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Homocoupling of Arylboronic Acids Catalyzed by a Simple Hydrophilic Palladium(II) Complex in Aqueous Media

Mengping Guo*, Liang Qi, Meiyun Lv, Xiuling Zhou, Hui Liang and Sanbao Chen

Institute of Coordination Catalysis, Engineering Center of Jiangxi University for Lithium Energy, Key Laboratory of Jiangxi University for Applied Chemistry and Chemical Biology, Yichun University, Yichun 336000, China

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Abstract: Homocoupling of arylboronic acids has been successfully carried out by using the inexpensive hydrophilic palladium(II) complex $PdCl_2(NH_2CH_2COOH)_2$ as catalyst in *i*-PrOH/H_2O (v/v=1:2) under aerobic atmosphere without elevated heating to give rise to symmetrical biaryls in moderate to good yields. The aqueous media, room temperature reaction and the low amounts of catalyst (0.5 mol%) show a practical and environmentally benign protocol. In addition, enhancement of yield was observed in the presence of 0.5 equiv. *p*-toluenesulfonyl chloride. Furthermore, the byproducts of this reaction were not observed while biaryl is the only product, which results in much more facile in the separation of the product symmetrical biaryls from arylboronic acids.

Keywords: Hydrophilic catalyst, homocoupling of arylboronic acids, aqueous media, green chemistry.

INTRODUCTION

The symmetrical biaryl motifs are common in the structures of many natural products, functional molecules and active ligands employed in catalysis [1-5]. The homocoupling of arylboronic acid derivatives represents a widely used approach to symmetrical biaryls [6-8], this is mainly due to commercial availability of a wide range of arylboronic acids [9-11]. So far, There has been a number of reports on homocoupling of arylboronic acids, where the catalysts and ligands were found essential to make the reaction proceed smoothly, for example, Au [6-7, 12-17], Cu [18-20], Cr [21], V [22], and Rh [5] can be used to mediate biaryl formation from arylboronic acids. However, Pd-based catalysts are most frequently used for the homocoupling of arylboronic acids. Although phosphine-based ligands have remained to be the most popular selection in the palladium-catalyzed homocoupling of arylboronic acids [23-26], the drawbacks of the catalyst, such as sensitivity to air, high costs, and toxicity, limit their application. The application of alternative ligands such as N-heterocyclic carbenes [27], nitrogen ligands [28-29], as well as ligand free systems [30-33], in the palladium-catalyzed homocoupling of arylboronic acids has opened new opportunities. The development of new catalytic systems that perform at mild reaction temperatures in short times using low catalyst loadings is still interesting. In addition, from environmental and economic points of view, water is an abundant, nontoxic, noncorrosive and nonflammable solvent, and the use of water as reaction medium is one of the latest challenges for modern chemists [34-35]. In this respect, the development of catalysis in aqueous media seems particularly suitable for the homocoupling of arylboronic acids due to the excellent stability of boronic acids in aqueous media. Despite the aqueous systems have been used previously for this homocoupling [29-31], no hydrophilic catalysts have been reported for this reaction in aqueous media. For this purpose, we expended all our efforts on the development of hydrophilic catalysts that can promote the homocoupling of arylboronic acids to prepare symmetrical aryl biphenyls. In this communication we wish to report the use of easily accessible, cheap and simple Glycine-ligated $PdCl_2$ to prepare $PdCl_2(NH_2CH_2COOH)_2$-catalyzed homocoupling reaction of arylboronic acids in aqueous media at room temperature under ambient atmosphere using low catalyst loadings.

RESULTS AND DISCUSSION

With the water-soluble catalyst $PdCl_2(NH_2CH_2COOH)_2$ in hand, we initially wanted to investigate the Suzuki-Miyaura cross coupling reaction of aryl bromides with arylboronic acids in pure water at room temperature under an air atmosphere as Suzuki-Miyaura cross coupling reaction in pure water with improved yield and simplify the reaction protocol still remains a major challenge [36]. The investigation was first carried out with 4-bromoanisole and phenylboronic acids as the model reaction using 0.5 mol% $PdCl_2(NH_2CH_2COOH)_2$ as the catalyst in pure water under ambient atmosphere. Surprisingly, when the reaction was observed using phenylboronic acid as the only substrate, $PdCl_2(NH_2CH_2COOH)_2$ as the catalyst, K_2CO_3 as the base and pure water as the solvent without following by the addition of 4-bromoanisole, all the product was symmetrical biphenyl which was confirmed by NMR. Therefore, this re-

*Address correspondence to this author at the Institute of Coordination Catalysis, Engineering Center of Jiangxi University for Lithium Energy, Key Laboratory of Jiangxi University for Applied Chemistry and Chemical Biology, Yichun University, Yichun 336000, China;
Tel: +86 0795 3200535; Fax: +86 0795 3200535;
E-mail: guomengping65@163.com

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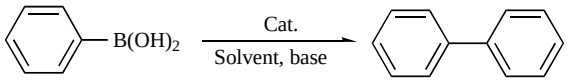
Table 1. Initial screening for solvent, the amount of catalyst $PdCl_2(NH_2CH_2COOH)_2$ and base effects on homocoupling reaction[a].



Entry	Solvent	$PdCl_2(NH_2CH_2COOH)_2$ (mol %)[b]	Base	Yield (%)[c]
1	H_2O	0.5	K_2CO_3	59
2	Methanol/H_2O	0.5	K_2CO_3	31
3	Ethanol/H_2O	0.5	K_2CO_3	76
4	*n*-PrOH/H_2O	0.5	K_2CO_3	67
5	*i*-PrOH/H_2O	0.5	K_2CO_3	90
6	*n*-Butanol/H_2O	0.5	K_2CO_3	50
7	*i*-PrOH	0.5	K_2CO_3	45
8	*i*-PrOH/H_2O	0.1	K_2CO_3	80
9	*i*-PrOH/H_2O	1.0	K_2CO_3	92
10	*i*-PrOH/H_2O	0.5	Na_2CO_3	65
11	*i*-PrOH/H_2O	0.5	NaF	55
12	*i*-PrOH/H_2O	0.5	NaOH	58
13	*i*-PrOH/H_2O	0.5	K_3PO_4	60
14	*i*-PrOH/H_2O	0.5	KOH	71
15	*i*-PrOH/H_2O	0.5	CH_3COONa	30
16	*i*-PrOH/H_2O	0.5	HCOONa	32
17	*i*-PrOH/H_2O	0.5	NEt_3	42
18	*i*-PrOH/H_2O	0.5	KH_2PO_4	21

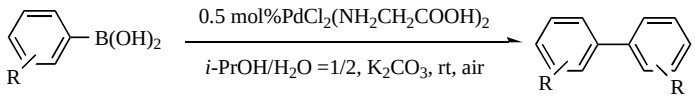
[a]Reaction conditions: phenylboronic acid (1 mmol), base (1 mmol), 0.1-1.0 mol% of cat. $PdCl_2(NH_2CH_2COOH)_2$, solvent/water 3 mL (v/v = 1/2), under air, room temperature, 12.5 h.
[b]Amounts of cat. $PdCl_2(NH_2CH_2COOH)_2$ based on phenylboronic acid.
[c]Isolated yield.

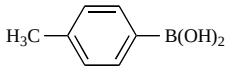
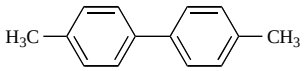
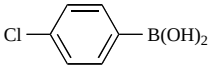
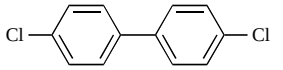
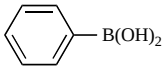
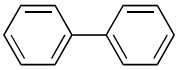
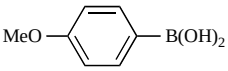
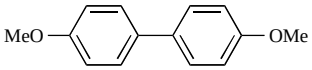
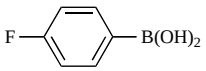
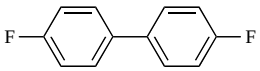
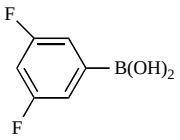
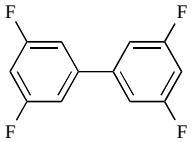
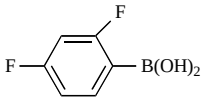
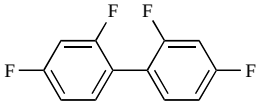
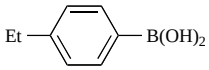
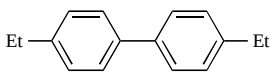
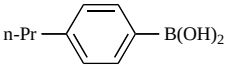
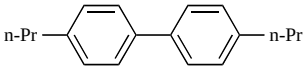
sult demonstrated that the homocoupling reaction of phenylboronic acid was performed in the present protocol. Unfortunately, only moderate homocoupling yield of 59% was achieved when used phenylboronic acid as substrate. Considering better solubility of arylboronic acids in alcohols, we investigated the influence of various alcohols and water (1: 2) on the reactions (Table **1**, entries 2-6). Among the solvent tested, methanol, ethanol, propanol, isopropanol and *n*-butanol, isopropanol was found to be the best (entry 5). The use of pure isopropanol led to lower yield (entry 7), which showed that the water could accelerate the oxidative dimerization of phenylboronic acid.

