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Ethanol-promoted reductive homocoupling reactions of aryl halides catalyzed by palladium on carbon (Pd/C)

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Homocoupling reactions of aryl bromides or iodides proceeded smoothly with palladium on carbon (Pd/C) catalyst, ethanol and base in dimethyl sulfoxide (DMSO) to afford exclusively symmetric biaryls in good to excellent yields. Ethanol was first used as a reducing agent *in situ* to reduce the Pd²⁺/C species into Pd⁰/C active species to complete the catalytic redox cycle. It was found that ethanol can promote the Pd/C-catalyzed reductive homocoupling of aryl iodides and bromides efficiently in the presence of base. A reaction mechanism has been put forward and discussed. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: palladium; biaryls; aryl halides; homocoupling; ethanol

Introduction

Biaryls and their heteroaromatic analogues have specific physicochemical properties which are widely used in the synthesis of conductive polymers, liquid crystals and important biaryl natural products.^[1-3] The Ullmann reductive homocoupling reactions of aromatic halides have been widely used to synthesize symmetrical biaryls (Scheme 1).^[4] However, the high reaction temperature (over 200 °C) and the stoichiometric amount of copper in the traditional Ullmann reaction limit its utility in the synthesis of biaryls with functional groups.

Based on the wide application of palladium (Pd)-catalyzed reductive coupling reactions in the formation of carbon–carbon bonds, a number of Pd-catalyzed Ullmann reactions have also been proposed as eco-friendly replacements for the stoichiometric Ullmann protocol.^[5,6] Pd-catalyzed Ullmann reactions are carried out under elevated temperatures in the presence of reducing agents, which facilitates the synthesis of functional biaryls. Normally, a reducing agent is required *in situ* to regenerate the Pd⁰ active species from Pd²⁺ species and complete the Pd⁰ < - > Pd²⁺ redox cycle. Until now, various reducing agents have been developed for the regeneration of Pd⁰, including hydrogen gas,^[7] zinc,^[8] indium,^[9] alcohol^[6,10] and formate salt.^[11]

Both homogeneous and heterogeneous Pd-based catalysts have been successfully applied in the Ullmann coupling reactions. The main drawback of homogeneous catalysis is the recycling of the catalyst, leading to difficulty in product purification and loss of expensive metals and ligands. In contrast, heterogeneous Pd catalysts can be easily handled, recovered from the reaction mixture by simple filtration and reused. Palladium on carbon



Scheme 1. Ullmann homocoupling reactions of aromatic halides.

(Pd/C) is the most commonly used Pd-based catalyst due to its commercial availability, low cost and easy regeneration. Thus, Pd/C can be used as an alternative choice to conventional homogeneous catalysts in the synthesis of symmetrical biaryls.^[12–15] Cravotto and his coworkers have reported that high-intensity ultrasound can promote the Pd/C-catalyzed coupling reaction and give the corresponding biaryls in good yields.^[12] Besides ultrasound, addition of metal, crown ether and phosphorus ligands can also be used to promote the Pd/C-catalyzed homocoupling reactions.^[13–15] However, all these methods have difficulties in industrial application.

Our recent work has demonstrated an efficient homocoupling of aryl iodides and bromides catalyzed by Pd^{2+} (dppf) (dppf = 1,1'-bis(diphenylphophino)ferrocene).^[16] The study shows that the Pd^{0} (dppf) active species were regenerated from Pd^{2+} (dppf) species by dimethyl sulfoxide (DMSO) without the need of any additional reducing agent. Pd/C was also studied with DMSO as a reducing agent, but the corresponding yield of biaryls was low under these reaction conditions. In this article, ethanol is first applied as a reducing agent to promote the Pd/C-catalyzed homocoupling reaction. It is well known that ethanol is nontoxic, cheap and easily disposed. By using ethanol as a reducing agent, we have developed a low-cost, simple and promising Pd/C-catalyzed system for further industrial application.

