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Research Article

SYNTHESIS AND CHARACTERIZATION OF 1-(THIOPHEN-2-YL)-N-(*P*-TOLYL) METHANIMINE AND ITS PALLADIUM(II) COMPLEX

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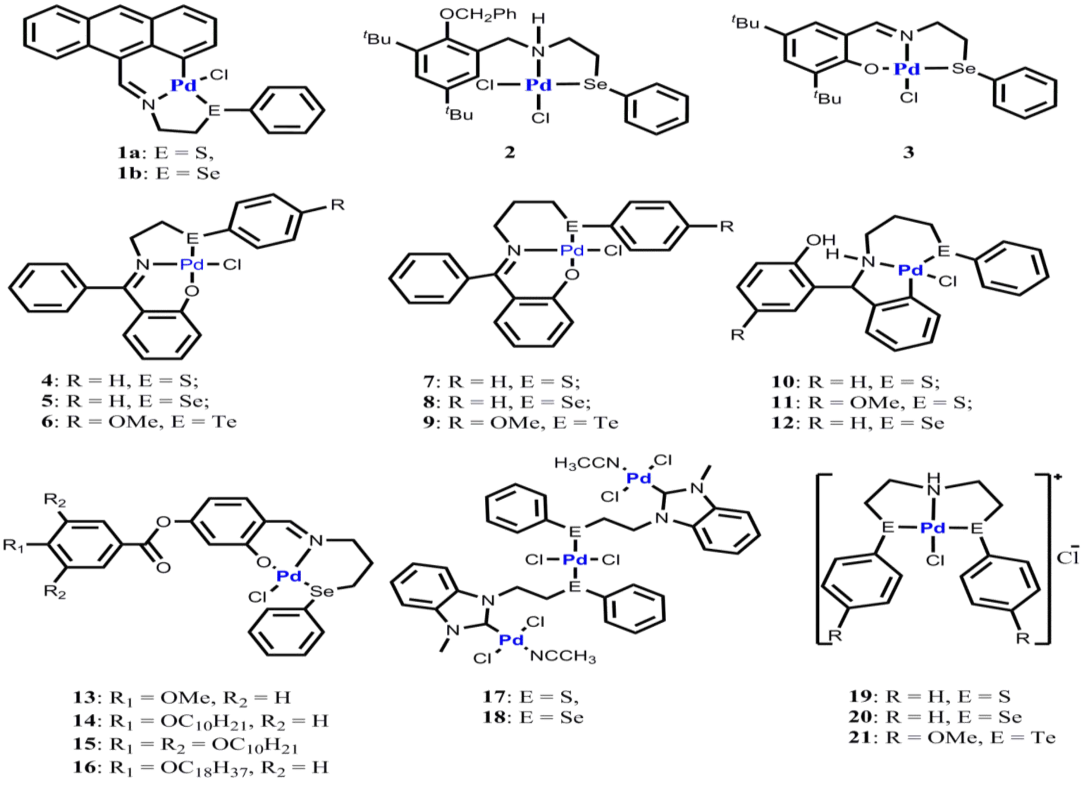
ABSTRACT

The synthesis and characterization of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine and bis[1-(thiophen-2-yl)-N-(*p*-tolyl) methanimine]$PdCl_2$ are reported here. Both compounds are well characterized with ^{1}H NMR, IR spectra and elemental analysis data. The reaction of thiophene-2-carbaldehyde reacted with *p*-toluidine in ethanol solvent at room temperature in 1:1 ratio afforded yellow colour solid of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine in excellent yield. The reaction of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine with Na_2PdCl_4 afforded 2:1 adduct of bis[1-(thiophen-2-yl)-N-(*p*-tolyl) methanimine]$PdCl_2$ complex. This manuscript is mainly concerned with the synthesis and characterization of a new bis[1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine]$PdCl_2$ complex bearing Schiff base, 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine ligand. In order to improve every aspect of the catalytic cycle in various coupling reactions like Suzuki, Heck, Stille cross couplings and Sonogashira reaction, it is necessary to develop novel highly stable organopalladium complexes as catalyst. The develop palladium complex can be used as a catalyst in several coupling reactions. The Schiff base ligand, 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine can also be employed in several metallation reactions. These metallated compounds can be used in development of a new sight of organometallic chemistry and synthesis of organic molecules.

Keywords: Synthesis, Palladium Complex, Schiff base, Room Temperature, Thiophene.

