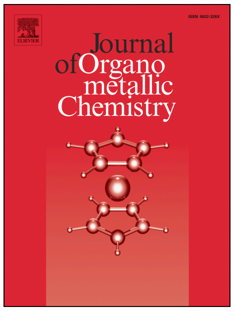

N-heterocyclic carbene-palladium(II) complexes with benzoxazole or benzothiazole ligands: synthesis, characterization, and application to Suzuki-Miyaura cross-coupling reaction

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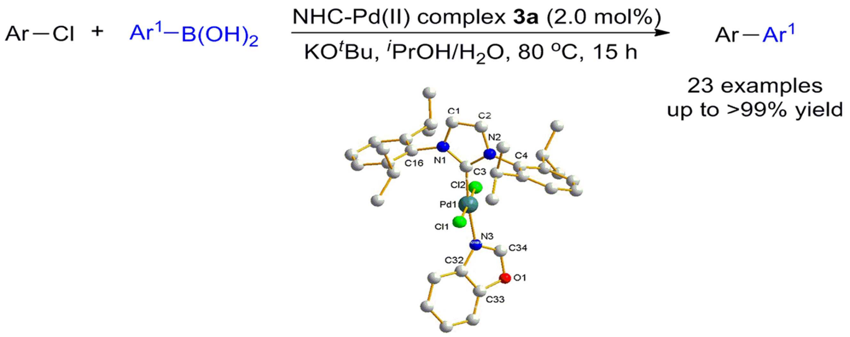
Ar—Cl
+
Ar1—B(OH)2
NHC-Pd(II) complex 3a (2.0 mol%)
KOtBu, iPrOH/H2O, 80 oC, 15 h
Ar—Ar1
23 examples
up to >99% yield
C1
C2
N2
N1
C4
C16
C3
Cl2
Pd1
Cl1
N3
C34
C32
O1
C33

N-heterocyclic carbene-palladium(II) complexes with benzoxazole or benzothiazole ligands: synthesis, characterization, and application to Suzuki-Miyaura cross-coupling reaction

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ABSTRACT: A series of novel *N*-heterocyclic carbene-palladium(II) complexes **3** were conveniently prepared from commercially available imidazolium salts, palladium chloride, and benzoxazole or benzothiazole in one step. All of the new complexes have been fully characterized by elemental analysis, ^{1}H, ^{13}C NMR, and IR spectra. In addition, the molecular structures of complexes **3a-d** have also been determined by X-ray single-crystal diffraction. The obtained palladium(II) catalysts showed efficient catalytic activity toward the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids. Under the optimal reaction conditions, the expected biaryl products were obtained in moderate to high yields.

Keywords: *N*-heterocyclic carbene; Palladium; Suzuki-Miyaura cross-coupling; Catalysis

1. Introduction

Palladium-catalyzed reactions have become one of the most important and frequently applied methods for the synthesis of useful organic compounds in agrochemistry, pharmaceutical chemistry, materials and synthetic chemistry.[1] *N*-heterocyclic carbene (NHC)-palladium complexes, as an important and fascinating subclass of palladium catalysts, have been developed and applied into numerous catalytic reactions such as

