Base-free efficient palladium catalyst of Heck reaction in molten tetrabutylammonium bromide

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Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday.

Abstract

Phosphine-free palladium precursors (PdCl$_2$, PdCl$_2$(PhCN)$_2$ and Pd(OAc)$_2$) in molten [^{n}Bu$_4$N]Br as the reaction medium and without addition of base were used as components for efficient catalytic systems for Heck coupling of bromobenzene with butyl acrylate. In all the systems under studies the yield of product, butyl cinnamate **1**, strongly depends on the concentration of palladium. The maximum yield of **1** was obtained for PdCl$_2$(PhCN)$_2$ at 0.09 mol% and for PdCl$_2$ and Pd(OAc)$_2$ at *ca.* 0.4 mol%. Lower yields were obtained below and over that concentration. Addition of bases (NaHCO$_3$, NaHCO$_2$, Et$_3$N or Bu$_3$N) caused an increase of acrylate conversion and formation of butyl β-phenyl cinnamate **2**. During recycling experiments the change of selectivity was observed with increase of **1/2** products ratio.
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Keywords: Heck coupling; Phosphorus-free palladium catalyst; Molten tetrabutylammonium salt; Palladium nanoparticles; Base-free Heck reaction

1. Introduction

The Heck coupling, one of the most important palladium-catalyzed C–C bond formation reactions, is a process also described as olefin arylation (Scheme 1) [1–6]. Arylated olefins, the final products of Heck reaction, have very broad application in synthesis of pharmaceuticals, agrochemicals, and natural products. In particular β-arylcinnamic acid derivatives were important intermediates in synthesis of medical products [7]. Therefore, very intensive research is addressed to elaboration of new, simple and efficient catalytic systems for Heck coupling reaction.

Typical palladium catalysts of Heck reaction contain phosphines, and the special place in this group of compounds is occupied by palladacycles [8,9] and PCP pincer complexes [10]. However, recently phosphine-free catalytic systems, economically profitable and environmentally friendly, have received increasing attention [11–20]. According to our and other [2,18] recently reported studies, it seems most probable that in phosphine-free systems the key role is played by colloidal (sol-uble) forms of Pd(0) nanoparticles. Such colloidal catalytic systems require the presence of stabilizing agents like polymers, dendrimers or ammonium salts. Their absence leads to catalyst deactivation as a result of the transformation of the Pd(0) colloid into inactive "palladium black". Recently published results concerning the Heck reaction with the participation of palladacycles seem to suggest the possibility of the presence of palladium nanoparticles also in these systems [13,21].

The Heck reaction can be performed not only in organic solvent but also in molten salts or ionic liquids [22–27]. One of the most effective ways to increase the Heck reaction yield was to apply the so-called Jeffery conditions, *i.e.* introduction of tetraalkylammonium salts to the reaction medium [28,29]. The use of tetraalkylammonium salts has made it possible to obtain very good results in a number of Heck reactions [23,24,30] as well as carbonylation and Suzuki reactions [31]. The role of tetraalkylammonium salts and their interactions with palladium catalyst was discussed by many authors who regarded ammonium salts as stabilizers of metal colloids formed in situ, preventing their aggregation to the bigger size particles, usually inactive or less active [32,34]. The effect of tetraalkylammonium salts as phase-transfer agents was also considered [28,29,35].

Typical catalytic system for Heck reaction also usually contains a base necessary to neutralize HX formed as a side reaction

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Scheme 1.

Fig. 1. Effect of palladium catalysts concentration on the yield of Heck reaction.
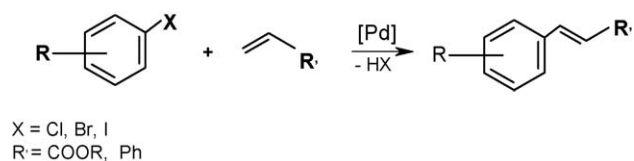
product (Scheme 1). Alkali metal carbonates (or bicarbonates) carboxylates (formates or acetates) or amines are used in most cases. Application of tetrabutylammonium acetate as a base in tetrabutylammonium bromide medium was also shown [33]. Very recently the system for Heck-type arylation of alkenes with aroyl chlorides without base was reported [36].

