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Synthesis, characterization and the Suzuki–Miyaura coupling reactions of *N*-heterocyclic carbene–Pd(II)–pyridine (PEPPSI) complexes

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ABSTRACT

N-heterocyclic carbenes (NHCs) are a significant and powerful class of ligands for transition metals. A new series of air and moisture-stable NHC–$PdCl_2$-pyridine complexes, (**2a**–**f**), have been described. With the development of a more efficient catalytic system for the cross-coupling of aryl halides in mind, the catalytic performance of the NHC–$PdCl_2$-pyridine complexes for Suzuki cross-coupling under mild conditions in aqueous *N*,*N*-dimethylformamide (DMF) was investigated. Electron-rich and electron-poor aryl chlorides were facilely coupled with boronic acids by NHC–$PdCl_2$-pyridine complexes.

Introduction

N-heterocyclic carbenes (NHCs) have led to important developments in transition metal chemistry due to their tunable steric and electronic properties. Arduengo et al. isolated and characterized the first stable free NHC in 1991 [1]. Since then, many metal-NHC complexes have been synthesized, leading to many applications in the field of transition metal catalysis such as hydrosilylation [2], Ru-catalyzed furan synthesis [3], transfer hydrogenation [4], olefin metathesis [5], and Pd-catalyzed cross-coupling reactions [6,7].

Herrmann [8], Nolan [9], Beller [10] and Sigman [11] have reported a series of monoligated Pd–NHC complexes that showed high activity in Pd catalyzed reactions.

The reported catalysts were prepared under an inert atmosphere due to the extreme oxygen and water sensitivity of isolated free NHCs that requires rigorously anhydrous reaction conditions [12]. The insitu preparation of active catalysts has proven to be a potent method in overcoming this problem. Organ et al. [13] reported easily-handled, air and moisture stable Pd–NHC complexes through the PEPPSI (**P**yridine-**E**nhanced **P**recatalyst **P**reparation **S**tabilization (and) **I**nitiation) method that featured Pd(II) species bearing an NHC ligand, two halides, and a labile ligand such as 3-chloro pyridine. After Organ's work, Doucet and Matt reported additional monoligated NHC-based palladium pyridine complexes [14,15].

Suzuki coupling, the reaction between boronic acid derivatives and organic electrophiles, is one of the most powerful and widely preferred reactions for C–C bond formation. Carbon–carbon and carbon-heteroatom bond-forming reactions have been catalyzed by structurally different palladium complexes. Recently, significant improvements have been made in the phosphine-ligated palladium catalyzed Suzuki–Miyaura reaction [16]. Fu et al. made a detailed study with alkylboranes and boronic acid derivatives and they took a step forward on the Suzuki–Miyaura reaction [17]. The first NHC-based Suzuki protocol was reported by Capretta et al. [18]. While less reactive and lacking in substrate range, ease of use and handling makes Pd–NHC catalysts attractive. However, preparation of Pd–NHC catalysts and Suzuki–Miyaura reactions require a rigorously inert atmosphere due to the sensitivity of isolated free carbenes [19]. To overcome this difficulty, active catalyst is produced in situ for most NHC-based Suzuki coupling reactions with couple of disadvantages [20]. However, with Organ's PEPPSI method, the synthesis of precatalysts was easily accomplished without air- or water-free conditions. Further studies on this topic have been published by other research groups [14,15].

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The Suzuki coupling reaction plays an important role in the synthesis of fine chemicals [21–26]. Non-toxic, air- and moisture-stable reagents as well as greener solvents are some of its advantages. Mixtures of water and organic solvents in Suzuki coupling promotes the solvation of mineral bases to support the Suzuki reaction by activating the aryl boronic acid and can the dissolve organic substrates and corresponding palladium catalysts. In this respect, water has economical and environmental advantages because it is relatively safe and easily separated from organic compounds. Several organic transformations use water as the solvent [27–43]. In 2010, Ying et al. discovered a novel, highly active pre-catalyst for the coupling of deactivated aryl chlorides and phenyl boronic acid at room temperature by using wet solvents (Dioxane/H_2O, THF/H_2O) in air [33]. Shao et al. reported a study that Pd–NHC complexes showed high catalytic activity in the Suzuki–Miyaura coupling reactions of aryl chlorides in aqueous media [44]. To date, Organ [13] and Cavell [45] groups have published imidazole and ring expanded NHC–Pd pyridine (PEPPSI) complexes and their catalytic activity on C–C, C–N cross coupling transformations. Herein, we would to understand catalytic activity of bezimidazol ligated palladium pyridine complexes on Suzuki reaction because benzimidazole ligands have different σ-donor function and more electrophylic than classical and ring expanded NHC ligands. Results showed that, this catalytic system could be applied to the Suzuki coupling of aryl chlorides in good yields, simply and efficiently.

