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Regiospecific cross-coupling of haloaryls and pyridine to 2-phenylpyridine using water, zinc, and catalytic palladium on carbon

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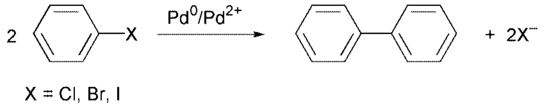
A novel and simple protocol for the reductive cross-coupling of halobenzenes (PhX; X = Cl, Br, I) with pyridine is presented, using catalytic (0.5 mol%) palladium on carbon. Catalyst regeneration is effected using molecular hydrogen generated *in situ* from the palladium-catalysed reduction of water with zinc powder. Notably, this transformation does not require the presence of reactive $B(OH)_2$ or $SnBu_3$ groups. Three separate processes are observed: cross-coupling (PhX + pyridine), homocoupling (PhX + PhX), and hydro-dehalogenation (reduction of PhX to PhH). The cross-coupling is regiospecific, forming only the 2-phenylpyridine isomer (*ca.* 50% isolated yield). The influence of various reaction parameters (temperature, reagent concentrations, and additives such as NaOH or a phase-transfer agent) on substrate conversion and product distribution is examined. Kinetic studies show the reaction rate is a function of zinc loading, catalyst loading, substrate concentration, and, above all, of the amount of water present. Possible mechanisms for the three processes in this system are discussed. It is proposed that the cross-coupling occurs *via* the formation of phenyl free-radicals, which subsequently react with pyridine molecules adsorbed on the catalyst surface.

Introduction

Carbon–carbon bond formation is one of the most sought-after transformations in organic chemistry. The synthesis of biphenyls, bipyridines, and cross-coupled moieties is of particular import, as these are key building blocks for many agrochemicals and pharmaceutical compounds.[1] The classic Ullmann[2a,b] and Suzuki[2c–e] protocols notwithstanding, cross-coupling remains a challenge, and attracts significant academic and industrial interest.[3] This is because the formation of an aryl–pyridine bond often requires substrates containing reactive functional groups, such as $–B(OH)_2$ and $–SnBu_3$,[4a] which are very expensive. Alternatively, stoichiometric metallic reagents may be used,[4b] but this means large amounts of waste by-products.

As we[5] and others[6] have shown, haloaryls (ArX; X = Cl, Br, I) easily undergo Ullmann-type homocoupling in the presence of catalytic amounts of Pd/C [eqn. (1)].[7] The elementary coupling



(1)

process involved requires stoichiometric Pd(0), and for a catalytic cycle it is necessary to regenerate the palladium catalyst using a reducing agent. Typically, hydrogen gas,[5a] hydrogen-generating agents (*e.g.* formate + water[5b] or zinc + water[5c]), or redox H-transfer agents (*e.g.* methanol,[8a] benzene,[8b,c] or hydroquinone[8d]) may be employed for this purpose.

In this study, we show that the above concept can also be applied to effect selective cross-coupling between haloaryls and pyridine, and interpret the kinetics and some of the mechanistic parameters of this interesting catalytic system.

Results

In a typical reaction (Scheme 1), PhX (X = Cl, Br, I), zinc, water (3 equiv.), pyridine (solvent), and catalytic amounts of 5% Pd/C were charged to an autoclave. After stirring ‡ for 8–20 h at 85–115 °C (depending on reaction conditions), 2-phenylpyridine **1** and biphenyl **2** were isolated as major products, together with small amounts of benzene **3** (hydro-dehalogenation product). No other phenylpyridine isomers were discernible by GC and ^1H NMR analysis. Control experiments confirmed that no reaction took place in the absence of either zinc, haloaryl, water, or palladium catalyst.

Under the same conditions, all three halobenzenes evidenced similar conversions (PhCl 68–70%; PhBr 70–75%; and PhI 78%, respectively), but product selectivity differed remarkably when the larger halides (Br, I) were used. Thus, with PhCl the product distribution was **1** 40–45%; **2** 50–52%; and **3** 8–10%. Conversely, when PhBr was used, the product distribution was **1** 12–15%; **2** 75–77%; and **3** 8–12%. With PhI, the product distribution was similar to that obtained with PhBr: **1** 19%; **2** 67%; and **3** 14%.

PhCl was chosen as a model substrate for the kinetics and process parameter studies. A first-order rate law was observed for fixed zinc and catalyst loading, *viz.* $-d[PhCl]/dt = k[PhCl]$.

