

Water-Soluble and Recyclable Cyclopalladated Ferrocenylimine for Suzuki Coupling Reaction

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A series of new water-soluble cyclopalladated ferrocenylimines were designed and prepared. They were efficient catalyst for Suzuki coupling reactions of aryl bromides and phenylboronic acid in neat water under ambient atmosphere. Among of these catalysts, the catalyst (**C₂D**) could be reused for 6 times for the Suzuki coupling reaction of 4-bromotoluene with phenylboronic acid in EtOH/H₂O under ambient atmosphere, in which no significant loss activity of **C₂D** was observed.

Keywords: Suzuki reaction; Water-soluble catalyst; Aqueous media; Recycle.

INTRODUCTION

The palladium-catalyzed Suzuki coupling reaction of aryl halides with arylboronic acids is an important and versatile method for the generation of C_{aryl}-C_{aryl} bonds,¹⁻⁴ which has extensive use in the synthesis of natural products, pharmaceuticals, herbicides, and advanced materials.⁵⁻⁶ The utility of the Suzuki reaction comes from its tractability, high stability, mild reaction conditions, broad functional group tolerance, as well as low toxicity associated with boron compounds.

Generally, the palladium-catalyzed Suzuki reaction is carried out in polar organic solvent under an inert atmosphere due to the solubility of the substrate, the instability of most catalysts. However, from an economic and environmental standpoint, it is desirable to use water as a solvent instead of hazardous, expensive organic solvents and it is also worthwhile to develop new highly active catalysts that are not sensitive to air and moisture as well as easy to recover and recycle.⁷⁻¹⁰ To satisfy these concerns, some significant advances have been made, including the use of heterogeneous catalysts, aqueous solution, phase-transfer catalysts, microwave technology, water-soluble catalysts etc.¹¹⁻¹⁷

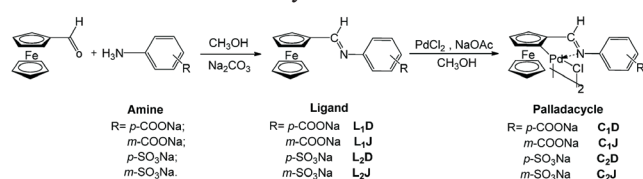
Cyclopalladated complexes had attracted much attention as exciting catalyst precursors to coupling reactions.¹⁸⁻²⁰ In our previous studies, we had synthesized series of cyclopalladated ferrocenylimines which showed satisfactory reactivity in Heck, Suzuki, Sonogashira and Kumada reactions etc.²¹⁻²⁹ However, it is still a considerable of interests in the development of new catalysts that can be used in neat

water or aqueous solution as well as easily separated from the product phase to realize the palladium catalysts recycling.^{30,31}

Recently, many researches were focused on the hydrophilic palladium complexes which were expected to perform as a recyclable and highly active catalyst system for Suzuki reaction in aqueous solvents. San Martin employed a new PCN palladium pincer complex containing a phosphinoamino group as good catalyst for Suzuki couplings in neat water.³² Chelate-stabilized palladium(II) complexes were used as catalysts for the Suzuki/Miyaura cross-coupling reaction of various aryl bromides with phenylboronic acid in water with extremely high turnover numbers.³³ Sulfonamide-based palladium complexes were employed for catalyzing Suzuki coupling reaction, in which high catalytic activity of these catalysts could be achieved.^{34,35} Additionally, cyclopalladated imine complex had proved to be efficient for Suzuki reactions in aqueous solvent with certain additive, such as water soluble phosphine ligand and TBAB.^{30,36} However, few ligand-free hydrophilic cyclopalladated ferrocenylimine complexes had been reported as efficient and recyclable catalytic precursors for Suzuki reaction in aqueous solution.

In previous studies, we discovered that cyclopalladated ferrocenylimine were efficient catalysts for carbon-carbon coupling reactions in aqueous medium. As a part of our program to explore cyclopalladated ferrocenylimines for carbon-carbon bond formation, we report here that the synthesis and characterization of four new cyclopalladated ferrocenylimines (Scheme I) with hydrophilic group and

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Scheme 1 The synthesis route of Cyclopalladated Ferrocenylimine

their application in Suzuki coupling reactions in neat water and in aqueous. It was found that the cyclopalladated complex (**C₂D**) was highly effective for Suzuki coupling reactions of aryl bromides with catalyst loadings of 0.5 mol % under ligand-free and ambient atmosphere in pure water. In addition, the application of Catalyst-H₂O-C₂H₅OH system as an efficient and reusable catalytic medium for the Suzuki coupling reaction was systematically investigated.

RESULTS AND DISCUSSION

Catalytic properties of hydrophilic cyclopalladated ferrocenylimine complexes for Suzuki reaction in neat water

Our main research was focused on the activation of steric hindrance as well as electron-rich aryl bromides under mild conditions. Thus, the coupling of the inactivated 4-bromotoluene with phenylboronic acid catalyzed by **C₂D** as a model system for the optimization were employed under aerial conditions. As shown in Table 1, KOH, NaOH and BuONa were found to be effective base, giving higher yields than K₂CO₃, Na₂CO₃ and K₃PO₄ (entries 5-7). With the appropriate base (NaOH), the relative activities of several cyclopalladated ferrocenylimine complexes (entries 10-12) for the same reaction were investigated, in which the **C₂D** complexes showed better activity than that of other complexes. Influence of phase transfer reagent and reaction temperature, time on the Suzuki coupling reaction in

Table 1. Investigation of Suzuki coupling reaction conditions^a

Entry	Base	Solvent	Catalyst (mol %)	Yield ^b (%)
1	K ₃ PO ₄	H ₂ O	0.5	88
2	K ₃ PO ₄ ·3H ₂ O	H ₂ O	0.5	85
3	Na ₂ CO ₃	H ₂ O	0.5	86
4	K ₂ CO ₃	H ₂ O	0.5	86
5	NaOH	H ₂ O	0.5	99
6	KOH	H ₂ O	0.5	99
7	BuONa	H ₂ O	0.5	99
8	NaOH	H ₂ O	0.2	86
9	NaOH	H ₂ O	0.1	76
10 ^c	NaOH	H ₂ O	0.5	96
11 ^d	NaOH	H ₂ O	0.5	96
12 ^e	NaOH	H ₂ O	0.5	92

^a Reaction conditions: 4-Bromotoluene (0.5 mmol), PhB(OH)₂ (0.75 mmol), Base (1.0 mmol), **C₂D** (0.5 mol %), H₂O (3.0 mL), PEG 2000 (0.5 mmol), 60 °C, 4 h. ^b Yield determined by GC, based on ArX. ^c Catalyst **C₁D**. ^d Catalyst **C₁J**. ^e Catalyst **C₂J**.

neat water was showed in Table 2, in which PEG2000 was selected as the best additive which acted not only as phase transfer reagent, but stability for Pd nanoparticles.

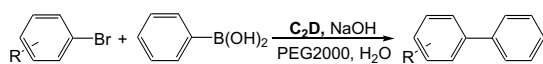
When the catalyst loading of **C₂D** was lowered to 0.1 mol% for Suzuki coupling reaction of 4-bromotoluene with phenylboronic acid, 76% GC yield could be obtained (Table 1, entry 9). The results obtained above showed that these catalysts could effectively catalyze Suzuki cross-coupling reaction between aryl bromide and phenylboronic acid in water under atmosphere.