Based on these results, we tested different base effects on homocoupling reaction such as KH_2PO_4, NEt_3, HCOONa, CH_3COONa, KOH, K_3PO_4, NaOH, K_2CO_3, NaF and Na_2CO_3(entries 5, 10-18). It can be seen that K_2CO_3 was the best choice of base and homocoupling of phenylboronic acid gave the highest yield (90%) (entry 5). Further, the effect of loading of $PdCl_2(NH_2CH_2COOH)_2$ on this reaction by running the homocoupling of arylboronic acids in a 1:2 mixture of *i*-PrOH/H_2O and K_2CO_3 as base was investigated (entries 8-9). Increasing catalyst loading to 1.0 mol% did not improve the homocoupling yield significantly (entry 9) and decreasing the catalyst loading to 0.1 mol% resulted in relatively low homocoupling yield (entry 8). These results indicated that the proper catalyst loading is 0.5 mol% to arylboronic acids (entry 5) and the catalyst is stable under the reaction conditions for long time.

With the optimized protocol, a variety of electronically and structurally diverse arylboronic acid was broadened in air. The results of the arylboronic acid homo-coupling study are summarized in Table **2**. Phenylboronic acid without any substituent group on the ring gave higher yield and shorter reaction time than that of containing groups in air without any additive (entry 3). For arylboronic acids, containing groups at the *para* position such as CH_3, Cl, F and OMe afford moderate to good yields of biaryl products in air without any additive (entries 1-2, entries 4-5). On the other hand, in the absence of an additive, homo-coupling occurs but the yield is poor (entries 6-10). As was the case with previous findings [29], addition of 0.5 equiv. *p*-toluenesulfonyl chloride improves the yield dramatically (96%, entry 5). The catalyst system that we showed is suitable for non-steric hindered arylboronic acids (entries 1-2, 4-6, 8-10), and for steric

Table 2. Homocoupling of various arylboronic acids[a].



Entry	$ArB(OH)_2$	Product	Yield (%)[b]
1			81 86[c]
2			66 66[c]
3[d]			90
4			63 73[c]
5			70 96[c]
6			32 69[c]
7			23 36[c]
8			38 74[c]
9			39 69[c]

[a]Reaction conditions: arylboronic acid (1 mmol), K_2CO_3 (1 mmol), 0.5 mol% of cat. $PdCl_2(NH_2CH_2COOH)_2$, *i*-PrOH /H_2O 3 mL (v/v = 1/2), under air, room temperature. All the reactions were carried out for 20 h.
[b]Isolated yield.
[c]*p*-Toluenesulfonyl chloride (0.5 mmol).
[d]12.5 h.

hindered arylboronic acids, only 36% isolated yield could be obtained (entry 7). Furthermore, the byproducts of this reaction were not observed while biaryl is the only product, which results in much more facile in the separation of the product biaryls from arylboronic acids.

CONCLUSION

In summary, we demonstrate the first simple hydrophilic palladium (II) complex $PdCl_2(NH_2CH_2COOH)_2$ as an effective catalyst for homocoupling reactions of arylboronic acids to synthesize symmetrical biaryls. Our catalytic system offers a mild, simple and environmentally benign alternative to the existing protocols since the homocoupling reaction is proceeded in aqueous media under aerobic atmosphere without elevated heating using low amounts of $PdCl_2(NH_2CH_2COOH)_2$ (0.5 mol%) without giving side products. The use of hydrophilic palladium(II) catalyst makes this aqueous system very attractive in view of its low cost, low catalyst loading and easy removal from the reaction mixture compared with other methods reported in the literature[29, 31]. Efforts to understand the reaction mechanism and to catalyze other carbon-carbon bond forming reactions of organoboron compounds are in progress.

EXPERIMENTAL SECTION

General

All the homocoupling reaction of arylboronic acids were performed without the protection of inert gas. All chemicals employed in the reaction were analytical grade, obtained commercially from Aldrich or Alfa Aesar and used as received without any prior purification. Analytical thin-layer chromatography was performed using glass plates with 200-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Petroleum ether is used as the eluting solvent for the preparative thin layer chromatography. ^1H NMR, ^{13}C

NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent.

Synthesis of Catalyst $PdCl_2(NH_2CH_2COOH)_2$

The catalyst ***$PdCl_2(NH_2CH_2COOH)_2$*** used in this work was prepared according to recently reported literature procedures summarized in Scheme **1** [35].

$$PdCl_2 + 2NH_2CH_2COOH \xrightarrow[\text{RT}]{\substack{CH_3CH_2OH \\ CH_3COOH}} PdCl_2(NH_2CH_2COOH)_2$$

Scheme 1. Synthesis of the catalyst.