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amination reactions, direct C-H bond arylation reactions, and cross-coupling reactions including Heck, Suzuki-Miyaura, Negishi, and Kumada-Tamao-Corriu(KTC) reactions.[2] In previous reports, it was found that the catalytic activity of *N*-heterocyclic carbene (NHC)-palladium complexes is dependent largely on the electronic properties and steric encumbrance of the NHC.[2a, 2d, 2f] Consequently, *N*-heterocyclic carbenes (NHCs) such as IPr, IXy, IMes, SIPr, SIXy, SIMes and other ligand architecture were successively designed. NHCs in Pd-catalyzed organic reactions have led to a number of exciting discoveries.[3] In addition to the NHC moieties, the ancillary ligands which are attached to the metal center also played key roles in the catalytic transformations of the NHC-Pd complexes. For example, Navarro and co-workers[4] explored the applications of the NHC-Pd(II)-Et_3N complex in Mizoroki-Heck couplings, providing the desired products in good yields without the need of an inert atmosphere and in relatively short reaction times. The groups of Organ[3c,3j], Tu[5], Thiel[3d] and Brenner[3h] demonstrated that the related NHC-Pd(II)-pyridine complexes were highly effective catalysts in several catalytic reactions. While the NHC-Pd(II)-2-phenylimidazole complexes[6] readily catalyzed the Suzuki-Miyaura cross-coupling reaction of aryl as well as benzyl chlorides with different boronic acids in excellent yields using very low catalyst concentrations of 0.05 mol%. Recently, Shao and Lu have successfully developed a well-defined *N*-heterocyclic carbene-Pd(II)-1-methylimidazole [NHC-Pd(II)-Im][7] complex, and found it to be an efficient catalyst for the Suzuki-Miyaura coupling,[3b,7a] arylation of symmetric dialkyl ketones,[7d] direct C-H bond arylation reactions[7b,7c]. Additionally, *N*-heterocyclic carbene-palladium(II)-4,5-dihydrooxazole complexes [NHC-Pd(II)-Ox] have been successfully applied to the amination of aryl chlorides.[8] Despite the impressive progress made so far in the *N*-heterocyclic carbene-palladium(II) complexes, however, we were interested in the development of easily prepared and highly reactive, and stable NHC-Pd(II) complexes, which can be readily tuned via variation of *N*-heterocyclic carbenes and efficient ancillary ligands. In our previous work, we reported the achiral CNN pincer Pd(II) complexes with *N*-substituted-2-aminomethyl-6-phenylpyridine ligands, which were used as effective catalysts for allylation of aldehydes as well as three-component allylation reactions of aldehydes, arylamines and allyltributyltin.[9] Very recently, some novel chiral

CNN pincer Pd(II) complexes based on 2-aryl-6-(oxazolinyl)pyridine ligands which were conveniently synthesized and well characterized by us, have proved to be excellent chiral catalysts for the asymmetric allylation of isatins with allyltributyltin (up to 86% *ee*) as well as asymmetric Suzuki-Miyaura coupling reaction (up to 68% *ee*).[10] Encouraged by the results mentioned above and also in continuation of our efforts to develop palladium complexes for organic synthesis, herein we would like to present facile synthesis and structural characterization of the *N*-heterocyclic carbene palladium(II) complexes with benzoxazole or benzothiazole as ancillary ligands, which can be prepared straightforward within only one step (Scheme 1). The application of the resulting bench-stable complexes in the Suzuki-Miyaura coupling of aryl and benzyl chlorides with arylboronic acids are also presented below.

Scheme 1. Synthesis of *N*-heterocyclic carbene-palladium(II) complexes.

2. Results and discussion

2.1. Synthesis and characterization of the palladium(II) complexes

According to the literature method reported,[3j,8] the synthesis of the required *N*-heterocyclic carbene-palladium(II) complexes **3** were easily done in a one-step sequence from commercially available imidazolium salts, palladium chloride, and benzoxazole or benzothiazole as shown in Scheme 1. The expected palladium(II) complexes **3** were isolated in good yields (65-76%) after purification and fully characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectra. Additionally, the NHC-Pd complexes exhibit generally high stabilities towards heat, air and moisture.

The molecular structures of Pd complexes **3a-d** were unambiguously determined by X-ray single crystal analysis. The molecules are illustrated in Figures 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 1. Complexes **3a-d** showed slightly distorted-square-planar configuration for the central palladium atom. The two chloride anions perpendicular to the plane of the NHC ligands and the benzoxazole or benzothiazole is trans to it. All of the bond lengths and angles around the Pd(II) center in the four complexes are similar. The values of bond lengths and angles also compare well to those of the related NHC-Pd(II) complexes with N-containing compounds.[8,11] The Pd-N bond lengths (around 2.090 Å) in complexes **3a-d** are slightly longer than that of Pd-$C_{carbene}$ (around 1.960 Å). The angles of $C_{carbene}$-Pd-N and Cl(1)-Pd-Cl(2) are almost close to 180°, while the $C_{carbene}$-Pd-Cl(1) angles, $C_{carbene}$-Pd-Cl(2) angles, N-Pd-Cl(1) angles and N-Pd-Cl(2) angles are almost close to 90 °.

Figure 1 Molecular structures of the Pd(II) complexes **3a** (left) and **3b** (right). Hydrogen atoms are omitted for clarity.

