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Data article

Synthesis of palladium(II) diimine complexes and their catalytic potential in sonogashira cross coupling reaction

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ABSTRACT

Cross-coupling reactions catalyzed by various transition metal complexes are the most powerful synthetic tools for the generation of C=C and C≡C bonds. Significant efforts have been put into the modification of ligands to increase the catalytic efficiency of the transition metal complexes. In most cases, attention is only paid to highly efficient catalysts and unsuccessful examples are often ignored. In this work, four diimine compounds, R-dab, were synthesized by condensation reaction and then reacted with the precursor $[PdCl_2(MeCN)_2]$ to form a palladium(II) diimine, $[PdCl_2(\text{R-dab})]$, complex. Our initial hypothesis was that the strong *trans*-effect from the diimine ligand in $[PdCl_2(\text{R-dab})]$ would enhance the rate of reductive elimination and subsequently promote the formation of cross coupling product. The catalytic efficiency of $[PdCl_2(\text{R-dab})]$ complexes in Sonogashira cross coupling reactions were examined at a temperature of 70 °C by reacting methyl-4-bromobenzoate and 2-methylbut-3-yn-2-ol for 5 hours under nitrogen conditions. Unfortunately, our results showed that the $[PdCl_2(\text{R-dab})]$ complexes are incapable of inducing the formation of cross coupling product. Despite the fact that these cross-coupling reactions were unsuccessful, we set out to explain the reasons for this failure herein

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so that these can serve as a reference for future researches of Pd-catalyzed Sonogashira cross coupling reactions.

Specifications Table

Subject area	*Inorganic chemistry – Catalysis*
Compounds	*Palladium(II) diimine, [$PdCl_2(R\text{-}dab)_2$], complexes*
Data category	*Catalysis results, yields, GCMS and NMR data*
Data acquisition format	*Mass and NMR spectra*
Data type	*Raw*
Procedure	*The catalytic efficiency of [$Pd(R\text{-}dab)Cl_2$] complexes in Sonogashira cross coupling reaction was examined at the temperature of 70 °C by reacting methyl-4-bromobenzoate and 2-methylbut-3-yn-2-ol for 5 hours.*
Data accessibility	*No. The data in this article was obtained from our catalysis experiments*

1. Rationale

Cross coupling reactions play a vital role in organic synthesis and have been widely used in the pharmaceutical, medicinal, polymer and advanced material industries [1–6]. Most cross coupling reactions employ palladium complexes as catalysts due to their ease of preparation, high stability in air and moisture, low loading as well as greater catalytic efficiency compared to other transition metal complexes [1,7–9].

In this work, we focused on the Sonogashira cross coupling reaction due to our interest in alkynylarenes synthesis, which have been used in metallacycle complex formation [10–13]. As illustrated in the catalytic cycle proposed by Sonogashira et al. (Fig. 1), two important components are involved in this cross-coupling reaction, namely (i) a pre-activation step in which Pd(II) is reduced to Pd(0), producing the homo-coupling product (R-CC-CC-R), and (ii) the main catalytic cycle involving oxidative addition, transmetallation and reductive elimination to give the cross-coupled product.

Despite the regular use of phosphine based compounds as ligands in Sonogashira cross coupling, a number of problems are frequently encountered when using with Pd catalyst systems. For example, phosphine ligands are usually moisture and air sensitive, highly toxic and also laborious to synthesize. Furthermore, during the reaction the degradation of P-C bonds can result in the deactivation of the catalyst as well as the scrambling of coupling partners with the phosphine substituent [14,15].

To counter all these disadvantages, efforts have been directed towards designing cost-effective catalysts that are readily accessible, moisture and air stable and function under ambient conditions. Therefore, R-dab ligands, also known as diimine ligands (Fig. 2) have been employed in palladium complexes as they can serve as metallomesogens or as homogeneous catalysts in carbon–carbon cross-coupling reactions owing to the versatility in their coordination behavior [16–19]. In addition, we initially expected that the diimine moiety in [$PdCl_2$(R-dab)] complexes is able to effect a strong *trans*-influence which can enhance the reductive elimination rate and subsequently reduce the formation of the homo-coupling product (R-CC-CC-R) thereby producing more cross-coupling product.

In this work, [$PdCl_2$(R-dab)] complexes were synthesized by reacting the precursor [$PdCl_2(CNMe)_2$] with R-dab as illustrated in Fig. 3. The catalytic effects in Sonogashira cross coupling reactions of these [$PdCl_2$(R-dab)] complexes were examined and compared to the [$PdCl_2(PPh_3)_2$] catalyst as the standard.

2. Procedures

2.1. General

All the infrared spectra (IR) were recorded as KBr pellets in the wavelength region from 400 to 4000 cm^{-1} using a Thermo Scientific Nicolet iS10 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra