Synthesis of Novel N-Heterocyclic Carbene-Oxazoline Palladium Complexes and Their Applications in Suzuki–Miyaura Cross-Coupling Reaction

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Received: 18.04.2013; Accepted after revision: 02.05.2013

Abstract: A series of novel N-heterocyclic carbene-oxazoline ligands were synthesized in six steps. Palladium complexes were obtained by deprotonation of the benzimidazole salts and subsequent ligation with $Pd(OAc)_2$ in THF. Different types of cyclic bis- and tetrapalladium complexes were achieved by modifying substituent of oxazoline group. The structures of these palladium complexes were characterized by NMR and X-ray diffraction analysis. Catalytic properties of these Pd-complexes were tested by Suzuki–Miyaura cross-coupling reaction.

Key words: N-heterocyclic carbene, oxazoline, palladium complex, Suzuki–Miyaura cross-coupling reaction

N-Heterocyclic carbenes (NHCs) and their transition metal complexes have rapidly been explored since the first synthesis of an isolable carbene species by Arduengo et al. in 1991.[1] N-Heterocyclic carbene ligands have quite different properties with general phosphine ligands by stronger σ-donor but weaker π-acceptor abilities.[2] NHC ligands can be easily used to complex with most of main group elements and transition metals, such as Pd,[3] Rh,[4] Ru,[5] Ir[6] and Au.[7] Especially, most of metal complexes ligated with NHC ligands are air/moisture stable, which makes handling of these complexes become much more convenient.[8] A range of very active catalysts ligated with NHC ligands have been obtained. Examples for the use of NHC ligands in modern synthesis are numerous, such as Grubbs NHC-Ru complexes catalyzed metathesis,[5a–c] Nolan's NHC-Pd and Organ's PEPPSI NHC-Pd complexes catalyzed coupling reactions,[9] NHC-Ir complexes catalyzed hydrogenations[6a] and hydrosilylation reactions catalyzed by Shi's NHC-Rh complexes,[4a,b] indicating the remarkable achievements with NHC ligated metal complexes.

Metallosupramolecular self-assembly has been a field of intensive research since Lehn first demonstrated the spontaneous formation of a double helical complex from bipyridine and Cu(I).[10] Subsequently a large number of metallosupramolecules have been obtained by self-assembly.[11] Among the early supramolecular assemblies were molecular square like $[\mathbf{A}]^{8+}$ (Figure 1), which was first synthesized by Fujita et al.[12] and subsequently studied by Stang[13] and others.[14] NHCs as an important class of ligands in organometallic chemistry have also been used in the field of supramolecular assembly.[15] Typical NHC–metal molecular squares like $[\mathbf{B}]^{8+}$ (Figure 1) has been obtained by Hahn and co-workers in 2012,[16] and the molecule was built up from four platinum corners by the ligation of four platinum atoms with the carbon atoms of two classical bis(diaminocarbene) and two di(NH, O-NHC) ligands. According to the related literature, the use of NHCs as building blocks in metal-directed supramolecular chemistry has only been explored recently.[15] Most of supramolecules were built by linear bidentate ligand and selected metal within at least two steps. Herein we wish to report an effective way to selectively synthesize tetranuclear or binuclear supramolecular complexes of nonlinear NHC-oxazoline ligand with $Pd(OAc)_2$ in only one step. Catalytic activities of these Pd catalysts were tested by Suzuki–Miyaura cross-coupling reaction.

Initially, we attempted to synthesize the desired chiral benzimidazole-oxazoline ligand **5**, and the synthetic route is shown in Scheme 1.[17] Methyl 3-aminobenzoate was used as the starting material to react with 1-bromo-2-nitrobenzene in the presence of $Pd(OAc)_2$/DPE-phos catalytic system to give the Buchwald coupling product **1** in 96% yield. Subsequently compound **1** with Pd/C under H_2 atmosphere (1 atm) was refluxed in methanol overnight to produce the desired compound **2** in 90% yield. Cyclization of compound **2** in the presence of triethyl orthoformate and a catalytic amount of TsOH at 100 °C gave the corresponding benzimidazole derivative **3** in 86% yield, which was further treated with chiral amino alcohol in the presence of Cs_2CO_3 in toluene to afford the corresponding amide **4**. Finally, cyclization of chiral amide **4** in the presence of thionyl chloride and MeONa gave the corresponding desired chiral benzimidazole-oxazoline compound **5** in good yield.