Figure 2 Molecular structures of the Pd(II) complexes **3c** (left) and **3d** (right). Hydrogen atoms and solvent molecules are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (deg) for complexes **3a-d**

	3a	**3b**	**3c**	**3d·CH_2Cl_2**
Pd(1)-C(3)/Pd(1)-C(8)	1.953(3)	1.967(2)	1.967(2)	1.974(4)
Pd(1)-N(3)/Pd(1)-N(1)	2.100(3)	2.097(2)	2.088(2)	2.097(3)
Pd(1)-Cl(1)	2.2754(9)	2.3015(8)	2.2948(7)	2.3013(10)
Pd(1)-Cl(2)	2.3011(9)	2.2948(8)	2.3045(8)	2.3020(11)
C(3)-Pd(1)-N(3)/C(8)-Pd(1)-N(1)	173.59(12)	174.44(10)	175.43(10)	173.36(14)
C(3)-Pd(1)-Cl(1)/C(8)-Pd(1)-Cl(1)	89.31(9)	91.38(8)	91.27(7)	92.10(11)
C(3)-Pd(1)-Cl(2)/C(8)-Pd(1)-Cl(2)	91.62(9)	88.22(8)	91.34(7)	90.43(11)
N(3)-Pd(1)-Cl(1)/N(1)-Pd(1)-Cl(1)	90.21(9)	91.13(8)	88.00(7)	89.86(9)
N(3)-Pd(1)-Cl(2)/N(1)-Pd(1)-Cl(2)	89.08(8)	89.26(8)	89.62(7)	87.88(9)
Cl(1)-Pd(1)-Cl(2)	177.84(4)	179.58(3)	176.11(3)	176.60(4)

2.2. Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids

The Suzuki-Miyaura coupling reaction stands out as one of the most powerful, convenient, and versatile methods to create carbon-carbon bonds and thus has found widespread applications in natural products, advanced materials and organic synthesis.[12] Although most of the successful examples concern the use of aryl iodides and bromides in the reaction, the application of aryl chlorides has recently attracted much attention mainly due to their good stability, low cost and wide availability. However, Suzuki-Miyaura coupling of aryl chlorides is still regarded as a challenging task because of high C-Cl bond strength. As a result, the development of known or new catalysts with excellent catalytic activities is in great demand to improve this transformation. Thus, we wonder whether the present NHC-Pd(II) complexes can behave better in the reaction. The coupling of 1-chloro-4-methoxybenzene with phenylboronic acid was chosen as a model to optimize the reaction conditions (Table 2). It was found that in the presence of 2.0 mol% of complex **3a** with KO^tBu, Cs_2CO_3 or NaO^tBu as the base in EtOH at 80 °C the corresponding biaryl product **6a** was isolated in high yield after 15 h (entries 1, 3, 5). When K_2CO_3 or K_3PO_4 was used as the base, the yield drastically decreased (entries 2, 6). With Na_2CO_3 as the base afforded trace amounts of product (entry 4). The drastically different yields between Na, K and Cs carbonate bases possible are due to the different basic character of the EtOH solutions.[13] In a word, base plays crucial role for the yield of the reaction. To our delight, EtOH mixed with different proportions of water still be able to provide good yields (entries 7-9). Several other solvents including THF, toluene, 1,4-dioxane and ^{i}PrOH mixed with an equal volume of water were tested, and ^{i}PrOH was found to be the most appropriate, giving the biaryl product in a >99% yield (entries 10-13). And a reduction in the catalyst loading from 2.0 mol% to 1.0 mol% led to decreased yield (entry 14). By reducing the reaction time to 12 h the product **6a** was obtained in a 85% yield (entry 15). In addition, complex **3b** showed an activity comparable to that of **3a** (entry 16), while **3c** and **3d** were less efficient under the same reaction conditions (entries 17 and 18). The nitrogen atoms of benzoxazole ligands coordinate more weakly to palladium than that of benzothiazole ligands. So the disassociation of benzoxazole ligands is relatively easier to occur during the reaction process which might lead to the higher reactivity of corresponding complexes.

Table 2 Optimization of reaction conditions for Suzuki-Miyaura reaction of 1-chloro-4-methoxybenzene with phenylboronic acid catalyzed by the NHC-Pd(II) complexes **3**[a]