The subject of studies reported in this paper are Heck reactions with palladium catalyst precursors not containing phosphorus ligands, like PdCl$_2$(PhCN)$_2$, in tetrabutylammonium bromide as reaction medium. The reaction of butyl acrylate with bromobenzene used in excess was the model reaction which allowed to obtain butyl cinnamate **1** and butyl β-phenylcinnamate **2** (Scheme 2). It was shown, for the first time, that reaction proceeds effectively in tetrabutylammonium bromide even without any base added, producing **1** as the main product, exclusively as *trans* form. Introduction of base to the catalytic system allows to obtain selectively product **1** or **2**, or both products in different ratios (Scheme 2).

1.1. Base-free Heck reaction in molten tetrabutylammonium bromide—effect of catalyst concentration

It was unexpectedly found that rather simple palladium compounds as PdCl$_2$(PhCN)$_2$, Pd(OAc)$_2$ or PdCl$_2$, catalyze Heck reaction in molten tetrabutylammonium bromide as reaction medium, even at the absence of bases.

In the reaction catalyzed by PdCl$_2$(PhCN)$_2$ (0.75 mol%) after 4 h product **1** was obtained with the yield of 66% (*trans* izomer). When similar concentrations of PdCl$_2$ and Pd(OAc)$_2$ have been used the yields of **1** were equal to 68% and 58%, respectively. The increase of PdCl$_2$(PhCN)$_2$ catalyst concentration up to 1.25 mol% caused significant decrease of the yield of product **1**, to 29%. The same effect of palladium concentration was also observed in a case of reactions catalyzed by PdCl$_2$ and Pd(OAc)$_2$ at increased concentration (Fig. 1).

In order to better understanding the observed effect of catalysts concentration on the yield of butyl cinnamate **1**, the reactions catalyzed by PdCl$_2$(PhCN)$_2$, PdCl$_2$ and Pd(OAc)$_2$ at different concentrations from 0.05 to 1.25 mol% have been studied.
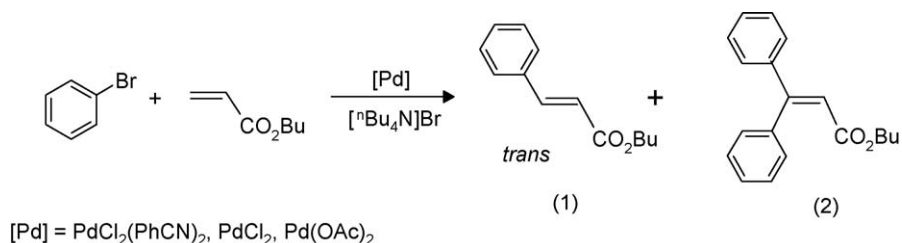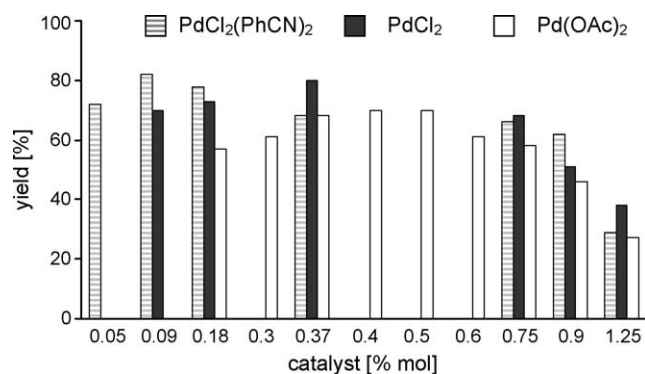
All reactions were carried out in molten tetrabutylammonium bromide in the absence of base. The results presented in Fig. 1 show characteristic non-linear dependence of the reaction yield on palladium concentration, similar for all three catalyst precursors used (Fig. 1). Interestingly, the optimum concentrations of three catalysts precursors that are associated with the highest yield of product, are different but the character of changes is similar. For reaction catalyzed by PdCl$_2$ the yield of 70% was achieved for catalyst concentration from 0.09 to 0.4 mol%. Similar range of concentrations, 0.05–0.4 mol%, was optimal also for PdCl$_2$(PhCN)$_2$ precursor whereas for Pd(OAc)$_2$ the maximum reaction yield was found for palladium concentration *ca.* 0.4–0.5 mol%. For all catalyst precursors applied decrease of the Heck reaction yield was observed for concentrations over 0.9 mol%. Similar behavior was observed earlier in Heck reaction catalyzed by Pd(OAc)$_2$ as well as by palladacycle and it was interpreted as the effect of palladium nanoparticles formation and their aggregation to "palladium black" at higher concentrations [13,14,21]. Therefore, increase of palladium catalyst concentration was accompanied with decrease of the reaction yield. However, formation of less reactive Pd(II) complexes, of dimeric or polymeric structure could also be considered as another explanation of the observed concentration effect. This explanation looks more likely than that considering aggregation of nanoparticles which should be diminished by the presence of [^{n}Bu$_4$N]Br, usually preventing aggregation of nanoparticles. Using XRD and/or TEM methods we have never observed aggregation of nanoparticles when initial concentration of palladium catalyst precursor increased [41].

