

Palladium-EDTA and palladium-EdteH₄ catalyzed Heck coupling reactions in pure water

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Abstract: Palladium-catalyzed Heck coupling reactions of styrene with bromoarene derivatives are carried out under aerobic conditions in water using water-soluble *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (EdteH₄) and ethylenediaminetetraacetic acid disodium salt (Na₂EDTA) as ligands. The effect of different bases, catalyst loading, and additives is also monitored. The olefination of bromoarenes with styrene affords the desired products in high yields. The Na₂PdCl₄- Na₂EDTA precatalyst system is also used for the preparative scale (50.0 mmol) synthesis of 4-acetyl-*trans*-stilbene and 4-styrylbenzaldehyde without a noticeable decrease in the activity. Recycling studies on the Na₂PdCl₄ - Na₂EDTA precatalyst system are also tested in the coupling of 4-bromoacetophenone with styrene.

Key words: Heck coupling, palladium, Na₂EDTA, EdteH₄, water

1. Introduction

The palladium-catalyzed coupling reaction of terminal alkenes with aryl or vinyl halides, the Mizoroki–Heck reaction, is a very important method for C-C bond formation.^{1–3} This powerful reaction has been widely used for coupling aryl halides with styrene or derivatives such as acrylic acid, alkyl acrylates, and acrylonitriles.^{4–8}

There has been much interest devoted to the use of water-soluble catalysts, since water is nontoxic, nonflammable, and relatively inexpensive when compared to organic solvents. Furthermore, simplifying the separation of the water-soluble catalyst and inorganic salts, which occurred during the reaction, from the product enables simple purification. In addition to the cost of the process, contamination of the product with ligands or palladium can be a problematic issue, especially in the case of the production of pharmaceuticals.^{9–15} Water has several drawbacks as a solvent: it is a poor solvent for most organic molecules, and it becomes waste itself when contaminated with the organic materials. However, organic-contaminated water can be cleaned by incineration since it is nonflammable. Thus, recycling of water used in chemical processes is an important element in the design of aqueous-phase processes on an industrial scale.¹⁶ Many efforts have been made to investigate the palladium-catalyzed Heck reaction in water both in homogeneous and heterogeneous conditions,^{17,18} by using different catalyst systems such as N-heterocyclic carbenes,^{19–21} palladacycles,^{22–24} P,N-ligands,²⁵ a benzothiazole ligand,²⁶ polymeric systems,^{27–29} palladium nanoparticles,^{30,31} and ionic liquids.^{32,33}

In 2005, Korolev and Bumagin investigated the PdCl₂-EDTA system in Suzuki–Miyaura coupling reactions.³⁴ Additionally, in our recent study, the water-soluble and chelate-stabilized palladium complex PdCl₂(EdteH₄), derived from EdteH₄, was synthesized and found to be a very efficient catalyst for the Suzuki–

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Miyaura cross-coupling reaction in water.³⁵ Encouraged by these previous results, we focused our attention on studying the water-soluble and chelating $\text{PdCl}_2(\text{EdteH}_4)$, $\text{Na}_2\text{PdCl}_4\text{-EdteH}_4$ and $\text{Na}_2\text{PdCl}_4\text{-Na}_2\text{EDTA}$ (Figure) catalyzed Heck coupling reactions of aryl bromides with styrene in water under aerobic conditions.

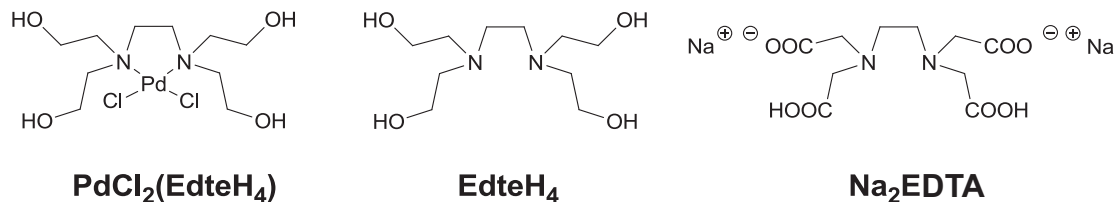
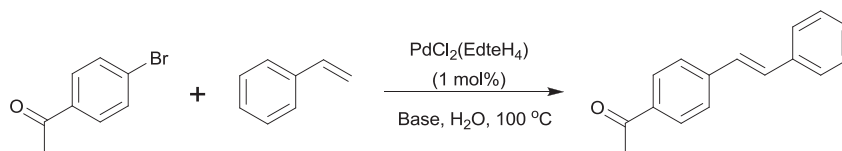


Figure. Structures of the palladium complex and ligands used in this study.