Next, the reaction of aryl-substituted benzimidazole-oxazoline compound **5** with methyl iodide in acetonitrile under reflux afforded the corresponding benzimidazole salts **6a** and **6b** in excellent yields (Scheme 2), which could be smoothly transformed to the corresponding NHC-oxazo-

SYNLETT 2013, 24, 1255–1259
Advanced online publication: 17.05.2013
DOI: 10.1055/s-0033-1338848; Art ID: ST-2013-R0358-C

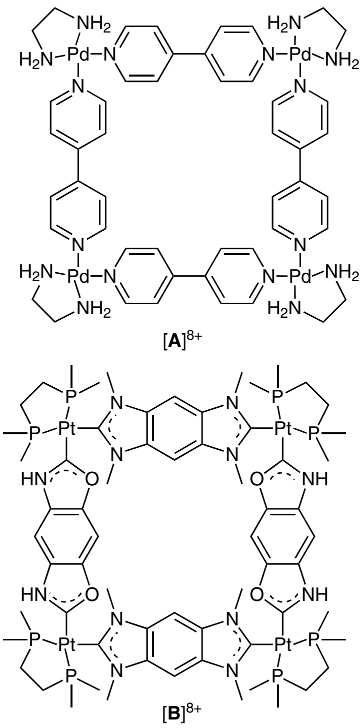
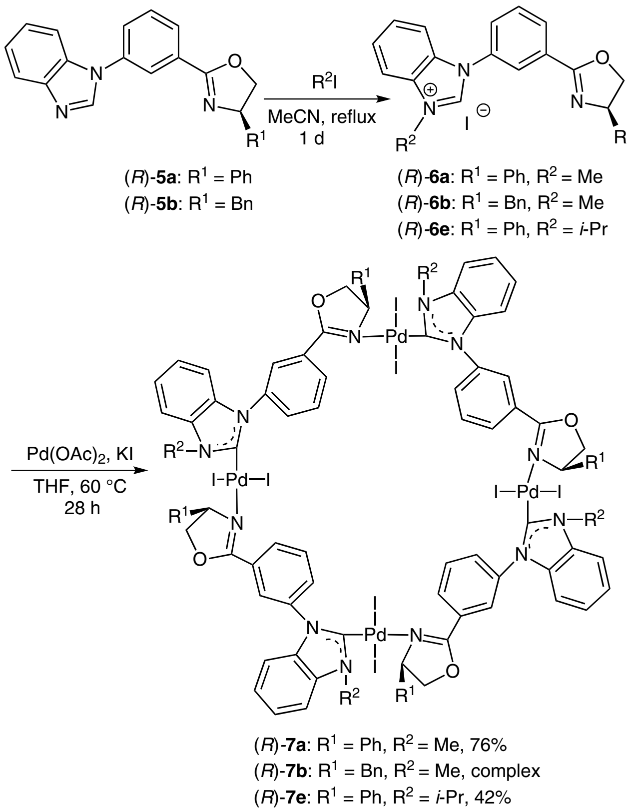


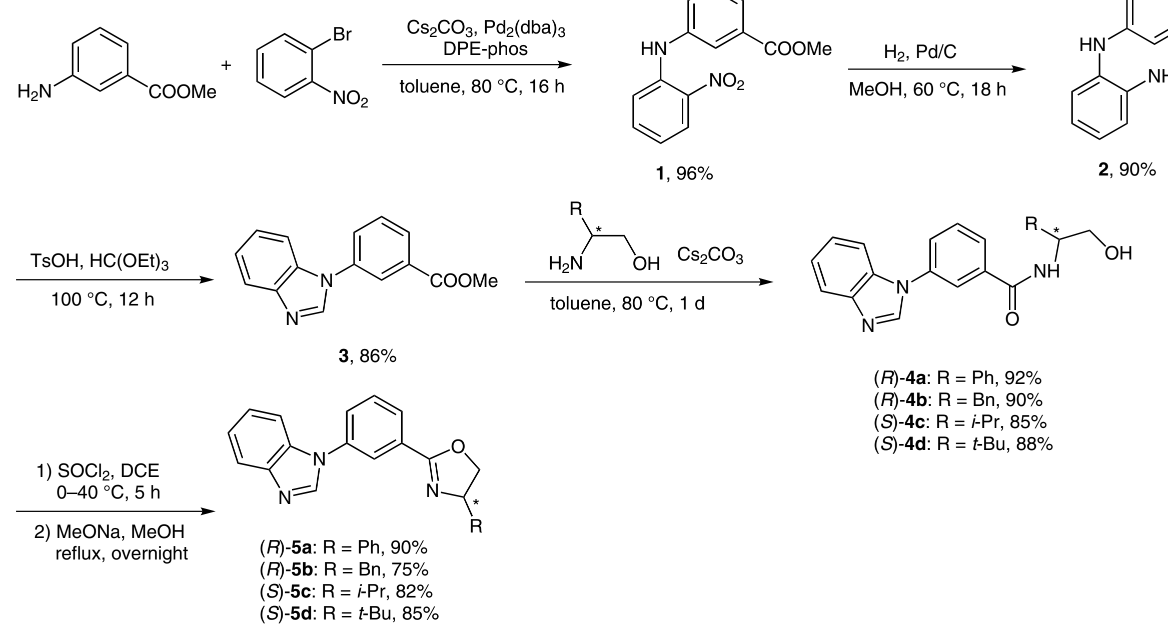
Figure 1 Structure of molecular squares $[\mathbf{A}]^{8+}$ and $[\mathbf{B}]^{8+}$

