



Synthesis and characterization of amide-functionalized N-heterocyclic carbene–Pd complexes

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ABSTRACT

Amide-functionalized N-heterocyclic carbene (NHC) precursors such as azolium compounds have been designed and synthesized. Reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with the NHC–Ag complex derived from the azolium salt gave $[(\text{NHC})\text{PdCl}_2]_2$ or $(\text{NHC})_2\text{PdCl}_2$, whereas $\text{PdCl}_2(\text{PPh}_3)_2$ reacted with the Ag complex to afford a mixed carbene/phosphine complex such as $(\text{NHC})(\text{PPh}_3)\text{PdCl}_2$ together with a cationic $[(\text{NHC})(\text{PPh}_3)_2\text{PdCl}]^+\text{Cl}^-$ whose structure was characterized by X-ray crystallographic studies. Thus, the library of NHC–Pd complexes with a tethered amide group has been successfully expanded.

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1. Introduction

In recent years, tremendous efforts have been made toward the synthesis of transition metal complexes bearing N-heterocyclic carbene (NHC) ligands [1]. Of particular interest is introduction of a pendent functional group to an NHC, since the functionalized NHC can anchor free carbene to a metal site, serve as a chelate ligand, control the stability of metal center, or introduce chirality [2]. In 2007, Lee and co-workers designed *amide-functionalized* NHC ligands and synthesized palladium(II) and nickel(II) complexes with chelating anionic amidate/NHC ligands [3]. Structurally similar anionic-tethered gold(I), silver(I) and nickel(II) complexes were introduced by Ghosh and co-workers [4]. More recently, Bouwman and co-workers subsequently reported on nickel(II) complexes bearing bidentate NHC ligands functionalized with anionic amidate moieties for the Kumada coupling reaction [5]. Gornitzka and Hemmert and co-workers introduced tridentate NHC ligands and their palladium(II) and nickel(II) complexes [6]. Thus, anionic amidate/NHC ligands have received considerable attention.

In 2008, we synthesized a novel *hydroxyamide-functionalized* azolium salt derived from chiral β -amino alcohol [7]. By using the azolium salt, new tridentate anionic amidate/NHC–Pd(II) and

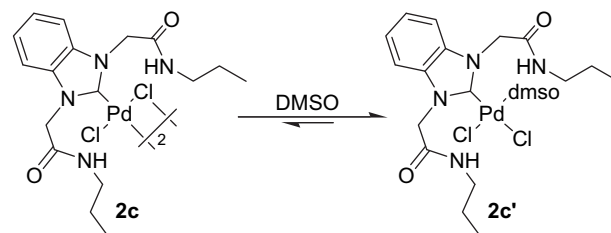
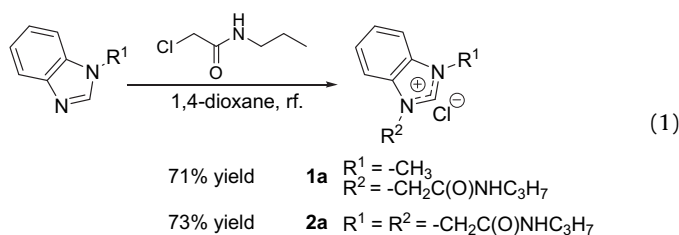
dianionic alkoxy/amidate/NHC–Pd(II) complexes have been developed. Importantly, the Pd(II) complex catalyzes an asymmetric oxidative Heck-type reaction with excellent enantioselectivity [8]. The above-mentioned anionic amidate/NHC–Pd(II) complexes by Lee and Ghosh were synthesized from *amide-functionalized* azolium compounds in the presence of an appropriate base such as K_2CO_3 [3,4]. In contrast, synthesis of the Pd(II) complex from the *hydroxyamide-functionalized* azolium salt does not require such a base [7]. These facts prompted us to examine the preparation of NHC–Pd(II) complexes from *amide-functionalized* azolium compounds in the absence of a base. During the course of this study, we found that various palladium complexes were synthesized by using $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ or $\text{PdCl}_2(\text{PPh}_3)_2$ as a palladium precursor. Herein, a systematic study on the synthesis of the NHC–Pd(II) complexes with amide functionalities is described.

2. Results and discussion

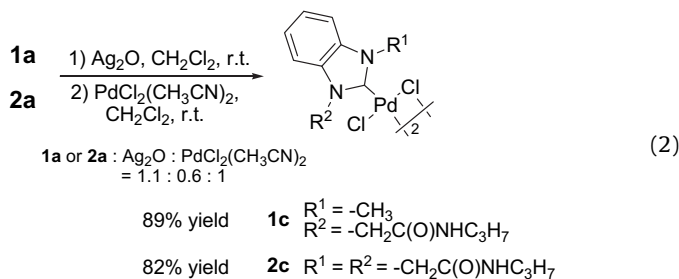
2.1. Synthesis of $[(\text{NHC})\text{PdCl}_2]_2$ complexes

The preparation of amide-functionalized NHC precursors such as 1-methyl-3-N-(propylacetoamido)benzimidazolium chloride (**1a**) and 1,3-N,N'-bis(propylacetoamido)benzimidazolium chloride (**2a**) is shown in Eq. (1). **1a** was prepared by reaction of 1-methylbenzimidazole with 2-chloro-N-propylacetamide in 1,4-dioxane under reflux. Similarly, **2a** was obtained in 73% yield.

