Inorganic Chemistry Communications 32 (2013) 78–81

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

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

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

Ping Li, Hai-Feng Zhou, Fang Liu, Zhao-Xia Hu, Hong-Xing Wang *

Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, PR China

A R T I C L E I N F O

Article history:
Received 5 January 2013
Accepted 8 March 2013
Available online 26 March 2013

Keywords:
Palladium
Mercury
Pincer
Transmetalation
Catalytic activity

A B S T R A C T

The unsymmetrical NCN ligand 1-(2-oxazolinyl)-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.

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-oxazolinyl)-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)$_2$Cl$_2$ resulted in 2-*m*-tolylpyridine **2** in a good yield (80%). An attempt to catalyze this coupling with Ni(acac)$_2$Cl$_2$ 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 ^{13}C 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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* Corresponding author. Tel./fax: +86 22 27403475.
E-mail address: hongxing_wang@tju.edu.cn (H.-X. Wang).

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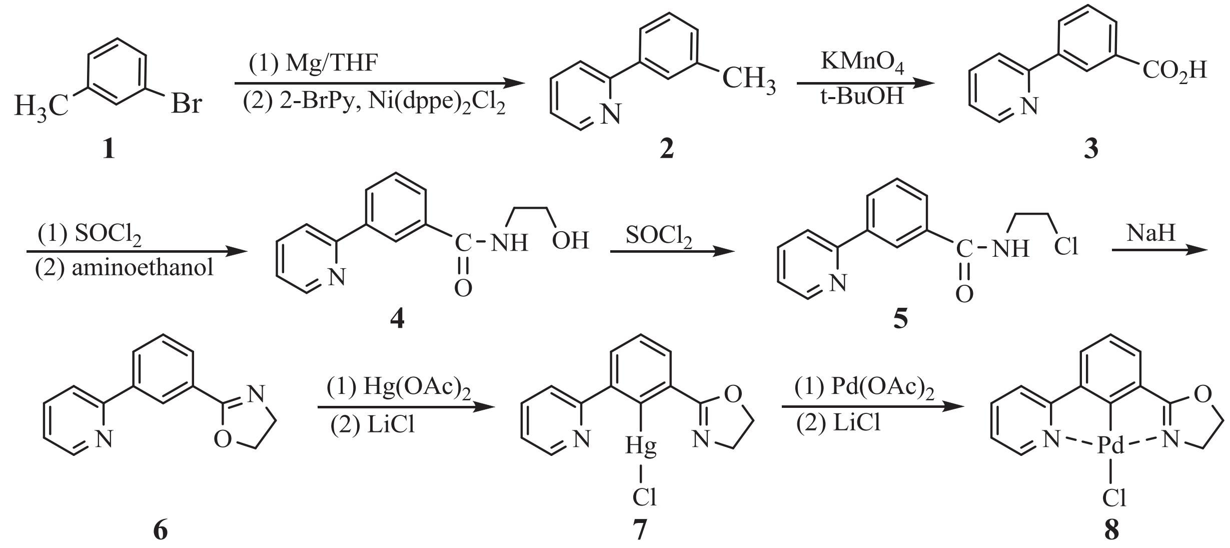
http://dx.doi.org/10.1016/j.inoche.2013.03.012



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

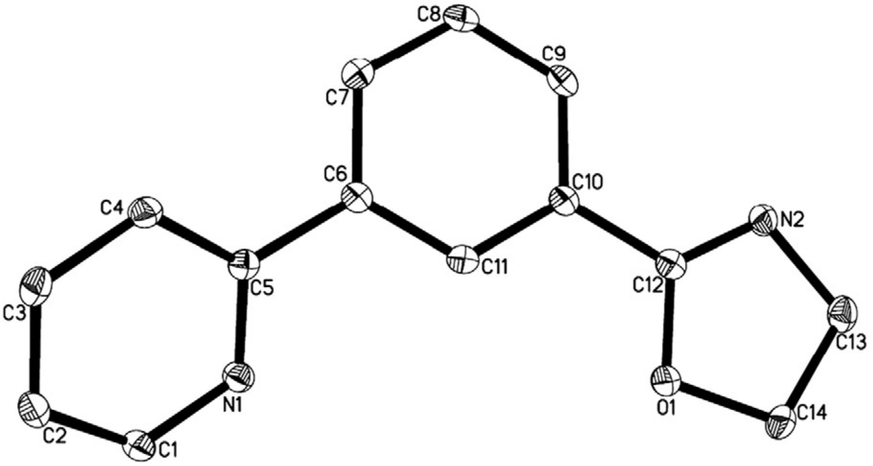


Fig. 1. Crystal structure of **6** (H atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): O1–C12 = 1.3584(2), O1–C14 = 1.4560(1), N2–C12 = 1.2734(2), N2–C13 = 1.4713(2), C12–O1–C14 = 105.82(9), C12–N2–C13 = 106.54(1), C9–C10–C12 = 119.54(1), C11–C10–C12 = 120.53(1).