2. Results and discussion

Initially, the performance of different bases was tested in the Heck coupling of 4-bromoacetophenone with styrene in water. The water-soluble $\text{PdCl}_2(\text{EdteH}_4)$ complex (1.0 mol%) was used as the precatalyst at 100 °C under aerobic conditions (Table 1). To compare the effect of different bases, inorganic bases such as NaOH, Na_2SiO_3 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, K_2CO_3 , K_3PO_4 , and NaOAc (Table 1, entries 1–6), and organic bases including NEt_3 and EdteH_4 (Table 1, entries 7 and 8) were used. The best result was obtained with K_3PO_4 as the base (Table 1, entry 5) with a conversion of 99% in 8 h. Although many different bases are used in Heck coupling reactions, there is no definitive evidence in the literature on the effect of different bases on the mechanism. Clearly, the choice of base could be influenced by the type of catalyst, substrate, and solvent; the basicity might not be the only reason behind obtaining the best result.

Table 1. Effect of different bases on the Heck coupling of 4-bromoacetophenone with styrene.^a

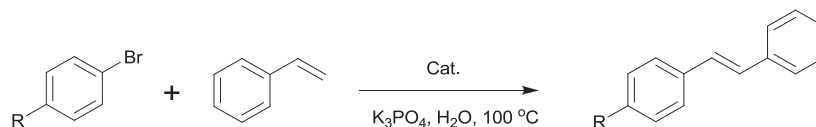


Entry	Base	Conversion (%) ^b
1	NaOH	59
2	Na_2SiO_3	32
3	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	15
4	K_2CO_3	91
5	K_3PO_4	99
6	NaOAc	47
7	NEt_3	51
8	EdteH_4	79

^a4-Bromoacetophenone (1.0 mmol), styrene (1.2 mmol), base (2.0 mmol), $\text{PdCl}_2(\text{EdteH}_4)$ (1.0 mol%), H_2O (3.0 mL), 8 h, 100 °C.

^bConversions determined by ^1H NMR spectroscopy based on 4-bromoacetophenone.

Next, we monitored the effect of precatalyst loading, and 88% and 99% conversions were obtained with 0.5 mol% and 1.0 mol% precatalyst loading respectively, in 8 h (Table 2, entry 1 and 2). By using 2.0 mol% of precatalyst we achieved 94% conversion in only 2 h (Table 2, entry 3).

Table 2. Heck coupling of different aryl halides with styrene.^a

Entry	R	Cat. [mol%]	Ligand (mmol)	Time (h)	Conv. (%) ^b	Yield (%) ^c
1	COCH ₃	PdCl ₂ (EdteH ₄) [0.5]	-	8	88	83
2	COCH ₃	PdCl ₂ (EdteH ₄) [1]	-	8	99	97
3	COCH ₃	PdCl ₂ (EdteH ₄) [2]	-	2	94	91
4	COCH ₃	Na ₂ PdCl ₄ [2]	EdteH ₄ (0.04)	2	84	80
5	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	99	96
6	COCH ₃	Na ₂ PdCl ₄ [2]	-	2	0	0
7 ^d	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	97	95
8 ^e	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	99	97
9 ^f	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	0	0
10 ^g	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	0	0
11 ^h	COCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	64	61
12	CHO	PdCl ₂ (EdteH ₄) [2]	-	2	96	93
13	CHO	Na ₂ PdCl ₄ [2]	EdteH ₄ (0.04)	2	91	87
14	CHO	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	100	98
15 ^d	CHO	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	2	99	96
16	OCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	12	76	73
17 ⁱ	OCH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	12	83	81
18	CH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	12	46	42
19 ⁱ	CH ₃	Na ₂ PdCl ₄ [2]	Na ₂ EDTA (0.04)	12	55	52

^a Aryl halide (1.0 mmol), styrene (1.2 mmol), K₃PO₄ (2.0 mmol), Pd, H₂O (3.0 mL), 100 °C.

^b Conversions determined by ¹H NMR spectroscopy.

^c Isolated yield.