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‡ To ensure that reaction rates were not mass-transfer controlled, control experiments were performed at various speeds of agitation, from 400 to 1000 rpm. Above 900 rpm, no increase in conversion was detected. Thus, all results hence pertain to reactions performed at 1000 rpm stirring.

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Table 1 Effect of various process parameters on PhCl conversion and product selectivity[a]

Entry	Parameter changed	PhCl conversion (%)	Product selectivity (%)[b] 1	2	3
	Temperature/°C				
1	85	34	54	39	7
2	95	46	53	38	9
3	105	58	52	37	11
4	115	68	52	40	8
5	125	68	52	38	10
	5% Pd/C/g				
6	0.50	43	47	46	7
7	1.00	68	52	40	8
8	1.50	69	53	39	8
9[c]	2.00	69	49	42	9
	Zinc/mmol				
10	50.0	31	51	42	7
11	90.0	64	49	40	11
12	133.0	68	52	38	10
13	200.0	68	45	47	8
	Phase-transfer agent				
14	THAC[d]	72	33	51	16
15	None	68	52	35	13
	NaOH/g				
16	3.00	77	44	49	7
17	None	68	52	40	8
	Water amount (mol H_2O : mol PhCl)				
18	None	0	0	0	0
19	3:1	68	52	40	8
20[e]	H_2O solvent	100	18	36	46

[a] *Standard reaction conditions*: PhCl, 10.0 g (88 mmol); Zn, 8.7 g (133 mmol), 5% Pd/C, 1.0 g (0.5 mol% relative to substrate), pyridine (solvent, total reaction volume 50 ml), 115 °C, 1000 rpm mechanical stirring for 20 h. [b] Based on GC area, corrected by the presence of an internal standard. [c] Conversion and selectivity after 12 h. [d] Tetrahexylammonium chloride (5 mol% of substrate). [e] Conversion and selectivity after 8 h.

The Arrhenius energy of activation was found to be $E_a = 50$ kJ mol^{-1} (12.5 kcal mol^{-1}, with $r^2 = 0.986$ for five measurements at 85, 95, 105, 115, and 125 °C), a typical value for a chemically controlled rate-determining step. Substrate conversions and product yields under various conditions are shown in Table 1.

Performing the reaction at higher temperatures (Table 1, entries 1–5, and Fig. 1), led, as expected, to higher conversion rates, but appreciable changes in product selectivity were not observed. The conversion was limited to 70% due to catalyst deactivation, but the catalyst was efficiently recycled at the end of the reaction (*vide infra*). Addition of a phase-transfer agent (entries 14, 15), or of a base (NaOH, entries 16, 17), increased substrate conversion, but, contrary to expectation based on previous work,[5a,b] did not enhance the selectivity to the coupling products. Similarly, using more zinc (entries 10–13) increased conversion but did not affect selectivity. Increasing catalyst loading, however (entries 6–9), shifted product selectivity towards the coupling products.

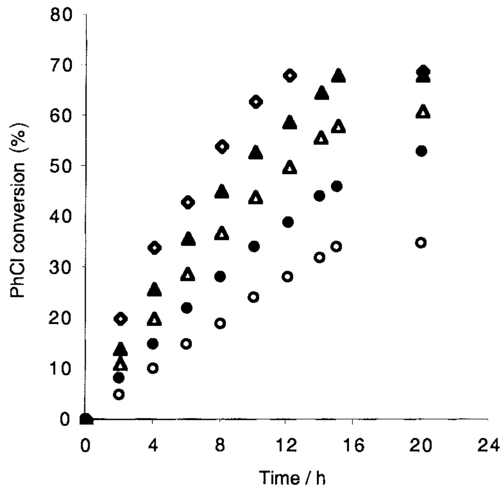


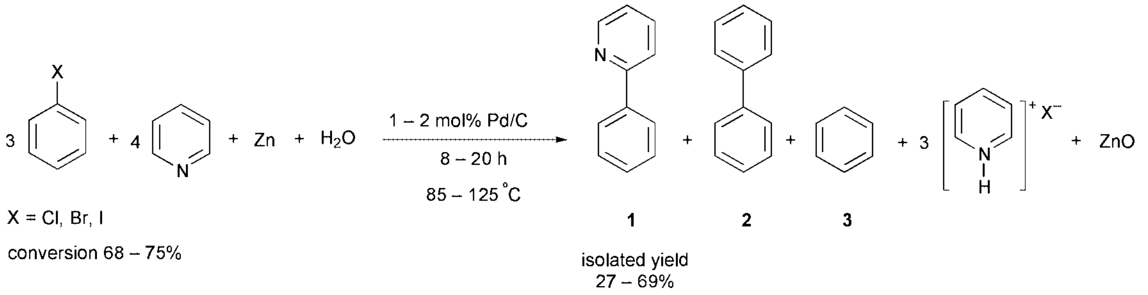
Fig. 1 Conversion of PhCl at different temperatures. Reaction conditions are given in Table 1. ○ 85 °C; ● 95 °C; △ 105 °C; ▲ 115 °C; ◇ 125 °C.