With the appropriate base (NaOH) and reaction temperature (60 °C), the scope and limitations of the protocol based on both aryl bromides and phenylboronic acids in the presence of 0.5 mol% cyclopalladated complex **C₂D** were examined (Table 3). The catalytic system selected can tol-

Table 2. Influence of catalyst and catalyst loading on Suzuki coupling reaction^a

Entry	Base	PTC	T (°C)	Time (h)	Yield ^b (%)
1	NaOH	—	25	24	10
2	NaOH	TBAB (0.1 mmol)	25	24	55
3	NaOH	TBAB (0.2 mmol)	25	24	64
4	NaOH	PEG2000 (0.1 mmol)	25	24	76
5	NaOH	PEG2000 (0.2 mmol)	25	24	63
6	NaOH	PEG4000 (0.1 mmol)	25	24	57
7	NaOH	PEG4000 (0.2 mmol)	25	24	49
8	NaOH	PEG2000 (0.1 mmol)	50	4	78
9	NaOH	PEG2000 (0.1 mmol)	60	4	99

^a Reaction conditions: 4-Bromotoluene (0.1 mmol), PhB(OH)₂ (0.15 mmol), Base (0.2 mmol), H₂O (3.0 mL), ^b Yield determined by GC, based on the product.

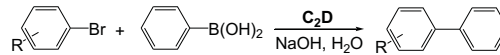
Table 3. Suzuki reaction of aryl bromides with phenylboronic acid in pure water^a


Entry	ArX	Product	Yield ^b (%)
1	<i>o</i> -CH ₃ -C ₆ H ₄ Br	<i>o</i> -CH ₃ -Ph-Ph	50 (47)
2	<i>p</i> -CH ₃ O-C ₆ H ₄ Br	<i>p</i> -CH ₃ O-Ph-Ph	97 (96)
3	<i>m</i> -CH ₃ O-C ₆ H ₄ Br	<i>m</i> -CH ₃ O-Ph-Ph	96 (94)
4	<i>o</i> -CH ₃ O-C ₆ H ₄ Br	<i>o</i> -CH ₃ O-Ph-Ph	83 (80)
5	<i>p</i> -NH ₂ -C ₆ H ₄ Br	<i>p</i> -NH ₂ -Ph-Ph	99 (96)
6	<i>m</i> -NH ₂ -C ₆ H ₄ Br	<i>m</i> -NH ₂ -Ph-Ph	90 (86)
7	<i>p</i> -CN-C ₆ H ₄ Br	<i>p</i> -CN-Ph-Ph	99 (98)
8	<i>o</i> -CN-C ₆ H ₄ Br	<i>o</i> -CN-Ph-Ph	97 (95)
9	<i>p</i> -CHO-C ₆ H ₄ Br	<i>p</i> -CHO-Ph-Ph	99 (99)
10	<i>o</i> -CHO-C ₆ H ₄ Br	<i>o</i> -CHO-Ph-Ph	98 (92)
11	<i>p</i> -NO ₂ -C ₆ H ₄ Br	<i>p</i> -NO ₂ -Ph-Ph	99 (97)
12	<i>p</i> -CF ₃ -C ₆ H ₄ Br	<i>p</i> -CF ₃ -Ph-Ph	99 (96)
13	1-Bromo-naphthalene	1-Naph-Ph	28 (24)
14	2-Bromo-pyridine	2-Py-Ph	99 ^c (96)
15	3-Bromo-pyridine	3-Py-Ph	99 ^c (97)
16	3-Bromo-thiophene	3-Th-Ph	trace
17	<i>p</i> -CHO-C ₆ H ₄ Cl	<i>p</i> -CHO-Ph-Ph	trace

^a Reaction conditions: 4-Bromotoluene (0.5 mmol), PhB(OH)₂ (0.75 mmol), Base (1.0 mmol), C₂D (0.5 mol %), H₂O (3.0 mL), PEG 2000 (0.5 mmol), 60 °C, 4 h. ^b Yield determined by GC, based on ArX (isolated yields are given in parentheses). ^c The reaction time was 10 h.

erate a broad range of functional groups, such as OMe, NH₂, CN, CHO, NO₂ and CF₃ groups, in which both electron-deficient and electron-rich aryl bromides could be coupled with phenylboronic acid in excellent yields in neat water except *o*-CH₃ group (entries 2, 3, and 5-12). However, the sterically hindered aryl bromides possessing ortho-substituents gave the coupled product in slightly lower yield (entries 1 and 4). Moreover, the N-heterocyclic compounds, excellent GC yield could also be obtained after 10 h (entries 14 and 15). 3-Bromo-thiophene was found to be poor coupling partners in the same reaction conditions. Coupling reaction of *p*-chlorobenzaldehyde with phenylboronic acid was also explored under the same reaction conditions, in which there was trace coupling product.

