



# Simple method for enhancement of the ligand-free palladium catalyst activity in the Heck reaction with non-activated bromoarenes

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## Abstract

Simple catalytic system is reported capable of catalyzing effectively the reaction of bromoarenes with styrene in air in the absence of any ligands. Quantitative yield of the product was achieved by the use of 0.04–1.6 mol% PdCl<sub>2</sub>, 18% HCOONa, 112% AcONa and six-fold excess of bromoarene (with respect to styrene) in DMF after 10 min at 140° or after 180 min at 100°. Confirmation was obtained of the earlier reported assumption that colloid palladium particles formed in the course of the reaction are the main “reservoir” of catalytically active homogeneous Pd(0) complexes.

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*Keywords:* Bromoarenes; Heck reaction; Phosphine-free condition

## 1. Introduction

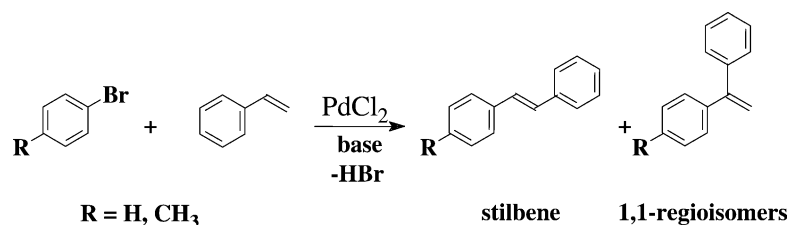
The Heck reaction is a perspective route to substituted alkenes [1,2]. Recent attention of chemists was focused on a search for catalytic systems capable of activation of more accessible but less reactive bromoarenes (see review [3]). This would make the Heck reaction much more acceptable for industrial use. In this connection, catalytic systems without ligands, in particular, the traditionally used phosphines, are of special interest. Systems of this type were reported in [3–5] where heterogeneous palladium catalysts were employed. A homogeneous catalytic system with tetraphenylphosphonium salts and dimethyl glycine used instead of phosphines has been investigated

[6]. In presented work, we report on the first example of catalytic system possessing no ligands and still capable of catalyzing effectively the reaction of bromoarenes with styrene in air (Scheme 1).

## 2. Experimental

Sixty millimoles bromobenzene, 10 mmol styrene, 11.2 mmol sodium acetate, 1.8 mmol sodium formate, 2 mmol naphthalene (as internal standard for GC analysis), 10 ml DMF (as solvent) and 1.6 mol% of PdCl<sub>2</sub> (with respect to styrene) were introduced in glass reactor. The reactor was placed into a pre-heated to 140 °C oil bath and the reaction mixture was vigorously stirred. The reaction was monitored by taking small samples for GC analysis. Maximum reaction rate was calculated by the graphical differentiation of the time–conversion curves. The gas–liquid

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Scheme 1. Heck coupling of bromoarenes with styrene.

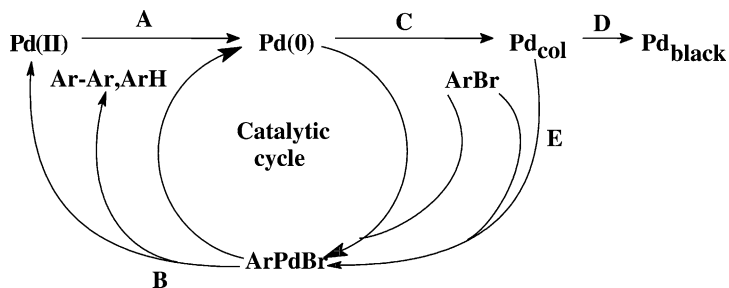
chromatograms were recorded on a chromatograph HP-4890 series equipped with a FID detector and a HP-5 column (cross-linked methyl, phenylsiloxane, 15 m × 0.53 mm × 1.5 μm film thickness). Products were identified by comparison with authentic samples.

### 3. Results and discussion

The key processes of the catalyzed Heck reaction are shown in the Scheme 2. The ratio of the rates of these processes plays the determining role in arylation by the use of non-reactive haloarenes. Reduction of Pd(II) to Pd(0) (Scheme 2, A) is necessary not only in the initial stage of the reaction but during the whole process because of persistent side reductive transformations of bromoarene to Ar–Ar and ArH (Scheme 2, B). This results in that in the reaction of iodobenzene with styrene even at 130° the major amount of palladium is present in the oxidized state [7]. The problem, however, can be solved by addition of catalytic amounts of reducing agent, e.g. sodium formate into the catalytic system [8]. Another undesirable process during the Heck reaction is aggregation of catalytically active Pd(0) complexes (Scheme 2, C, D) favored by low reactivity of ArBr. The process of aggregation

as depicted in the Scheme 2 proceeds via intermediate formation of particles of colloid palladium whose formation in the Heck reaction was unequivocally established by Reetz and Westermann [9]. An important role of colloid palladium will be clarified below. Note that partial recovery of aggregated palladium into the catalytic cycle is possible (Scheme 2, E) by its reaction with haloarene [9,10]. A competition between the process of aggregation and the catalytic cycle allows one to assume that an increase of concentration of ArBr would favor the increase of the current concentration of palladium in the catalytic cycle.

