Journal of Organometallic Chemistry 817 (2016) 1–14

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Fluxional Pd(II) NHC complexes – Synthesis, structure elucidation and catalytic studies

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ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form
14 April 2016
Accepted 2 May 2016
Available online 4 May 2016

Keywords:
Palladium(II)
NHC complexes
Dynamic NMR
DFT calculations
Catalytic studies

ABSTRACT

Four catalytically relevant Pd(II) complexes involving N-heterocyclic carbenes (NHCs) and bidentate N- and P-donor ligands were synthesized and characterized. The structures and conformations of the complexes were elucidated on the basis of combination of dynamic NMR and DFT studies. Conformational studies in respect to hindered rotation around C-N_{donor} and Pd-C_{NHC} bonds were performed resulting in surprisingly good agreement between the calculated and the experimental results. The results from dynamic NMR and DFT studies confirm hindered rotation around the C-N bond in 1,3-disubstituted imidazole complexes. The fluxional behavior of P-donor ligands includes exchange between left-handed and right-handed phosphine propellers. The catalytic studies of 1,3-disubstituted 4,5-fused imidazole complexes produced excellent activities in Suzuki–Miyaura Reaction.

1. Introduction

N-Heterocyclic carbenes (NHC) are state of the art ligands in organometallic chemistry [1–6] and catalysis [7–10]. The nitrogen atoms in the heterocycle offer possibilities for tuning the ligand structure – through changes in the N substituents, the steric demands and electronic properties of the ligand can be modified to provide complexes with enhanced catalytic performances [11–14]. Also, various functional groups can be introduced, resulting in complexes with wider applications [15,16]. The introduction of a suitable donor group can lead to versatile structures in ditopic complexes or enhanced catalytic performance of complexes with hemilabile ligands [17–22]. Potentially antibacterial compounds have also been synthesized by the introduction of a biologically active function [23–25]. In addition, complexes of bifunctional ligands can be immobilized or their solubilities altered by suitable functionalization to afford recoverable catalysts [26–30].

During the last decade, numerous applications of N-heterocyclic carbenes (NHCs) as ligands in all areas of transition metal catalysis have been found [7,31–33]. NHCs are strong, neutral σ-donor ligands which form very stable bonds with the majority of transition metals [7,33]. NHC complexes also possess greater thermal stability than their phosphane analogues, which benefits the catalyst stability. The most successful NHC cores are derived from imidazolium and 4,5-dihydroimidazolium salts, that have bulky substituents at both nitrogen atoms [31,34]. The steric and electronic properties NHCs can be tuned independently, because the N-substituents, are not directly connected to the carbene carbon atom and their influence on the electronic density of this atom is small [35,36]. The heterocyclic core determines the electronic properties of the carbene [37] and fusing an additional aromatic ring provides further possibilities for fine tuning of the electronic properties of the NHCs [38].

Recently 4-amino-3-nitro substituted 1,8-naphthalimides as potential photoactive sensors and starting compounds for further transformations to fluorescent sensors have been reported [39]. The application of 1,8-naphthalimide derivatives as the photoactive units for design of optical chemosensors for metal cations and protons with different mechanisms of analyte binding signal transduction and different receptors was recently reviewed [40]. In an ongoing investigation on catalysis we synthesized carbene complexes based on the fluorescent naphthalimide core connected/

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http://dx.doi.org/10.1016/j.jorganchem.2016.05.002
0022-328X/© 2016 Published by Elsevier B.V.

fused to an imidazolium salt. Since the fluxional behavior of a molecule may have a dramatic impact on the relaxation pathways from its respective excited states, it was important to study the dynamics of these newly synthesized compounds in details. In this study we introduce the 1,8-naphthalimides as an *N* substituent and as a fused aromatics to the NHC to form catalytically relevant Pd(II) complexes with additional bidentate *N*- and *P*-donor ligands to the metal.

Herein, we report the synthesis of novel Pd N-heterocyclic carbene complexes. Two of them, **1** and **2** (Fig. 1), are 1,3-disubstituted imidazole NHC complexes (*1,3-disubstituted*), while the others two are the corresponding 1,3-disubstituted 4,5-fused imidazole NHC complexes (*4,5-fused*), **3** and **4**. Conformational exchanges occurred in solution at rates that were intermediate on the NMR time scale. The ^{1}H NMR signals of complexes **1, 2** and **4** were broad at room temperature and therefore, it was necessary to study their NMR spectra at lower temperatures. The NMR spectra of complex **3** were recorded at room temperature due to the presence of the single preferred conformer. The possible conformers, exchange routes and the origin of the observed exchanged were studied by combination of dynamic NMR and DFT calculations.