Water was found to be a critical parameter in this system (Table 1, entries 18–20). Near-stoichiometric amounts of water enabled high selectivity towards the desired coupling products (working with less than 3 molar equivalents of water to substrate proved ineffectual, due to technical mixing problems associated with the solid zinc reagent). Conversely, when water was used as a solvent (*i.e.* at a molar ratio where $[H_2O] \gg [Zn]$), only 18% of **1** was obtained.

As we recently reported, the zinc–water–palladium system can be regarded as an *in situ* source of molecular hydrogen.[9] It was expected, therefore, that substituting the zinc and water with gaseous hydrogen should enable the above cross-coupling. This was found to be the case, although only 14% conversion of PhCl was measured after 12 h under 1 atm H_2 (the yield of 2-phenylpyridine was 48%, comparable to the yields obtained using the zinc–water system).

In the presence of 5% (w/w) of BHT (2,6-di-*tert*-butyl-4-methylphenol), the reaction rate was slowed down by more than two orders of magnitude (<11% conversion of PhCl after 20 h). This suggests the participation of free-radicals in the rate-determining step. Notably, chlorobiphenyl products were not observed (in fact, chlorobiphenyls were not detected even in the absence of pyridine, in the homocoupling of PhCl to biphenyl[5c]), which supports our hypothesis that the free-radical species interact in the vicinity of the catalyst surface, rather than in the solvent bulk.

The resulting solid Pd/C + Zn + ZnO mixture, after filtration and drying, was found to be inactive in subsequent runs. However, following pretreatment of this solid cake with hydrogen gas in MeOH, 40% conversion of PhCl was obtained in a second run. We suggest that the catalyst may be deactivated



Scheme 1 Stoichiometry of cross-coupling between halobenzenes and pyridine.

partly by pyridine poisoning and partly due to coating of ZnO on the catalyst surface.[9]

Discussion

In the interests of clarity, it is best to consider each of the three chemical transformations in this complex system, namely the homocoupling, the reduction, and the cross-coupling, separately.

Homocoupling of halobenzenes

The coupling of two PhX molecules in this system has been recently discussed in detail,[5b] and is thought to proceed *via* two consecutive SET processes. *In situ* catalyst regeneration, in this case, occurs through the formation of hydrogen gas in the palladium-catalysed reaction of zinc with water [eqns. (2)–(5)].

$$\mathrm{Pd^0 + 2PhCl \longrightarrow Ph{-}Ph + Pd^{2+} + 2Cl^-} \qquad (2)$$

$$\mathrm{Zn_{(s)} + H_2O_{(l)} \xrightarrow{Pd^0/C} ZnO_{(s)} + H_{2(g)}} \qquad (3)$$

$$\mathrm{H_2 + Pd^{2+} \longrightarrow Pd^0 + 2H^+} \qquad (4)$$

$$\mathrm{Zn_{(s)} + H_2O_{(l)}PhCl \xrightarrow{Pd^0/C} ZnO_{(s)} + Ph{-}Ph + 2HCl} \qquad (5)$$

Reduction (hydro-dehalogenation) of halobenzenes

This reaction depends on the effective concentration of dihydrogen molecules at the active catalyst sites, which controls the formation of active hydride species. At low H_2 concentrations the reduction of Pd(II) to Pd(0) [eqn. (4)] is sufficiently fast so that none of the dihydrogen is available to adsorb on Pd(0) sites as hydride [eqn. (6)].

$$\mathrm{H_2 + Pd^0 \longrightarrow Pd^{II}(H^-)_2} \qquad (6)$$

$$\mathrm{Pd^{II}(H^-)_2 + Ar{-}X \longrightarrow Pd^{II}(H^-)(X^-) + Ar{-}H} \qquad (7)$$

At higher H_2 concentrations, however, eqn. (6) becomes dominant, and the number of $Pd(II)(H^-)_2$ sites increases. A haloaryl molecule that diffuses to a $Pd(II)(H^-)_2$ site can then undergo reduction [eqn. (7)]. Indeed, when the amount of water (and subsequently, the local concentration of hydrogen at the palladium surface) was increased, the conversion of PhCl was much faster, but the selectivity to the coupling products (both homocoupling and cross-coupling) was significantly lower than when water was used in near-stoichiometric amounts.

