



## Note

# Synthesis and characterization of new (pyrazolyl)aryl phosphinite PCN pincer palladium(II) complexes

An-Ting Hou, Yan-Jing Liu, Xin-Qi Hao, Jun-Fang Gong\*, Mao-Ping Song\*

Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Zhengzhou University, Zhengzhou 450052, PR China

## ARTICLE INFO

## Article history:

Received 15 March 2011

Received in revised form

26 April 2011

Accepted 28 April 2011

## Keywords:

Unsymmetrical

PCN pincer palladium(II) complex

Pyrazolyl

Phosphinite

## ABSTRACT

Two unsymmetrical PCN pincer Pd(II) complexes **3a–3b** which are based on (pyrazolyl)aryl phosphinite ligands and contain two fused six-membered palladacycles have been synthesized from 3-(3,5-dimethylpyrazol-1-ylmethyl)benzyl alcohol (**2**) by one-pot phosphorylation/palladation reaction via C–H bond activation of the related ligands. The pyrazole-coordinated phosphine-free Pd(II) complex (**4**) was also isolated in the preparation of pincer complex **3a**. The new complexes were characterized by elemental analysis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR (for pincer complexes) and IR spectra. And the molecular structures of **3b** and **4** have been further determined by X-ray single-crystal diffraction. The pincer Pd complexes **3a** and **3b** exhibited rather low activity in the allylation of benzaldehyde.

© 2011 Elsevier B.V. All rights reserved.

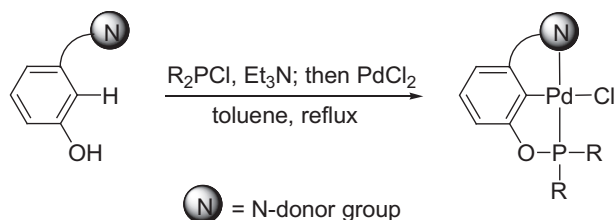
## 1. Introduction

Pincer palladium complexes with monoanionic terdentate ligands have found wide applications in organometallic homogeneous catalysis [1]. For example, they have been used as efficient catalysts for a variety of C–C bond forming reactions including allylation of aldehydes and imines with allylic stannanes [2–8], palladium-catalyzed cross-coupling reactions such as the Heck reaction [9–12], Suzuki–Miyaura [13–18] and Sonogashira couplings [14,19] as well as  $\alpha$ -arylation of ketones [20]. Palladium pincers have also been successfully applied to the synthesis of organometallic reagents such as allyl [2] or allenyl [21] stannanes, where in most cases they cannot be replaced with simple Pd sources like Pd(OAc)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>(dba)<sub>3</sub>. Among the pincer Pd catalysts, the most common ones are symmetrical ECE type with two identical donor groups (E = PR<sub>2</sub>, OPR<sub>2</sub>, NR<sub>2</sub>, pyridine, N-containing heterocycles, SR, etc.) in the side arms of the central aryl ring and two equivalent five-membered palladacycles, particularly those of PCP and NCN Pd pincers. The reactivities of the Pd center in these symmetrical complexes can be easily tuned by appropriate choice of substituents on the heteroatom donors or/and heteroatom donors. Nonetheless, introduction of two different donors in the pincer ligand, which gives unsymmetrical pincer Pd complexes, also seems to be an appealing strategy to improve the properties of the ensuing complexes [22–25]. In fact, it has been found that some