^d Aryl bromide (50.0 mmol), styrene (60.0 mmol).

^e Reaction carried out under Ar atmosphere.

^f Using 1.5 mmol of NaIO₄ as the reoxidant.

^g Using 1.5 mmol of Cu(OAc)₂ as the reoxidant.

^h Two drops of Hg(0) were added at the beginning of the reaction.

ⁱ n-Bu₄NBr (5.0 mol%).

Having observed that the PdCl₂(EdteH₄) complex, with a chelating EdteH₄ ligand, was active for this conversion, we aimed to prepare simple in situ generated water-soluble precatalyst systems. For this purpose, a water-soluble palladium salt, Na₂PdCl₄, was mixed with 2 equivalents of EdteH₄ or Na₂EDTA, which are both chelating amine ligands possessing alcohol or carboxylic acid functional groups, to give very clear yellow solutions in water. The above-mentioned water-soluble precatalysts, PdCl₂(EdteH₄), Na₂PdCl₄-EdteH₄, and Na₂PdCl₄-Na₂EDTA, were used to examine the Heck coupling reactions of electronically activated and deactivated aryl bromides with styrene using K₃PO₄ as the base at 100 °C in water (Table 2). Three of these systems were found to be active precatalysts for the coupling of styrene with electronically activated aryl bromides such as 4-bromoacetophenone (Table 2, entries 3–5) and 4-bromobenzaldehyde (Table 2, entries 12–14). Furthermore, to prove the effect of these water-soluble ligands in the catalytic Heck coupling reaction, a ligand-free experiment was carried out. There was no conversion observed to the expected (*E*)-1-(4-styrylphenyl)ethanone under these conditions (Table 2, entry 6).

The Na_2PdCl_4 - Na_2EDTA system was found to be the most active precatalyst of these 3 systems. This system was also used for a preparative scale (50.0 mmol) synthesis of (*E*)-1-(4-styrylphenyl)ethanone (Table 2, entry 7) and (*E*)-4-styrylbenzaldehyde (Table 2, entry 15) without a noticeable decrease in the activity when compared with the 1 mmol scale.

The reactions of electronically deactivated 4-bromoanisole and 4-bromotoluene with styrene were also examined and required prolonged reaction times to reach moderate to good yields (Table 2, entries 16–19). Generally, electron-donating substituents on the aryl halides made the oxidative addition step of the catalytic cycle more difficult and, as a result, substrates with electron-withdrawing groups (activated) gave higher yields than those with electron-donating (deactivated) substituents.^{7,32} However, we observed better activity in the presence of 5.0 mol% of tetra-*n*-butylammonium bromide (*n*- Bu_4NBr) (Table 2, entries 17 and 19). The addition of *n*- Bu_4NBr might enhance the solubility or the mobility of the substrates into the aqueous phase, increasing the reaction rate or the stability of the active species.^{6,34,36,37}

Although Heck reactions are usually performed under an inert atmosphere, there are many examples of this reaction performed under aerobic conditions.^{20,27,28,32,38–48} When the conversions under aerobic conditions (Table 2, entry 5) and inert reaction conditions (Table 2, entry 8) are compared, no difference between the activities was observed. This could be because all the ligands and complexes are nonsensitive to oxygen. All manipulations for performing the reaction and separating the products from the water phase could be handled without an inert atmosphere.

A simplified Pd(0) / Pd(II) mechanism for the Heck coupling reaction between aryl halides and alkenes is often referred to as the classical mechanism.^{7,48,49} There is also an alternative mechanism involving Pd(II) / Pd(IV) species.^{50,51} The Heck reaction occurring in the presence of different oxidants suggests that a catalytic cycle involving Pd(II) / Pd(IV) species might be the possible pathway.⁴⁷ Sumimoto et. al. investigated theoretically the $\text{PdCl}_2(\text{dppe})$ -catalyzed Heck reaction between bromobenzene and ethylene using DFT.⁵² This mechanism involves oxidative addition of bromobenzene to the Pd center, followed by alkene insertion into the Pd-C bond. The next step is β -H abstraction and elimination of the product to generate the active catalyst for the next cycle.

