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Suzuki cross-coupling catalyzed by palladium (II) complexes bearing 1-aryl-3,4,5,6-tetrahydropyrimidine ligands

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ABSTRACT

A novel highly efficient monodentate imine palladium catalyst system has been tested for Suzuki cross-coupling reaction. Under the standard conditions, a series of aryl halides, including phenyl iodide, aryl bromides and phenyl chloride, were coupled with phenylboronic or 1-naphthylboronic acid, producing the corresponding biaryls in good to excellent yields. High-resolution transmission electron microscopy (HR-TEM) study of the recycled catalyst showed the formation of palladium nano particles in the catalytic system.

1. Introduction

The palladium-catalyzed Suzuki cross-coupling between organoboronic acid and halides has been evolved into one of the most important and powerful methods for carbon–carbon bond formation because of the versatility and the potentiality of the products formed [1–4]. The area that has perhaps received most research is the development of new catalysts and ligands for Suzuki cross-coupling reaction, and the use of these catalytic systems in the synthesis of pharmaceutical agents, organic materials, and natural products [5–13]. Until now, phosphine-based ligands have remained to be the most popular selection in the palladium-catalyzed cross-coupling reactions [14–21]. However, their sensitivity to air and moisture is known to limit their stability and shelf-life. Recent application of alternative ligands such as *N*-heterocyclic carbenes (NHCs) [22–28], as well as ligand free systems [29–32], in the coupling reactions has opened new opportunities in catalysis. Nitrogen ligands, such as amine [33–36], diazabutadienes [37], oxazolines [38–40], and hydrazones [41] have attracted considerable interest due to their stability and excellent activity. Examples of Schiff base derived systems, such as cyclopalladated imine [42,43], multi- or bi-dentate imine ligands [44–49] have been extensively investigated and successfully employed in catalytic transformations, while research on monodentate imine ligand remains scarce to date [50]. Here we report a highly efficient catalyst system for Suzuki cross-coupling using simple monodentate imine palladium complexes.

2. Results and discussion

Our group is interested in the preparation of new *N*-heterocyclic carbene (NHC) ligands based on substituted 1,4,5,6-tetrahydropyrimidine and their palladium complexes. In the course of preparing the palladium complexes of some bi-dentate NHC ligand, we observed that the reaction of the methylene bridged tetrahydropyrimidine salts with $Pd(OAc)_2$, under unoptimized reaction conditions, afforded novel monodentate imine coordinated palladium complexes, *trans*-bis-(1-aryl-3,4,5,6-tetrahydropyrimidine)dibromopalladium(II) (**1** and **2**) (Scheme 1) [51]. Aiming at finding versatile, robust, and easy-to-prepare catalytic systems suitable for a wide range of carbon–carbon bond forming processes, we investigated the activity of the new imine palladium complexes toward the Suzuki cross-coupling.

Initially, we conducted a brief base and solvent screening by running the cross-coupling of bromobenzene and phenylboronic acid as a model (Scheme 2). Among the bases tested, NEt_3, K_2CO_3, Na_2CO_3, $NaHCO_3$, and *t*-BuOK all produced good yields (Table 1, entries 1–5). Tests of different solvents showed that toluene, dioxane, DMF or a 1:1 mixture of DMF/H_2O are all efficient system

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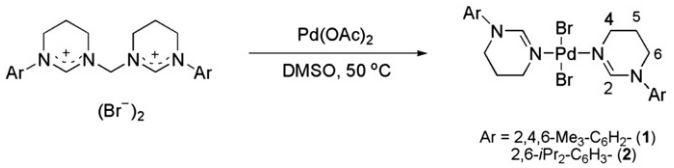


Scheme 1. Synthesis of complexes **1** and **2**.

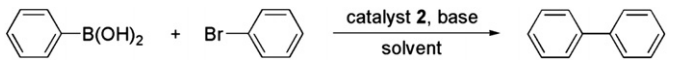
for the cross-coupling, producing the product biphenyl in yields around 90%, while the reaction in pure water resulted in a relatively low yield of 60% (Table 1, entries 5–9).