The coupling of 4-bromotoluene with phenylboronic acid in neat water was selected as a model reaction to explore the recyclability of C₂D. A little palladium black was found after the reaction was in progress for certain times. It appeared that the aggregation of palladium nanoparticles took place with increasing reaction time. At the end of reaction, a large amount of palladium black precipitated was gained. In order to insight into the temperature ef-

 Table 4. Influence of temperature and reaction time on Suzuki coupling reaction in water^a


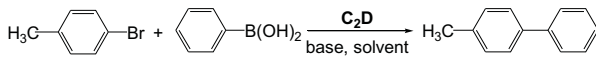
Entry	T (°C)	Time (h)	Yield ^b (%)
1	80	4	99
2	70	4	99
3	60	4	99
4	50	4	78
5	60	3	85
6	50	5	88

^a Reaction conditions: 4-Bromotoluene (0.5 mmol), PhB(OH)₂ (0.75 mmol), Base (mmol), C₂D (0.5 mol %), H₂O (3.0 mL), PEG 2000 (0.5 mmol). ^b Yield determined by GC, based on ArX.

fect on the aggregation of palladium nanoparticles, we investigated the changes of reaction temperature on the activity of C₂D. Palladium black could be observed with increasing of reaction temperature (Table 4, entries 1-4). It's clear that the reaction rate could be improved by rising the reaction temperature, but the degradation rate of C₂D also be increased, which resulted in formation of palladium black. Therefore, the recycle of catalyst C₂D in water could not be realized.

Catalytic properties of C₂D for Suzuki reaction in C₂H₅OH/H₂O

We tried to explore the recycle of C₂D for Suzuki coupling reaction in mixed solvent. The coupling reaction of 4-bromotoluene with phenylboronic acid was chosen as a model reaction for screening the reaction conditions, and the results are summarized in Table 5. The reaction in pure water without PEG2000 afforded 4-methylbiphenyl in a very low yield (entry 1). However, the activity of catalyst was improved due to the addition of incremental amounts of organic solvent and nearly quantitative yield was obtained even in 1h at room temperature (entries 5-7). C₂H₅OH/H₂O (2:1) mixed solvent was selected because of ethanol's safety, economy, and environmental friend. Desired product with high yields were obtained under different bases, including K₃PO₄, K₃PO₄·3H₂O, Na₂CO₃, NaOH, KOH, K₂CO₃, and BuONa (entries 5, 10-13). A quantitative yield of product could be obtained in the presence of 0.1 mol % C₂D. Moreover, an excellent 96% yield of the coupling product could also be gained even in lowering the catalyst loading to 0.05 mol %. A modest yield of 80% was obtained when the loading of C₂D was decreased to 0.01 mol %, indicating that the C₂D-H₂O-C₂H₅OH catalytic sys-

Table 5. Influence of solvent, base, and amount of catalyst on Suzuki coupling reaction^a


