

Heterogeneous Palladium Chloride Catalyzed Ligand-free Suzuki-Miyaura Coupling Reactions at Ambient Temperature

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A mild and efficient ligand-free Suzuki-Miyaura coupling reaction catalyzed by heterogeneous palladium chloride was developed at room temperature in a short reaction time under air atmosphere. Various phenyl iodides, bromides and activated chlorides were coupled with sodium tetraphenylborate or phenylboronic acids efficiently to afford the corresponding cross-coupled products in good to excellent yields. Furthermore, the catalyst could be recycled up to four times without loss of its activity.

Keywords Suzuki-Miyaura reaction, ligand-free, palladium chloride, heterogeneous catalyst

Introduction

The Suzuki-Miyaura reaction has become a mainstay of modern synthetic organic chemistry for the preparation of biaryl compounds¹ and has been broadly applied to synthesis of natural products, agrochemicals, pharmaceuticals, and polymers, such as organic electroluminescence (EL) materials.^{1a,2} The utility of the Suzuki-Miyaura reaction comes from its high stability of precursors, tolerance to a wide range of functional groups, low toxicity associated with boron compounds, and easy handling of reagents and by-products. Since its invention, the development of efficient and selective catalytic systems for the Suzuki-Miyaura cross-coupling reaction has attracted much more attention. Traditional Suzuki-Miyaura coupling reactions generally employ homogeneous palladium catalysts along with phosphine ligands in the presence of a base.³ However, many of the phosphine ligands are toxic and sensitive to air and moisture and the expensive palladium complexes are often lost by the end of the reaction. Furthermore, the products are frequently contaminated by residual palladium black and ligands, which can be difficult to separate from the end products.⁴ Thus, development of phosphine-free palladium catalytic systems is still a promising area for organic chemists. Fortunately, a number of efficient phosphine-free catalytic systems, such as *N*-heterocyclic carbene-palladium catalysts,⁵ thiourea-palladium catalysts,⁶ diazabutadiene-palladium catalyst,⁷ amine-palladium catalysts,⁸ guanidine-palladium catalyst,⁹ and other phosphine-free palladium catalysts,¹⁰ even though ligand-less palladium catalytic systems,¹¹ have been reported recently. From an eco-

nomical and environmental point of view, catalytic systems that can be efficiently recovered and recycled while keeping the intrinsic activity and selectivity of the active center have been received much more attention. Heterogeneous palladium catalysts immobilized on activated carbon,¹² silica¹³ or organic polymers¹⁴ have been recently reported, which represent attractive alternatives to the homogeneous systems. To the best of our knowledge, there are few ligand-free palladium chloride catalyzed heterogeneous Suzuki-Miyaura coupling reactions in the literature.

Sodium tetraphenylborate, as a new type of borate source, is a stable and commercially available reagent. It has been discovered that its four phenyl groups can all be coupled with phenyl halides to generate the corresponding products efficiently for the Suzuki-Miyaura reaction.¹⁵ Herein, we would like to report a mild and efficient ligand-free palladium chloride catalyzed Suzuki-Miyaura coupling reaction of phenyl iodides, bromides and activated chlorides with sodium tetraphenylborate, as well as with phenylboronic acids at room temperature in methanol under air atmosphere. The reactions generated the corresponding coupling products in good to excellent yields when bromide, iodide acted as a leaving group with sodium tetraphenylborate and phenylboronic acids.

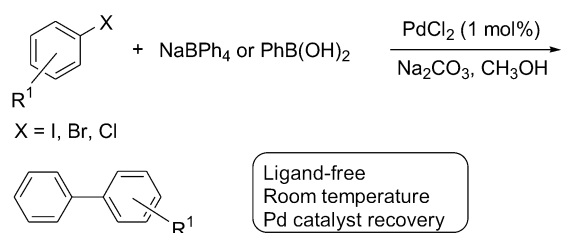
Results and discussion

In order to find a better catalytic system for the synthesis of asymmetrical biaryls, a cross-coupling reaction of 4-bromoanisole with sodium tetraphenylborate was chosen as a model one for our investigation. The