Entry	Cat.	Base	Solvent	Yield (%)[b]
1	**3a**	KO^tBu	EtOH	> 99
2	**3a**	K_2CO_3	EtOH	53
3	**3a**	Cs_2CO_3	EtOH	> 99
4	**3a**	Na_2CO_3	EtOH	trace
5	**3a**	NaO^tBu	EtOH	> 99
6	**3a**	K_3PO_4	EtOH	80
7	**3a**	KO^tBu	$EtOH/H_2O$ (2/1)	> 99
8	**3a**	KO^tBu	$EtOH/H_2O$ (1/1)	84
9	**3a**	KO^tBu	$EtOH/H_2O$ (1/2)	60
10	**3a**	KO^tBu	THF/H_2O (1/1)	67
11	**3a**	KO^tBu	$Toluene/H_2O$ (1/1)	19
12	**3a**	KO^tBu	1,4-dioxane/H_2O (1/1)	88
13	**3a**	KO^tBu	$^iPrOH/H_2O$ (1/1)	> 99
14[c]	**3a**	KO^tBu	$^iPrOH/H_2O$ (1/1)	72
15[d]	**3a**	KO^tBu	$^iPrOH/H_2O$ (1/1)	85
16	**3b**	KO^tBu	$^iPrOH/H_2O$ (1/1)	91
17	**3c**	KO^tBu	$^iPrOH/H_2O$ (1/1)	72
18	**3d**	KO^tBu	$^iPrOH/H_2O$ (1/1)	25

[a] All reactions were carried out using **4a** (0.50 mmol), **5a** (0.75 mmol), base (2.0 equiv), **3** (2.0 mol%) in solvent (2.0 mL) at 80 °C for 15 h. [b] Isolated yields. [c] Cat. (1.0 mol%). [d] Reaction time was 12 h.

With optimized conditions in hand, we next set out to explore the substrate scope of the cross coupling of aryl chlorides and aryl boronic acids. As shown in Table 3, a series of aryl chlorides **4** and aryl boronic acids **5** were investigated in ^{i}PrOH-H_2O in the presence of 2.0 mol% complex **3a** and 2.0 equiv KO^{t}Bu at 80 ^{o}C for 15 h (Table 3). Gratifyingly, most of the coupling reaction proceeded rapidly and efficiently to provide the corresponding biaryl products in excellent yields. Both electron-donating and electron-withdrawing groups in the phenyl ring of aryl chlorides were tolerated and good results were obtained (entries 1-10). Roughly, the electron-donating group in the phenyl ring of aryl chlorides showed some beneficial effect on the yields of the catalysis products. The position of the group on the aryl ring did not seem to affect the product yields apparently. For example, the reaction was quite feasible with ortho-substituted aryl chlorides when the phenylboronic acid was used (entries 3 and 6). Particularly, when heteroaromatic aryl chlorides such as 2-chloropyridine and 3-chloropyridine were used as the substrates, high yield of the corresponding products was always observed (entries 9-10). Subsequently, the scope of complex **3c** catalytic system was further investigated with respect to arylboronic acids (entries 11-17). In most cases, the reaction worked well and approached to corresponding products in very high yield. However, electron-deficient and sterically hindered boronic acids resulted in a significant decrease in yields (entries 15 and 17). In addition, in the case of 3-pyridinylboronic acid or 4-pyridinylboronic acid afforded trace amounts of product under the present reaction conditions (data not shown in Table 3). It was believed that possible reason for this was these substrates bearing ligating atoms which may deactivate the catalyst. Overview, the results indicated that complex **3a** was still efficient in the catalytic process.

Inspired by these results and our attention was next turned to the cross coupling reaction of benzyl chlorides and aryl boronic acids. As shown in Table 4, the reactions proceed smoothly to afford diarylmethanes in excellent yields. Particularly, when electron-deficient boronic acids such as 4-trifluoromethyl-phenylboronic acid were used as the substrates, high yield of the corresponding product was always observed (98% yield, entry 5). The above results confirm that the NHC-Pd complexes are really effective catalysts for the Suzuki-Miyaura reaction. It is worth pointing out that the present NHC-Pd(II) catalysts invariably provided much higher yields than the related catalysts[3h, 14] under similar reaction conditions.

Table 3 Substrate scope for the catalytic Suzuki-Miyaura reaction of aryl chlorides using the NHC-Pd(II) complex **3a** as the catalyst^a