The values of the reaction yields presented in Fig. 1 are not the maximum ones and when reaction time was elongated total conversion of acrylate was achieved and product **2** appeared. In

Scheme 2.

reaction catalyzed with $PdCl_2(PhCN)_2$ (0.09 mol%) in 0.5–6 h the yield of product **1** gradually increased. After 8 h conversion of acrylate attained 100% and *ca.* 10% of product **2** was obtained. Similar studies have been conducted with $Pd(OAc)_2$ (0.75 mol%) and in all cases only product **1** was obtained at the conversion of acrylate lower than in reactions catalyzed with $PdCl_2(PhCN)_2$ (Fig. 2).

Results presented in Fig. 2 additionally verify conclusions drew out from the experimental data presented in Fig. 1 and point out on higher activity of $PdCl_2(PhCN)_2$ catalyst precursor compared with $Pd(OAc)_2$, that is frequently used in Heck reaction. The lower activity of $Pd(OAc)_2$ is surprising since it undergoes self-reduction at elevated temperature to produce nanosize Pd(0) colloid [18], ready for catalytic function. The difference between both precursors requires additional studies.

1.2. Effect of Bu3N on Heck reaction rate

Bu_3N can be formed as product of $[^nBu_4N]Br$ decomposition at elevated temperature, therefore, we wanted to learn if tributylamine being potential reducing agent for Pd(II) can affect on the reaction course. Reaction of Pd(II) with amines may lead to formation of Pd(0) species as it was shown in our earlier studies of $PdCl_2(P(OPh)_3)_2$ reduction with Et_3N in which Pd(0) complexes of formula $Pd(Et_3N)_x(P(OPh)_3)_{4-x}$ were formed [37,38].

The effect of Bu_3N on conversion of butyl acrylate in Heck reaction catalyzed by $PdCl_2(PhCN)_2$ was studied in molten $[^nBu_4N]Br$ (140 °C) or in DMF. The reaction in molten $[^nBu_4N]Br$ without Bu_3N was considered as reference. At such reaction conditions product **1** was obtained with the yield of 44% after 2 h (Table 1, entry 1), and after 4 and 6 h the yields increased to 61% (entry 2) and 82% (entry 3), respectively. Addition of Bu_3N caused the increase of reaction rate that was demonstrated by the increase of butyl acrylate conversion and appearance of product **2**. Even small amounts of Bu_3N (6.28×10^{-4} mol) resulted in increase of *ca.* 20% the yield of product **1** after 2 h although the final yield (after 6 h) was the same as in the reaction performed without Bu_3N and equal to 82% (entries 4–6).