The assignment of VT NMR spectra of studied complexes is a challenging task that required combination of dynamic NMR study and DFT calculation. Dynamic NMR study using 2D EXSY spectra provides information about the exchange routes and the corresponding rate constants can be calculated directly from the volume integrals. The DFT calculations of GS structures provide information about thermodynamic stability of possible conformers. Calculating the theoretical populations and comparing them with the experimental one allows the conformers assignment. If given NMR chemical shifts are sensitive to the exchange, comparison of DFT calculated and the experimental values can confirm the assignment of conformers. The comparison of experimental and DFT calculated barriers can reveal the exchange mechanism. This integrated approach, which combines methods of dynamic NMR spectroscopy and computational chemistry was successfully applied recently for studying the structure and exchange mechanism of *ortho*-diphenylphosphinobenzenecarboxamide ligands [41] and atropisomers of 2,2′-diaryl-1,1′-binaphthalenes containing three stereogenic axes [42].

2. Results and discussion

2.1. Synthesis of complexes

The first step of synthesis of the desired *1,3-disubstituted* Pd(II) NHC complexes **1** and **2** was preparation of imidazolium salt **NHC·HBr**, which was synthesized from commercial 4-bromo-1,8-naphthalic anhydride (Scheme 1). 6-Bromo substituted naphthalimide **II** was prepared by reaction of 2,6-diisopropylaniline and 4-bromo-1,8-naphthalic anhydride in refluxing acetic acid according the literature [43]. The naphthalimide **II** reacts with imidazole in the presence of CuI, proline-based ligand and Cs_2CO_3 in DMF to obtain compound **III** [44], which was quaternized with 3,3-dimethylallyl bromide in ethyl acetate to yield the corresponding imidazolium bromide salt (**NHC·HBr**).

The desired Pd(II) NHC complexes were synthesized in good yields using a well-established procedure (Scheme 2), via generation of carbene *in situ* from the relevant imidazolium salt by a weak base in the presence of corresponding dimeric palladacycles [45,46].

2.2. Conformations and exchange mechanisms of complexes 1–4

The structures of the newly synthesized complexes **1**–**4** were confirmed by 1D and 2D NMR spectra. Conformational exchanges occurred in solution at rates that were intermediate on the NMR time scale. For complexes **1**, **2** and **4** the signals were broad at room temperature and therefore, it was necessary to measure NMR spectra at lower temperatures. However, the spectra of complex **3** were recorded at room temperature due to the presence of a single preferred conformer.

Four conformers are predictable for *1,3-disubstituted* Pd(II) NHC complexes **1** and **2** (Scheme 3): two conformers due to rotation around the C-N bond and two conformers due to rotation around C-Pd bond. The ^{1}H, ^{13}C and ^{31}P NMR spectra of complex **2** showed the expected four conformers, while the ^{1}H and ^{13}C NMR spectra of complex **1** showed only two conformers. Therefore it can be concluded that restricted rotation around only one of the two possible bonds occurs, while in complex **2** the inversion of phosphine helicity is responsible for additional conformers.

The decrease of observed number of conformers in *4,5-fused* Pd(II) NHC complexes **3** and **4** (one and two, respectively) compared to *1,3-disubstituted* Pd(II) NHC complexes **1** and **2** (two and four, respectively) can be explained by the restricted rotation around C-N bond (Fig. 2). Further this conclusion was confirmed by comparison of experimental and DFT calculated rotational barriers around C-N and C-Pd bonds.

In Scheme 4 the potential diastereomers of complex **2** as viewed down the C-Pd-P bonds are presented. The diastereomers are related horizontally by rotation around C-N amine bond and vertically by inversion of phosphine helicity. The top conformers are right-handed twist (Δ) propellers and bottom conformers are left-handed twist (Λ) propellers. Similar inversion of phosphine

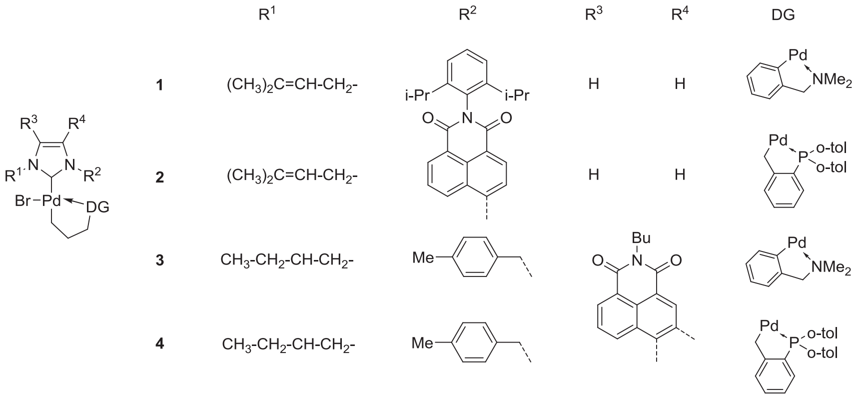

Fig. 1. Complexes **1**–**4** (*o*-tol = *ortho*-tolyl).