The effect of catalyst loading on the model reaction was then investigated by running the cross-coupling of bromobenzene and phenylboronic acid in a 1:1 mixture of DMF/H_2O, using complex **2** as catalyst and *t*-BuOK as base. As shown in Table 2, compared to the blank reaction, addition of 0.5 mol% complex **2** accelerated the cross-coupling efficiently, improving the biphenyl yield from 16% to 90% (Table 2, entries 1, 5). Increasing catalyst loading to 1.0 mol%, 1.5 mol% or 2.0 mol% increased the reaction rate, lead to more than 50% conversion within 0.25 h and high TOF (Turn Over Frequency), but did not improve the yield significantly (Table 2, entries 2–17). While decreasing the catalyst loading resulted in relatively low yields and slow reaction rate, as long as 24 h were needed to obtain high yields, either for bromobenzene or iodobenzene (Table 2, entries 18–21). These results indicated that the proper catalyst loading is 0.5 mol% to phenylhalides and the catalyst is stable under the reaction conditions for long time.

Under the standard conditions, using *t*-BuOK as base and a 1:1 mixture of DMF/H_2O as solvent, the catalytic activity of complexes **1** and **2** toward Suzuki cross-coupling of series aryl halides, including phenyl iodide, aryl bromides and phenyl chloride, with phenylboronic acid and 1-naphthylboronic acid was investigated and the results were summarized in Table 3 (Scheme 3). The results showed that complexes **1** and **2** presented almost equally high catalytic efficiency, producing the target biaryls in high yields in nearly all the cases.

Due to the bulky space effect of 1-naphthyl, the cross-coupling of arylbromides with 1-naphthylboronic acid resulted in relatively low yields than the corresponding cross-coupling with phenylboronic acid (Table 3, entries 2–3, 5–6, 9–10, 13–14, 17–18). In the cross-coupling with iodobenzene, the difference is even more obvious, which can be tentatively attributed to the bulkiness of both iodo and 1-naphthyl (Table 3, entries 21–22). Due to the low activity of chlorobenzene, prolonging the cross-coupling with 1-naphthylboronic acid to 48 h only resulted in a moderate yield of 50%.

From Table 3, it can be seen that as expected, the effect of the substituent on the *para*-position of the arylhalides is mainly depending on the electronegativity of the substituent, electron-withdrawing substituents leading to relatively high yields in the cross-coupling reaction (Table 3, entries 4, 5, 6, 8, 9, 10), while electron-donating substituents resulting in relatively low yields (Table 3, entries 12, 13, 16, 17). While effect of the substituent on the *ortho*-position of the arylbromide is mainly depending on the size of the substituent, bulky *ortho*-substituted arylbromide afforded biaryls in relatively low yields, and the yields decreased according to the size increment of the substituent (Table 3, entries 7, 15, 19). In the case of 2-$COCH_3$ substituted phenyl bromide, due to the opposite effect of electronegativity and space effect, the overall effect is negligible (Table 3, entries 1, 11).



Scheme 2. Base and solvent screening of the catalytic system.

Table 1
Base and solvent effect on the cross-coupling of bromobenzene with phenylboronic acid.

Entry[a]	Catalyst loading (mol%)	Base	Solvent	Reaction time (h)	GC yield (%)	TON
1	0.5	NEt_3	DMF/H_2O	2	74	148
2	0.5	K_2CO_3	DMF/H_2O	2	88	176
3	0.5	Na_2CO_3	DMF/H_2O	2	87	174
4	0.5	$NaHCO_3$	DMF/H_2O	2	85	170
5	0.5	*t*-BuOK	DMF/H_2O	2	90	180
6	0.5	*t*-BuOK	Toluene	2	86	172
7	0.5	*t*-BuOK	Dioxane	2	89	178
8	0.5	*t*-BuOK	DMF	2	88	176
9	0.5	*t*-BuOK	H_2O	2	60	120

[a] Reaction condition: 1.0 mmol bromobenzene, 1.0 mmol phenylboronic acid, 1.5 mmol base, 3 mL solvent, 100 °C. All reactions were monitored by GC.

As there are many examples of the formation of palladium nano particles from the palladium complexes with nitrogen ligands [52]. We studied the recycled catalyst through electron microscopic techniques to determine the possibility of palladium nano particles formation in our system. Indeed high-resolution transmission electron microscopy (HR-TEM) study of the recycled catalyst showed the formation of palladium nano particles (diameter around 20 nm) (Fig. 1), which maybe the true active species and responsible for the similar activities of complexes **1** and **2**.