Entry	Base	Solvent (V/V)	Catalyst (mol %)	Yield ^b (%)
1	K ₃ PO ₄	Pure H ₂ O (3)	0.1	10
2	K ₃ PO ₄	CH ₃ OH/H ₂ O (1:1)	0.1	80
3	K ₃ PO ₄	CH ₃ OH/H ₂ O (2:1)	0.1	93
4	K ₃ PO ₄	C ₂ H ₅ OH/H ₂ O (1:1)	0.1	89
5	K ₃ PO ₄	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	99
6	K ₃ PO ₄	acetone/H ₂ O (1:1)	0.1	99
7	K ₃ PO ₄	DMF/H ₂ O (1:1)	0.1	99
8	K ₃ PO ₄ ·3H ₂ O	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	93
9	Na ₂ CO ₃	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	92
10	NaOH	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	99 (99)
11	KOH	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	99
12	K ₂ CO ₃	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	99
13	BuONa	C ₂ H ₅ OH/H ₂ O (2:1)	0.1	99
14	NaOH	C ₂ H ₅ OH/H ₂ O (2:1)	0.05	96
15	NaOH	C ₂ H ₅ OH/H ₂ O (2:1)	0.02	86
16	NaOH	C ₂ H ₅ OH/H ₂ O (2:1)	0.01	80

^a Reaction condition: 4-Bromotoluene (0.5 mmol), PhB(OH)₂ (0.75 mmol), base (1.0 mmol), C₂D (0.1 % mol), solvent (3 mL), 1 h, rt. ^b GC yields based on bromotoluene (isolated yields are given in parentheses).

tem has highly activity for the Suzuki coupling reaction.

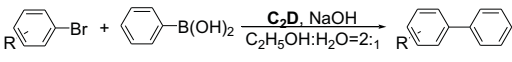
A variety of aryl bromides with different substituent could be efficiently coupled with phenylboronic acid under the optimized reaction conditions (Table 6). In the case of the steric hindrance aryl bromides, such as 2-bromotoluene, 2-bromoanisole as substrates, cross-coupling products were obtained in modest yields (entries 1, 4). The electron-deficient aryl bromides showed an excellent reactivity and the products with high yields (entries 7-12) could also be obtained. Moreover, in the case of the heterocyclic compounds, such as 1-bromonaphthalene, 2-bromopyridine, 3-bromopyridine, the cross-coupling products were also obtained from modest to excellent yields (entries 13-15). 3-Bromo-thiophene was still found to be poor coupling partners in the same reaction conditions, giving only trace coupled products. When we employed p-chlorobenzaldehyde under our optimized conditions for aryl bromides, only trace products were observed.

Recycling

The recyclability of C₂D was also investigated for Suzuki reactions in neat water and mixed solvent respectively. In the case of pure water, higher yields could be obtained, while a large amount of palladium black precipitates appeared after the reaction. Two control experiments

were performed, one directly carried out recycling experiments following general procedure, only trace coupled products were found. Another experiment was carried out for recycling experiments in the same reaction conditions after palladium black precipitates were removed by filtering, which gave 28% yield at second recycle and trace coupled products at third recycle respectively. The results of control experiments revealed that the catalyst recycle with C₂D-H₂O-PEG2000 system could not be realized because of aggregation of palladium nanoparticles.

However, 6 times cycles could be realized for Suzuki coupling of 4-bromotoluene at room temperature in the C₂D-H₂O-C₂H₅OH system, in which no significant loss of catalyst activity was observed (Table 7, runs 1–6). Control experiments were also performed to discuss the influence of Pd black, the aqueous layer (contain catalyst C₂D) separated from experiments was filtered before recycling experiments, then substrates were added in the same reaction conditions, which gave 96% yield at second recycle and 84% yield at third recycle. Palladium black almost could not be observed in the recycle experiments. These results suggested that the recyclability of the catalyst C₂D was determined by solvent and temperature which could affect the properties of aggregation of Pd nanoparticles.