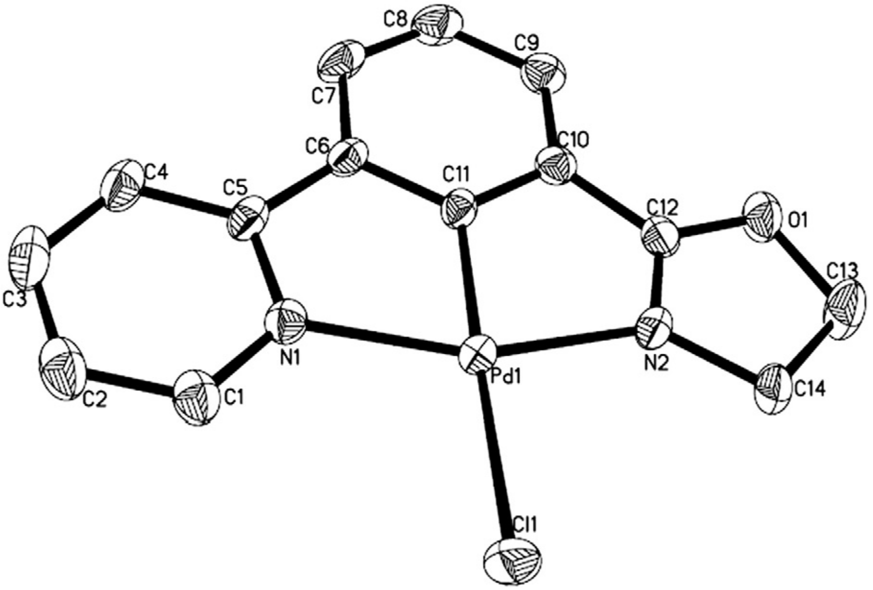


Fig. 2. Crystal structure of **8** (H atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): N1–Pd1 = 2.066(3), N2–Pd1 = 2.055(3), C11–Pd1 = 1.917(4), Cl1–Pd1 = 2.4178(1), C11–Pd1–N2 = 79.36(1), C11–Pd1–N1 = 79.65(1), N2–Pd1–N1 = 159.01(1), C11–Pd1 –Cl1 = 177.82(1).

Table 1
Crystal data and structure refinement parameters for **6** and **8**.

Structure parameters	6	8
Empirical formula	$C_{14}H_{12}N_2O$	$C_{14}H_{11}ClN_2OPd$
Formula weight	224.26	365.10
$F(000)$	472	360
Crystal size/mm	$0.18 \times 0.12 \times 0.10$	$0.08 \times 0.06 \times 0.04$
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2(1)/c$	Triclinic, $P1$
a/(Å), b/(Å), c/(Å)	5.7024(11), 9.4926(19), 20.010(4)	6.7703(1), 9.762(2), 9.864(2)
$\alpha/(°)$, $\beta/(°)$, $\gamma/(°)$	90, 92.23(3), 90	103.47(3), 90.55(3), 100.41(3)
$V/(Å^3)$	1082.3(4)	622.6(2)
Z	4	2
Calculated density/$Mg{\cdot}m^{-3}$	1.376	1.947
θ range for date collection	$1.13° \le \theta \le 25.01°$	$2.13° \le \theta \le 25.01°$
Limiting indices	$-5 \le h \le 6, -10 \le k \le 11, -23 \le l \le 23$	$-8 \le h \le 8, -11 \le k \le 10, -10 \le l \le 11$
Reflections collected/unique	6957/1889 [$R(int) = 0.0311$]	4506/2156 [$R(int) = 0.0238$]
Data/restraints/parameters	1889/0/154	2156/0/173
R indices (all data)	$R1 = 0.0398$, $wR2 = 0.1015$	$R1 = 0.0345$, $wR2 = 0.0741$
Final R_1, $wR_2[I > 2\sigma(I)]$	0.0361, 0.0980	0.0307, 0.0715
Largest diff. hole and peak	0.189, −0.195e. $Å^{-3}$	1.973, −0.353e. $Å^{-3}$