unsymmetrical pincer Pd complexes do outperform the related symmetrical ones on catalytic activity under certain circumstances. For example, Klein Gebbink and Szabó et al. have demonstrated that the unsymmetrical PCS palladium pincer is the fastest catalyst in aldol condensation reaction between benzaldehyde and methyl isocyanacetate among the three pincer complexes including symmetrical SCS and PCP complexes [26]. We have also found that in the Suzuki couplings conducted at 40–50 °C, the unsymmetrical (pyrazolyl)aryl phosphinite or (imino)aryl phosphinite PCN Pd complexes exhibit much higher activity than the related symmetrical bis(phosphinite) PCP complexes [27,28]. Despite the facts, reports on the unsymmetrical Pd complexes are relatively few compared to the symmetrical ones and one obvious reason for this is their relatively complicated synthesis. Recently, we have developed a facile, direct method based on one-pot phosphorylation/palladation reaction for the preparation of unsymmetrical PCN pincer palladium complexes containing a phosphinito group (Scheme 1) [27–30]. By using this method, a variety of achiral and chiral Pd pincers which comprise pyrazolyl-, amino-, imino- or chiral imidazolyl as a N-donor and phosphinito as a P-donor have been conveniently synthesized in good yields (42–72%). Among them, the (pyrazolyl)aryl phosphinite PCN compound **1** (Scheme 2) containing fused five- and six-membered metallacycles was obtained by the reaction of pyrazolyl-containing *m*-phenol derivative, which was derived from *m*-hydroxybenzaldehyde, with diphenylchlorophosphine in the presence of Et<sub>3</sub>N, followed by the addition of PdCl<sub>2</sub> [27]. In continuation of this investigation, herein we would like to report the synthesis of new (pyrazolyl)aryl phosphinite PCN

\* Corresponding authors. Tel.: +86 371 67763869; fax: +86 371 67766667.

E-mail addresses: [gongjf@zzu.edu.cn](mailto:gongjf@zzu.edu.cn) (J.-F. Gong), [mpsong@zzu.edu.cn](mailto:mpsong@zzu.edu.cn) (M.-P. Song).



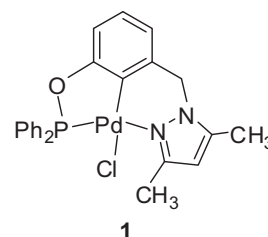
**Scheme 1.** One-pot phosphorylation/palladation reaction for the synthesis of the unsymmetrical PCN pincer palladium(II) complexes.

Pd(II) complexes **3a–3b** containing two six-membered metallacycles by one-pot phosphorylation/palladation reaction of pyrazolyl-containing *m*-benzyl alcohol derivative **2** (Scheme 3). The pincer Pd complexes were applied to the allylation of aldehydes. The results are shown as below.

## 2. Results and discussion

### 2.1. Synthesis and characterization

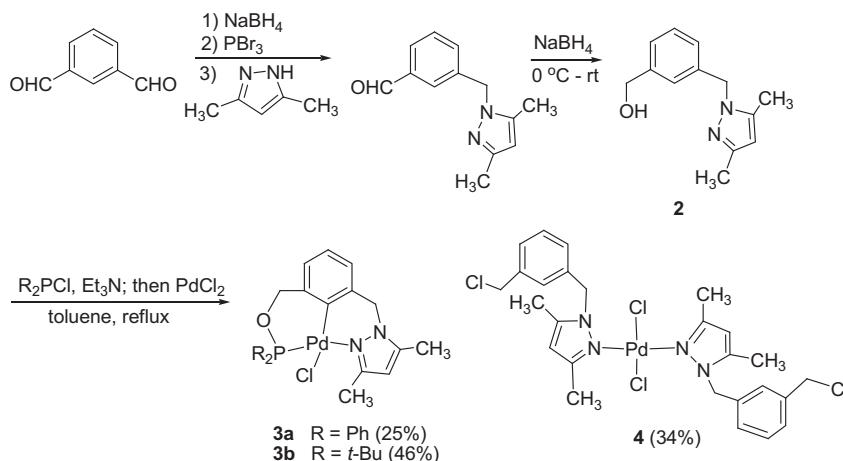
Starting from inexpensive, commercially available isophthalaldehyde, the 3-(3,5-dimethylpyrazol-1-ylmethyl)benzaldehyde could be prepared after selective reduction of one aldehyde to hydroxymethyl, bromination and nucleophilic substitution with 3,5-dimethylpyrazole according to the published procedure [31] (Scheme 3). Then reduction of the remaining aldehyde group by NaBH<sub>4</sub> easily gave the required 3-(3,5-dimethylpyrazol-1-ylmethyl)benzyl alcohol **2**. The following “one-pot phosphorylation/palladation reaction” was carried out in a way similar to that of 3-(3,5-dimethylpyrazol-1-ylmethyl)phenol. Thus, **2** reacted with diphenylchlorophosphine or di-*tert*-butylchlorophosphine in the presence of triethylamine in toluene at reflux for 8 h, followed by the addition of palladium chloride and reflux for another 18 h. The expected new PCN pincer palladium complexes **3a** and **3b** with two six-membered metallacycles were successfully obtained as white solids after chromatography on silica gel in 25% and 46% yields, respectively. Interestingly, the hydroxymethyl-chlorinated and pyrazole-coordinated phosphine-free Pd(II) complex **4** was also isolated in the preparation of pincer complex **3a**, which led to the lower yield of **3a**. Prolonging the reaction time of **2** with Ph<sub>2</sub>P-Cl for phosphorylation could not inhibit effectively the formation of compound **4**, although it was not observed in the synthesis