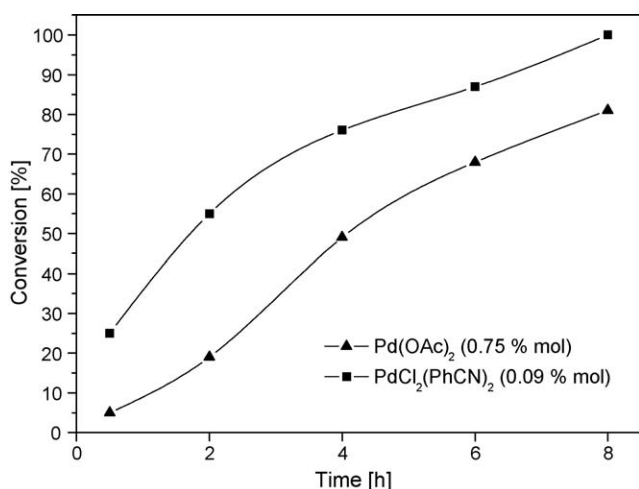

Fig. 2. Effect of palladium catalysts concentration on the conversion of butyl acrylate in Heck reaction.

Table 1

Effect of Bu_3N addition on the yield of Heck coupling of bromobenzene with butyl acrylate in molten $[^nBu_4N]Br$

Entry	[Bu$_3$N] ($\times 10^{-3}$ mol)	Time (h)	Yield of products (mol%)	
			1	**2**
1	–	2	44	–
2	–	4	61	–
3	–	6	82	–
4	0.628	2	67	–
5	0.628	4	70	–
6	0.628	6	82	–
7	1.25	2	78	–
8	1.25	4	91	–
9	1.25	6	87	13
10	2.3	2	58	42
11	2.3	4	54	46
12	2.3	6	57	43
13	4.36	2	58	42
14	4.36	4	54	46
15	4.36	6	46	54
16[a]	2.3	4	28	–
17[a]	2.3	6	36	–

$PdCl_2(PhCN)_2$ (1.41×10^{-5} mol); PhBr (4.36×10^{-3} mol); butyl acrylate (1.89×10^{-3} mol); $[^nBu_4N]Br$ (2.3×10^{-3} mol); mesitylene as internal standard; 140 °C.

[a] Reaction in DMF.

At higher amount of Bu_3N (1.25×10^{-3} mol) after 6 h, 100% conversion of butyl acrylate has been achieved with *ca.* 13% of product **2** (entry 9). Further increase of Bu_3N concentration up to 2.3×10^{-3} mol allowed to attain 100% conversion of butyl acrylate after 2 h with the yield of products **1** and **2** equal to 58% and 42%, respectively. Further twice increase of Bu_3N concentration had no influence on the reaction yield and products **1** and **2** ratio. The reaction carried out in DMF (instead of $[^nBu_4N]Br$) was much less effective and at concentration of Bu_3N 2.3×10^{-3} mol after 4 h 28% of **1** (entry 16) was obtained and in the reaction prolonged to 6 h the yield was only 36% (entry 17).

Results presented in Table 1 show that Bu_3N has positive influence on the Heck reaction yield catalyzed by $PdCl_2(PhCN)_2$, however at relatively high concentration. This observation allows to conclude that the effect of eventually formed Bu_3N as the product of thermal decomposition of $[^nBu_4N]Br \rightarrow Bu_3N + BuBr$ can be neglected. However, one cannot exclude the role of Bu_3N in reduction of Pd(II) to Pd(0) as it was earlier proved for Et_3N [37,38].