Entry	**4** (Ar^1)	**5** (Ar^2)	Product	Yield (%)^b
1	**4a** (4-MeO-C_6H_4)	**5a** (Ph)	**6a**	> 99
2	**4b** (3-MeO-C_6H_4)	**5a** (Ph)	**6b**	99
3	**4c** (2-MeO-C_6H_4)	**5a** (Ph)	**6c**	99
4	**4d** (4-Me-C_6H_4)	**5a** (Ph)	**6d**	> 99
5	**4e** (3-Me-C_6H_4)	**5a** (Ph)	**6e**	99
6	**4f** (2-Me-C_6H_4)	**5a** (Ph)	**6f**	92
7	**4g** (4-CH_3CO-C_6H_4)	**5a** (Ph)	**6g**	86
8	**4h** (4-NO_2-C_6H_4)	**5a** (Ph)	**6h**	93
9	**4i** (2-Pyridyl)	**5a** (Ph)	**6i**	97
10	**4j** (3-Pyridyl)	**5a** (Ph)	**6j**	96
11	**4a** (4-MeO-C_6H_4)	**5b** (4-Me-C_6H_4)	**6k**	98
12	**4a** (4-MeO-C_6H_4)	**5c** (3-Me-C_6H_4)	**6l**	97
13	**4a** (4-MeO-C_6H_4)	**5d** (2-Me-C_6H_4)	**6m**	92
14	**4a** (4-MeO-C_6H_4)	**5e** (4-F-C_6H_4)	**6n**	98
15	**4a** (4-MeO-C_6H_4)	**5f** (4-CF_3-C_6H_4)	**6o**	68
16	**4a** (4-MeO-C_6H_4)	**5g** (1-Naphthyl)	**6p**	> 99
17	**4a** (4-MeO-C_6H_4)	**5h** (2-Naphthyl)	**6q**	50

^{a}All reactions were carried out using **4** (0.50 mmol), **5** (0.75 mmol), KO^{t}Bu (2.0 equiv), **3a** (2.0 mol%) in ^{i}PrOH/H_2O (2.0 mL, V:V = 1:1) at 80 °C for 15 h. ^{b}Isolated yields.

Table 4 Substrate scope for the catalytic Suzuki-Miyaura reaction of benzyl chlorides using the NHC-Pd(II) complex **3a** as the catalyst^a

Entry	**5** (Ar^2)	Product	Yield (%)^b
1	**5b** (4-Me-C_6H_4)	**8a**	> 99
2	**5c** (3-Me-C_6H_4)	**8b**	98
3	**5d** (2-Me-C_6H_4)	**8c**	98
4	**5e** (4-F-C_6H_4)	**8d**	99
5	**5f** (4-CF_3-C_6H_4)	**8e**	98
6	**5g** (1-Naphthyl)	**8f**	> 99

^{a}All reactions were carried out using **7** (0.50 mmol), **5** (0.75 mmol), KO^{t}Bu (2.0 equiv), **3a** (2.0 mol%) in ^{i}PrOH/H_2O (2.0 mL, V:V = 1:1) at 80 °C for 15 h. ^{b}Isolated yields.

3. Conclusion

In summary, four new *N*-heterocyclic carbene-palladium(II) complexes based on benzoxazole or benzothiazole ligands have been conveniently synthesized and well characterized. These complexes have been utilized as the catalysts for the Suzuki-Miyaura coupling of aryl chlorides and benzyl chlorides with arylboronic acids, producing the corresponding biaryl products in high yields (up to 99%). Also, the NHC-Pd complexes include benzoxazole as ligand was found to exhibit much higher activity than the related NHC-Pd complexes with benzothiazole in the Suzuki-Miyaura coupling. Further modification of the *N*-heterocyclic carbene-palladium(II) complexes and their applications in other reactions are in progress.

4. Experimental

4.1. General

Reactions for the preparation of *N*-heterocyclic carbene-palladium(II) complexes as well as all the catalytic reactions were carried out under nitrogen atmosphere. Solvents were dried with standard methods and freshly distilled prior to use if needed. All other chemicals were used as purchased. Melting points were measured on a XT4A melting point apparatus and were uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using TMS as an internal standard. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer.

4.2. General procedure for the synthesis of N-heterocyclic carbene-palladium(II) complexes

Under an N_2 atmosphere, the mixture of imidazolium salts **1** (1.1 mmol), benzoxazole or benzothiazole (2.0 mmol), $PdCl_2$ (1.0 mmol) and K_2CO_3 (1.1 mmol) was stirred in anhydrous THF (10 mL) under reflux for 16 h. After cooling, filtration and evaporation, the residue was puried by preparative TLC on silica gel plates eluting with CH_2Cl_2 to afford the corresponding *N*-heterocyclic carbene-palladium(II) complexes **3a-d**.