**Scheme 2.** Structure of the (pyrazolyl)aryl phosphinite PCN pincer Pd(II) complex **1** containing fused five- and six-membered palladacycles.

of complex **3b**. The results indicated that phosphorylation of hydroxymethyl with dialkylchlorophosphine was relatively difficult compared to that of phenolic-hydroxy group under similar conditions.

All of the new Pd complexes are air- and moisture- stable both in the solid state and in solution. They were well characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>31</sup>P {<sup>1</sup>H} NMR (for pincer complexes) and IR spectra. The formation of the pincer complexes was confirmed by the single resonance at  $\delta$  about 117 ppm (for Ph<sub>2</sub>PO) or 160 ppm (for *t*-Bu<sub>2</sub>PO) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra and the absence of the singlet corresponding to the central aryl proton located ortho to both –CH<sub>2</sub>OR and –CH<sub>2</sub>Pz in the <sup>1</sup>H NMR spectra. In addition, the –CH<sub>2</sub>Pz protons appeared as a singlet at  $\delta$  5.13 ppm and the –CH<sub>2</sub>OH protons appeared as a doublet at 4.60 ppm in the PCN ligand precursor **2**. While in the Pd complexes **3a** and **3b**, the two protons of –CH<sub>2</sub>Pz appeared in two different positions including the doublet at  $\delta$  5.49 and the multiplet at  $\delta$  4.96–4.85 ppm (5.59 and 4.95–4.83 ppm, respectively for **3b**), and the –CH<sub>2</sub>OPR<sub>2</sub> protons were observed as one doublet of doublets at  $\delta$  5.10 ppm and one multiplet at  $\delta$  4.96–4.85 ppm (only one multiplet at  $\delta$  4.95–4.83 ppm for **3b**). The <sup>13</sup>C NMR spectra of the pincer complexes exhibited intensive <sup>31</sup>P–<sup>13</sup>C couplings. On the other hand, although X-ray analysis clearly indicates that the non-cyclometallated compound **4** adopts a *trans*-geometry in the solid state with the two chloride ligands being in a *trans*-position (vide infra), its <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra demonstrated more signals than expected, suggesting the presence of isomers in solution. For example, the <sup>1</sup>H NMR spectrum of **4** showed two singlets at  $\delta$  6.16 and 5.74 ppm, respectively for –CH<sub>2</sub>Pz protons as well as two singlets at  $\delta$  4.59 and 4.46 ppm, respectively for –CH<sub>2</sub>Cl protons. The signals for the pyrazole proton were observed at  $\delta$  5.90 and 5.94 ppm, respectively as two singlets and the four singlets at  $\delta$  2.51,



**Scheme 3.** Synthesis of the new (pyrazolyl)aryl phosphinite PCN pincer Pd(II) complexes **3a–b** with two fused six-membered palladacycles.

Download English Version:

<https://daneshyari.com/en/article/1323970>

Download Persian Version:

<https://daneshyari.com/article/1323970>

[Daneshyari.com](https://daneshyari.com)