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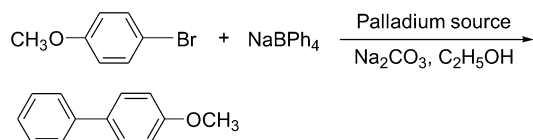
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reactions were carried out in the presence of different palladium sources, sodium carbonate as a base, and ethanol as a solvent at room temperature. The results are summarized in Table 1. Among the various palladium sources tested, the use of PdCl_2 gave the corresponding cross-coupling product in the highest yield (Table 1, Entry 1). Although Pd/C is one of the most common heterogeneous catalysts¹⁶ and many applications of Pd/C to Suzuki-Miyaura coupling reactions have been reported,¹⁷⁻²⁰ palladium powder (submicron) could not catalyze the reaction in our system (Table 1, Entries 2 and 3). It is probably that catalytic activity of palladium black powder is determined by its size. $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2$, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ and $\text{Pd}(\text{PPh}_3)_4$ were found to be inferior (Table 1, Entries 4–7). However, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ or $\text{Pd}(\text{PPh}_3)_2\text{Br}_2$ gave the disappointing results (Table 1, Entries 8 and 9). Consequently, PdCl_2 was chosen as the catalyst for further optimization for its high efficiency.

Table 1 Effect of palladium source on the Suzuki-Miyaura reaction^a



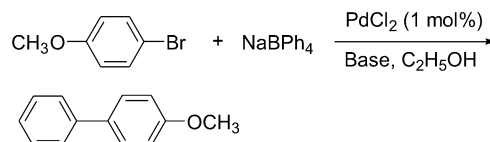
Entry	Palladium source	Yield ^b /%
1	PdCl_2	81
2	Pd/C	73
3	Palladium powder (submicron)	NR
4	$\text{Pd}(\text{OAc})_2$	51
5	$\text{Pd}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2$	65
6	$\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$	70
7	$\text{Pd}(\text{PPh}_3)_4$	66
8	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	Trace
9	$\text{Pd}(\text{PPh}_3)_2\text{Br}_2$	Trace

^a 4-Bromoanisole (1.00 mmol), NaBPh_4 (0.25 mmol), palladium source (0.01 mmol), Na_2CO_3 (2.00 mmol) in $\text{C}_2\text{H}_5\text{OH}$ (2.0 mL) at room temperature under air atmosphere for 100 min. ^b Isolated yield.

As known, a well-chosen base is essential to the success of the coupling reaction. Several different bases for the Suzuki-Miyaura coupling reaction were examined. Na_2CO_3 was found to be the most effective one and gave the desired product in an 81% yield (Table 2, Entry 1). Other bases, such as K_2CO_3 , K_3PO_4 , Na_3PO_4 ,

NEt_3 and DABCO, were substantially less effective (Table 2, Entries 2–6). Strong bases, such as Cs_2CO_3 , LiOH and NaOH failed to promote the reaction and gave a trace of coupling products (Table 2, Entries 7–9).

Table 2 Effect of base on the Suzuki-Miyaura reaction^a

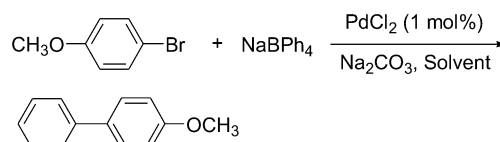


Entry	Base	Yield ^b /%
1	Na_2CO_3	81
2	K_2CO_3	60
3	K_3PO_4	65
4	Na_3PO_4	76
5	NEt_3	63
6	DABCO	61
7	LiOH	Trace
8	NaOH	Trace
9	Cs_2CO_3	Trace

^a 4-Bromoanisole (1.00 mol), NaBPh_4 (0.25 mol), PdCl_2 (0.01 mol), base (2.00 mol) in $\text{C}_2\text{H}_5\text{OH}$ (2.0 mL) at room temperature under air atmosphere for 100 min. ^b Isolated yield.