Typical Experimental Procedure for Homocoupling Reaction of Aryl Boronic Acids

To a stirred ***i-PrOH /H_2O*** 3 mL (v/v = 1/2) solution of ***arylboronic acid*** (1.0 mmol), ***$PdCl_2(NH_2CH_2COOH)_2$*** (0.5 mol%), ***potassium carbonate*** (1 mmol) and ***ρ-Toluenesulfonyl chloride*** (0.5 mmol). The solution was stirred at room temperature under ambient atmosphere for 20 h. ***Ethyl acetate*** (3×25 mL) was added to extract the product. The combined organic phase was dried with ***$MgSO_4$***, filtrate, solvent was removed on a rotary evaporator, and the product was isolated by preparative thin layer chromatography on silica gel. The purified products were identified by ^{1}H NMR, ^{13}C NMR spectroscopy. All the biaryl products are known compounds, Spectral data for symmetrical biaryls:

4, 4'-Dimethylbiphenyl [29]**:** ^{1}H NMR ($CDCl_3$): δ_H 2.45 (6H, s, $2CH_3$), 7.29 ($4H_{arom}$, d, *J*=7.2 Hz, 4CH), 7.54 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH); ^{13}C NMR ($CDCl_3$): δ_C 21.11, 126.8, 129.5, 136.7, 138.3.

Biphenyl[29]**:** ^{1}H NMR ($CDCl_3$): δ_H 7.66 ($4H_{arom}$, d, *J*=7.2 Hz, 4CH), 7.49 ($4H_{arom}$, d, *J*=7.6 Hz, 4CH), 7.42 ($2H_{arom}$, t, *J*=7.2 Hz, 2CH); ^{13}C NMR ($CDCl_3$): δ_C 127.2, 127.3, 128.8, 141.3.

4, 4'-Dimethoxybiphenyl [29]**:** ^{1}H NMR ($CDCl_3$): δ_H 3.87 (6H, s, $2CH_3$), 6.99 ($4H_{arom}$, d, *J*=8.8 Hz, 4CH), 7.51 ($4H_{arom}$, d, *J*=8.8 Hz, 4CH); ^{13}C NMR ($CDCl_3$): δ_C 55.3, 114.2, 127.7, 133.5, 158.7.

4, 4'-Difluorobiphenyl [30]**:** ^{1}H NMR ($CDCl_3$): δ_H 7.43 ($4H_{arom}$, d, *J*=8.8 Hz, 4CH), 7.50 ($4H_{arom}$, d, *J*=8.8 Hz, 4CH); ^{13}C NMR ($CDCl_3$): δ_C 128.1, 129.1, 133.7, 138.4.

4, 4'-Diethylbiphenyl [37]**:** ^{1}H NMR ($CDCl_3$): δ_H 1.28 (6H, t, *J*=7.6 Hz, $2CH_2CH_3$), 2.69 (4H, q, *J*=7.6 Hz, $2CH_2CH_3$), 7.26 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH), 7.50 ($4H_{arom}$, d, *J*=8.4 Hz, 4CH); ^{13}C NMR ($CDCl_3$): δ_C 15.6, 28.5, 126.9, 128.2, 138.6, 143.0.

4, 4'-Dipropylbiphenyl [39]**:** ^{1}H NMR ($CDCl_3$): δ_H 0.97 (6H, t, *J*=7.2 Hz, $2CH_2CH_2CH_3$), 1.63-1.72 (4H, m, $2CH_2CH_2CH_3$), 2.62 (4H, t, *J*=7.2 Hz, $2CH_2CH_2CH_3$), 7.23 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH), 7.50 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH); ^{13}C NMR ($CDCl_3$): δ_C 13.9, 24.6, 37.7, 126.8, 128.8, 138.6, 141.5.

4, 4'-Dichlorobiphenyl [30]**:** ^{1}H NMR ($CDCl_3$): δ_H 7.43 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH), 7.50 ($4H_{arom}$, d, *J*=8.0 Hz, 4CH).

3, 5, 3', 5'-Tetrafluorobiphenyl [19]**:** ^{1}H NMR ($CDCl_3$): δ_H 7.1-7.2 ($6H_{arom}$, m, 6CH).

2, 4, 2', 4'-Tetrafluorobiphenyl [38]**:** ^{1}H NMR ($CDCl_3$): δ_H 6.74 ($4H_{arom}$, m, 4CH), 7.35 ($2H_{arom}$, m, 2CH).

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIALS

Supplementary material is available on the publisher's web site along with the published article.

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