Complex (3a): 458.4 mg, 67% yield, orange solids. mp: 139-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H, OCH=N), 8.02-8.00 (m, 1H, ArH), 7.51 (t, *J* = 7.8 Hz, 2H, ArH), 7.40-7.36 (m, 5H, ArH), 7.30-7.23 (m, 2H, ArH), 7.16 (s, 2H, NCH=), 3.25-3.15 (m, 4H, C*H*(CH_3)$_2$), 1.49 (d, *J* = 6.6 Hz, 12H, C*H*$_3$CHCH$_3$), 1.13 (d, *J* = 6.9 Hz, 12H, CH$_3$CHC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5(Pd-Ccarbene), 153.5, 148.4, 145.9, 134.1, 129.3, 125.3, 125.1, 124.0, 123.7, 123.0, 120.5, 27.8, 25.4, 22.1. IR (KBr, cm^{-1}): υ 3122, 3091, 2965, 2927, 2866, 1593, 1529, 1454, 1414, 1382, 1348, 1137, 800, 756, 708. Anal. Calcd. for $C_{34}H_{41}Cl_2N_3OPd$: C, 59.61; H, 6.03; N, 6.13. Found: C, 59.58; H, 6.08; N, 6.09%.

Complex (3b): 532.1 mg, 76% yield, orange solids. mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H, SCH=N), 8.26 (d, *J* = 7.2 Hz, 1H, ArH), 7.69 (d, *J* = 6.8 Hz, 1H, ArH), 7.58-7.54 (m, 2H, ArH), 7.42-7.40 (m, 4H, ArH), 7.37-7.31 (m, 2H, ArH), 7.18 (s, 2H, NCH=), 3.26-3.16 (m, 4H, C*H*(CH_3)$_2$), 1.47 (d, *J* = 6.6 Hz, 12H, C*H*$_3$CHCH$_3$), 1.13 (d, *J* = 6.9 Hz, 12H, CH$_3$CHC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5(Pd-Ccarbene), 153.5, 148.4, 145.9, 134.1, 129.3, 125.3, 125.1, 124.0, 123.7, 123.0, 120.5, 27.8, 25.4, 22.1. IR (KBr, cm^{-1}): υ 3171, 3136, 3105, 2921, 2851, 1603, 1530, 1491, 1459, 1412, 1383, 1345, 1237, 1021, 928, 864, 826, 762, 730, 709, 426. Anal. Calcd. for $C_{34}H_{41}Cl_2N_3SPd$: C, 58.25; H, 5.89; N, 5.99. Found: C, 58.15; H, 5.96; N, 5.85%.

Complex (3c): 390.1 mg, 65% yield, orange solids. mp: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, OCH=N), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.32-7.23 (m, 2H, ArH), 7.10 (s, 2H, NCH=), 7.08 (s, 4H, ArH), 2.40 (s, 6H, CH_3), 2.38 (s, 12H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7(Pd-Ccarbene), 139.3, 136.5, 135.1, 129.3, 126.3, 125.1, 124.2, 121.7, 111.0, 21.3, 19.2. IR (KBr, cm^{-1}): υ 3122, 3089, 2963, 2929, 2869, 1605, 1529, 1466, 1457, 1411, 1382, 1362, 1346, 1332, 1267, 1205, 944, 923, 800, 758, 731, 699, 425. Anal. Calcd. for $C_{28}H_{29}Cl_2N_3OPd$: C, 55.97; H, 4.86; N, 6.99. Found: C, 55.63; H, 5.06; N, 6.72%.

Complex (3d): 462.0 mg, 75% yield, orange solids. mp: >250 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H, SCH=N), 8.09 (d, *J* = 7.4 Hz, 1H, ArH), 7.71 (d, *J* = 7.1 Hz, 1H, ArH), 7.37-7.31 (m, 2H, ArH), 7.12 (s, 6H, ArH and NCH=), 2.45 (s, 6H, CH_3), 2.38 (s, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4(Pd-Ccarbene), 139.3, 136.7, 135.1, 129.3, 126.4, 126.2, 124.6, 124.2, 121.6, 21.3, 19.2. IR (KBr, cm^{-1}): υ 3162, 3133, 3122, 2954, 2918, 2855, 1607, 1529, 1487, 1455, 1408, 1378, 1370, 1341, 1302, 1280, 1247, 1234, 1160, 1132, 1099, 930, 870, 863, 848, 745, 734, 703. Anal. Calcd. for $C_{28}H_{29}Cl_2N_3SPd$: C, 54.51; H, 4.74; N, 6.81. Found: C, 54.31; H, 4.96; N, 6.63%.