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Table 1.	Effect	of	ethanol	amount	on	Pd/C-catalyzed	reductive
homocou	pling of	fiod	lobenzen	ne ^a			

	Ethanol	Conversionb	Yield (%)		
Entry	(mmol)	(%)	Biphenyl ^c	Benzene ^b	
1	0	43.24	39.60	2.76	
2	0.50	98.57	68.90	26.92	
3	0.86	100	85.79	11.12	
4	1.71	100	78.63	12.62	
5	2.57	100	74.94	18.40	
6	3.43	100	69.90	25.12	
7	6.00	100	63.30	30.20	
8	8.56	100	64.14	30.40	
9	12.0	100	65.65	27.60	
10	17.1	100	61.40	32.10	
11	5.00 ^d	61.83	36.47	13.12	

 $^{\rm a}$ Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/C catalyst, 7.5 mmol CsF and predetermined amount of ethanol in 5 ml DMSO at 120 $^\circ$ C for 3.0 h.

^b lodobenzene conversions and phenyl yields were determined from the GC/MS measurements by the area normalization method.

^c Biphenyl yield was determined from the GC/MS measurements by the external standard method.

^d A 5 ml aliquot of ethanol was used as the solvent.

Results and Discussion

A series of palladium catalysts have been studied for the reductive homocoupling of iodobenzene in DMSO.^[16] Unfortunately, when Pd/C was used as the catalyst, the yields of biaryls were comparably low. Isopropanol has been reported to be an effective reducing agent for the homogenous palladium catalyst.^[6,10] Compared with isopropanol, ethanol is cheap, nontoxic and easily removed. Thus, ethanol was studied as the reducing agent to promote the Pd/C-catalyzed homocoupling reaction of aryl halides in this article.

First, we examined the Pd/C-catalyzed homocoupling reaction of iodobenzene to biphenyl by varying the amount of ethanol (Table 1). It was found that both the biphenyl yield and the iodobenzene conversion could be greatly increased by a small amount of ethanol (0.86 mmol). However, further addition of ethanol could lead to an increase in self-reduction product (phenyl). When ethanol was used as the solvent, both the biphenyl yield and the iodobenzene conversion decreased. Therefore, 0.86 mmol of ethanol is clearly the best amount for this reaction and was chosen for the subsequent studies.

In the palladium-catalyzed reductive reactions, base is indispensable to neutralize the generated acidic byproduct, otherwise the reaction will be suppressed due to the increased medium acidity.^[17] It was indeed observed that the pH value of the reaction system decreased as the reaction proceeded. As shown in entry 1 of Table 2, no homocoupling product (biphenyl) was formed in the absence of base, indicating that a suitable base is indispensable for successful progress in palladium-catalyzed reductive reactions. Interestingly, acetates, carbonates, bicarbonates and hydroxides can also be used as bases to promote the Pd/C-catalyzed homocoupling reaction of iodobenzene in DMSO. Examination of entries 2–7 of Table 2 shows that the cesium salts are better than the corresponding potassium salts, which in turn are better than the corresponding sodium salts at promoting the Pd/C-catalyzed homocoupling reactions. The relative effectiveness of these salts

Table 2.	Effects of base on Pd/C-catalyzed reductive homocoupling
ofiodobe	nzene ^a

Entry	Base	Biphenyl yield ^b (%)
1	No base	0
2	CsF	85.79
3	KF	19.76
4	NaF	7.60
5	Cs ₂ CO ₃	84.80
6	K ₂ CO ₃	77.88
7	Na ₂ CO ₃	34.01
8	NaHCO ₃	28.85
9	KOAc	71.75
10	КОН	44.71
11	KCI	0
12	KBr	0
13	Et_3N	54.46

^a Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/C catalyst, 0.86 mmol ethanol, 7.5 mmol base in 5 ml DMSO at 120 $^{\circ}$ C for 3.0 h. ^b Biphenyl yields were determined from the GC/MS measurements by the external standard method.

is determined by their solubility and basicity, which is associated with the size of their metal cations.^[16]

The cesium salts are similarly good at promoting the Pd/Ccatalyzed homocoupling reaction of iodobenzene. The biphenyl yields are 85.79% for CsF (entry 2 of Table 2) and 84.80% for Cs₂CO₃ (entry 5 of Table 2), respectively. However, when potassium and sodium salts were used as the base, the corresponding yields of biaryls varied obviously. This is due to the fact that the solubility and basicity of cesium salts are mainly affected by the cesium cation in DMSO, while those of potassium and sodium salts are affected by their anion. Examination of entries 3, 6 and 9–12 of Table 2 shows that the carbonate anion is the most effective anion at promoting the homocoupling reaction of iodobenzene. The alkali chloride and bromide salts have no effect due to their low basicity (entries 11 and 12 of Table 2). Triethylamine was also studied for its excellent solubility in DMSO but was not as ideal as expected due to its weak basicity (entry 13 of Table 2).