Table 6. Suzuki reaction of aryl bromides with phenylboronic acid^a


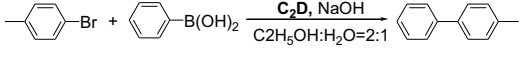
Entry	ArX	Product	Yield ^b (%)
1	<i>o</i> -CH ₃ -C ₆ H ₄ Br	<i>o</i> -CH ₃ -Ph-Ph	74 (70)
2	<i>p</i> -CH ₃ O-C ₆ H ₄ Br	<i>p</i> -CH ₃ O-Ph-Ph	99 (99)
3	<i>m</i> -CH ₃ O-C ₆ H ₄ Br	<i>m</i> -CH ₃ O-Ph-Ph	99 (97)
4	<i>o</i> -CH ₃ O-C ₆ H ₄ Br	<i>o</i> -CH ₃ O-Ph-Ph	63 (60)
5	<i>p</i> -NH ₂ -C ₆ H ₄ Br	<i>p</i> -NH ₂ -Ph-Ph	99 (97)
6	<i>m</i> -NH ₂ -C ₆ H ₄ Br	<i>m</i> -NH ₂ -Ph-Ph	96 (93)
7	<i>p</i> -CN-C ₆ H ₄ Br	<i>p</i> -CN-Ph-Ph	99 (99)
8	<i>o</i> -CN-C ₆ H ₄ Br	<i>o</i> -CN-Ph-Ph	94 ^c (90)
9	<i>p</i> -CHO-C ₆ H ₄ Br	<i>p</i> -CHO-Ph-Ph	99 (99)
10	<i>o</i> -CHO-C ₆ H ₄ Br	<i>o</i> -CHO-Ph-Ph	98 (96)
11	<i>p</i> -NO ₂ -C ₆ H ₄ Br	<i>p</i> -NO ₂ -Ph-Ph	99 (96)
12	<i>p</i> -CF ₃ -C ₆ H ₄ Br	<i>p</i> -CF ₃ -Ph-Ph	99 (96)
13	1-Bromo-naphthalene	1-Naph-Ph	99 (98)
14	2-Bromo-pyridine	2-Py-Ph	99 ^d (94)
15	3-Bromo-pyridine	3-Py-Ph	61 ^d (57)
16	3-Bromo-thiophene	3-Th-Ph	trace
7	<i>p</i> -CHO-C ₆ H ₄ Cl	<i>p</i> -CHO-Ph-Ph	trace

^a Reaction condition: ArX (0.5 mmol), PhB(OH)₂ (0.75 mmol), NaOH (1.0 mmol), C₂D (0.1% mol), CH₃CH₂OH/H₂O (2:1) (3 mL), 1 h, room temperature. ^b GC yields based on ArX (isolated yields are given in parentheses). ^c The reaction temperature was 50 °C. ^d The reaction temperature was 90 °C.

EXPERIMENTAL SECTION

Agent and Measurement. All chemicals were purchased from various commercial companies. MeOH was distilled after being dried with MgSO₄. DMF was distilled at reduced pressure, and stored on 4 Å molecular sieves. IR spectra were recorded on a Bruker VECTOR22 spectrometer, in KBr pellets. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. ¹H and ¹³C NMR spectra were performed with a Bruker DPX-400 spectrometer, using DMSO-d₆ or D₂O as a solvent and TMS as an internal standard.

General synthesis. Synthesis of Ligands. A mixture of FcCHO (0.257 g, 1.2 mmol), *p*-aminobenzoic acid (0.137 g, 1.0 mmol) or *m*-aminobenzoic acid (0.137 g, 1.0 mmol) or sulfanilic acid (0.173 g, 1.0 mmol) or metanilic acid (0.173 g, 1.0 mmol), Na₂CO₃ (0.053 g, 0.5 mmol) and CH₃OH (30 mL) was refluxed for 12 h under nitrogen atmosphere. The volume of the solution was reduced to ca. 10 mL. Addition of diethyl ether (30 mL) on the concentrated solution gave brown precipitates, which were isolated, washed with moderate diethyl ether, and then dried in vacuum. Compound **L₁D**: Reddish-brown solid; m.p. >250 °C. IR (KBr): 3054, 1632, 1407, 1282, 1179, 1103, 788 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.40 (s, 1H), 7.88 (d, *J* = 1.6 Hz, 2H),