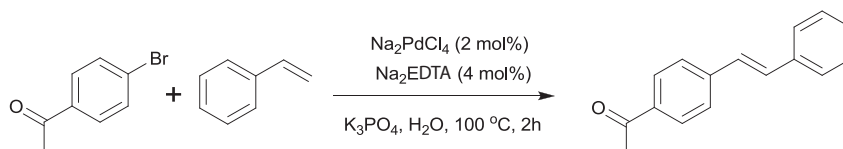
We investigated the effect of different oxidants on the reaction of styrene and 4-bromoacetophenone in order to understand the mechanism of the reaction. In the presence of 1.5 equiv. of NaIO_4 or $\text{Cu}(\text{OAc})_2$, no product formation was observed (Table 2, entries 9 and 10) and the starting materials were recovered. These results may indicate that a catalytic cycle involving Pd(II) / Pd(IV) species might not be operating.⁴⁷ Therefore, the alternative mechanism for this reaction could be the classical Pd(0) / Pd(II) pathway.^{48,49,52}

Homogeneous and heterogeneous Heck reactions can be catalyzed by species produced from preformed palladium nanoparticle PdNPs stabilized by various organic or inorganic stabilizers, in particular tetraalkylammonium salts, ligands, macromolecules, ILs, and micelles, or solid oxides of a variety of elements.^{53,54} It is known that Pd(0) complexes with conventional diamine ligands are not stable, because the required back donation does not exist in these cases. However, the chelating EdteH_4 and Na_2EDTA system may play a stabilizing role in Pd(0) complexes or PdNPs. Consistent with these observations, the used EdteH_4 and Na_2EDTA ligands might stabilize the Pd(0) species formed upon the reduction of Pd(II). The mercury poisoning of metal(0) particles, by amalgamating the metal, is a widely used test for heterogeneity or homogeneity of catalysis.^{6,18,55–57} Thus, we applied this procedure to our system and observed that addition of excess Hg(0) at the beginning of the catalytic reaction decreased the conversion from 99% to 64% (Table 2, entry 11). This result suggests that the

heterogeneously active Pd(0) species may also play an important role and a heterogeneous mechanism might be probable in this case. This result also indicates that the increased efficiency of the precatalyst by adding *n*-Bu₄NBr could be explained by its nanoparticle-stabilizing ability.⁵⁸

Recycling of the Na₂PdCl₄ (2 mol%) - Na₂EDTA (4 mol%) precatalyst system was tested for the coupling of 4-bromoacetophenone (1.0 mmol) with styrene (1.2 mmol) using K₃PO₄ (2 mmol) as the base at 100 °C in water (3.0 mL) (Table 3). On completion of the reaction, the mixture was cooled to room temperature and then extracted with Et₂O (3 × 5 mL). The organic phase was separated, and then 4-bromoacetophenone (1.0 mmol), styrene (1.2 mmol), and K₃PO₄ (2 mmol) were added to the solution. After the necessary reaction time, the product was isolated. The results indicated that the precatalyst was not very stable and that the activity decreased considerably after the second run. Addition of 5.0 mol% *n*-Bu₄NBr under the same conditions increased the precatalyst stability and the precatalyst could be recycled 5 times without any considerable loss in activity.^{6,55–58}

Table 3. Recycling of the precatalyst.



Run	Yield ^a	Yield ^b
1st	96	98
2nd	91	97
3rd	69	94
4th	58	91
5th	43	89

^a: Isolated yield without any additive.

^b: Isolated yield with 5.0 mol% of *n*-Bu₄N⁺Br as additive.

In conclusion, water-soluble precatalysts, including the previously synthesized PdCl₂(EdteH₄) complex and in situ prepared Na₂PdCl₄- EdteH₄ and Na₂PdCl₄- Na₂EDTA have been found to be effective precatalysts in the Heck coupling of electronically activated aryl bromides with styrene under aerobic conditions in water. This procedure adds value from a cost and environmental viewpoint and simplifies the separation of the catalyst from the products. Of the 3 catalyst systems tested, Na₂PdCl₄- Na₂EDTA was found to be the most active precatalyst. In the case of electronically deactivated aryl bromides the catalytic activity increased on the addition of 5.0 mol% of *n*-Bu₄NBr. The addition of 5.0 mol% of *n*-Bu₄NBr also increased the catalyst stability in the recycling studies; the precatalyst could be recycled 5 times without any considerable loss in the activity.

3. Experimental

3.1. General comments

All reactions were performed in open air. Reagents and solvents were purchased from Merck, Alfa Aesar, and Acros Organics. ¹H and ¹³C NMR spectra were recorded in CDCl₃ with tetramethylsilane as an internal reference using a Varian AS 400 Mercury instrument. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) in Hz. Melting points were determined with an electrothermal melting point detection apparatus.