Besides the basicity and solubility, the amount of base also plays an important role. In theory, stoichiometric quantity of a base is enough for the Pd/C-catalyzed homocoupling reaction of aryl halides. However, due to the incomplete solubility of the base, stoichiometric quantity of a base is not enough. As can be seen from Fig. 1, the iodobenzene conversion and the biphenyl yield increased rapidly with the amount of CsF when the base was consumed in three molar equivalents relative to iodobenzene. The further addition of CsF had negligible enhancement of the coupling biphenyl yields, suggesting that three molar equivalents of base is enough to neutralize the acidic products in the Pd/C-catalyzed homocoupling reactions. As the number of molar equivalents of CsF was increased to 6.0, biphenyl was obtained in good yield and the addition of more molar equivalents of CsF had no obvious positive effect in the yield of biphenyl.

Having realized the optimal type and quantity of base for the coupling reaction, attention was turned to the evaluation of the optimal reaction temperature and time. As shown in Fig. 2, we found that high temperature was beneficial to both the iodobenzene conversion and the biphenyl yield. At 60 $^{\circ}$ C, the reaction proceeded slowly and the conversion of iodobenzene was



Figure 1. Effect of base amount on Pd/C-catalyzed reductive homocoupling of iodobenzene. Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/C catalyst, 0.86 mmol ethanol and predetermined amount of CsF in 5 ml DMSO at 120 °C for 3.0 h. lodobenzene conversions were determined from the GC/MS measurements by the area normalization method and biphenyl yields were determined from the GC/MS measurements by the external standard method.



Figure 2. Effect of temperature on Pd/C-catalyzed reductive homocoupling of iodobenzene. Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/C catalyst, 0.86 mmol ethanol, 6.0 mmol CsF and in 5 ml DMSO for 3.0 h. Iodobenzene conversions were determined from the GC/MS measurements by the area normalization method and biphenyl yields were determined from the GC/MS measurements by external standard method.

found to be only 9.23% after 3 h, while at 100 $^{\circ}$ C, iodobenzene was completely consumed within the same time. Since low reaction temperature facilitates the synthesis of biaryls with functional groups, finally a reaction temperature of 120 $^{\circ}$ C was determined for the following experiments.

As shown in Fig. 3, the homocoupling reaction proceeded slowly in the first half hour and then rapidly in the next half hour. Pachón *et al.*^[18] have reported that there was an induction period for the palladium-catalyzed coupling reaction due to the involvement of palladium clusters. After the formation of 'optimal particle size' of palladium clusters in the first half-hour, the reaction could be greatly enhanced in the next half-hour. After 2 h, the



Figure 3. Time dependence of Pd/C-catalyzed reductive homocoupling of iodobenzene. Reaction conditions: 1.0 mmol iodobenzene, 0.05 mmol Pd/C catalyst, 0.86 mmol ethanol, 6.0 mmol CsF in 5 ml DMSO at 120 °C. Iodobenzene conversions were determined from the GC/MS measurements by the area normalization method and biphenyl yields were determined from the GC/MS measurements by external standard method.

homocoupling reaction had almost completed. Thus, ethanol again proved to be an effective reducing agent for promoting the Pd/C-catalyzed homocoupling reaction of iodobenzene.

Finally, having determined the optimal conditions for the homocoupling reaction, the scope and limitations of this Pd/C-catalyzed homocoupling protocol were also studied. Several substituted aromatic halides were tested as substrates having electron-withdrawing and electron-donating groups in *ortho, meta* and *para* positions. Reaction conditions were modified according to the nature of substituents. The results are summarized in Table 3.

As described above, 0.86 mmol ethanol is the optimal amount for the Pd/C-catalyzed homocoupling reaction of iodobenzene. However, this amount of ethanol is not as good as we have assumed for the Pd/C-catalyzed homocoupling reactions of some aryl bromides and iodides. Examination of entries 6, 7, 12 and 15 in Table 3 shows that the addition of ethanol can increase the yields of biaryls and decrease the reaction time for some aryl bromides and iodides. Because of steric hindrance, the yields of 2,2'-methoxyl biphenyl are very low as the homocoupling products from the ortho-methoxyl group substituted iodobenzene and bromobenzene (entries 4 and 10 of Table 3). However, the steric effect of small substituents (ortho-methyl, ortho-fluoro) is negligible and excellent biaryl yields could also be obtained from the Pd/C-catalyzed homocoupling of the corresponding substituted aromatic halides (entries 9 and 12 of Table 3). Furthermore, entries 17-19 show that this Pd/C-catalyzed system is also effective for heteroaryl iodides and bromides. In general, the reaction is tolerant for both electron-rich and electron-deficient aryl substrates to provide the corresponding biaryls in good to excellent yields by using the appropriate amount of ethanol.