The solvent also played an important role in the present method. Various solvents were investigated for the Suzuki-Miyaura reaction and the results are listed in Table 3. No desired cross-coupling products were observed while reactions were carried out in cyclohexane,

Table 3 Effect of solvent on the Suzuki-Miyaura reaction^a



Entry	Solvent	Yield ^b /%
1	Cyclohexane	NR
2	Ethyl ether	NR
3	Toluene	NR
4	CH_2Cl_2	NR
5	1,4-Dioxane	20
6	DMF	15
7	CH_3CN	20
8	Acetone	67
9	Ethanol	81
10	Methanol	91
11	H_2O	23

^a 4-Bromoanisole (1.00 mmol), NaBPh_4 (0.25 mmol), PdCl_2 (0.01 mmol), base (2.00 mmol) in solvent (2.0 mL) at room temperature under air atmosphere for 100 min. ^b Isolated yield.

ethyl ether, toluene and dichloromethane (Table 3, Entries 1–4). Very little product was isolated when the reactions were performed in aprotic polar solvents, such as dimethylformamide (DMF), acetonitrile and dioxane (Table 3, Entries 5–7). Fortunately, an excellent yield of the coupling product was obtained as the reaction was carried out in methanol, whereas ethanol was less effective than methanol (Table 3, Entries 9 and 10). However, the reaction only gave a poor yield of the product in pure water (H₂O), because of low dissolubility of substrates in water (Table 3, Entry 11).

During the course of our further optimization of the reaction conditions, when using 1 mol% of PdCl₂, the reactions were generally completed in a matter of minutes, but the time, as expected, was inversely proportional to the temperature. An ambient temperature was found to be optimal. Thus, the optimized reaction conditions for this reaction are PdCl₂ (1 mol%) in methanol at room temperature for 100 min.

We next explored the scope and limitation of substrates for the Suzuki-Miyaura coupling reaction under the optimized reaction conditions by using 1 mol% of PdCl₂ in methanol. The catalyst system was applicable to a wide range of phenyl iodides and bromides. The results are shown in Table 4. The electron-neutral, electron-rich and electron-deficient phenyl iodides reacted with NaBPh₄ and afforded almost quantitative corresponding cross-coupling products under the standard reaction conditions (Table 4, Entries 1–5). Phenyl bromides bearing electron-withdrawing groups, such as

Table 4 PdCl₂ catalyzed the Suzuki-Miyaura reaction^a

Entry	Phenyl halide	Organoboron source	Yield ^b /%
1	C ₆ H ₅ I	NaBPh ₄	99
2	<i>m</i> -CH ₃ C ₆ H ₄ I	NaBPh ₄	98
3	<i>p</i> -CH ₃ C ₆ H ₄ I	NaBPh ₄	97
4	<i>p</i> -CH ₃ OC ₆ H ₄ I	NaBPh ₄	97
5	<i>m</i> -CNC ₆ H ₄ I	NaBPh ₄	99
6	C ₆ H ₅ Br	NaBPh ₄	95
7	<i>p</i> -CH ₃ C ₆ H ₄ Br	NaBPh ₄	93
8	<i>p</i> -CH ₃ OC ₆ H ₄ Br	NaBPh ₄	91
9	<i>p</i> -CNC ₆ H ₄ Br	NaBPh ₄	97
10	<i>p</i> -C ₂ H ₅ CO ₂ C ₆ H ₄ Br	NaBPh ₄	96
11	<i>p</i> -NO ₂ C ₆ H ₄ Br	NaBPh ₄	95
12	<i>m</i> -NO ₂ C ₆ H ₄ Br	NaBPh ₄	94
13	<i>p</i> -CH ₃ COC ₆ H ₄ Br	NaBPh ₄	98
14	<i>p</i> -CNC ₆ H ₄ Cl	NaBPh ₄	67
15	C ₆ H ₅ Br	C ₆ H ₅ B(OH) ₂	93
16	C ₆ H ₅ Br	<i>p</i> -CH ₃ OC ₆ H ₄ B(OH) ₂	96
17	C ₆ H ₅ Br	<i>o</i> -CH ₃ OC ₆ H ₄ B(OH) ₂	89
18	C ₆ H ₅ Br	<i>p</i> -CH ₃ CO ₂ C ₆ H ₄ B(OH) ₂	92

^a Phenyl halide (1.00 mmol), NaBPh₄ (0.25 mmol) or boronic acid (1.00 mmol), palladium chloride (0.01 mmol), Na₂CO₃ (2.00 mmol) in CH₃OH (2.0 mL) under air atmosphere at room temperature for 100 min. ^b Isolated yield.