1.3. Effect of bases on the selectivity of Heck reaction catalyzed by PdCl2 and PdCl2(PhCN)2

From the results collected in Table 2 it may be concluded that different bases (also other than amines) added to the catalytic system accelerate the formation of both products **1** and **2** when compare with reaction carried out in molten $[^nBu_4N]Br$ only.

Within 4 h of reaction catalyzed by $PdCl_2$ in molten $[^nBu_4N]Br$ without base, only product **1** was obtained with

Table 2
Effect of bases on the yield of products **1** and **2** in Heck reaction of butyl acrylate with bromobenzene

Entry	Catalyst	Base	Time (h)	Yield of products (mol%)	
				1	**2**
1	PdCl$_2$	–	4	68	–
2		NaHCO$_3$	2	5	95
3		NaHCO$_3$	4	1	99
4		Na(OAc)	4	40	60
5		NaHCO$_2$	2	93	–
6		NaHCO$_2$	4	98	–
7	PdCl$_2$(PhCN)$_2$	–	4	66	–
8		–	6	92	–
9		NaHCO$_3$	2	4	96
10		NaHCO$_3$	4	–	100
11		Et$_3$N	4	8	92
12		NaOAc	4	17	83
13		NaHCO$_2$	4	56	44
14		NaHCO$_2$	6	29	71
15		Cs$_2$CO$_3$	4	92	8
16		Cs$_2$CO$_3$	6	13	87
17		Na$_2$C$_2$O$_4$	4	75	–
18		Na$_3$PO$_4$	4	22	–

Catalyst (1.41×10^{-5} mol); [^{n}Bu$_4$N]Br (2.3×10^{-3} mol); PhBr (4.36×10^{-3} mol); base (4.36×10^{-3} mol); butyl acrylate (1.89×10^{-3} mol); mesitylene as internal standard; 140 °C.

the yield 68% (Table 2, entry 1). Addition of bases caused an increase of butyl acrylate conversion to *ca.* 100%, with the ratio of **1/2** fluctuating, depending on the kind of base used. In reaction with NaHCO$_2$ only product **1** was formed (Table 2, entries 5 and 6). At the presence of NaOAc the comparable amounts of **1** and **2** were obtained (Table 2, entry 4). In the most efficient system, with NaHCO$_3$, already after 2 h *ca.* 95% of **2** was formed (Table 2, entry 2).

In analogous conditions the Heck reaction with PdCl$_2$(PhCN)$_2$ as catalyst precursor have been studied. The reaction carried out in molten [^{n}Bu$_4$N]Br in the absence of base produced only **1** with the yield similar to that with PdCl$_2$ precursor (66%, Table 2, entry 7). Increase of butyl acrylate conversion up to 100% with domination of product **2** was obtained after 4 h of the reaction with addition of NaHCO$_3$ (Table 2, entry 10), Et$_3$N (Table 2, entry 11), or NaOAc (Table 2, entry 12). In reactions with addition of NaHCO$_2$ or Bu$_3$N the mixtures containing comparable amounts of products **1** and **2** were obtained (Table 2, entry 13, Table 1, entry 14).

Comparison of reactions catalyzed with PdCl$_2$ and PdCl$_2$(PhCN)$_2$ in the presence of NaHCO$_2$ allowed to observe differences in catalytic activity of both systems under studies. In reaction catalyzed by PdCl$_2$(PhCN)$_2$ the mixture of products **1** and **2** was obtained whereas under the same conditions PdCl$_2$ precursor generates only product **1**. Contrastingly, in the presence of NaHCO$_3$ both precursors were acting in a similar way and only **2** was obtained as the main product just after 2 h.

