



NCN palladium pincer *via* transmercuration. Synthesis of [2-(2-oxazoliny)-6-(2-pyridyl)] phenylpalladium(II) chloride and its catalytic activity in Suzuki coupling

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ABSTRACT

The unsymmetrical NCN ligand 1-(2-oxazoliny)-3-(2-pyridyl)benzene **6** was synthesized starting from *m*-bromotoluene after a series of transformations. The reaction of **6** and mercury (II) acetate resulted in mercurial derivative **7** which was transformed into the corresponding NCN palladium pincer **8** *via* transmercuration. The ultraviolet spectra of **6–8** in acetonitrile were also studied. The structures of **6** and **8** were further confirmed by X-ray single crystal diffraction. The carbon–carbon cross coupling reactions between aryl halides and phenylboronic acid catalyzed by **8** were investigated. The results indicate that this palladium pincer is more highly active to the coupling of aryl bromides than aryl chlorides.

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As an important class of pincers, palladium complexes have been widely used in organic synthesis and material sciences [1,2]. Their synthesis normally includes C–H bond activation, oxidative addition and transmetalation. C–H bond activation is very useful for preparation of PCP, SCS and some NCN pincers bearing the side arms, because without this requirement, such activation for NCN ligands will occur at the 4-, 6-positions [3]. The latter two methods have no such limitation, but both oxidative addition and most of transmetalation reactions *via* organostannanes and organolithiums require the comparatively expensive 2-halo substituted starting material and low reaction temperature (–78 °C) [4]. Though there are also reports on the synthesis of palladium pincers *via* organomercurials, the examples in this aspect are still rare [5]. As we know, mercury (II) salts are cheap and easily available, and react normally under mild reaction. Moreover, their good functions on site-directing and transmetalation are documented very well in literatures [6]. Thus, to prepare the palladium pincers *via* mercurials will become an attractive choice. Herein, we present an example of unsymmetrical NCN palladium pincer, *i.e.* [2-(2-oxazoliny)-6-(2-pyridyl)]phenylpalladium (II) chloride *via* transmercuration. In addition, the photophysical properties of the ligand, its mercurial and the corresponding palladium pincer and catalytic activity of this pincer in Suzuki coupling between aryl halides and phenylboronic acid were also investigated.

The synthetic route for the unsymmetrical NCN palladium pincer **8** was shown in Scheme 1. The coupling reaction between Grignard

reagent derived from *m*-bromotoluene **1** and 2-bromopyridine catalyzed by Ni(dppe)₂Cl₂ resulted in 2-*m*-tolylpyridine **2** in a good yield (80%). An attempt to catalyze this coupling with Ni(acac)₂Cl₂ was not successful [7]. The NCN ligand **6** was synthesized starting from phenylpyridine **2** after a series of transformations including oxidation [8], acylation/amination, chlorination as well as ring closure. Elemental analysis and IR spectrum (ν 1647 cm^{–1}, C=N) as well as the NMR (δ 149.24 ppm, O=C=N) of **6** confirmed its structure. The reaction of **6** with one equivalent of mercury (II) acetate was carried out in refluxing methanol and followed by treatment with lithium chloride to give out organomercurial **7** in 44% yield after purification. In ¹³C NMR of **7**, a signal at δ 167.51 ppm corresponds to the C1, implying that the mercuration of ligand **6** occurs at the expected position. Transmetalation reaction of **7** with palladium (II) acetate was carried out in the same manner as the mentioned mercuration previously. The pure palladium pincer **8** was isolated in the yield of 35%.

In order to obtain unambiguous characterizations of **6–8**, the single crystal X-ray diffraction study of **6** and **8** was undertaken (Figs. 1 and 2). Fig. 1 clearly demonstrates that a dihedral angle 29.18° exists between pyridyl and phenyl rings in the ligand. After the introduction of palladium atom, these two rings are closed to be coplanar (dihedral angle: 0.2° in **8**). In addition, it is also observed that the moieties of O=C=N in both **6** and **8** are coplanar with their corresponding phenyl rings (dihedral angle: 0.29° in **6**, 0.3° in **8**, respectively). The C–Pd bond length (1.917(4) Å) and the average length of N–Pd bond (2.061 Å) are the same as those already reported NCN palladium pincers (Table 1) [9].

UV-vis spectra. The UV-vis spectra of **6–8** in acetonitrile were recorded (Fig. 3) and the data were tabulated in Table 2. From Table 2,