NO₂, CN, COOC₂H₅ and COCH₃, coupled with NaBPh₄ and generated the corresponding products in high yields (Table 4, Entries 9–13), while phenyl bromides bearing electron-donating groups, such as CH₃ and CH₃O, gave good yields of the corresponding cross-coupling products accompanied with a trace amount of the homo-coupling product of NaBPh₄ as a side product (Table 4, Entries 7 and 8).

Encouraged by the results of phenyl iodides and bromides, we would like to extend the scope of the activity of phenyl chlorides. The activated 4-chlorobenzonitrile was first applied as the Suzuki-Miyaura coupling partner. Under the optimized conditions, however, the coupling reaction generated the desired cross-coupling product in a 67% yield and biphenyl was formed as a by-product from the self-coupling of NaBPh₄ (Table 4, Entry 14). Unfortunately, the electron-rich phenyl chlorides were inactive.

The effect of the phenylboronic acid partner on the Suzuki-Miyaura reaction was also investigated (Table 4, Entries 15–18). It could be seen from Table 4 that both active phenylboronic acids with an electron-donating group and deactivated phenylboronic acids with an electron-withdrawing group exhibited excellent reactivity to the Suzuki-Miyaura reaction (Table 4, Entries 15–18). In addition, this cross-coupling was also tolerant to *ortho* substitution in phenylboronic acids, leading to a good yield (89% isolated yield).

The reusability of PdCl₂ is a great advantage in the cost reduction of process chemistry. The reuse of PdCl₂ in the coupling reaction by using 4-bromoanisole and sodium tetraphenylborate as substrates was surveyed (Table 5). Although, the catalytic activity was gradually diminished, the yield was still not less than 86% even in the third reuse without any activating procedure.

Table 5 Investigation on the reuse of PdCl₂ in the Suzuki-Miyaura reaction^a

Entry	PdCl ₂	Yield ^b /%
1	Fresh	91
2	First reuse	90
3	Second reuse	88
4	Third reuse	86

^a 4-Bromoanisole (1.00 mmol), NaBPh₄ (0.25 mmol), PdCl₂ (0.01 mmol), Na₂CO₃ (2.00 mmol) in methanol (2.0 mL) at room temperature under air atmosphere for 100 min. ^b Isolated yield.

Conclusion

In conclusion, we have developed a ligand-free and heterogeneous PdCl₂ catalyzed Suzuki-Miyaura coupling reaction under mild reaction conditions. Sodium

tetraphenylborate and phenylboronic acids could smoothly couple with various phenyl iodides, bromides and activated chlorides in high yields at room temperature in a short reaction time (less than 2 h) under air atmosphere. Furthermore, palladium chloride could be recycled four times without loss of its activity via a simple decantation procedure. This methodology will provide a facile, efficient, and environmentally friendly process for the Suzuki-Miyaura coupling reaction because of its wide applicability to various substrates, the use of less toxic reagents, and mild reaction conditions.

Experimental

Physical measurements and materials

Melting points were recorded on a WRS-2B melting point apparatus and uncorrected. All ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer. Chemical shifts were given as δ values with reference to tetramethylsilane (TMS) as an internal standard. Products were purified by flash column chromatography on 230–400 mesh silica gel, SiO_2 .

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and used without purification prior to use.

General procedure for the Suzuki-Miyaura cross-coupling reaction

Under air atmosphere, phenyl halide (1.00 mmol), NaBPh_4 (0.25 mmol) or phenylboronic acid (1.00 mmol), Na_2CO_3 (212 mg, 2.00 mmol), PdCl_2 (1.8 mg, 0.01 mmol) and methanol (2.0 mL) were added to a test tube with a stirring bar, and the reaction system was sealed with a rubber stopper. The reaction was stirred at room temperature for 100 min. After the reaction was completed, palladium black and other inorganics precipitated to the bottom of the test tube. After decantation of the reaction solution, the residue was washed with methanol (2 mL \times 3), and then was subjected to a second run of the Suzuki-Miyaura reaction by recharging with the substrates, Na_2CO_3 and methanol without further addition of PdCl_2 . The filtrate was concentrated in vacuum and purified by flash column chromatography on silica gel to give the desired biphenyl compound.