line Pd(II) complexes **7a** and **7b** upon treating with Pd(OAc)$_2$ and KI in THF, respectively. The ^{1}H NMR spectra of complex **7a** indicated two methyl signals at δ = 3.46 ppm and 3.38 ppm and the ratio of the two methyl signals was 1:1 along with two sets of alkyl group signals. Unfortunately pure Pd complex **7b** could not be obtained by column chromatography or recrystallization, although its crude ^{1}H NMR spectra also showed the characteristic two sets of alkyl group signals as those of complex **7a** (see Supporting Information).



Scheme 2 Synthesis of NHC-oxazoline tetra-Pd complexes **7a**, **7b** and **7e**

However, the accurate structures of these Pd complexes could not be confirmed. Attempts to get single crystals of complex **7a** for X-ray diffraction were not successful because the single crystals of complex **7a** obtained from the



Scheme 1 Synthesis of chiral benzimidazole-oxazoline pre-ligands **5**

n-hexane–CH_2Cl_2 solvent system effloresced easily within a few seconds after they were removed from mother liquor. The collected diffraction data did not allow a completely anisotropic refinement of the model. But they turned out to be sufficient enough to solve the structure which was obtained as a cyclic tetrapalladium molecule. Encouraged by the result, many solvent systems such as Et_2O, EtOAc, acetone, $CHCl_3$, and acetonitrile were chosen to stabilize the single crystals. Unfortunately, high-quality single crystals suitable for the X-ray diffraction could not be obtained. Next, we tried to change the N-substituent of benzimidazole from methyl group to isopropyl group in order to increase the steric hindrance which might improve the stability of the Pd complex. Then we followed the previous synthetic route shown in Scheme 2 simply by exchanging methyl iodide with isopropyl iodide to smoothly prepare complex **7e** as a yellow powder. Its ^{1}H NMR spectra showed the similar two sets of alkyl group signals. Finally its stable single crystal was obtained from the mixed solvent of *n*-hexane and chloroform. The structure of complex **7e** has been confirmed by X-ray diffraction. The ORTEP drawing is shown in Figure 2 and the CIF data are presented in the Supporting Information. According to the crystal data, the complex **7e** is built up from four neutral palladium(II) corners that are connected by bonds formed between palladium and the ligands end to end. The NHC ligand and another oxazoline ligand are *trans*-chelated with Pd atom and the Pd complex seems to be a distorted square molecule. The Pd complexes of **7a** and **7e**, having *S*-configuration, could be also obtained using (*S*)-**5a** as the starting materials. Their spectroscopic data are consistent with their enantiomers, suggesting that the absolute configuration had no effect on the coordination mode of these palladium complexes.

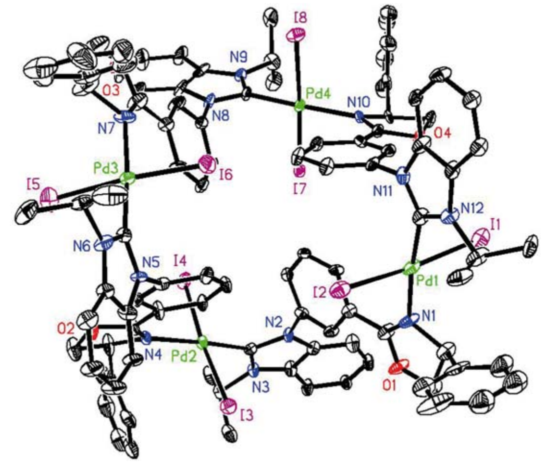
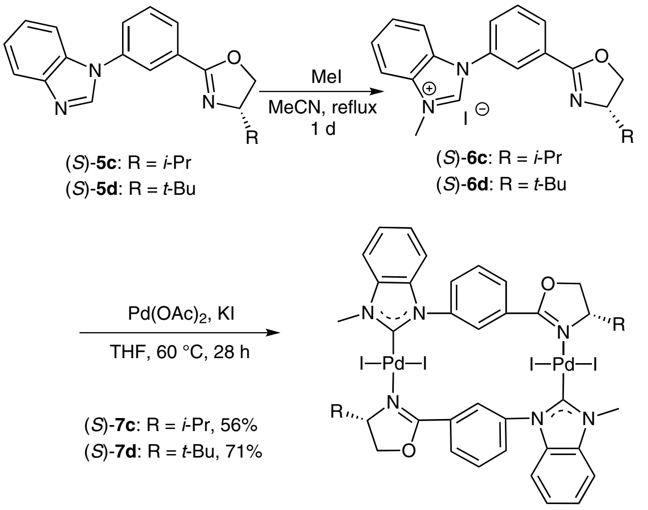