3.2. Preparation of precatalyst system

The PdCl₂(EdteH₄) precatalyst was prepared according to our previously published procedure.³⁵ The precatalysts Na₂PdCl₄-EdteH₄ and Na₂PdCl₄-Na₂EDTA were prepared in situ using 1:2 molar ratios of Na₂PdCl₄ and the appropriate amine ligands. All the precatalyst systems were used from 2 × 10⁻² M stock solutions in distilled water.

3.3. General procedure for the Pd-catalyzed Heck reaction

In a typical run, a reaction vessel was charged with bromoarene (1.0 mmol), styrene (1.2 mmol), a solution of the Pd precatalyst in H₂O, and the base (2 mmol), followed by the addition of more H₂O until the total volume reached 3 mL. The mixture was then stirred vigorously at 100 °C for desired reaction time in the open air under reflux conditions. After the required reaction time, the solution was allowed to cool to room temperature and then extracted with Et₂O (3 × 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent evaporated. The residue was purified by column chromatography on silica gel using a mixture of hexane and EtOAc (4:1) as eluent. The melting points and ¹H NMR and ¹³C NMR data for the isolated compounds (*E*)-1-(4-styrylphenyl)ethanone,²⁵ (*E*)-4-styrylbenzaldehyde,²⁷ (*E*)-1-methyl-4-styrylbenzene,²⁵ and (*E*)-1-methoxy-4-styrylbenzene²⁵ are comparable with those reported in the literature.

3.4. Characterization of products

(*E*)-1-(4-Styrylphenyl)ethanone:²⁵ White solid. Mp = 142–143 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.58 (2 H, d, *J* = 8.4 Hz, Ph-H), 7.54 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.30–7.38 (3 H, m, Ph-H), 7.22 (1 H, d, *J* = 16.0 Hz, CH), 7.12 (1 H, d, *J* = 16.0 Hz, CH), 2.59 (3 H, s, COCH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃)δ 197.6, 142.5, 137.0, 136.2, 129.1, 129.0, 128.7, 128.5, 127.7, 127.1, 126.7, 126.4, 26.8 ppm.

(*E*)-4-Styrylbenzaldehyde:²⁷ White solid. Mp = 115–116 °C. ¹H NMR (400 MHz, CDCl₃)δ 9.94 (1 H, s, CHO), 7.84 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.61 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.52 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.39–7.31 (3 H, m, Ph-H), 7.22 (1 H, d, *J* = 16.0 Hz, CH), 7.14 (1 H, d, *J* = 16.0 Hz, CH) ppm. ¹³C NMR (100.6 MHz, CDCl₃)δ 193.7, 143.6, 136.8, 135.6, 132.4, 130.4, 129.1, 128.7, 128.6, 128.0, 127.5, 127.1, 126.4 ppm.

(*E*)-1-Methyl-4-styrylbenzene:²⁵ White solid. Mp = 115–117 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (2 H, d, *J* = 8.4 Hz, Ph-H), 7.38 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.32 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.09–7.21 (3 H, m, Ph-H), 7.22 (1 H, d, *J* = 16.4 Hz, CH), 6.94 (1 H, d, *J* = 16.4 Hz, CH), 2.39 (3 H, s, CH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃)δ 137.6, 137.3, 134.6, 130.5, 129.6, 128.6, 127.9, 127.1, 126.3, 126.0, 22.8 ppm.

(*E*)-1-Methoxy-4-styrylbenzene:²⁵ White solid. Mp = 136–138 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (2 H, d, *J* = 8.0 Hz, Ph-H), 7.36 (2 H, d, *J* = 8.4 Hz, Ph-H), 7.16–7.27 (3 H, m, Ph-H), 7.02 (1 H, d, *J* = 16.0 Hz, CH), 6.92 (1 H, d, *J* = 16.4 Hz, CH), 6.86 (2 H, d, *J* = 8.0 Hz, Ph-H), 3.79 (3 H, s, OCH₃) ppm. ¹³C NMR (100.6 MHz, CDCl₃)δ 160.3, 138.6, 131.2, 129.7, 128.2, 127.6, 127.3, 126.8, 126.3, 117.2, 58.3 ppm.

Acknowledgments

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