Attempts to extend this catalytic system to chlorobenzene and fluorobenzene failed due to the much stronger carbon-chlorine and carbon-fluorine bond strength.^[19,20] Therefore, it is not unexpected to find that 4,4'-dichlorobiphenyl formed as the sole homocoupling product from 4-chloroiodobenzene (entry 8 of Table 3) and 4-chlorobromobenzene (entry 16 of Table 3). Similarly, difluorobiphenyl formed from the corresponding fluoro-

iodides and bromides ^a				
		Ethanol		
Entry	Substrate	(mmol)	Time (h)	Biaryl yield ^o (%)
1	C ₆ H ₅ I	0.86	3	85.79 ^c
2	C_6H_5Br	8.56	22	90.43
3	4-CH ₃ -C ₆ H ₅ I	0.86	8.5	99.79
4	2-CH ₃ O-C ₆ H ₄ I	8.56	66	46.94
5	3-CH ₃ O-C ₆ H ₄ I	0.86	22	93.50
6	4-CH ₃ O-C ₆ H ₅ I	0.86	9.5	71.38
		8.56	4	100.00
7	4-F-C ₆ H ₅ I	0.86	14.5	84.66
		8.56	14.5	96.90
8	4-CI-C ₆ H ₄ I	8.56	52.5	98.10
9	$2-CH_3-C_6H_4Br$	8.56	40.5	84.74
10	2-CH ₃ O-C ₆ H ₄ Br	8.56	66	64.58
11	4-CH ₃ O-C ₆ H ₄ Br	8.56	22	83.65
12	2-F-C ₆ H ₄ Br	0.86	66	84.88
		8.56	40.5	96.34
13	3-F-C ₆ H ₄ Br	0.86	28	84.12
14	4-F-C ₆ H ₄ Br	0.86	66	76.50
		8.56	40.5	94.54
15	$4-F_3C-C_6H_4Br$	0.86	66	86.89
		8.56	14.5	90.58
16	4-CI-C ₆ H ₄ Br	8.56	40.5	94.49
17	$2-I-C_5H_4N^d$	0.86	28	100.00
18	2-Br-C ₅ H ₄ N ^e	0.86	28	90.61
19	$2\text{-}CH_3O\text{-}5\text{-}Br\text{-}C_5H_4N^f$	8.56	14.5	99.67

 Table 3
 Pd/C-catalyzed reductive homocoupling of various and

 a Reaction conditions: 1.0 mmol aryl iodides or bromides, 0.05 mmol Pd/C catalyst, 6.0 mmol CsF and predetermined amount of ethanol in 5 ml DMSO at 120 $^\circ$ C.

^b Biaryl yields were determined from the GC/MS measurements by the area normalization method.

^c This data is from the entry 3 of Table 1.

^d 2-lodopyridine.

^e 2-Bromopyridine.

^f 2-methoxyl-5-bromopyridine.



Scheme 2. Mechanism for the Pd/C-catalyzed reactions of aryl halides.

substituted iodobenzene (entry 7 of Table 3) and bromobenzene (entries 12–14 of Table 3).

As reported by Hassen *et al.*,^[6] when the isopropanol was used as the reducing agent, the isopropanol was oxidized into acetone *in situ* to regenerate the Pd⁰ active species from Pd²⁺ species. However, the oxidation product of ethanol is acetaldehyde, which is more reactive than ethanol and the reactions were carried out under argon and in a waterless environment. After careful examination of the reaction product mixture, small amounts of acetaldehyde and ethyl acetate were detected by gas chromatography/mass spectroscopy (GC/MS). Therefore, it can be concluded that ethanol indeed acted as the reducing agent in the reaction as expected.