1. INTRODUCTION

Numerous type of pincer ligands have been employed in the last two decades to isolate organopalladium complexes in 0, II, III, and IV oxidation state by many research groups. These pincer ligands have several types of donor atoms (O, S, Se, Te, N, and P) [1-9]. Singh and co-workers have reported a number of palladacycles bearing metal chalcogen bond and explore its catalytic property [10-17]. The CNE (E = S, Se) pincer ligand bearing palladium complexes can be prepared by the treatment of schiff bases, $[PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ and $[PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_9]$ with Na_2PdCl_4 in mixture of acetone and water solvent at room temperature to give rise $[PhS(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_8\text{-}(1\text{-}Pd(II)Cl)]$, **1a** and $[PhSe(CH_2)_2C{=}N\text{-}9\text{-}C_{14}H_8\text{-}(1\text{-}Pd(II)Cl)]$ **1b** organo-palladium compounds respectively [10]. Both complex **1a** & **1b** are thermally stable, moisture and air-insensitive. Both palladium complexes can be employed as efficient catalyst in transfer hydrogenation reaction. At room temperature observed conversion rate was 90% in transfer hydrogenation reaction [10]. However in 2014 same group have reported adduct formation, take place through the reaction of sterically hindered selenoether ligand, $[2\text{-}PhCH_2O\text{-}3,5\text{-}(t\text{-}Bu)_2\text{-}C_6H_2\text{-}CH_2\text{-}NH\text{-}(CH_2)_2SePh]$ and $PdCl_2$ in 1:1 ratio. In which $PdCl_2$ molecule is coordinated through Se and N atom of the selenoether ligand. Almost analogous sterically hindered schiff base ligand, $[2\text{-}HO\text{-}3,5\text{-}(t\text{-}Bu)_2\text{-}C_6H_2\text{-}CH{=}N\text{-}(CH_2)_2SePh]$, treated with Na_2PdCl_4 in methanol solvent can afford palladium(II) complexes, $[2\text{-}(Cl\text{-}Pd(II)\text{-}O)\text{-}3,5\text{-}(t\text{-}Bu)_2\text{-}C_6H_2\text{-}CH{=}N\text{-}(CH_2)_2SePh]$, **3** by the O-H bond activation in place of C-H bond. Both palladium complex **2** & **3** are demonstrated as catalyst for Suzuki-Miyaura C-C coupling reactions. The efficiency of catalyst **3** in this coupling reaction is somewhat better than that of catalyst **7** [11]. In 2009 same group have also reported a series of schiff bases of 2-hydroxybenzophenone and their palladium(II) complexes **4-9.** In these complexes, ligands were also coordinated in the same manner as in case complex **9**. Complexes **4-6** & **8** are also employed as catalyst in Heck and Suzuki reaction [12]. Thereafter in 2010 and 2013 Singh and coworkers have reported reaction of tridentate thio/selenoether ligands, 2-HO-4-R-C_6H_3-(C_6H_4) CHNH$(CH_2)_3EC_6H_5$, [R = H/MeO & E = S; R = H & E = Se] with Na_2PdCl_4, to give rise a series of palladacycles, **10**-**12** respectively. These palladacycle are coordinated as tridentate ligand (N, S/Se, C). These complexes exhibit as excellent catalyst in Suzuki-Miyaura coupling reaction of phenyl boronic acid with aryl halides. During catalysis generated a nano size particle of $Pd_{16}S_7$&$Pd_{17}Se_{15}$, probably these nanoparticle are actually playing a role as catalyst in the catalytic cycle [13, 14]. In 2012 same research group have published the selenated schiff bases which differ in the chain length of non-coordinating substituent and their square planar palladium(II) complexes (**13-16**). These schiff bases are behaving as tridentate (Se,N,O$^-$) pincer ligands. All four complexes have been found suitable to catalyze Suzuki-Miyaura coupling reactions under gentle circumstances. Among these complex **16** show highest catalytic activity due to presence of longest chain. In this article author concluded that the length of the pendent alkyl chain present in the complex molecule controls the catalytic activity [15]. Recently same group have published trimelallic Palladium(II) complexes **17** & **18** by using same method from 3‑methyl‑1‑(2‑(phenylthio) ethyl)‑1H‑benzo[d]‑imidazol‑3‑ium iodide and 3‑methyl‑1‑(2‑(phenylselenyl)‑ethyl)‑1H‑benzo[d]imidazol‑3‑ium iodide respectively [16]. These trimetallic complexes were reported as efficient catalysts for nitrile‑amide interconversion and Sonogashira coupling reactions. These cationic complexes were also employed as catalyst in Suzuki-Miyaura coupling (SMC) reactions by use of various aryl bromides with phenylboronic and *para* substituted phenylboronic acid [17]. Complexes **19** and **20** show better catalytic activity than **21**. Representative well characterized palladium complexes are shown in **Fig. 1**. These seminal discoveries have inspired us to develop easiest methodology to isolate highly stable palladium complex in excellent yield even in presence of air and moisture. Herein, we report the synthesis and characterization of a new schiff base 1-(thiophen-2-yl)-N-(*p*-tolyl) methanimine, **22** and its Pd(II) complex [1-(thiophen-2-yl)-N-(*p*- tolyl)methanimine]$PdCl_2$ **23** in excellent yield. The Schiff base is characterized by ^{1}H-NMR and IR spectra. The reaction of 1- (thiophen-2-yl)-N-(*p*-tolyl) methanimine with Na_2PdCl_4 in methanol, afforded 2:1 adduct of its Pd(II) complex. The developed Schiff base ligand, 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine and its Pd(II) complex can be utilized in several type of metalltion reaction and demonstrated as a good catalyst in reduction of several functional groups respectively.