Cross-coupling

We propose that when a PhX molecule adsorbs onto a Pd(0) site, an SET process occurs, and a $[PhX]^{\bullet -}$ radical anion is formed. This radical anion can eject X^-, leaving a $Ph^\bullet$ radical on the catalyst surface (a discussion of this mechanism has been published previously;[5b,10] alternatively, the results can also be explained through a heterogeneous Heck-type reaction,[11] and the formation of ArPdX, which also displays the characteristics of a phenyl radical). In presence of an excess of pyridine, it is likely that an adjacent site to the $Ph^\bullet$ radical would be occupied by a pyridine molecule, and cross-coupling to 2-phenylpyridine can occur. This approach can also explain the remarkable difference in the product distribution between PhCl and PhBr/PhI. With PhBr or PhI, the formation of the $Ph^\bullet$ radical would be much faster[12] than that from PhCl, so at any given time the available concentration of $Ph^\bullet$ radicals adjacent to the catalyst surface would be higher, decreasing the chances of cross-coupling to a pyridine molecule (and indeed, much higher selectivity to the homocoupling product is observed). It may also be that both the zinc and the palladium play an active part in activating the pyridine molecule, which would account for the slow reaction observed in the presence of 1 atm hydrogen gas (without zinc).

This unusual activity evidenced by pyridine may stem from the low electron density of the heteroaromatic ring, which would make it susceptible (when absorbed onto the palladium catalyst) to attack by $Ph^\bullet$ radicals produced from the dismutation of $PhCl^{\bullet -}$ radical anions. In such a case, similar reactions could be expected between PhCl and electron-deficient aromatic rings (although a stoichiometric amount of base would be required to neutralize the HCl formed). Such analogous reaction systems are currently under investigation in our laboratory.

Conclusions

Heterogeneous palladium on carbon can catalyze the regiospecific coupling of aryl halides and pyridine under moderate conditions. This system enables the clean formation of 2-phenylpyridine in good yields without requiring expensive and wasteful boron or tin reagents. The ease of product and catalyst separation promotes this approach as a potential alternative pathway to the conventional cross-coupling methods. Furthermore, the above examples substantiate our claim that palladium-catalysed coupling using zinc and water is in fact a system where *in situ* generated hydrogen gas closes the catalytic cycle, rather than "direct metal-to-metal electron transfer" as was recently speculated.[13] The unusually high reactivity of aryl *chlorides* enhances the economical viability of our protocol, as these substrates are both cheaper and incur much lower E-factors[14] than aryl bromides or iodides.

Experimental

Melting points were measured in glass capillaries using an Electrothermal 9100 instrument and are uncorrected. ^1H NMR spectra were measured on a Bruker AMX 300 instrument at 300.13 MHz. GC and GCMS analyses were performed using an HP-5890 gas chromatograph with a 50% diphenyl- 50% dimethyl-polysiloxane packed column (25 m × 0.53 mm). All chemicals were purchased from commercial firms (>98% pure) and used without further purification. Products **1** and **2** were isolated and identified by comparison of their GCMS and ^1H NMR spectra to standard samples (*vide infra*). Reactions were performed in a 300 ml stainless steel Parr autoclave, equipped with a six-bladed impeller, an external heating mantle and a gas cooling system.

General procedure for cross-coupling

Example: 2-phenylpyridine from PhCl and pyridine: 10 g (88.6 mmol) PhCl, 8.7 g (133 mmol) plain zinc powder (40–60 mesh size), 4.8 g (270 mmol) water, 1 g (0.4 mmol) 5% Pd/C (0.5 mol% of Pd relative to PhCl), and pyridine (solvent, total reaction volume 50 ml) were charged to an autoclave which was heated to 115 °C. The autogeneous pressure was 19–21 psi. Reaction progress was monitored by GC. The slurry was stirred (1000 rpm) for 20 h, and filtered hot to remove the unreacted Zn, ZnO and Pd/C solid mixture. The filtrate was then acidified with HCl. Benzene, PhCl, and biphenyl were extracted in CH_2Cl_2 (3 × 30 ml). The aqueous acidic extract was evaporated to dryness, to obtain a mixture of hydrochloride salts of pyridine and 2-phenylpyridine. The solid mixture was basified with NaOH–MeOH, and pyridine was distilled from the solution under vacuum to give the crude 2-phenylpyridine (7.1 g, 52 mol% based on PhCl). Pure 2-phenylpyridine (light oil, >99% pure by GC and ^1H NMR) was obtained by column chromatography on silica (Merck K-100) using 20% ether in petroleum ether as eluent. δ_H ($CDCl_3$; Me_4Si) 8.69–8.71 (m, 1H), 7.96–8.0

