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The effect of Al_2O_3 and ionic liquids in palladium catalyzed arylation of cyclohexene. Interaction of Hg(0) with immobilized palladium.

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Graphical abstract:

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Highlights:

- Pd/Al₂O₃, modified with ionic liquid, efficiently catalyzes formation of 4phenylcyclohexene.
- The addition of Al₂O₃ to the homogeneous catalytic system remarkably increased the yield of product.
- Hg(0) added to the Heck reaction mixture forms Pd-Hg amalgam immobilized on Al₂O₃.
- Ionic liquids changed the surface properties of Pd/Al₂O₃.

Abstract

Three-component systems containing Pd(OAc)₂, Al₂O₃, and an IL (IL = ionic liquid) were applied in the Heck arylation of cyclohexene. The highest productivity and selectivity to 4phenylcyclohexene was noted in reaction catalyzed by Pd/Al₂O₃ in the presence of a small amount of an IL, dimethyldidodecylammonium lactate (C). The addition of Al₂O₃ alone to the reaction catalyzed by soluble precursors, PdCl₂(PhCN)₂ or Pd(OAc)₂ and IL, remarkably increased conversion to 4-phenylcyclohexene. Hg(0) inhibited the reaction catalyzed by Pd/Al₂O₃ by formation of Pd-Hg amalgam immobilized on Al₂O₃. SEM/EDX studies of Pd/Al₂O₃ performed after treatment with Hg(0) showed that the IL modified the surface properties of Pd/Al₂O₃.

Key words: palladium; Heck coupling; cyclohexene; ionic liquids; Hg(0); TEM; SEM.

1. Introduction

The Heck reaction belongs to the most important and intensively studied processes leading to the formation of C–C bonds [1–8]. This is because the Heck procedure enables the efficient synthesis of arylated olefins, important materials in the chemical and pharmaceutical industries [7]. According to this procedure, aryl halides are coupled with linear [4, 9-11] and cyclic olefins [12-17], allyl alcohols [18, 19], unsaturated esters and acids. A particular interest in the arylation of cyclic olefins is related to the possible formation of a stereogenic center in the reaction product [20-22]. The most extensively studied cyclic olefins are cyclopentene [15, 23, 24], 2,3-dihydrofuran [12-14, 20], and cyclohexene [25-35]. However only for 2,3-dihydrofuran and dihydropyran has successful enantioselective Heck coupling been reported [20]. For example, the employment of a chiral IL makes it possible to obtain the product of 2,3-dihydrofuran arylation with ee > 99 [13].

Very good results have been obtained in the Heck coupling of cyclic olefins catalyzed by heterogeneous palladium catalysts supported on TiO_2 [36], mixed oxides [34-38], and zeolites [41]. In our previous studies, palladium supported on Al_2O_3 appeared more efficient in the arylation of cyclohexene than homogeneous catalysts [25].

In this work, we concentrated our efforts on the studies of three-component catalytic systems, containing a palladium precursor, Al_2O_3 , and IL (IL = ionic liquid), in the Heck coupling of cyclohexene. Our concept was to apply Al_2O_3 as a support for a heterogeneous palladium catalyst and also as an additive to the homogeneous system to form a heterogenized palladium catalyst *in situ*. By introducing selected IL, we expected to improve the stability and selectivity of palladium catalysts, following a synergistic effect of the support and ILs observed recently in the Suzuki–Miyaura reaction [42].

2. Results and discussion

The Heck arylation of cyclohexene with iodobenzene is schematically shown in Figure 1. In this reaction, two groups of products can be expected, namely mono- and diarylated ones [23, 25]. In these studies, the temperature of 100 °C was used in order to increase the selectivity to monoarylated products, aryl-cyclohexenes. Actually, at 140 °C, up to 22% of diarylated products were formed [25], while preliminary studies showed that their formation was totally retarded at 100 °C.

2.1. A heterogeneous system, $Pd/Al_2O_3 + IL$

The catalyst Pd/Al₂O₃, prepared by the immobilization of Pd(OAc)₂ on Al₂O₃, was tested in the arylation of cyclohexene at 100 °C. Under these conditions, 4-phenylcyclohexene (III) was formed as the main product together with small amounts of 1-phenylcyclohexene (I) and biphenyl. Interestingly, product II, which was identified at 140 °C, was not found here (Fig. 2).

In the reference reaction performed without an IL, the total conversion of iodobenzene was 62%, and selectivity to III was 90% (Table 1).