Table 7. Recycling of C₂D for Suzuki cross-coupling reaction^a


Run	Solvent	Yield ^{b,c,d} (%)
1	CH ₃ CH ₂ OH:H ₂ O = 2:1	99
2	CH ₃ CH ₂ OH:H ₂ O = 2:1	99
3	CH ₃ CH ₂ OH:H ₂ O = 2:1	99
4	CH ₃ CH ₂ OH:H ₂ O = 2:1	97
5	CH ₃ CH ₂ OH:H ₂ O = 2:1	95
6	CH ₃ CH ₂ OH:H ₂ O = 2:1	94
7	CH ₃ CH ₂ OH:H ₂ O = 2:1	81
8	CH ₃ CH ₂ OH:H ₂ O = 2:1	64

^a Reaction condition: 4-Bromotoluene (0.5 mmol), PhB(OH)₂ (0.75 mmol), NaOH (1.0 mmol), C₂D (0.1% mol), CH₃CH₂OH/H₂O (2:1) (3 mL), 1 h, room temperature. ^b GC yield of product extracted with *n*-hexane. ^c Cycles 2-8 used the aqueous solution remaining after the previous cycle. ^d After cycle 3, the reaction time was increased to 3-10 h.

7.05 (d, *J* = 1.2 Hz, 2H), 4.81 (s, 2H), 4.53 (s, 2H), 4.27 (s, 5H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 161.5, 152.1, 132.8, 130.1, 118.7, 79.9, 70.5, 68.5, 68.3; MS: 332 [M-Na]. Compound **L₁J**: Reddish-brown solid; m.p. >250 °C. IR (KBr): 3109, 1623, 1397, 1173, 1105, 785 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.42 (s, 1H), 7.74, 7.72 (d, *J* = 7.2 Hz, 1H), 7.67 (s, 1H), 7.29, 7.27, 7.26 (t, 1H), 7.09, 7.08 (d, *J* = 7.2 Hz, 1H), 4.81 (s, 2H), 4.53 (s, 2H), 4.27 (s, 5H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 160.2, 151.39, 132.8, 131.6, 127.7, 121.2, 80.0, 70.5, 68.6, 68.3; MS: 332 [M-Na]. Compound **L₂D**: Reddish-brown solid; m.p. >250 °C. IR (KBr): 3084, 1621, 1401, 1193, 1127, 1042, 834 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.41 (s, 1H), 7.60, 7.58 (d, *J* = 8.0 Hz, 2H), 7.08, 7.06 (d, *J* = 8.0 Hz, 2H), 4.82 (s, 2H), 4.55 (s, 2H), 4.28 (s, 5H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 161.3, 151.8, 148.4, 126.1, 119.2, 79.7, 70.7, 68.9, 68.4; MS: 368 [M-Na]. Compound **L₂J**: Reddish-brown solid; m.p. >250 °C. IR (KBr): 3102, 1619, 1387, 1149, 1114, 1031, 794 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.422 (s, 1H), 7.748, 7.745 (d, 2H, *J* = 1.2 Hz), 7.292 (s, 1H), 7.095, 7.079 (d, 1H, *J* = 6.4 Hz), 4.819 (s, 2H), 4.524 (s, 2H), 4.261 (s, 5H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 161.2, 151.2, 147.4, 128.1, 127.4, 121.7, 120.7, 79.7, 70.7, 68.9, 68.4; MS: 368 [M-Na].

Synthesis of Palladacycle. A mixture of PdCl₂ (0.177 g, 1 mmol), sodium acetate (0.082 g, 1 mmol), Ligand (1.1 mmol) in methanol (10 mL) was stirred for 24 h at room temperature. The volume of the solution was reduced to ca. 3 mL. Addition of diethyl ether (30 mL) on the concentrated solution gave precipitates, which were isolated, washed with a little ethanol, and then dried in vacuum. When carboxylate-functionalized ligands **L₁D**

and **L₁J** were reacted with PdCl₂, rufous precipitates were obtained. But these material could not be easy characterized due to its insolubility in most solvents tested (water, methanol, methylene chloride, DMSO).