Product **1** was dominating in reaction catalyzed by PdCl$_2$(PhCN)$_2$ in the presence of Cs$_2$CO$_3$ (92%, Table 2, entry 15), but after elongation of reaction time to 6 h product **1** was converted to **2** (87%, Table 2, entry 16). Also in reaction with addition of Na$_2$C$_2$O$_4$ formation of **1** was preferred, although
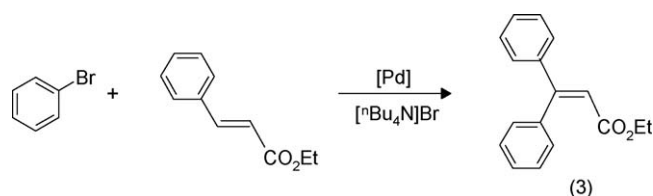
Scheme 3.

lower butyl acrylate conversion suggested slower reaction rate (75%, entry 17). Na$_3$PO$_4$ demonstrated inhibiting effect and only 22% of **1** was formed (Table 2, entry 18), less than in base-free system.

1.4. Synthesis of ethyl β-phenylcinnamate

The results presented above led to the conclusion that Heck reaction carried out in molten [^{n}Bu$_4$N]Br with simple Pd(II) catalyst precursors can be used for preparation of β-phenylcinnamates. It is an attractive synthesis method of the important products directly from acrylate and bromobenzene. Alternatively, appropriate cinnamates and aryl halides could be used as substrates. To verify the applicability of the studied catalytic systems in such process the reaction of ethyl cinnamate with bromobenzene has been selected (Scheme 3).

The product **3** was obtained according to Scheme 3 with a good yield (66%) with PdCl$_2$(PhCN)$_2$ as catalyst precursor in molten [^{n}Bu$_4$N]Br, in the absence of base. At comparable reaction conditions with PdCl$_2$ as catalyst precursor only 17% of product **3** was obtained (Table 3). The efficiency of both catalysts increased significantly after addition of bases. The 100% yield was obtained after addition of Et$_3$N to both catalyst precursors whereas addition of NaHCO$_3$ allowed to obtain 100% yield of product only in the system with PdCl$_2$(PhCN)$_2$ as catalyst precursor (Table 3). Other bases were slightly less effective however allowed to obtain reasonable yields of ethyl β-phenylcinnamate from 75% (for NaHCO$_2$) to 97% (for Bu$_3$N) (Table 3).

1.5. Effect of [^{n}Bu$_4$N]Br on the Heck reaction yield

Reaction of butyl acrylate with bromobenzene catalyzed by PdCl$_2$(PhCN)$_2$ in DMF in the presence of NaHCO$_3$ proceeds with rather low conversion (22%) and leads to the formation

Table 3
Yield of ethyl β-phenylcinnamate (mol%) obtained in Heck reaction (Scheme 3) catalyzed by PdCl$_2$(PhCN)$_2$ and PdCl$_2$ in the presence of bases in molten [^{n}Bu$_4$N]Br

Base	PdCl$_2$(PhCN)$_2$	PdCl$_2$
–	66	17
NaHCO$_3$	100	84
NaHCO$_2$	75	97
NaOAc	95	80
Et$_3$N	100	100
Bu$_3$N	97	87

PdCl$_2$(PhCN)$_2$ (1.41×10^{-5} mol); PhBr (2.0×10^{-3} mol); ethyl cinnamate (1.89×10^{-3} mol); base (4.36×10^{-3} mol); mesitylene as internal standard, 4 h, 140 °C.

Table 4
Effect of [$^nBu_4N$]Br amount on the composition of Heck reaction products **1** and **2** (Scheme 2)

Entry	[[$^nBu_4N$]Br] ($\times 10^{-4}$ mol)	Yield of products (mol%)	
		1	**2**
1	–	22	–
2	2.32	60	–
3	2.79	90	10
4	5.58	2	98
5	11.2	–	100
6[a]	23.0	1	99

PdCl$_2$(PhCN)$_2$ (1.41 × 10^{-5} mol); PhBr (4.36 × 10^{-3} mol); butyl acrylate (1.89 × 10^{-3} mol); NaHCO$_3$ (4.36 × 10^{-3} mol); mesitylene as internal standard; DMF, 4 h, 140 °C.