Formation of 4-phenylcyclohexene (III) as the main product corresponds well with the fact that III represents the thermodynamically most stable isomer [15]. In contrast, 3-phenylcyclohexene (II) was probably fast underwent isomerization to I or to III. Our studies indicated on the influence of KOH in this process [25]. The role of the added base on the selectivity of cyclohexene arylation was also mentioned in the literature [16]. Alternatively, a H-Pd complex might be considered as a palladium form responsible for the double-bond migration [33, 34]. However in our system a strong base, KOH, could quickly remove H-Pd.

It was expected that further improvement could be achieved by the introduction of chiral IL. In particular, its presence could facilitate not only the higher conversion but also the enantioselective formation of 4-phenylcyclohexenes. On the basis of our earlier experience, indicating the positive effect of chiral anions on the asymmetric Heck arylation of 2,3-dihydrofuran, we selected three ILs bearing chiral anions for further studies [12, 13]. The ILs A and B contained a morpholinium cation and a chiral anion, 2-phenyl-2-hydroxyacetate of R and S configuration, whereas a lactate anion was present in the IL C (Fig. 3).

Unfortunately, the addition of ILs did not result in an increase in enantioselectivity, and in all cases only a racemic mixture of 4-phenylcyclohexenes (III) was found. It can be assumed that chiral anions did not coordinate to a palladium active species and consequently they had no influence on the reaction selectivity. A complementary explanation of the lack of asymmetric induction could be the higher conformational freedom of the six-membered olefin than the five-membered one [43]. Nevertheless, the addition of ILs caused a remarkable improvement in PhI conversion, to 91%. The selectivity to III remained high, 82–87% (Table 1).

2.2. A homogeneous system with Al₂O₃ additive.

The promising results obtained with a heterogenized palladium catalyst encouraged us to check whether similar efficiency could also be achieved using Pd/Al_2O_3 formed *in situ*. To the best of our knowledge, the procedure involving the addition of Al_2O_3 alone to the homogeneous system in order to trap palladium has not been described in the literature. On the other hand, an enhancement of the Heck reaction was observed when SiO₂ was added to a reaction catalyzed by Pd(acac)₂ [44]. The transfer of Pd between the solvent and the support under Heck reaction conditions has also been reported [45].

It was expected that Al_2O_3 added to the reaction would trap soluble palladium species from the solution slowing down their uncontrolled reduction and agglomeration to larger Pd NPs. As a result, the productivity of the system should increase because smaller Pd clusters are more active than larger ones [46, 47].

In order to estimate an effect of the addition of Al₂O₃ to the homogeneous system, first, two palladium precursors, Pd(OAc)₂ and PdCl₂(PhCN)₂, were tested without and with ILs, using KOH as a base (Table 2). An average conversion of ca. 60% was achieved with III as the main product formed with ca. 90% selectivity. An effect of the addition of ILs was less spectacular than in reactions catalyzed by Pd/Al₂O₃, although some conversion increase was observed after the addition of the ILs A and B. Interestingly, the IL B was more efficient and produced 64% of III in reaction with PdCl₂(PhCN)₂, whereas 44% was formed in the presence of A. The different activities of the two enantiomers of the chiral ligand were rather surprising; however, some examples have scarcely been reported in the literature [40].

The results collected in Table 2 show that the addition of Al_2O_3 to the reaction catalyzed by $Pd(OAc)_2$ caused a remarkable increase in the conversion of PhI to 70–82% and the simultaneous increase in the yield of III. In reactions performed without ILs, after the addition of Al_2O_3 , the conversion of PhI increased from 45% to 72% and conversion to III also increased from 43 to 58%. These results are even better than those obtained with Pd/Al₂O₃ (Table 1). When reactions with ILs are considered, the best result, 72% of III, was obtained in the system containing the IL C and the additive Al_2O_3 (Table 2). Moreover, in reactions performed in the presence of ILs, a decrease in the yield of a side product, biphenyl, from 10 to 5–6%, was noted. It is also worth noting that selectivity to III was very good (86–88%) in all experiments (Table 2).

Conversions obtained with the application of immobilized Pd/Al_2O_3 modified with ILs were higher than in the system formed *in situ* by introduction of an IL and Al_2O_3 to $Pd(OAc)_2$. Nevertheless, it should be pointed out that the simple *in situ* procedure offers a real improvement of the homogeneous catalytic system.

It can be proposed that metallic core of Pd NPs supported on Al₂O₃ is surrounded by a protective shell composed of cations and anions of IL what positively influenced on the reaction yield.

2.3. TEM and SEM analyses of catalysts 1C and 2C

In order to learn more about the nature of the studied three-component catalytic systems, SEM and TEM measurements were undertaken.