4.3. General procedure for the catalytic Suzuki-Miyaura coupling reaction

A Schlenk flask was charged with aryl chlorides (0.20 mmol), arylboronic acids (0.30 mmol), *N*-heterocyclic carbene-palladium(II) complex **3** (2 mol %), KO^tBu (2.0 equiv), ^{i}PrOH (1 mL) and H_2O (1 mL). The mixture was stirred at 80 °C for 15 h under N_2. After cooling, the reaction mixture was evaporated and the product was isolated by preparative TLC on silica gel plates. The purified products were identified by ^1H NMR spectra and their analytical data are given in Supporting Information.

4.4. Crystal structure determination and data collection

Crystals of **3a-d** were obtained by recrystallization from CH_2Cl_2/*n*-hexane at ambient temperature. Their data were collected on an Oxford Diffraction Gemini E diffractometer with graphite-monochromated Cu Kα (λ = 1.5418 Å, for **3a-b**) or Mo Kα radiation (λ = 0.7107 Å, for **3c-d**). The structures were solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique, which used the SHELXL-97 crystallographic software package.[15] The hydrogen atoms were included but not refined. Details of the crystal structure determination of the Pd(II) complexes are summarized in Table 5. CCDCs 1413911, 1413912, 1413913 and 1413782 contain the crystallographic data for complexes **3a**, **3b**, **3c** and **3d**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table 5 Crystal data and structure refinement parameters for complexes **3a-d**

	3a	**3b**	**3c**	**3d**$\cdot CH_2Cl_2$
Empirical formula	$C_{34}H_{41}Cl_2N_3OPd$	$C_{34}H_{41}Cl_2N_3SPd$	$C_{28}H_{29}Cl_2N_3OPd$	$C_{29}H_{31}Cl_4N_3SPd$
Mr	685.00	701.06	600.84	701.83
temperature (K)	291.15	291.15	291.15	291.15
wavelength (Å)	1.54184	1.54184	0.71073	0.71073
crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
cryst size (mm)	0.20 x 0.20 x 0.18	0.18 x 0.16 x 0.13	0.25 x 0.20 x 0.17	0.20 x 0.18 x 0.16
a (Å)	14.33347(13)	10.7554(5)	10.10616(14)	40.9687(13)
b (Å)	33.7182(3)	12.4577(6)	32.1576(6)	11.9097(2)
c (Å)	15.71676(14)	12.8064(6)	16.5544(3)	14.9999(4)
α (^{o})	90	84.337(4)	90	90
β (^{o})	100.4678(9)	88.720(4)	90	119.779(4)
γ (^{o})	90	83.079(4)	90	90
V (Å^3)	7469.47(12)	1694.99(14)	5380.03(15)	6352.4(4)
Z	8	2	8	8
space group	P2(1)/n	P-1	Pccn	C(2)/c
D_{calcd} (g cm^{-3})	1.218	1.374	1.484	1.468
μ (mm^{-1})	5.525	6.638	0.914	1.009
θ range (^{o})	3.15-72.39	3.468-67.08	3.031-26.37	3.021-26.37
F(000)	2832.0	724.0	2448.0	2848.0
no. of data collected	28773	12167	19649	25263
no. of unique data	14512	6052	5500	6488
R(int)	0.0243	0.0291	0.0276	0.0318
final R indices	$R_1 = 0.0411$	$R_1 = 0.0323$	$R_1 = 0.0333$	$R_1 = 0.0439$
($I > 2\sigma(I)$)	$wR_2 = 0.1093$	$wR_2 = 0.0773$	$wR_2 = 0.0719$	$wR_2 = 0.1089$
R indices (all data)	$R_1 = 0.0502$	$R_1 = 0.0391$	$R_1 = 0.0427$	$R_1 = 0.0571$
	$wR_2 = 0.1149$	$wR_2 = 0.0814$	$wR_2 = 0.0768$	$wR_2 = 0.1173$

Largest diff peak and hole (e·Å^{-3})	1.42 and -0.86	0.32 and -0.40	0.49 and -0.43	0.67 and -0.76

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/xxxxxx.