[a] Reaction carried out in [$^nBu_4N$]Br, without DMF.

Table 5
Recycling of Pd-catalyst (PdCl$_2$(PhCN)$_2$ as precursor) in molten [$^nBu_4N$]Br

Entry	Run	Conversion of acrylate (%)	Yield of products (mol%)	
			1	**2**
1	0	100	–	100
2	1	100	18	82
3	2	95	76	19
4	3	88	59	29
5	4	80	70	10
6	5	51	44	6
7	6	33	33	–

PdCl$_2$(PhCN)$_2$ (1.41 × 10^{-5} mol); PhBr (4.36 × 10^{-3} mol); butyl acrylate (1.89 × 10^{-3} mol); NaHCO$_3$ (4.36 × 10^{-3} mol); mesitylene as internal standard; [$^nBu_4N$]Br (2.3 × 10^{-3} mol), 4 h, 140 °C.

of only product **1** (Table 4, entry 1). Replacement of DMF with [$^nBu_4N$]Br under the same reaction conditions allowed to obtain 99% of product **2** at 100% conversion of butyl acrylate (Table 4, entry 6). In the following experiments the effect of [$^nBu_4N$]Br concentration on butyl acrylate conversion in the system containing PdCl$_2$(PhCN)$_2$ and NaHCO$_3$ has been studied in DMF during 4 h. The conversion of butyl acrylate, as well as the rate of formation of product **2**, increased significantly with increase of [$^nBu_4N$]Br concentration compared with reaction proceeding in DMF as the only reaction medium.

Addition of small amounts of [$^nBu_4N$]Br (2.32 × 10^{-4} mol) caused an increase of acrylate conversion up to 60%. Conversion of 100% and the yield 90% of product **1** were attained when 2.79 × 10^{-4} mol of [$^nBu_4N$]Br was added to the catalytic system. Further addition of tetrabutylammonium salt caused formation of product **2** in higher yield. Addition 5.58 × 10^{-4} mol or more of [$^nBu_4N$]Br allowed to obtain from 98% to 100% of product **2** which was practically the only reaction product (Table 4, entries 2–5). The most favorable concentration ratio of [$^nBu_4N$]Br versus palladium found as *ca.* 40 seems to be sufficient for stabilization of palladium nanoparticles formed "in situ" in reaction medium.

1.6. Catalyst recycling

One of the great advantages of the use of molten salts as reaction medium is possibility of catalyst recycling. The manifold use of catalyst requires however its separation from the reaction products via careful extraction with diethyl ether. Catalyst recycling was studied for the system composed with PdCl$_2$(PhCN)$_2$ as catalyst precursor and NaHCO$_3$ as the base. In four consecutive runs (Table 5, entries 2–5) conversion of acrylate dropped from 100% to 80%. In the next experiments (entries 6 and 7) both conversion of butyl acrylate as well as the yield of product **2** decreased significantly (Table 5). These observations may suggest decrease of activity of catalyst. Similar tendency was observed in our earlier studies of recycling of two quite different catalytic systems: Pd(0) colloid supported on PVP polymer and Pd/Al$_2$O$_3$ heterogeneous catalyst [39]. All the above mentioned Pd-catalysts used in similar reaction conditions in which Pd(II) (in a case of PdCl$_2$(PhCN)$_2$) or Pd(0) (in a case of Pd(0) colloid

or Pd/Al$_2$O$_3$) were acting in the presence of [$^nBu_4N$]Br, base (NaHCO$_3$) and PhBr and butyl acrylate, CH$_2$=CHC(O)OBu, as reaction substrates. In our opinion the reason of the observed decrease of catalytic activity is associated with accumulation of NaBr, the side reaction product, which is not extracted with diethyl ether from reaction mixture during recycling procedure.