Recyclability of PdCl_2

After the reaction, the reactor was kept silent for 10 min, palladium black and other inorganics precipitated to the bottom of the reactor. After decantation of the reaction solution, the residue was washed with methanol (2 mL \times 3) and then could be reused directly without further purification.

Biphenyl: m.p. 69–70 °C (lit.²¹ 69–70 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.58–7.28 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 141.2, 128.7, 127.2, 127.1.

3-Methylbiphenyl: m.p. 42–44 °C (lit.²² 42–43 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.64–7.12 (m, 9H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 141.5, 138.7, 137.3, 129.8, 129.0, 127.31, 127.29, 21.4.

4-Methylbiphenyl: m.p. 46–48 °C (lit.²³ 46–47 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.58–7.21 (m, 9H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 20.1.

4-Methoxybiphenyl: m.p. 86–87 °C (lit.²⁴ 86 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.59–7.54 (m, 4H), 7.46–7.41 (m, 2H), 7.35–7.30 (m, 1H), 7.02–6.99 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Cyanobiphenyl: m.p. 83–85 °C (lit.²⁵ 82–84 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.75–7.71 (m, 4H), 7.62–7.60 (d, $J=7.2$ Hz, 2H), 7.53–7.44 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.1, 118.9, 110.8.

4-Nitrobiphenyl: m.p. 110–111 °C (lit.²⁶ 112–113 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 8.29–8.26 (d, $J=8.4$ Hz, 2H), 7.73–7.70 (d, $J=8.4$ Hz, 2H), 7.63–7.60 (d, $J=7.2$ Hz, 2H), 7.52–7.44 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 147.5, 146.9, 138.6, 129.1, 128.8, 127.7, 127.3, 124.0.

3-Nitrobiphenyl: m.p. 60–62 °C (lit.²⁷ 59 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 8.40 (s, 1H), 8.17–8.14 (d, $J=7.5$ Hz, 1H), 7.87–7.86 (d, $J=7.2$ Hz, 1H), 7.59–7.57 (m, 3H), 7.46–7.44 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 148.5, 142.6, 138.4, 132.9, 129.6, 129.0, 128.4, 127.0, 121.9, 121.7.

4-Acetylbiphenyl: m.p. 120–121 °C (lit.²⁸ 119–120 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 8.05–8.03 (d, $J=8.4$ Hz, 2H), 7.70–7.62 (m, 4H), 7.50–7.40 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 197.7, 145.7, 139.8, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.7.

3-Cyanobiphenyl: m.p. 45–46 °C (lit.²⁹ 43–45 °C); ^1H NMR (300 MHz, CDCl_3) δ : 7.80–7.76 (m, 2H), 7.60–7.57 (m, 1H), 7.53–7.50 (m, 3H), 7.47–7.39 (m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 142.2, 138.6, 131.3, 130.5, 130.4, 129.4, 128.9, 128.2, 126.9, 118.7, 112.7.

2-Methoxybiphenyl: Oil (lit.³⁰ oil); ^1H NMR (CDCl_3 , 300 MHz) δ : 7.55–7.52 (m, 2H), 7.43–7.38 (m, 2H), 7.34–7.30 (m, 3H), 7.05–6.97 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 156.4, 138.5, 130.9, 130.6, 129.5, 128.6, 127.9, 126.9, 120.8, 111.1, 55.5.

Ethyl 4-phenylbenzoate: m.p. 48–49 °C (lit.³¹ 49.2–49.6 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 8.16–8.14 (d, $J=8.1$ Hz, 2H), 7.69–7.62 (m, 4H), 7.50–7.38 (m, 3H), 4.46–4.39 (q, $J=7.2$ Hz, 2H), 1.46–1.41 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 166.3, 145.3, 139.9, 129.9, 129.1, 128.8, 128.0, 127.1, 126.8, 60.8, 14.2.

Methyl 4-phenylbenzoate: m.p. 118–120 °C (lit.³² 119–120 °C); ^1H NMR (CDCl_3 , 300 MHz) δ : 8.12–8.09 (m, 2H), 7.67–7.61 (m, 4H), 7.49–7.37 (m, 3H), 3.94 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 167.0, 145.6, 140.0, 130.0, 128.9, 128.8, 128.1, 127.2, 127.0, 52.1.

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