1a: E = S,
1b: E = Se

2

3

4: R = H, E = S;
5: R = H, E = Se;
6: R = OMe, E = Te

7: R = H, E = S;
8: R = H, E = Se;
9: R = OMe, E = Te

10: R = H, E = S;
11: R = OMe, E = S;
12: R = H, E = Se

13: R_1 = OMe, R_2 = H
14: R_1 = $OC_{10}H_{21}$, R_2 = H
15: R_1 = R_2 = $OC_{10}H_{21}$
16: R_1 = $OC_{18}H_{37}$, R_2 = H

17: E = S,
18: E = Se

19: R = H, E = S
20: R = H, E = Se
21: R = OMe, E = Te

Fig. 1: Representation of various type Pd-II Complexes

2. EXPERIMENTAL

All manipulations of the complexes were carried out using standard Schlenk techniques under a nitrogen atmosphere. All solvents were freshly distilled and used solvents were purified and dried by standard techniques. All chemicals, e.g. Na_2PdCl_4 and thiophene-2-carbaldehyde, *p*-toluidine (Sigma-aldrich), ethanol, (S D Fine) were reagent grade and used as received. The ^{1}H NMR spectra were recorded on Bruker 400 MHz instruments at ambient temperature and the chemical shifts were measured in ppm relative to TMS for ^{1}H NMR. FTIR spectra were recorded on Perkin–Elmer Spectrum GX spectrophotometer in KBr window. Elemental analyses were performed on a CarloErba model 1106 elemental analyzer.

2.1. Synthesis of 1-(thiophen-2-yl)-N-(p-tolyl) methanimine (22)

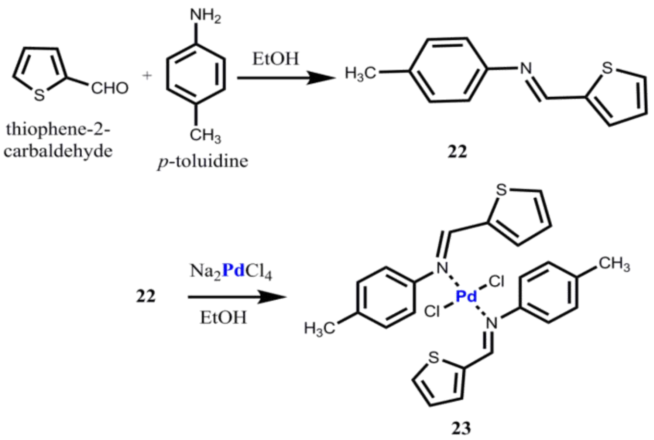
To a solution of thiophene-2-carbaldehyde (2.2 ml, 20.0 mmol) in freshly distilled dry ethanol (40 ml), a solution of *p*-toluidine (2.1 ml, 20.0 mmol) in the same solvent (40 ml) was added drop-wise. After 3h, the resulting yellow solid suspension was filtered and washed with dry ethanol (20mL). The filtrate was concentrated by removing the solvent under vacuum. This resulted in a yellow solid residue, which was purified by Colum chromatography to yield as a yellow solid. Yield: 94% M.P. 42°C ^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ2.36 (s, 3H, CH_3), 7.10-7.19 (m, 5H, aryl-H), 7.44-7.49 (m, 2H, aryl-H), 8.56 (s, 1H, CH=N). FT-IR (KBr) 531, 577, 712, 768, 824, 1043, 1100, 1193, 1384, 1426, 1500, 1615, 1898, 2870, 2924, 3409 cm^{-1}. Anal. Calcd. For $C_{12}H_{11}NS$: C, 71.61; H, 5.51; N, 6.96. Found C, 71.50; H, 5.80; N, 7.00.