Figure 2 Molecular structure of complex **7e**. Ellipsoids are shown at 30% probability. All hydrogen atoms and solvent molecular are omitted for charity. Selected bond lengths [Å] and angles [°] for **7e** are as follows: Pd1–N1 2.053(7), Pd1–C91 1.960(9), Pd1–I1 2.6296(13), N2–C16 1.381(10), C91–Pd1–N1 173.5(3)°, C91–Pd1–I2 88.3(3)°, N1–Pd1–I1 91.3(3)°, C10–C11–C12 116.5(7)°.

Encouraged by this finding, we next started to investigate the influence of the substituent on oxazoline ligand. Isopropyl- and *tert*-butyl-substituted pre-ligands **5c** and **5d** were obtained with the same synthetic method as shown in Scheme 1. Then their benzimidazole salts were obtained smoothly and were used to complex with $Pd(OAc)_2$, affording the corresponding NHC-oxazoline Pd complexes **7c** and **7d** in good yields (Scheme 3).



Scheme 3 Synthesis of NHC-oxazoline bis-Pd complexes **7c** and **7d**

The ^{1}H NMR spectra of complexes **7c** and **7d** only gave one set of alkyl group signals, suggesting that the structures of complexes **7c** and **7d** are totally different from that of Pd complex **7e**. The structure of oxazoline-NHC Pd complex **7d** was confirmed by the X-ray diffraction. Suitable single crystals were obtained from *n*-hexane–CH_2Cl_2 solvent system. The ORTEP drawing is shown in Figure 3. The complex **7d** is built up from two neutral palladium(II) corners formed in same way as that in complex **7e**. The NHC ligand and another oxazoline ligand are also *trans*-chelated with palladium atom and the molecule is twisted as a rectangle. The structure of complex **7d** is highly symmetrical and all the corresponding bond lengths and angles are exactly the same; for example, the bond lengths of Pd1–C1 and Pd1A–C1A are both 1.947(3) Å. The one set of alkyl group signals in the ^{1}H NMR spectra can be appropriately explained by its X-ray crystal structure.

The catalytic activities of these NHC bis- or tetrapalladium complexes were evaluated by Suzuki–Miyaura cross-coupling reaction. Initially, we tested the Suzuki coupling of phenyl bromide and 4-methoxyphenylboronic acid using palladium catalysts **7a**, **7c**, **7d** and **7e** under the standard reaction conditions [80 °C, isopropanol as solvent, potassium *tert*-butoxide (1.5 equiv) as base].[18] The corresponding biaryl products were obtained in good yields (Table 1, entries 1–4). Obviously phenyl-substituted catalyst **7a** showed the best catalytic activity with the isolated yield of 86% (Table 1, entry 1). Next we chose Pd complex **7a** as the catalyst to test the influence of halogen substituent. Phenyl iodide showed excellent reactivity with quantitative yield (Table 1, entry 6). The biaryl products

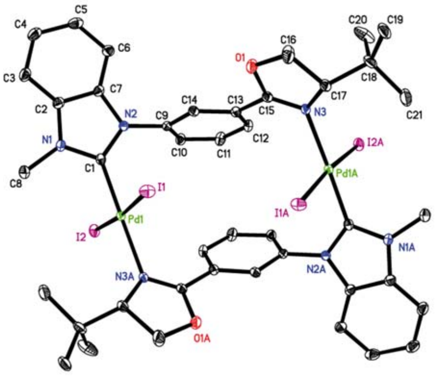


Figure 3 Molecular structure of complex **7d**. Ellipsoids are shown at 30% probability. All hydrogen atoms are omitted for charity. Selected bond lengths [Å] and angles [°] for **7d** are as follows: Pd1–C1 1.947(3), Pd1–N3A 2.127(2), Pd1–I1 2.5929(3), N1–C1 1.355(3), N3–C15 1.267(3), C1–Pd1–N3A 173.87(11)°, C1–Pd1–I1 86.68(8)°, N1–C1–N2 106.5(2)°, I1–Pd1–I2 174.365(9)°.

