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HIGHLY EFFICIENT Pd(II) SCHIFF BASE CATALYST FOR SONOGASHIRA REACTION

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ABSTRACT

Five symmetrical Schiff bases were successfully synthesized from the condensation reaction between salicylaldehyde and its derivatives (X= H, F, Cl, CH_3 and OCH_3) with 2,2-dimethyl-1,3-propanediamine. The synthesized ligands were reacted with palladium (II) acetate in 1:1 ratio, yielding palladium (II) Schiff base complexes. They were characterized through elemental analysis CHN, melting point, molar conductivity, infrared, UV-Vis, ^1H nuclear magnetic resonance (NMR) spectroscopy and magnetic susceptibility. All Pd(II) complexes were tested as catalysts in the Sonogashira reaction. The optimization of reaction conditions was done by varying the type of bases and the amount of catalysts. The bases used for optimization were triethylamine ($C_6H_{15}N$), potassium carbonate (K_2CO_3), pyridine (C_5H_5N) and potassium hydroxide (KOH) where the latter was found to be at the optimum base. The amount of catalyst was varied at 0.5, 1.0, 1.5 and 2.0 mmol% respectively. The 2.0 mmol% of catalyst was found to be the best amount of catalyst indicated by the highest percent conversion of iodobenzene in 12 hours monitored using GC-FID. The temperature set for the optimization were room temperature (30°C), 60°C, 100°C and 120°C. The best temperature of reaction found was 120°C. Pd(AD1F) showed the highest percent conversion of iodobenzene with 100% conversion after 3 hours of reaction at 120°C. Hence, the Pd (II) Schiff base complex was found to be a good catalyst without the presence of Cu(I) co-catalyst. The absence of a co-catalyst avoids product contamination and eliminates the need for by-product separation.

Keyword: *Catalyst, Palladium, Schiff base, Sonogashira*

1. INTRODUCTION

The condensation of primary amine, aldehyde or ketone in a specific solvent can easily produce a Schiff base compound (Kargar et al., 2021). Structurally, the aldehyde or ketone's carbonyl group (C=O) is replaced by an imine or azomethine group (Brodowska & Łodyga-Chruścińska, 2014). To form metal complexes, the Schiff base ligand is added to a metal precursor in an appropriate ratio, along with suitable experimental conditions (Yusuf et al., 2021). Commonly, the multidentate Schiff bases coordinate to metals through the imine nitrogen and another nitrogen or oxygen atom from a proper functional group from its neighborhood (Gondia & Sharma, 2018). Due to their fascinating physical and chemical properties, Schiff base complexes that have synthetic sensitivity, selectivity, and flexibility have become important compounds in coordination chemistry (Karaoğlan, 2022).

Sonogashira coupling reaction is one of a blooming cross-coupling reactions that is used to form C(sp)-C(sp^2) bonds (Naeimi & Kiani, 2019). For the formation of terminal and internal alkynes, the Sonogashira reaction is one of the most efficient and straightforward processes (Anitha et al., 2015; Nasresfahani & Kassaee, 2021). This reaction involves the coupling of terminal alkynes, i.e., phenylacetylene with aryl or vinyl halides assisted by catalyst, co-catalyst and an amine base. Diphenylacetylene is a major product that is expected to be observed from this coupling reaction. This cross-coupling reaction is used in a variety of fields such as natural product synthesis, agrochemicals, synthetic materials, biologically active molecules, non-linear optical and molecular electronics, dendrimer and polymeric materials, acetylene macrocycles and polyalkynated molecules (Devkule et al., 2017). The original Sonogashira reaction was generally carried out in organic solvents in the presence of palladium and copper(I) iodide as co-catalysts. The presence of copper increases the reactivity of acetylene by forming copper acetylide. However, the presence of copper co-catalyst induces Glaser-type homocoupling of the terminal alkyne, causing product contamination and the side products (diynes) are generally difficult to separate from the desired products (Zhu et al., 2018). Therefore, in this study, the reaction will be applied without the presence of a co-catalyst and observe the catalytic performance of the Pd (II) catalyst.

2. METHODOLOGY

2. 1 Synthesis of Pd (II) Complexes

In a clean round bottom flask, 1 mmol of ligand was added together with 10 mL acetonitrile. Then, 10 mL of acetonitrile solution of 0.225 g (1 mmol) $Pd(CH_3COO)_2$ was put into the flask containing the ligand solution, then stirred and refluxed for 4 hours. The precipitate produced was carefully filtered off, washed with a small amount of cold ethanol, and was air-dried.

2.2 Sonogashira Coupling Reaction

In several clean tubes, 0.203 g (2.0 mmol) of triethylamine (Et_3N) was added to the solvent DMSO (7 mL). Then the reactants, 0.153 g (1.5 mmol) of phenylacetylene and 0.204 g (1 mmol) of iodobenzene, were added. In each tube, different Pd(II) complexes (1.0 mmol%) were added separately as potential catalysts and the mixture was placed on the Radley's 12-place reaction carousel. The mixture was stirred under aerobic conditions and heated at 100 °C for 12 h. The reaction progress was monitored by GC-FID for every 0, 3, 6, 9 and 12 h to determine the percentage of conversion of iodobenzene.

Three (3) reaction parameters namely the type of base, amount of catalysts and reaction temperature are varied to find the optimum reaction conditions between iodobenzene and phenylacetylene. There are four (4) different bases *viz*. KOH, K_2CO_3, pyridine and Et_3N. Upon obtaining the optimum base, the optimization process continues to search for the optimum amount of catalyst or catalyst loading. The amount of catalyst varies at 0.5, 1.0, 1.5 and 2.0 mmol%. After identification of the optimum base and amount of catalyst, the optimization process continued to figure out the optimum temperature of the reaction. The temperature will be varied at room temperature, 60 °C, 100 °C and 120 °C.

3. FINDINGS

It was found that the best base for the reaction is KOH, while the best amount of catalyst is 2.0 mmol% at 120 °C. Pd(AD1F) was found to be the best catalyst in the optimum conditions as it shows the highest percent conversion of iodobenzene 100% after 3 hours of reaction. The catalyst contains an electron-withdrawing group which is fluoro (-F). The electron-withdrawing effect in the metal complex might favor the oxidative addition of aryl halides (iodobenzene), which accelerates its coupling with phenylacetylene to the final product (Zhang *et al*., 2015). Besides, the presence of electron-withdrawing substituents in the complexes increases the acidity of hydrogen in the metal-acetylide complex, facilitating elimination reaction.

4. CONCLUSION

Five tetradentate Pd(II) complexes were successfully synthesized as confirmed by the characterization via physicochemical and spectroscopic analysis. Schiff base ligands coordinated through phenolic oxygen and azomethine nitrogen atoms as tetradentate chelates as indicated by the spectral data. Pd(AD1F) displayed properties of good catalysts for the Sonogashira reaction, with up to 100% conversion of iodobenzene after 3 h of reaction time at 120°C with the presence of KOH and 2.0 mmol% of the catalyst.

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