3. Conclusion

In conclusion, we presented here the novel monodentate imine palladium complexes as a new and highly efficient catalyst system for Suzuki cross-coupling reactions. Under the standard conditions, using *t*-BuOK as base, 1:1 mixture of DMF/H_2O as solvent, the palladium complexes showed high catalytic activity for the cross-coupling of series of phenylboronic acids and 1-naphthylboronic acid with aryl halides (including phenyl iodide, aryl bromides and phenyl chloride). HR-TEM study of the catalyst residue showed that

Table 2
Catalyst loading effect on the cross-coupling of bromobenzene with phenylboronic acid.

Entry[a]	Catalyst loading (mol%)	Reaction time (h)	GC Yield (%)	TON	TOF (h^{-1})
1	0	2	16	/	/
2	0.5	0.25	40	80	320
3	0.5	0.5	60	120	240
4	0.5	1	90	180	180
5	0.5	2	90	180	90
6	1.0	0.25	55	55	220
7	1.0	0.5	70	70	140
8	1.0	1	90	90	90
9	1.0	2	91	91	46
10	1.5	0.25	62	41	164
11	1.5	0.5	78	52	104
12	1.5	1	89	59	59
13	1.5	2	92	61	31
14	2.0	0.25	64	32	128
15	2.0	0.5	80	40	80
16	2.0	1	90	45	45
17	2.0	2	92	46	23
18	0.25	24	81	324	14
19	0.10	24	77	770	32
20	0.05	24	75	1500	63
21[b]	0.05	24	86	1720	72

[a] Reaction condition: 1.0 mmol bromobenzene, 1.0 mmol phenylboronic acid, 1.5 mmol *t*-BuOK, 3 mL DMF/H_2O (1/1, V/V) 100 °C. All reactions were monitored by GC.

[b] Iodobenzene was used as aryl halide.

Table 3
Suzuki cross-coupling of aryl halides with phenylboronic acid and 1-naphthylboronic acid.

Entry[a]	Ar-X	Ar′	Cat. (0.5 mol%)	Reaction time (h)	GC yield (%)
1	C_6H_5Br	Phenyl	**1**	1	88
2	C_6H_5Br	Phenyl	**2**	1	90
3	C_6H_5Br	1-Naphthyl	**2**	1	74
4	4-NO_2-C_6H_4-Br	Phenyl	**1**	1	94
5	4-NO_2-C_6H_4-Br	Phenyl	**2**	1	97
6	4-NO_2-C_6H_4-Br	1-Naphthyl	**2**	1	87
7	2-NO_2-C_6H_4-Br	Phenyl	**2**	2	78
8	4-$COCH_3$-C_6H_4-Br	Phenyl	**1**	1	94
9	4-$COCH_3$-C_6H_4-Br	Phenyl	**2**	1	98
10	4-$COCH_3$-C_6H_4-Br	1-Naphthyl	**2**	1	84
11	2-$COCH_3$-C_6H_4-Br	Phenyl	**2**	3	89
12	4-OCH_3-C_6H_4-Br	Phenyl	**1**	1	87
13	4-OCH_3-C_6H_4-Br	Phenyl	**2**	1	86
14	4-OCH_3-C_6H_4-Br	1-Naphthyl	**2**	1	76
15	2-OCH_3-C_6H_4-Br	Phenyl	**2**	2	82
16	4-CH_3-C_6H_4-Br	Phenyl	**1**	1	88
17	4-CH_3-C_6H_4-Br	Phenyl	**2**	1	87
18	4-CH_3-C_6H_4-Br	1-Naphthyl	**2**	1	75
19	2-CH_3-C_6H_4-Br	Phenyl	**2**	1	91
20	C_6H_5I	Phenyl	**1**	1	94
21	C_6H_5I	Phenyl	**2**	1	98
22	C_6H_5I	1-Naphthyl	**2**	1	79
23	C_6H_5Cl	Phenyl	**1**	24	75
24	C_6H_5Cl	Phenyl	**2**	24	71
25	C_6H_5Cl	1-Naphthyl	**2**	48	50

[a] Reaction condition: 1.0 mmol aryl halide, 1.5 mmol arylboronic acid, 1.5 mmol *t*-BuOK, 0.005 mmol catalyst, 3 mL DMF/H_2O (1/1, V/V), 100 °C. All reactions were monitored by GC.

the true active species maybe palladium nano particles formed in the catalytic system. Further studies on the applicability of this catalyst system in other coupling reactions such as Heck, Sonogashira and amination are currently under investigation in our laboratory.