Compound **C₁D**: rust solid; m.p.: >200 °C. IR (KBr): 2932, 1583, 1402, 1190, 1136, 1021, 836 cm⁻¹; MS: 992 [M+H]⁺. Compound **C₁J**: rust solid; m.p.: >200 °C. IR (KBr): 3002, 1639, 1379, 1138, 1121, 1025, 879, 796, 701 cm⁻¹; MS: 992 [M+H]⁺. Compound **C₂D**: Atropurpureus Solid; m.p. >250 °C. IR (KBr): 2920, 1579, 1400, 1187, 1126, 1008, 833 cm⁻¹; ¹H NMR (DMSO-d₆, 400 MHz): δ 8.40 (s, 2H), 7.60, 7.58 (d, *J* = 8.0 Hz, 4H), 7.09, 7.07 (d, *J* = 8.4 Hz, 4H), 4.82 (d, *J* = 1.2 Hz, 2H), 4.54 (s, 2H), 4.43, 4.40 (d, *J* = 12.9 Hz, 2H), 4.28 (s, 10H); MS: 1080 [M+H₂O]. Compound **C₂J**: Atropurpureus Solid; m.p. >250 °C. IR (KBr): 2943, 1546, 1385, 1174, 1109, 1001, 815 cm⁻¹; MS: 1080 [M+H₂O].

General procedure for the Suzuki coupling reaction of aryl bromides with phenyl boronic acid. Aryl bromides (0.5 mmol), phenylboronic acid (0.75 mmol), Base (1 mmol), PEG 2000 (0.5 mmol), catalyst **C₂D** (0.5 mol %) and H₂O (3.0 mL) were stirred 4 h at 60 °C, Or Aryl bromides (0.5 mmol), PhB(OH)₂ (0.75 mmol), NaOH (1.0 mmol), **C₂D** (0.1% mol) and CH₃CH₂OH/H₂O (2:1) (3 mL) were stirred 1 h at room temperature. The reaction mixture was stirred to complete reaction, and then diluted with water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic phase was dried with MgSO₄, filtrate, solvent was removed on a rotary evaporator, and the product was isolated by thin layer chromatography. The purified products were identified by ¹H NMR spectroscopy and melting points with the literature data.

General procedure for recycling experiments for C₂D catalyzed Suzuki cross-coupling reaction of 4-bromotoluene with phenylboronic acid in H₂O/C₂H₅OH. 4-Bromotoluene (0.5 mmol), phenylboronic acid (0.75 mmol), Base (1 mmol), catalyst **C₂D** (0.1 mol %) and H₂O/C₂H₅OH (3.0 mL) was stirred 1 h under air, and then extracted with n-hexane. The aqueous layer (contain catalyst **C₂D**) was separated for recycling experiments. The combined organic phase (contain reactants and products) was dried with MgSO₄, filtrate, solvent was removed on a rotary evaporator, and the product was isolated by thin layer chromatography. The equivalent of 4-bromine toluene, phenyl boric acid and NaOH mixed in the separated aqueous phase (contain catalyst **C₂D**), stirred under air. That could achieve catalyst cycle repeat above steps.

CONCLUSION

A series of new water-soluble cyclopalladated ferro-

cenylimine were designed and prepared from ferrocenylimine ligands with hydrophilic functional group. These catalysts could effectively catalyze Suzuki cross-coupling reaction of aryl bromide and phenylboronic acid in neat water. Although catalyst (**C₂D**) exhibited high activity, recycling of catalyst could not be proceeded because that a large amount of palladium black precipitates were formed after reaction at experiment condition, which indicates that the **C₂D** was sensitive to temperature in water. For **C₂D**-H₂O-C₂H₅OH catalytic system, not only higher yields of coupling products with a wide range of substrates could be obtained at ambient, but also 6 times recycling could be achieved, in which suggested that the recyclability of the catalyst **C₂D** for Suzuki coupling reaction was determined by solvent and temperature.

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