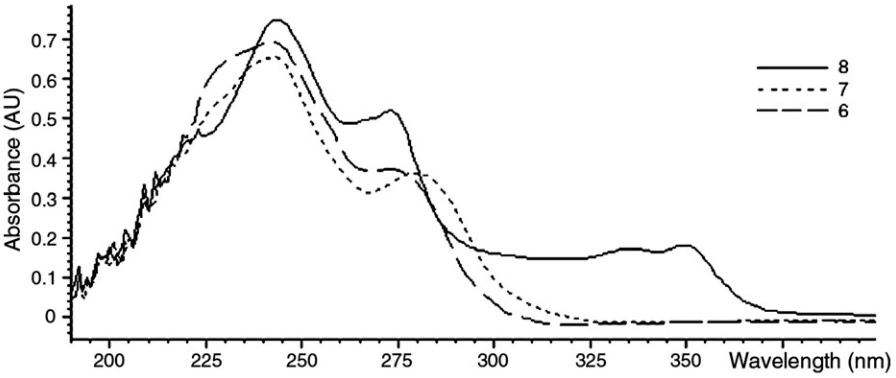


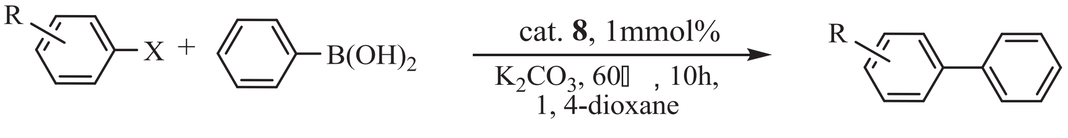
Fig. 3. UV−vis spectra of **6**–**8**. Substance concentration: 1.27×10^{-4} mol/L(**6**), 1.15×10^{-4} mol/L(**7**), 1.77×10^{-4} mol/L(**8**). Solvent: CH_3CN.

Table 2
UV absorption data of **6**–**8**.

Complex	6	7	8
λmax (nm)	242, 273	243, 280	244, 273, 336, 350

it can be seen that the absorption bands of **6**–**8** at λ_{max} ~ 243 and 273 nm, respectively are ascribed to the $\pi \rightarrow \pi^*$ electron transition from the O–C=N moiety of the oxazolinyl ring to the phenyl ring and these results are in good agreement with the fact as discussed in X-ray crystal analysis. The absorption bands at $\lambda_{max} = 336$, and 350 nm in **8** are most likely caused by coplanarity between pyridyl and phenyl rings. It is worth noting that a small red shift from λ_{max} 273 nm (**6**) to 280 nm (**7**) indicates that a weak N–Hg interaction might exist in **7** between nitrogen atom in the O–C=N moiety and mercury atom, and this phenomenon is in consistence with other nitrogen-containing organomercurials [6,10].

Suzuki coupling. A variety of pincer palladium complexes were emerging as a new class of efficient catalysts for the carbon–carbon bond formation reactions. In order to test the catalytic activity of **8**, the Suzuki coupling between aryl halides with phenylboronic acid were assessed (Scheme 2). All the experiments were carried out under the same optimized conditions (1,4-dioxane, 60 °C for 10 h, K_2CO_3 as the base, catalyst loading: 1 mmol%) and the results were summarized in Table 3. From Table 3, a good catalytic activity of **8** was observed, and as expected, aryl bromides (Entries 1–8) were more reactive than their chlorides congeners (Entries 9–15). It was also found that the couplings of aryl bromides bearing electron-withdrawing groups (Entries 4–8) were easier than those bearing electron-donating groups (Entries 1–3) and a similar phenomenon was observed in the couplings of aryl chlorides (Entries 11–14 *vs* Entry 9).



Scheme 2. Suzuki coupling between aryl halides and phenylboronic acid.

Table 3
The Suzuki couplings of aryl halides and phenylboronic aicd catalyzed by **8**.[a]

Entry	X	R	Yield (%)[b]
1	Br	4-MeO	90.3
2		4-Me	91.0
3		3-Me	90.5
4		4-O_2N	92.4
5		4-Cl	91.3
6		4-$COCH_3$	95.3
7		4-CO_2CH_3	94.8
8		2-Py	91.9
9	Cl	4-MeO	43.2
10		H	56.6
11		4-CH_3CO	68.2
12		4-O_2N	73.7
13		4-$COCH_3$	78.1
14		4-CO_2CH_3	77.3
15		2-Py	73.0

[a] Reagents: ArX (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (2.0 mmol), and 1,4-dioxane (10 ml).
[b] Isolated yields, average two runs.

Acknowledgments

We are grateful to Li-Ke Chemical Corporation limited (China) for the financial support for this project.

Appendix A. Supplementary material

The syntheses and characterizations of **2**–**8** and catalytic experiment of **8** can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche. CCDC 916904 and 916905 contain the supplementary crystallographic data for complexes **6** and **8**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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