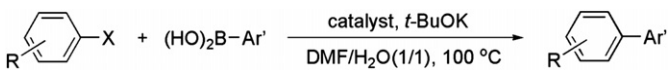
4. Experimental

4.1. Materials and methods

The *N*,*N*-methylene-*N*′,*N*′-bis-aryl-1,4,5,6-tetrahydropyrimidinium dibromides were prepared in our lab. All other chemicals were used as purchased. Solvents were dried and freshly distilled prior to use. Suzuki cross-coupling reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were obtained from a Thermo Flash EA 1112 elemental analyzer. ^1H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker DPX-400 spectrometer using TMS as an internal standard. The catalyst stock solution for Suzuki cross-coupling was prepared by dissolving exactly weighed complexes **1** or **2** in 5 mL DMF.

4.2. General procedure for the synthesis of complexes *1* and *2*

$Pd(OAc)_2$ (101 mg, 0.45 mmol) was added to a solution of *N*,*N*-methylene-*N*′,*N*′-bis-aryl-1,4,5,6-tetrahydropyrimidinium dibromides (0.45 mmol) in DMSO (3 mL). The mixture was then heated at 50 °C for 5 h. After cooling, the solvent was removed completely under vacuum. The residue was then dissolved in $CHCl_3$, and filtered. Evaporation of the filtrate afforded orange solids. Recrystallization from acetonitrile/diethyl ether gave the analytically pure complexes **1** and **2**, respectively.



Scheme 3. Suzuki cross-coupling of aryl halides with arylboronic acids.

4.2.1. Bis-[1-(2,4,6-trimethyl-phenyl)-3,4,5,6-tetrahydropyrimidine) dibromopalladium (*1*)

Orange solid; yield, 56%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.97 (m, 4H, H5), 2.20 (s, 12H, CH_3), 2.26 (s, 6H, CH_3), 3.28 (t, $J = 5.78$ Hz, 4H, H6), 3.47 (t, $J = 5.62$ Hz, 4H, H4), 6.87 (s, 4H, ArH), 7.27 (s, 2H, H2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9 (CH_3), 20.9 (CH_3), 21.5 (C5), 45.4 (C6), 47.4 (C4), 129.4, 135.9 138.2, 147.2 (ArC), 155.4 (C2). Anal. Calcd for $C_{26}H_{36}Br_2N_4Pd(H_2O)_{0.5}$: C, 45.93; H, 5.49; N, 8.24. Found : C, 45.96; H, 5.30; N, 8.10.

4.2.2. Bis-[1-(2,6-diisopropyl-phenyl)-3,4,5,6-tetrahydropyrimidine) dibromopalladium (*2*)

Orange solid; yield, 60%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, $J = 5.48$ Hz, 12H, CH_3), 1.26 (d, $J = 6.76$ Hz, 12H, CH_3), 1.99 (m, 4H, H5), 2.96(m, 4H, C*H*(CH_3)$_2$), 3.31 (t, $J = 5.68$ Hz, 4H, H6), 3.51 (t, $J = 5.70$ Hz, 4H, H4), 7.15 (m, 6H, ArH), 7.30 (t, $J = 7.76$ Hz, 2H, H2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3 (CH_3), 24.8 (CH_3), 28.2 (CH(CH_3)$_2$), 29.7 (C5), 46.8(C6), 47.5 (C4), 124.3, 129.3, 138.2, 147.2 (ArC), 155.4 (C2). Anal. Calcd for $C_{32}H_{48}Br_2N_4Pd(Et_2O)_{0.25}$: C, 51.24; H, 6.58; N, 7.24; Found : C, 51.47; H, 6.36; N, 7.21.

4.3. General procedure for Suzuki cross-coupling

A Schlenk tube was charged with the appropriate aryl halide, arylboronic acid and base under nitrogen. The required amount of the catalyst stock solution and additional solvent were added to obtain a total volume of 3 mL. The reaction mixture was heated at 100 °C for specified time, and then allowed to cool. The reaction mixture was extracted three times with diethyl ether, and the combined organic extracts were washed with water, dried ($MgSO_4$), and evaporated to dryness. Internal standard was added to the residue and the yield was then measured by GC. The products were isolated by flash chromatography on silica gel, and characterized by m.p. and ^1H NMR.

4.3.1. Biphenyl

White plate, m.p. 70 °C, Lit. 70–71 °C [53]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (m, 4H), 7.46–7.42 (m, 4H), 7.35–7.32 (m, 2H).