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Scheme 1. Tentative structure of (NHC)(dmsO)PdCl₂ **2c'** in DMSO.

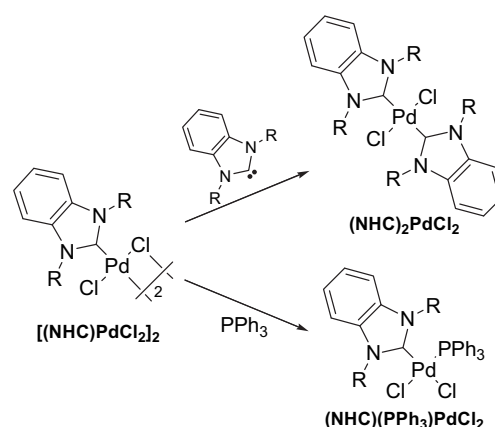
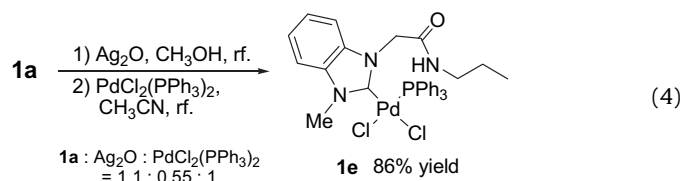
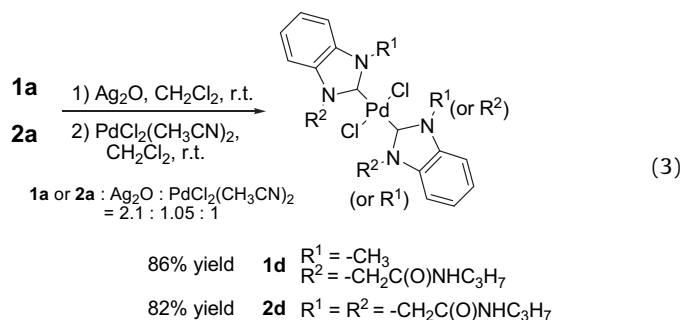
NHC complexes were successfully synthesized according to the Ag₂O method that was introduced by Lin et al. [9]. Ag₂O particularly serves as a mild base, reacting predominantly at the C₂ position of the azolium salt without deprotonation of other acidic protons. Treatment of **1a** with Ag₂O in CH₂Cl₂ at room temperature gave a white solid. The ¹H NMR spectrum of the solid without further purification suggests that NHC–Ag complex **1b** was obtained in almost pure form. The ¹³C NMR spectrum of **1b** contains the characteristic carbene signal at δ 191.4 ppm. Since the silver complexes **1b** and **2b** have light-sensitive character, synthesis of NHC–Pd complexes **1c** and **2c** was carried out by a one-pot procedure without purification of the NHC–Ag intermediates from **1a** and **2a**, respectively (Eq. (2)). After treatment of **1a** with Ag₂O, the resulting silver complex **1b** was allowed to react with PdCl₂(CH₃CN)₂ at room temperature to give the corresponding neutral amide-functionalized NHC–Pd complex **1c** in good yield. NHC–Pd complex **2c** was obtained in 82% yield from the NHC precursor **2a**. Synthesis of a similar iodo-bridged dimeric monodentate NHC–Pd complex by reaction of Pd(OAc)₂ with an imidazolium salt in the presence of NaI and NaOEt has been reported [10]. It should be noted that no anionic amidate/NHC–Pd type complex was formed from the reaction with *amide-functionalized* azolium salts **1a** and **2a**. These facts would strongly indicate that the hydroxyl group on a *hydroxylamide-functionalized* azolium salt is crucial for the formation of an anionic palladium amidate complex [7].



Interestingly, the ¹H NMR spectrum of **2c** in (CD₃)₂SO indicates that it exists as a mixture of two NHC–Pd compounds, whereas the spectrum in CD₃OD indicates that it exists only a single compound (Fig. 1). Attention should be paid to the signal of the methylene proton adjacent to the carbonyl group. In CD₃OD, it appears as a singlet at δ 5.65 ppm. In (CD₃)₂SO, it appears as two kinds of signals: an A₂ system (δ 5.60 ppm) and an AX system [δ 5.62 and 5.33 ppm (*J* = 16.4 Hz)], in the ratio 17:83, as determined by integration. This might indicate that in (CD₃)₂SO the major component (83%) is a new NHC–Pd complex **2c'** (Scheme 1). Indeed, it was reported that the donor numbers of (CH₃)₂SO, CH₃OH, H₂O, and CH₃CN are 30, 19, 18, and 14, respectively [11], indicating that (CH₃)₂SO can strongly coordinate with a metal.

2.2. Synthesis of (NHC)₂PdCl₂ and (NHC)(PPh₃)PdCl₂ complexes

Because the chloride-bridged dimeric monodentate NHC–Pd complex **2c** was found to vary in the presence of a strongly coordinating donor such as (CH₃)₂SO, we speculated that it might be possible to synthesize (NHC)₂PdCl₂ or (NHC)(PPh₃)PdCl₂, which is an analog of **2c'**, from [(NHC)PdCl₂]₂ **2c** in the presence of an additional NHC or PPh₃ ligand, respectively (Scheme 2).

Scheme 2. Working hypothesis for conversion of dimeric NHC–Pd complex into (NHC)₂PdCl₂ or (NHC)(PPh₃)PdCl₂.

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