Results and discussion

Preparation of benzimidazolium salts

According to Scheme 1, **1a**–**f** was synthesized in approximately quantitative yield by quaternization of 1-alkyl-benzimidazole in DMF with corresponding aryl and morpholine chlorides [46]. **1c**, **1d** and **1f** benzimidazolinium salts have already been reported in the literature [47,48]. The ^{1}H- NMR shifts of **1a**, **1b** and **1e** are similar to other characterized benzimidazolium salts [49–54]. In the ^{1}H-NMR spectra of **1a**, **1b** and **1e**, the NC*H*N protons were observed as sharp singlets at 12.15, 11.59, and 11.29 ppm respectively. The imino carbons (NCHN) were detected as typical singlets in the ^{1}H-decoupled mode at 139.5, 142.7, and 156.9 ppm. The IR data of **1a**, **1b** and **1e** clearly support the presence of the C–N group with ν(C–N) vibrations at 1545, 1570 and 1623 cm^{-1}.

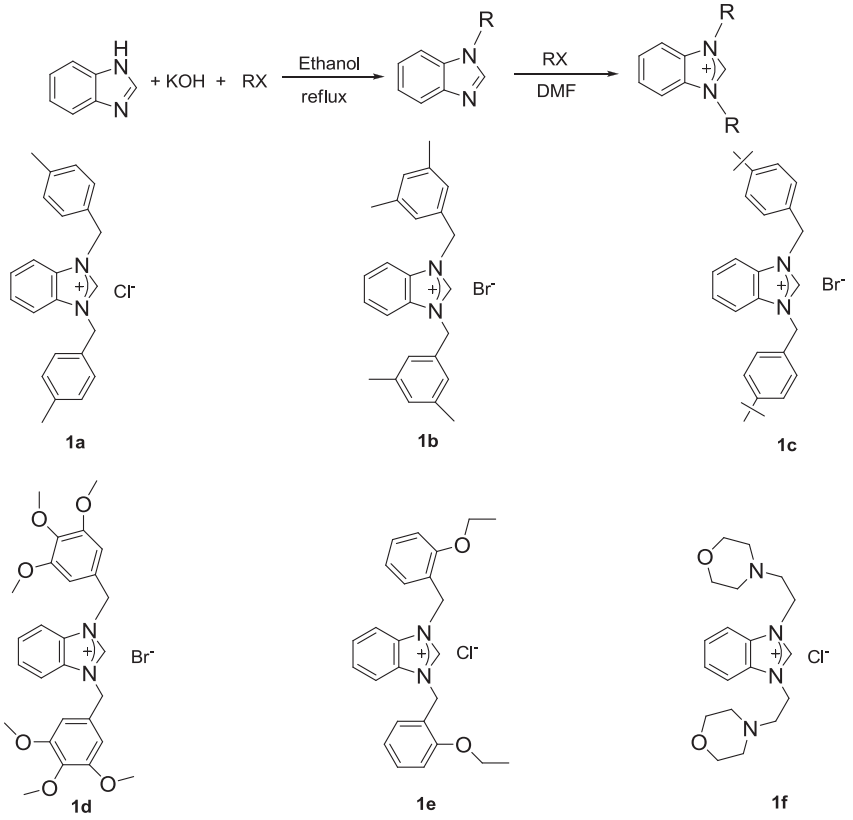
*Preparation of NHC–palladium–pyridine complexes **2a**–**f***

NHC–Pd-pyridine complexes (Scheme 2)were synthesized according to the method described by Organ et al. [13]. Structural definitions of **2a**–**f** were determined by NMR, IR spectroscopy, LC-MS (ESI) spectrometry, and elemental analysis. The ^{1}H NMR spectra for **2a**–**f** reveal disappearance of the distinctive NC*H*N proton signals. Also, ^{13}C{^{1}H} NMR spectra prove a increasing downfield shift of the NCN carbon from **1a**–**f** to **2a**–**f**: for example, the ^{13}C{^{1}H} N–C–N shifts of **1a** and **2a**, which are 139.5 and 162.7 ppm, respectively. This observation is confirmed by previous study [14].

In order to demonstrate the utility of these NHC–$PdCl_2$–pyridine complexes, we used them as co-catalysts in Suzuki–Miyaura coupling reactions, which are common industry-applicable processes.

Suzuki coupling reaction

We performed a series of the Suzuki coupling reactions with 4-chloroacetophenone and phenylboronic acid as a model reaction to



Scheme 1. Synthesis of symmetrical benzimidazole based-NHC ligand precursors, **1a**–**f**.