from bromo- and chlorobenzene were obtained in 90% and 43% yields, respectively (Table 1, entries 5 and 7). Nolan's NHC-Pd catalysts have obtained excellent results under mild conditions in the same coupling reaction.[9a,b] We assumed that the coordinated iodine atom and the coordination mode may cause lower catalytic activity in the coupling reaction than those of Nolan's catalysts, which were also consistent with our previous work.[3d] Finally, different types of substituent were tested under the standard conditions. The coupling product from 2-bromotoluene and phenylboronic acid was achieved in 86% yield (Table 1, entry 8), but the product from 2-fluorophenyl bromide was obtained in 70% yield (Table 1, entry 9).[19]

In conclusion, a series of novel NHC-oxazoline ligands on phenyl scaffold were synthesized in six steps, and the corresponding palladium complexes were obtained from ligation of these ligands with $Pd(OAc)_2$. Two different types of cyclic bis- and tetrapalladium complexes were obtained by changing the substituent of oxazoline from alkyl group to phenyl group. The examples of square Pd supramolecular synthesis in one step are quite rare. In fact, we have found another effective method for the synthesis of metallosupramolecule by self-assembly. We assumed that these phenomena may be due to the fact that the tetrapalladium complexes could be stabilized by the substituted aryl group in oxazoline moiety. Finally, the catalytic activities of these palladium catalysts were tested by Suzuki–Miyaura cross-coupling reaction. The palladium complex **7a** showed the best catalytic activity and the corresponding biaryl products were obtained in moderate to excellent yields.

Acknowledgment

We thank the Shanghai Municipal Committee of Science and Technology (11JC1402600), the National Basic Research Program of China [(973)-2010CB833302], the Fundamental Research Funds for the Central Universities, and the National Natural Science Foundation of China for financial support (21072206, 20472096, 20872162, 20672127, 21102166, 21121062 and 20732008).

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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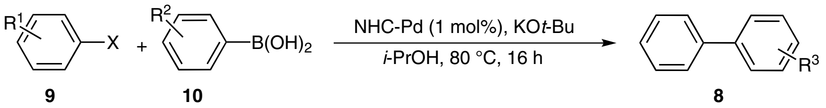
Table 1 NHC-Pd(II) Complexes Catalyzed Suzuki–Miyaura Reaction



Entry[a]	Pd cat.	R^1	X	R^2	R^3	Yield (%)[b]
1	**7a**	H	Br	*p*-OMe	*p*-OMe	**8a**, 86
2	**7c**	H	Br	*p*-OMe	*p*-OMe	**8a**, 72
3	**7d**	H	Br	*p*-OMe	*p*-OMe	**8a**, 73
4	**7e**	H	Br	*p*-OMe	*p*-OMe	**8a**, 80
5	**7a**	H	Br	H	H	**8b**, 90
6	**7a**	H	I	H	H	**8b**, 99
7	**7a**	H	Cl	H	H	**8b**, 43
8	**7a**	*o*-Me	Br	H	*o*-Me	**8c**, 86
9	**7a**	*o*-F	Br	H	*o*-F	**8d**, 70

[a] Reactions of NHC-Pd (1 mol% Pd), aryl halides (0.5 mmol), arylboronic acids (0.6 mmol), potassium *tert*-butoxide (0.75 mmol) in *i*-PrOH (2 mL) were carried out at 80 °C for 16 h.
[b] Isolated yield.

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(19) **General Procedure of the NHC-Pd Catalyzed Suzuki–Miyaura Cross-Coupling Reaction**: NHC-Pd (1.25 or 2.5 μmol, 1 mol% Pd), aryl halide (0.5 mmol, 1 equiv), arylboronic aid (0.6 mmol, 1.2 equiv), potassium *tert*-butoxide (0.75 mmol, 1.5 equiv) were added into a tube under argon, and the solvent *i*-PrOH (2 mL) was added into the tube via a syringe. The mixture was stirred for 16 h at 80 °C. After the reaction completed, H_2O was added to the mixture, and the aqueous phase was extracted with EtOAc (3 ×). The combined organic solvent was dried over anhyd Na_2SO_4 and removed in vacuo. The residue was purified by flash column chromatography on silica gel column with petroleum ether as an eluent to give the desired biaryl products **8** in good to excellent yields.