2. Comments and conclusions

The results presented above proved that Heck reaction can be effectively realized with application of rather simple catalytic system containing phosphine-free palladium precursor and molten [$^nBu_4N$]Br as reaction medium, even without base addition.

From characteristic non-linear dependence of reaction yield on catalyst concentration one may conclude that Pd(0) nanoparticles act as reactive form of catalyst. Nanoparticles are formed as reduction products of Pd(II) in PdCl$_2$(PhCN)$_2$ or in [$^nBu_4N$]$_2$[PdCl$_x$Br$_{4-x}$]. The second Pd(II) complex was obtained in reaction of Pd(0) with PhBr and [$^nBu_4N$]Br during catalytic process. It is not well understood how Pd(II) is reduced but it was proved that one of the potential reducing agents could be Bu$_3$N, formed in situ by decomposition of [$^nBu_4N$]Br during Heck reaction at 140 °C. In reaction carried out in the presence of bases their contribution in reduction of Pd(II) is also possible. Our recent studies have shown that palladium in PdCl$_2$(PhCN)$_2$ was reduced only by NaHCO$_2$ whereas NaOAc and NaHCO$_3$ require contribution of [$^nBu_4N$]Br [39]. Our earlier studies of reaction of Pd(0) colloid with aryl halides (PhX) have shown, with application of TEM and XPS methods, that size of nanoparticles significantly decreased after their reaction with PhX due to the formation of Ph–Pd–X species [15]. These products of oxidative addition of PhX to Pd(0) (in colloid) may react with [$^nBu_4N$]Br forming soluble Pd(II) complexes of [$^nBu_4N$]$_2$[PdX$_3$Ph] type, as it was proved by XPS studies [15]. These complexes, similarly like starting PdCl$_2$(PhCN)$_2$ precursor can be reduced again to Pd(0) monomolecular complex of PdL$_4$ type if suitable L ligands are present in the system or to Pd(0) colloid usually of much smaller size than initial particles. According to the above presented description tetrabutylammonium salt is playing important role both in the formation of intermediate complexes of [$^nBu_4N$]$_2$[PdX$_3$Ph] type as well as

in stabilization of Pd(0) nanoparticles preventing their aggregation and deactivation. Therefore, in real catalytic process both forms of palladium, Pd(0) colloid and Pd(II) complexes are taking part.

3. Experimental

The Heck reactions of bromobenzene with butyl acrylate were carried out in a $50 \, cm^3$ Schlenk tube with magnetic stirring. Reagents: catalyst ($PdCl_2(PhCN)_2$, $Pd(OAc)_2$ or $PdCl_2$, 1.41×10^{-5} mol), PhBr $0.24 \, cm^3$ (2.3×10^{-3} mol) or $0.46 \, cm^3$ (4.36×10^{-3} mol), butyl acrylate $CH_2{=}CHC(O)OBu$ $0.27 \, cm^3$ (1.9×10^{-3} mol), [$^nBu_4N$]Br 0.75 g (2.3×10^{-3} mol), base $NaHCO_3$, Et_3N, Bu_3N, NaOAc, Cs_2CO_3, $Na_2C_2O_4$, Na_3PO_4 (4.36×10^{-3} mol) were introduced to the Schlenk tube under the N_2 atmosphere. The reaction was carried out at $140 \, °C$ for 4 h. Afterwards, organic products were separated by extraction with diethyl ether (three times with $10 \, cm^3$) and GC–MS analyzed (Hewlett Packard 8452A) with mesitylene as internal standard. On the basis of ^1H and ^{13}C NMR spectra (Bruker 300 MHz) product **1** was identified as *trans* butyl cinnamate and product **2** as butyl β-phenylcinnamate [39,40].

The Heck reaction of bromobenzene (2.0×10^{-3} mol) with ethyl cinnamate (1.89×10^{-3} mol) was performed in a similar way. The yield of β-phenylcinnamate was determined by GC analysis.

Acknowledgements

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