The TEM pictures of the catalyst 2C, obtained by catching palladium directly from the Heck reaction mixture in which $Pd(OAc)_2 + C$ acted as a catalyst, are shown in Figure 4. Palladium was present in the form of relatively big NPs, 10–49 nm in diameter, partially agglomerated and distributed not uniformly on the surface. The size distribution of Pd(0) NPs is presented in Figure 5. Most probably, these nanoparticles were formed from the $Pd(OAc)_2$ precursor during the catalytic reaction in solution and next attracted by the support.

The TEM picture obtained for the catalyst 1C isolated after the Heck reaction differs remarkably from that for 2C (Fig. 6). The surface of the catalyst 1C was black, Pd(0) NPs were smaller and showed symmetrical size distribution with maximum ca. 20 nm (Fig. 7). Thus, as expected, the application of immobilized palladium as the catalyst (1C) made it possible to better control the size of the NPs and keep them smaller.

SEM measurements with an EDX analysis made it possible to detect the distribution of palladium on the surface of Al_2O_3 in 1C more precisely (Fig. 8). Palladium is not uniformly distributed on the support, and the highest concentration of Pd, 19 weight %, was found in point 6 (Fig. 8). The lowest amount of Pd, 1.7 weight %, as determined in point 2.

The analysis of the cross-section of a piece of the catalyst 1C showed that the Pd content inside was remarkably lower than that on the surface and varied from 0 to 1.7% (Fig. 9). In general, as expected, more Pd gathered near the surface.

2.4. Treatment of the Pd catalysts with Hg(0).

The presence of Pd NPs, experimentally evidenced in the studied systems, not unambiguously indicated their dominating role in the catalytic cycle [46-48]. For example, NPs can act as a source of soluble palladium forms which catalyze the reaction according to the homogeneous pathway [46-48]. In fact, it is generally admitted that, in C–C cross-coupling reactions, Pd(0) NPs act mainly as a source of soluble palladium species [49]. One of the most useful tests used to get a closer insight into the type of catalytically active forms is the reaction with Hg(0) [50-52]. The procedure involves adding an Hg(0) excess to the reaction mixture and observing possible changes in the reaction yield. The application of the Hg(0) test was first recommended to distinguish between the homogeneous and the heterogeneous reaction mechanisms, in principle in the hydrogenation process [50, 51]. Nowadays, it is assumed that the inhibiting effect of Hg(0) is caused by the formation of an amalgam with Pd NPs and underligated Pd(0) species [48, 52]. Consequently, both these forms of palladium are eliminated from the catalytic cycle.

The Hg(0) test was performed for two systems containing Pd/Al₂O₃, namely for the catalysts 1 and 1C. In both cases, a strong inhibition of the reaction was observed and conversion decreased to 17-18% (Table 3). Selectivity to III also decreased to 65-67%.

According to the literature, an inhibiting effect of Hg(0) indicated that the soluble forms of palladium leached from the support taks part of catalytic cycle [52]. Similarly, a homogeneous reaction pathway was proposed for the Heck coupling of cyclohexene [15, 25]. This is in agreement with the fact that no products were formed in reactions performed with the catalysts 1 and 1C separated from the reaction mixture after the Heck reaction.

2.5. SEM/EDX studies of Pd/Al₂O₃ catalysts separated after Hg(0) treatment.

It was also interesting to check whether there was any interaction between Hg(0) and Pd supported on Al_2O_3 . As far as we know, such an aspect of the Hg(0) test has not discussed in the literature. Thus, the catalysts 1 and 1C were separated from the solution after the catalytic reaction performed in the presence of Hg(0) and analyzed by the SEM/EDX method.

The analysis of the surface of the catalyst 1C unexpectedly showed the presence of Pd and Hg in the same places, indicating the covering of Pd by Hg (Fig. 10). In most cases, the amount of

Pd on the surface exceeded the amount of Hg, and this tendency was even more pronounced inside the catalyst piece. The Pd/Hg ratios calculated from the weight % estimated by EDX varied from 0.77 to 1.77 (Fig. 10).

Interestingly, the Pd/Hg ratios in the catalyst 1 (without an IL) were lower than in the catalyst 1C because the relative amount of Hg was always higher than that of Pd (Fig. 11). All the estimated Pd/Hg ratios were below 0.9. The difference between 1 and 1C consists only in the presence of the IL C, and, therefore, it can be assumed that the IL C modified the properties of the catalyst (1C) preventing Hg bonding. Such a modifying effect of the IL correlates well with the enhancement of the catalytic activity observed in the presence of an IL (Table 1).