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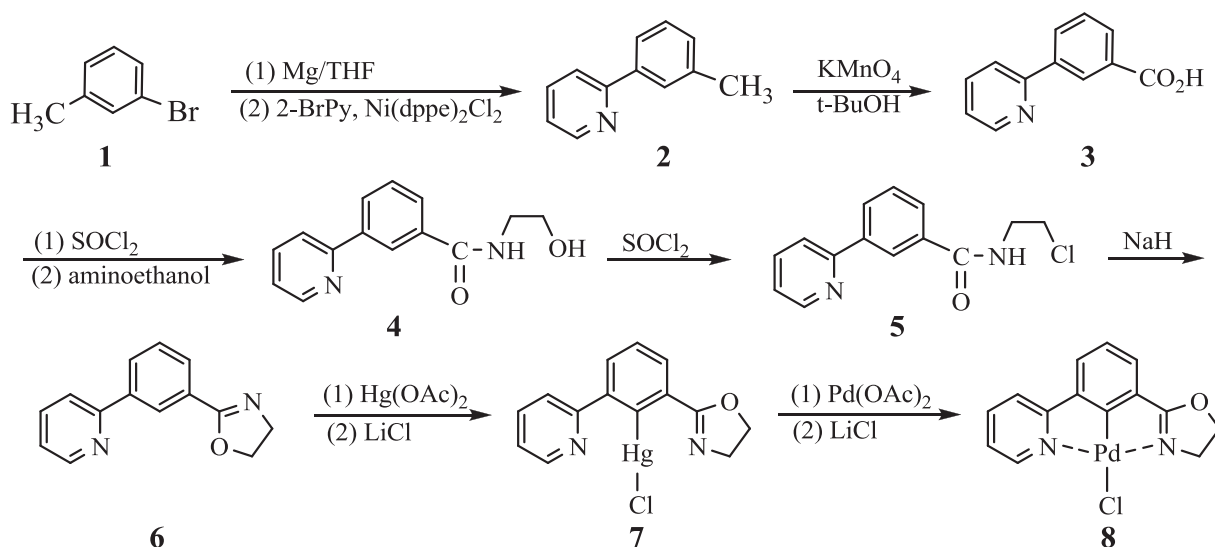
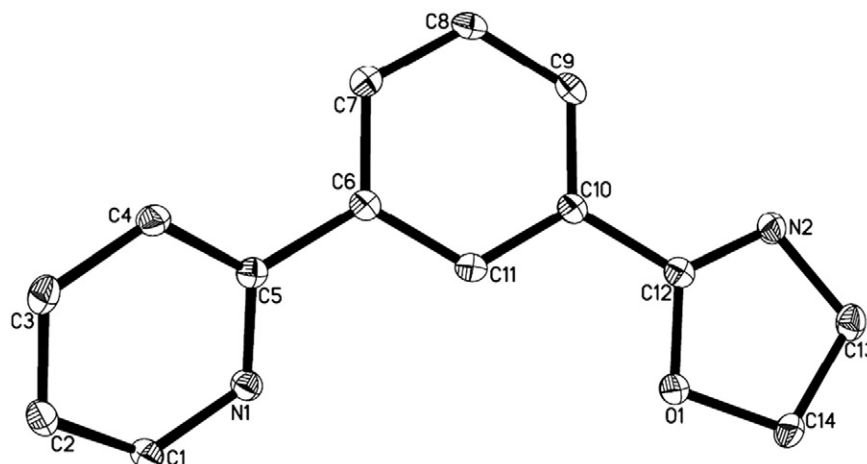
Scheme 1. Synthesis of the unsymmetrical NCN palladium pincer **8**.

Fig. 1. Crystal structure of **6** (H atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): O1–C12 = 1.3584(2), O1–C14 = 1.4560(1), N2–C12 = 1.2734(2), N2–C13 = 1.4713(2), C12–O1–C14 = 105.82(9), C12–N2–C13 = 106.54(1), C9–C10–C12 = 119.54(1), C11–C10–C12 = 120.53(1).

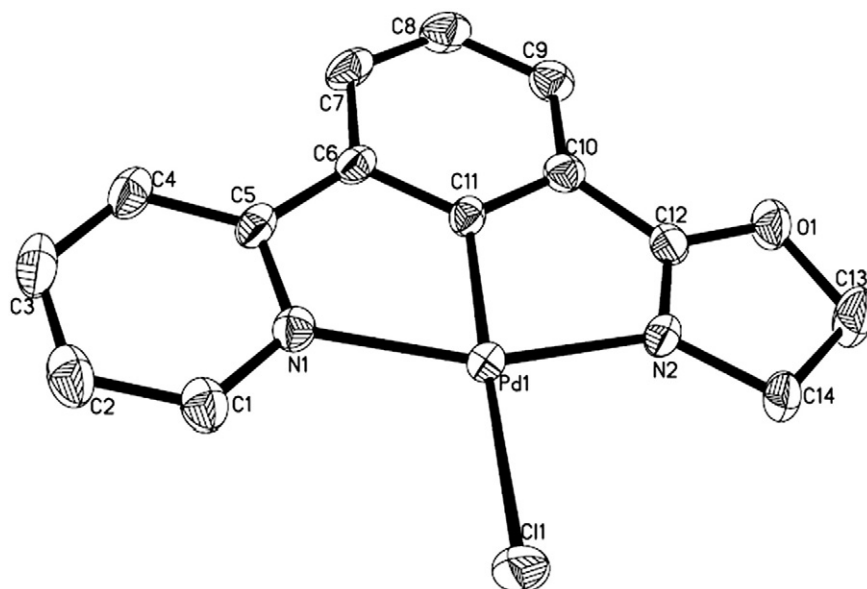


Fig. 2. Crystal structure of **8** (H atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): N1–Pd1 = 2.066(3), N2–Pd1 = 2.055(3), C11–Pd1 = 1.917(4), Cl1–Pd1 = 2.4178(1), C11–Pd1–N2 = 79.36(1), C11–Pd1–N1 = 79.65(1), N2–Pd1–N1 = 159.01(1), C11–Pd1–Cl1 = 177.82(1).

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