(m, 2H), 7.20–7.79 (m, 2H), 7.39–7.51 (m, 3H), 7.21–7.26 (m, 1H).[15] Biphenyl was isolated from the organic layer by distilling out CH_2Cl_2, benzene and PhCl, followed by recrystallization from cold EtOH. Mp 69 °C (lit.,[16] 69–71 °C). Found: C, 93.31; H, 6.58. $C_{12}H_{10}$ requires C, 93.46; H, 6.54%. δ_H ($CDCl_3$; Me_4Si) 7.36 (2H, tt, aromatic 4,4′-H, *J* 7.1 and 1.2), 7.46 (4H, tt, aromatic 3,3′,5,5′-H, *J* 7.2 and 1.1), 7.56 (4H, dq, aromatic 2,2′,6,6′-H, *J* 7.0 and 1.2), good agreement was found with literature values.[17]

Catalyst recycling

The reaction was performed as above, after which the liquids were filtered and the solid cake containing Zn, ZnO, and Pd/C was washed with hot H_2O (3 × 40 ml) and then washed with MeOH (3 × 20 ml) at 25 °C. Then the mixture was heated to 120 °C in an autoclave in 60:40 MeOH–H_2O under 5 atm hydrogen pressure. The pretreated catalyst batch retained >63% of its activity when reused with a fresh batch of zinc for the same reaction, though no efforts were made to separate the Pd catalyst from the unreacted Zn powder.

Kinetic studies

Example: 10 g (88.6 mmol) PhCl, 8.7 g (133 mmol) plain zinc powder, 1 g (0.4 mmol, 0.5 mol% of PhCl) 5% Pd/C, and pyridine (solvent, total reaction volume 50 ml) were charged to an autoclave which was heated to 115 °C. Reaction progress was monitored by GC. The following parameters were studied: (i) initial PhCl concentration (3 experiments at 10% w/v, $k_{obs} = 1.8 \times 10^{-5}$ s^{-1}, $r^2 = 0.997$ for 9 observations; 20% w/v, $k_{obs} = 2.08 \times 10^{-5}$ s^{-1}, $r^2 = 0.999$ for 9 observations; and 30% w/v, $k_{obs} = 2.18 \times 10^{-5}$ s^{-1}, $r^2 = 0.997$ for 9 observations); (ii) catalyst loading (4 experiments using 0.5 g of 5% w/w Pd/C, $k_{obs} = 1.04 \times 10^{-5}$ s^{-1}, $r^2 = 0.996$ for 9 observations; 1.0 g, $k_{obs} = 2.07 \times 10^{-5}$ s^{-1}, $r^2 = 0.99$ for 9 observations; 1.5 g, $k_{obs} = 2.2 \times 10^{-5}$ s^{-1}, $r^2 = 0.97$ for 9 observations; and 2.0 g, $k_{obs} = 2.38 \times 10^{-5}$ s^{-1}, $r^2 = 0.93$ for 9 observations); (iii) Zn loading (4 experiments using 50 mmol Zn, $k_{obs} = 6.8 \times 10^{-6}$ s^{-1}, $r^2 = 0.998$ for 9 observations; 90 mmol Zn, $k_{obs} = 1.8 \times 10^{-5}$ s^{-1}, $r^2 = 0.996$ for 9 observations; 133 mmol Zn, $k_{obs} = 2.07 \times 10^{-5}$ s^{-1}, $r^2 = 0.999$ for 9 observations; and 200 mmol Zn, $k_{obs} = 2.3 \times 10^{-5}$ s^{-1}, $r^2 = 0.998$ for 9 observations); (iv) reaction temperature (5 experiments at 85 °C, $k_{obs} = 7.58 \times 10^{-6}$ s^{-1}, $r^2 = 0.998$ for 9 observations; 95 °C, $k_{obs} = 1.14 \times 10^{-5}$ s^{-1}, $r^2 = 0.999$ for 9 observations; 105 °C, $k_{obs} = 1.6 \times 10^{-5}$ s^{-1}, $r^2 = 0.99$ for 9 observations; 115 °C, $k_{obs} = 2.08 \times 10^{-5}$ s^{-1}, $r^2 = 0.999$ for 9 observations; and 125 °C, $k_{obs} = 2.68 \times 10^{-5}$ s^{-1}, $r^2 = 0.997$ for 9 observations).

Acknowledgements

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