The above theoretical analysis was completely corroborated experimentally (Table 1). As anticipated, the use of catalytic system PdCl<sub>2</sub> + AcONa resulted in a low yield of the reaction product (Run 1). Addition of sodium formate accelerated the reaction but had no effect on the yield of stilbene (Run 2). In contrast, the use of the four-fold excess of bromobenzene increased the yield to 41% (Run 3) and with its six-fold excess styrene was for the first time quantitatively converted to stilbene in 10 min in the air and without usage of any ligands (Run 4). Addition of the reducing agent also accelerated the reaction (Runs 4 and 5). That high catalytic activity allowed us to substantially reduce the amount of the catalyst, from 1.6 to 0.04 mol%



Scheme 2. The key processes of the Heck reaction.

Table 1

Effect of the reducing agent and excess of PhBr on Heck reaction (Scheme 1, 140 °C)

Run	Catalytic system	Styrene:PhBr ratio	Time, (min) <sup>a</sup>	Maximum rate (mol <sup>-1</sup> min <sup>-1</sup> ) × 10 <sup>2</sup>	Conversion of PhBr to Ph–Ph + PhH (%) <sup>b</sup>	Conversion of styrene to stilbene (%) <sup>b</sup>
1	PdCl <sub>2</sub> + AcONa	1:1	45	2.1	1.0	26
2	PdCl <sub>2</sub> + AcONa + HCOONa	1:1	5	6.0	3.0	24
3	PdCl <sub>2</sub> + AcONa + HCOONa	1:4	15	4.2	1.0	41
4	PdCl <sub>2</sub> + AcONa + HCOONa	1:6	10	18	1.5	95
5	PdCl <sub>2</sub> + AcONa	1:6	80	5.2	1.3	94
6	PdCl <sub>2</sub> + AcONa + HCOONa <sup>c</sup>	1:6	180	2.0	0.8	93
7	PdCl <sub>2</sub> + AcONa + HCOONa <sup>d</sup>	1:6	180	1.5	0.2	70
8	PdCl <sub>2</sub> + AcONa <sup>d</sup>	1:6	180	0.6	–	8
9	PdCl <sub>2</sub> + AcONa + HCOONa <sup>d</sup>	1:1	60	1.4	1.0	10
10	PdCl <sub>2</sub> + AcONa + HCOONa <sup>e</sup>	1:6	120	12	0.4	70
11	Pd/C + AcONa + HCOONa <sup>f</sup>	1:6	260	0.4	1.3	95
12	Pd/C + AcONa <sup>f</sup>	1:1	180	0.1	1.0	12

<sup>a</sup> The reaction completion time after which the concentration of all the components remains constant.<sup>b</sup> ArBr and styrene were only converted into Ph–Ph, PhH, stilbene and into 1,1-regioisomers, yield of which did not exceed 3% in all experiments.<sup>c</sup> PdCl<sub>2</sub>: 0.04 mol%.<sup>d</sup> Reaction was carried out at 100 °C.<sup>e</sup> Heck reaction with *p*-bromotoluene (Scheme 1).<sup>f</sup> The 5 wt.% Pd/C was prepared according to [13].

(Run 6) and to perform the reaction at 100 °C (Run 7). Note that according to [3] the temperature for the Heck reaction with bromoarenes is normally as high as 140 °C. Runs 7 and 8 show that the presence of the reducing agent is a necessary condition for attaining good yields when the reaction is carried out at 100 °C. Substitution of less reactive *p*-bromotoluene for bromobenzene results in a decrease of the reaction rate (Run 10). However, the yield of the reaction product remains high. The use of heterogeneous Pd/C instead of PdCl<sub>2</sub> was also successful when sodium format and an excess of PhBr were applied (Runs 11 and 12). The homogeneous catalysis is possible as well because of Pd leaching [4,5,11,12].

Comparison of the reaction rate for equimolar ratio of the reagents with that for excess of bromobenzene allows an assumption to be made on the mechanism of the Heck reaction for non-reactive haloarenes. The matter is that it is impossible to explain the increase of the reaction product only by acceleration of the steps with participation of ArBr and/or an increase of the turnover frequency of the catalytic cycle as a result of the increased palladium concentration. Actually, the increase of bromobenzene concentration at 140 °C gives rise to three-fold increase of the reaction rate but to almost four-fold increase

of the yield of arylation products (Runs 2 and 4). The effect is even more pronounced at 100 °C when the yield increased by a factor of 7 with the reaction rate virtually constant (Runs 7 and 9). This is indicative of the increase of the yield being attained due to prolonged performance of the catalyst rather than increased palladium concentration in the catalytic cycle. The observed trends, in our opinion, can be explained by the fact that, in spite of increasing concentration of bromobenzene, aggregation of Pd(0) still occurs (Scheme 2, C). However, due to competition between processes E and D (Scheme 2), an increase of concentration of ArBr leads to retardation of irreversible aggregation (Scheme 2, D) and occurrence of palladium mainly in an intermediate, capable of regeneration, state (Scheme 2, E). It may be suggested according to [9] that this state will be colloid particles of palladium.

#### 4. Conclusions

The use of reducing agent and excess of bromoarene allowed for the first time to attain quantitative yield of the product and to reduce the temperature of the Heck reaction without utilization of any ligands and

an inert atmosphere. An earlier assumption [9] was corroborated that colloid palladium particles formed in the course of the reaction are the main “reservoir” of catalytically active homogeneous Pd(0) complexes (Scheme 2).

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