The influence of an IL (C) on the physical properties of Pd/Al₂O₃ was also confirmed by the analyses of the cross-section of the catalysts 1 and 1C. The Table 4 presents the Pd/Hg ratios determined at ten different points of the cross-sections of 1 and 1C. The Pd/Hg ratios for the catalyst 1C are in the range 2.2–6.4, indicating that the amount of Pd is always higher than of Hg. It means that the IL C prevents the bonding of Hg on the surface of Pd. A different situation exists in the catalyst 1, which contains more Hg. Consequently, Pd/Hg ratios were lower and ranged from 0.4 to 1.7.

In the next step of the studies, the stability of the Pd/Hg composites (most probably Pd-Hg amalgam) present on the surface of the catalysts was monitored. Samples of the catalysts 1 and 1C, separated after the Heck reaction performed with an Hg(0) additive, were heated at a given temperature under vacuum and analyzed by SEM/EDX. Of course, it could be expected that, during heating, Hg(0) would be removed; however, in this experiment, we wanted to estimate whether the presence of an IL had any influence on this process.

Heating the catalyst 1C to 80 °C only slightly changed the distribution of Pd and Hg on the surface (Fig. 12). In points 1, 2, and 6, the amounts of Pd exceeded those of Hg, whereas in points 3, 4, and 5, the Hg content was higher. An increase of the Hg content in some points could be explained by its migration on the surface at a higher temperature.

In the catalyst 1, the amount of Hg was smaller than that of Pd in points 1, 2, or 3, suggesting the partial removal of Hg from the surface. In all the remaining places, the amount of Pd was

higher than the amount of Hg, and the Pd/Hg ratios were similar to the not-heated sample (Fig. 13).

The results obtained for the catalyst 1C heated to 150 °C showed an increase in the Pd/Hg ratios, which even exceeded 4 at two points (Fig. 14).

Conversely, in the catalyst 1, the amount of Hg remained high and the Pg/Hg ratios were in most cases below 1 (Fig. 15). Thus, again, the difference between the catalysts 1 and 1C should be underlined. At 150 °C, Hg was removed faster from 1C (containing IL) than from 1.

Heating to 200 °C facilitated the removal of Hg from both catalysts and, consequently, the Pd/Hg ratios became similar for 1C and 1. Nevertheless, the Hg content in 1C (Fig. 16) was lower than in 1 (Fig. 17). This is illustrated by the higher ratios of Pd/Hg for 1C than for 1.

The performed studies showed that Hg was bonded rather strongly to the immobilized palladium and could be removed at a temperature higher than 150 °C. Interestingly, this process proceeded more easily for the catalyst 1C, containing an IL, than for 1. Thus, the presence of IL facilitated a weaker bonding of Hg.

As far as we know, the interaction of Pd with Hg on the surface of catalyst has not been discussed before in the context of poisoning test. On the other hand Pd/Al_2O_3 was shown as an efficient sorbent for elemental mercury capture [53, 54]. We demonstrated that Hg(0) present in the catalytic reaction mixture covers Pd and blocks the contact of the catalyst with the substrates. In consequence, the catalytic activity of the heterogeneous catalyst can decrease remarkably in the presence of Hg(0). Most probably, Pd-Hg amalgam (alloy) was formed in the catalytic reaction conditions and next decomposed during heating. Interestingly, an IL strongly influenced the distribution of Hg as well the stability of the resulting alloys. Such effect might be related to the formation of the protective IL shell on the surface of Pd NPs.

3. Experimental

Materials

All reactants were obtained from Aldrich "for synthesis" quality or higher and were used without further purification or drying.

Heck reaction procedure (with ILs):

The Heck reactions of iodobenzene with cyclohexene were carried out in a 50 cm³ Schlenk tube with magnetic stirring under a N₂ atmosphere. The reagents: base KOH (0.1403g ; $2.5 \cdot 10^{-3}$ mol), palladium catalyst: Pd(OAc)₂ (0.01203 g; $5.36 \cdot 10^{-5}$ mol) or PdCl₂(PhCN)₂ (0.02056 g; $5.36 \cdot 10^{-5}$ mol) or Pd/Al₂O₃ ; IL; iodobenzene (0.3 cm³; $2.68 \cdot 10^{-3}$ mol), cyclohexene (0.5 cm³; $8.77 \cdot 10^{-3}$ mol) and solvent - DMF (5 cm³) were introduced to the Schlenk tube in this order. The tube was closed, and the reaction was carried out at 100 °C for 4 h. Afterwards, the sample was quenched with water (10 cm³), the organic products were separated by extraction with diethyl ether (2 x 15 cm³) and analyzed by GC–MS (Hewlett Packard 8452A) with mesitylene (0.15 cm³) as internal standard. Products I, III and biphenyl were identified by comparison of the MS spectra and the retention times with the literature data.