Based on the above experimental results, a mechanism for the Pd/C-catalyzed homocoupling reaction of aromatic halides is proposed (Scheme 2). It was initially thought that formation of the biaryl product is achieved by ligand exchange of two molecules of intermediate 1, which is similar to the literature.^[8,11,13,16] However, after careful density functional theory (DFT) calculations,^[21] the ligand exchange of two molecules of intermediate 1 is unlikely to happen due to the high energy requirement and the proposed mechanism (path I in Scheme 2) is a much more feasible mechanism. The Pd²⁺ species is reduced into Pd⁰ active species by ethanol, followed by oxidative insertion of aromatic halide and then group exchange of X⁻ by CH₃CH₂O⁻ to produce intermediate 2. From intermediate 2, formation of intermediate 3 occurs and the biaryl product is finally formed via the reductive elimination process with the regeneration of Pd⁰ active species *in situ* to furnish the catalytic redox cycle. In addition, with alcohol as the reducing agent, Pd⁰ was detected in the reaction system by X-ray photoelectron spectroscopic (XPS).

Although the dehalogenation product is negligible for this reaction, we also investigated the mechanism of the formation of dehalogenation product (path II in Scheme 2). DFT calculation shows that intermediate 2 is also formed for the formation of dehalogenation product, and then the hydrogen transfer of intermediate 2 occurs to give intermediate 4. Finally, reductive elimination occurs and enables the formation of the dehalogenation product and regeneration of Pd⁰ active species at the same time.

Conclusion

In this work, ethanol was first used as an efficient reducing agent to promote the Pd/C-catalyzed homocoupling reactions of aryl bromides and iodides. This Pd/C-catalyzed system was successfully applied to a variety of aryl bromides and iodides with electron-donating and electron-withdrawing groups in relatively mild reaction conditions. According to the experimental results, a mechanism for the catalytic cycle was proposed. The ease of product separation and catalyst recycling promote this method as a promising Pd/C-catalyzed system in industrial applications.

Experimental Section

Chemicals

All solvents and Chemicals were analytical grade. Palladium on carbon (Pd/C, 5 mol%) was purchased from Zhejiang Metallurgical Research Institute. DMSO solvent was treated with potassium hydroxide (KOH) pellet overnight and then distilled under a reduced pressure before use.

Typical Experimental Procedure for the Pd/C-catalyzed Homocoupling Reactions

In a 20 ml tubular reactor containing DMSO (5.0 ml), aryl halide (1.0 mmol), Pd/C-catalyst (0.05 mmol), CsF (6.0 mmol) and ethanol

(0.86 mmol) were added under argon atmosphere. The reactor was placed in a preheated oil bath at 120 $^{\circ}$ C under vigorous stirring. TLC was used to monitor the homocoupling reaction until the disappearance of the aryl halide starting materials for Table 3. After reaction, the reaction mixture was cooled to room temperature. The samples for GC/MS measurements were filtrated from the reaction mixture directly.

The product isolation was as follows: after the reaction was completed, the reaction mixture was cooled to room temperature and quenched with 10 ml of water, and then extracted three times with ethyl acetate (3 × 20 ml). The combined organic layers were washed with water (3 × 20 ml) and saturated brine (3 × 20 ml), and then dried over anhydrous Na₂SO₄. Solvents were evaporated under reduced pressure, and the residue was purified by chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (v:v, 1:1) as eluent to afford the corresponding coupling product. All the biaryls were characterized by their spectroscopic data (¹H NMR and GC/MS) and melting point, which were identical to those found in the literature.^[16,21,22]

The biphenyl yields were determined by external standard method of GC/MS. A series of biphenyl solutions in DMSO were prepared with different concentrations. A working curve was obtained according to the corresponding biphenyl peak areas from GC/MS spectra of the biphenyl solutions. By this working curve, the biphenyl yields of samples were determined from the biphenyl peak area of their GC/MS spectra.

Characterizations

The quantitative analysis was performed on an Agilent GC/ MS instrument (Agilent 6890N/5975I) with a programmable split/splitless injector. The injector-port temperature was set at 270 °C. The oven-temperature program was initially set at 140 °C and ramped to 270 °C at 10 °C/min, and maintained for 2 min at every step. NMR spectra were recorded in CDCl₃ on an Avance III 400 MHz spectrometer. ¹H NMR chemical shifts are reported in parts per million relative to TMS, with the residual solvent peak as the internal reference. Melting points were measured on a Buchi 510 in open capillary tubes and were not calibrated.

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