)-Pd(1)-N(1)	90.27(3)
N(1)-C(8)	1.4695(10)	N(1A)-Pd(1)-N(1)	94.20(4)
O(1)-C(1)	1.3092(9)	C(1)-O(1)-Pd(1)	119.13(5)
O(2)-C(3)	1.3637(10)	C(3)-O(2)-C(12)	117.06(7)
O(2)-C(12)	1.4366(11)	C(7)-N(1)-Pd(1)	121.25(5)
C(2)-C(3)	1.3835(11)	C(8)-N(1)-Pd(1)	120.32(5)
C(2)-H2A	0.9500	C(7)-N(1)-C(8)	118.40(7)

Catalytic testing of homogeneous Mizoroki-Heck cross-coupling reaction: After confirming the exact structure of the synthesized complex **PdL$_{SB}$**, the catalytic activity of organic reaction was then tested by using 4-bromoacetophenone and methyl acrylate in the presence of sodium acetate as base and solvent at optimum reaction temperature (120 ºC) for 12 h. The reaction was carried out in a Radleys 12-placed carousel reactor vessel whilst continuously flushed with nitrogen gas. However, the temperature must be carefully controlled to avoid the palladium black formation that will inhibit the catalytic cycle if the temperature was too high [16]. The catalyst loading was kept to 1.0 mmol % so as to produce an expected turnover number (TON) of 100 if 100 % conversion was achieved. The reaction was monitored by using GC-FID. A controlled experiment indicated that a small amount of the cross coupling product was observed without any catalyst.

As expected, the result demonstrated excellent catalytic activity and efficiency of **PdL$_{SB}$** as a homogeneous catalyst with 70 % conversion of starting material to the desired Mizoroki-Heck product after 12 h reaction time probably due to the presence of electron donating (-OCH_3) group that can accelerate the oxidative addition of aryl halide. However, the conversion might not reach up 100 % and was found to be time independent. To extend the research work scope, more optimization conditions for catalytic study in Mizoroki-Heck reaction should be considered by using a variety of reaction parameters such as different bases, temperature, catalyst loading and solvent in order to increase the percentage of C-C coupling yield. It is worth mentioning here that these findings indicated the synthesized palladium(II) complex (**PdL$_{SB}$**) can act as a potential homogeneous catalyst in the Mizoroki-Heck reaction. The catalytic data (Table-5) showed that **PdL$_{SB}$** efficiently catalyzed the Mizoroki-Heck reaction of 4-bromoacetophenone with methyl acrylate.

TABLE-5
PdL$_{SB}$ CATALYZED MIZOROKI-HECK COUPLING REACTION OF 4-BROMOACETOPHENONE WITH METHYL ACRYLATE

Reaction condition	Control	Catalyst (**PdL$_{SB}$**)
Temperature (°C)	120	120
Reaction time (h)	24	12
Catalyst loading (mmol %)	0.00	1.00
% Conversion of 4-bromoacetophenone	17	70

Conclusion

In this study, N,N'-*bis*(4-methoxysalicylidene)-2,2-dimethylpropane-1,3-diamine (**L$_{SB}$**) and its palladium(II) complex (**PdL$_{SB}$**) were successfully synthesized with high percentage of yields. Under the present experimental condition, the homogeneous catalyst was found to efficiently catalyze Mizoroki-Heck reaction of 4-bromoacetophenone into the coupled product.

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