2.2. Synthesis of bis[1-(thiophen-2-yl)-N-(p-tolyl) methanimine]$PdCl_2$ (23)

A solution of Schiff base 22 (0.273 g, 1 mmol) in ethanol (10 ml), Na_2PdCl_4 (0.15 g, 0.51 mmol) in the same solvent (10 ml) was added slowly. A yellow solid was separated immediately then allowed to 6 h at room temperature the yellow solid was filtered, washed with ethanol and dried. Yield: 84%. M.p.: 268°C. FT-IR (KBr) 566, 605, 754, 819, 1056, 1195, 1384, 1498, 1611, 1732, 2295, 2857, 2921, 3406 cm^{-1}. Anal. Calcd. For $C_{24}H_{22}N_2S_2PdCl_2$: C, 47. 71; H, 3.82; N, 4.83. Found C, 47.50; H, 3.90; N, 4.70.

3. RESULTS AND DISCUSSION

The syntheses of Pd(II) complexes carried out at room temperature are summarized in **Scheme1**. Schiff base **22** were prepared by reaction of thiophene-2-carbaldehyde with *p*-toluidine in ethanol at room temperature in 1:1 ratio afforded yellow colour solid of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine in excellent yield. The Schiff base 1-(thiophen-2-yl)-N-(*p*-tolyl) methanimine is characterized by ^{1}H-NMR and IR spectra. The reaction with **22** and Na_2PdCl_4 in acetone and water mixture (5:2) has resulted in bis[1-(thiophen-2-yl)-N(*p*- tolyl)methanimine]$PdCl_2$Complex. The complex **23** was isolated as bright yellow powdered solids and has poor solubility in $CHCl_3$, DMSO and common organic solvents.



Scheme 1: Synthesis of Schiff base bearing new Pd-II complex.

3.1. Spectroscopic Studies

3.1.1. NMR and IR Spectroscopic studies

1-(thiophen-2-yl)-N-(p-tolyl)methanimine molecule is a yellow colour solid, ^{1}H-NMR spectrum show two singlets at 2.36 and 8.56 ppm for methyl and methylene proton respectively. Aryl region exhibited two sets of multiplets at 7.10-7.19 for five aryl protons and at 7.44-7.49 show multiplets for 2 aryl-protons. IR spectrum of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine shows characteristic imine C=N singlet peak at 1615 cm^{-1}. Its palladium complex IR spectrum shows at 1611 cm^{-1}. However palladium complex are insoluble in most of the common organic solvent so we are unable to study in solution state as well as single crystal x-ray studies. Our main objective is to develop a highly stable organopalladium complex that can be employed as homogeneous catalyst in several coupling reactions and development of new pharmaceutical molecules. The developed palladium complex can be reused as catalyst in several catalytic cycles since the palladium complex is highly stable even in presence of air and water.

4. CONCLUSION

The treatment of thiophene-2-carbaldehyde with *p*-toludine in ethanol solvent at room temperature afforded yellow colour solid of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine in excellent yield. The reaction of 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine with Na_2PdCl_4 afforded yellow colour solid of bis[1-(thiophen- 2-yl)-N(*p*-tolyl)methanimine]$PdCl_2$ complex in good yield. The Pd(II) complex is poor solubility in most of the common organic solvent so we are unable to study in solution state as well as single crystal x-ray studies. The Schiff base, molecule and its palladium complex has been characterized by ^{1}H-NMR, IR spectrum and elemental analysis. The developed palladium complex can be used as a catalyst in several coupling reactions like Suzuki, Heck, Stille cross couplings and Sonogashira reaction. The Schiff base ligand, 1-(thiophen-2-yl)-N-(*p*-tolyl)methanimine can also be employed in several metallation reactions. These metallated compounds can be used in development of a new sight of organometallic chemistry and synthesis of organic molecules.

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Conflict of Interest

Authors don't have any types of conflict related to this article.

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