4.3.2. 1-Phenylnaphthalene

Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, $J = 8.4$ Hz, 1H), 8.12 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.75–7.62 (m, 9H).

4.3.3. 4-Nitrobiphenyl

Yellow needle, m.p. 113–114 °C, Lit. 112–114 °C [53]; ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.5$ Hz, 2H), 7.62 (d, $J = 7.5$ Hz, 2H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 1H).

4.3.4. 2-Nitrobiphenyl

Yellow solid, m.p. 37–38 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (m, 1H), 7.65–7.58 (m, 1H), 7.47–7.43 (m, 5H), 7.33–7.29 (m, 1H).

4.3.5. 1-(4-Nitrophenyl)naphthalene

White solid, m. p. 131 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, $J = 8.4$ Hz, 2H), 7.98–7.96 (m, 2H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.61–7.45 (m, 4H).

4.3.6. 4-Acetylbiphenyl

White solid, m.p. 118 °C, Lit. 116–118 °C [53]; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.66 (d,

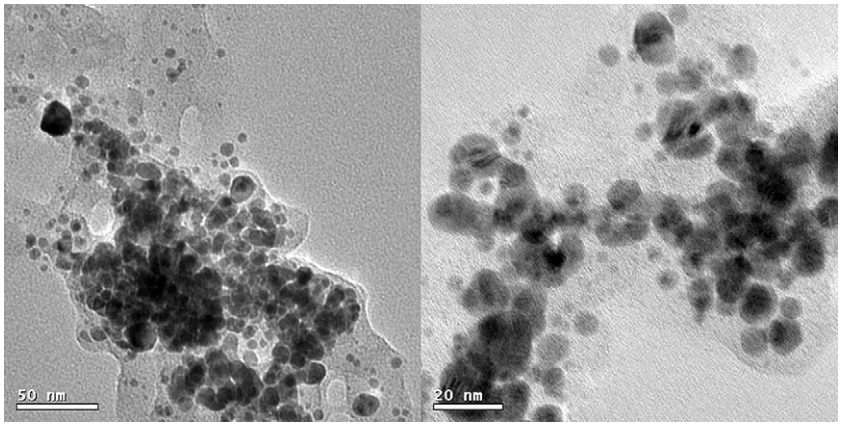


Fig. 1. HR-TEM micrographs of palladium nano particles formed in the Suzuki reaction.

$J = 7.2$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.44 (t, $J = 7.2$ Hz, 1H), 2.67 (s, 3H, $COCH_3$).

4.3.7. 2-Acethylbiphenyl

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (m, 1H), 7.47–7.44 (m, 1H), 7.38–7.32 (m, 5H), 7.30–7.28 (m, 1H).

4.3.8. 1-(4-Acetylphenyl)naphthalene

White solid, m.p. 101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, $J = 8.4$ Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.78–7.61 (m, 6H), 7.55 (d, $J = 7.6$ Hz, 2H), 2.71 (s, 3H, $COCH_3$).

4.3.9. 4-Methoxybiphenyl

White solid, m.p. 90–91 °C, Lit. 91–92 °C [53]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52 (m, 4H), 7.50–7.35 (m, 2H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 8.5$ Hz, 2H), 3.85 (s, 3H, OCH_3).

4.3.10. 2-Methoxybiphenyl

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.50 (m, 2H), 7.39–7.36 (m, 2H), 7.30–7.28 (m, 3H), 7.04–6.94 (m, 2H), 3.77 (s, 3H).

4.3.11. 1-(4-Methoxyphenyl)naphthalene

White solid, m.p. 112–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.94 (m, 2H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.56–7.45 (m, 6H), 7.08 (d, $J = 8.8$ Hz, 2H), 3.94 (s, 3H, OCH_3).

4.3.12. 4-Methylbiphenyl

White solid, m.p. 46–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, $J = 7.6$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.45–7.40 (m, 2H), 7.35–7.30 (m, 1H), 7.25 (d, $J = 7.6$ Hz, 2H), 2.40 (s, 3H).

4.3.13. 2-Methylbiphenyl

Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.35 (m, 2H), 7.33–7.26 (m, 3H), 7.25–7.20 (m, 4H), 2.25 (s, 3H, CH_3).

4.3.14. 1-(4-Methylphenyl)naphthalene

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, $J = 8.0$ Hz, 2H), 7.94 (t, $J = 8.2$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.59–7.45 (m, 4H), 2.18 (s, 3H, CH_3).

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