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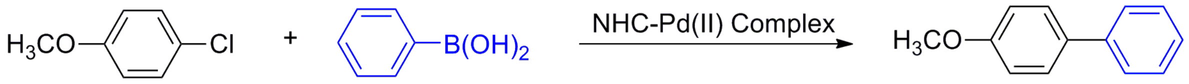
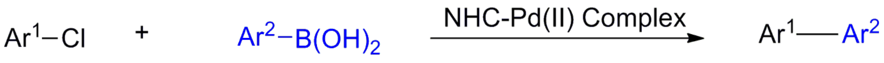
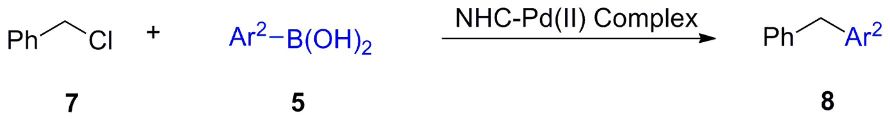


4a **5a** **6a**



4 **5** **6**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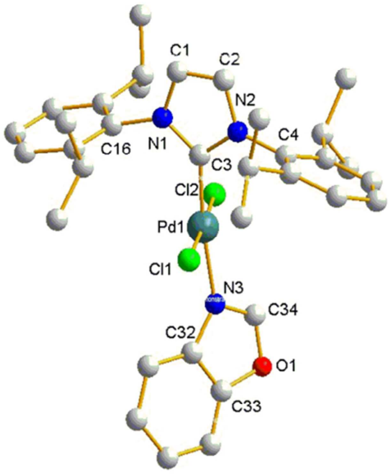
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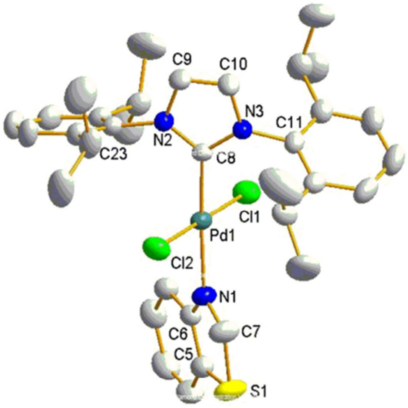
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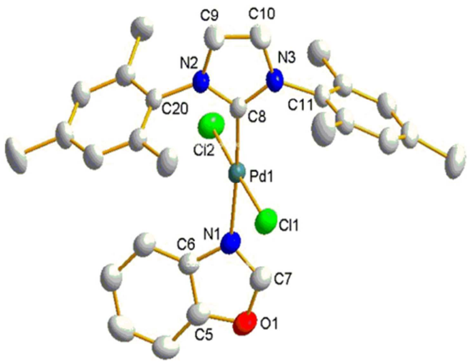
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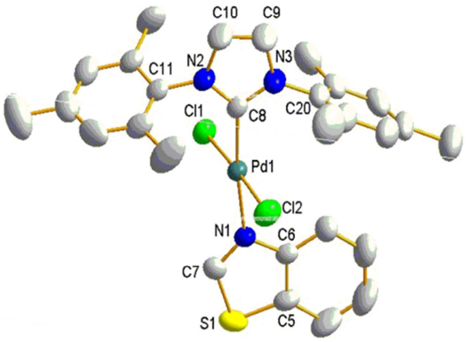
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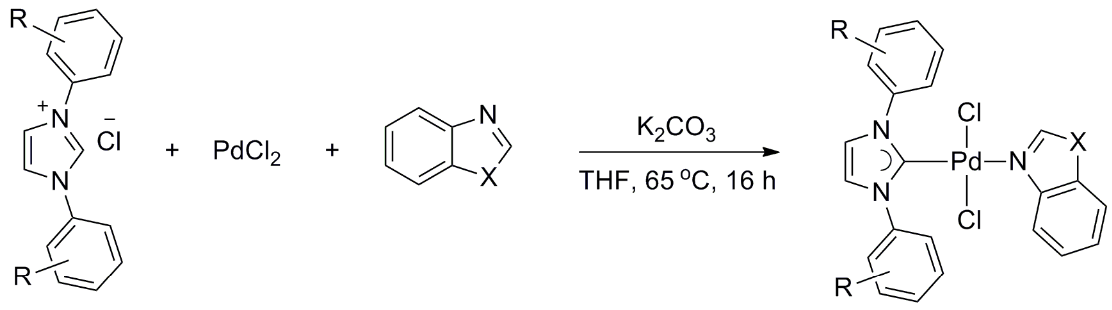

1 **2** **3**

3a R = o,o'-^{i}Pr$_2$, X = O (67%)
3b R = o,o'-^{i}Pr$_2$, X = S (76%)
3c R = o,p,o'-Me$_3$, X = O (65%)
3d R = o,p,o'-Me$_3$, X = S (75%)

Highlights

- Four new *N*-heterocyclic carbene-palladium(II) complexes based on benzoxazole or benzothiazole ligands have been conveniently synthesized.
- All of the new complexes have been well characterized.
- The catalytic activity of Pd(II) complexes in the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids are investigated.