Heck reaction with $(Pd(OAc)_2 + IL) + Al_2O_3$ catalysts was performed according to the above procedure with addition of Al_2O_3 (0.25 g).

Preparation of Pd/Al₂O₃: First, the support (1.5 g) was impregnated, with stirring, in Pd(OAc)₂ solution in the acetone (0.53 g in 50 cm³). After 2 days the solution was decanted, and the catalyst was washed three times with water and acetone and dried. The palladium content was estimated by the ICP method after mineralization of the weighted sample with *aqua regia*. The amount of Pd was 3.8%.

ICP measurements were performed using a ARL instrument Model 3410+ICP Fisons Instruments.

TEM measurements were performed using a FEI Tecnai G220 X-TWIN electron microscope operating at 200 kV and providing 0.25 nm resolution. A sample of supported Pd catalyst was isolated after the Heck reaction and triturated in agate mortar. In the second step suspension of Al_2O_3 supported catalyst in methanol was prepared and sonicated for 2 minutes. A droplet of suspension was placed on a carbon coated microscope grid and dried in air.

SEM measurements were performed using Hitachi S-3400N SEM instrument with EDS Noran System 7 analyser with Thermo Scientific Ultra Dry detector. Samples weren't dusted neither gold nor carbon so measurements were carried out using low vacuum – 30 Pa and BSE detector.

The BET specific surface area, total pore volume and pore size distribution of the Al_2O_3 supported catalysts were determined by the corresponding N_2 adsorption desorption isotherms (at the liquid nitrogen temperature) using an Surface Area and Porosity Analyzer Micromeritics ASAP 2020 V4.02. Before measurements the samples were degassed at 350 °C in vacuum for 4h. Textural properties of Al_2O_3 and supported Pd catalysts after Heck reaction are presented in Table 5.

4. Conclusions

The Heck coupling of iodobenzene with cyclohexene performed at 100 $^{\circ}$ C with homogeneous and heterogeneous palladium catalysts and small amounts of an IL made it possible to obtain the high conversion of substrates to 4-phenylcyclohexene. A positive influence of Al₂O₃ used as an additive to the homogeneous reaction was shown. The addition of Al₂O₃ caused an

increase of PhI conversion from 45% to 72% and to 82% when an IL (C) was introduced. Similarly, in the presence of ILs in a reaction catalyzed by heterogeneous Pd/Al_2O_3 , the conversion of PhI increased to 87–91%. It can be anticipated that the observed positive influence of the Al_2O_3 additive can be also used in other Heck reactions to increase the yield of the products. The reaction selectivity under applied conditions is better than in our previous system [25] because double-arylated products were not formed.

Recycling of the studied catalysts failed as a result of palladium leaching under the reaction conditions. Consequently, we proposed the main role of the Pd species dissolved in solution in the arylation of cyclohexene, similarly as it was also proposed earlier [15, 25]. Accordingly, the reaction was suppressed in the presence of Hg(0). Interestingly, SEM analyses showed that Hg covered the surface of Pd NPs supported on Al_2O_3 forming Pd-Hg amalgam. Thus, not only the elimination of soluble Pd forms but also the blocking of the heterogenized Pd were responsible for the drop in the yield at the presence of Hg(0). Experiments performed at higher temperatures (80–200 °C) made it possible to conclude that the removal of Hg from the support was easier in the presence of IL. Such a conclusion indicated the interaction of the IL with the supported Pd catalyst, which influenced not only the reaction with Hg but also the catalytic activity of the three-component catalytic system.

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Fig. 1. Scheme of the Heck arylation of cyclohexene. Monoarylated (I-III) and diarylated (IV-VIII) products.



Fig. 2. Products of cyclohexene arylation at 100 °C.



Fig. 3. ILs used in the Heck arylation of cyclohexene.

N-benzyl-N-methylmorpholinium 2-phenyl-2(R) - (-) hydroxyacetate (A); N-benzyl-N-methylmorpholinium 2-phenyl-2(S) - (+) hydroxyacetate (B); dimethyldidodecylammonium lactate (C).

Fig. 4. TEM image of 2C after Heck reaction.







Fig. 6. TEM image of 1C after Heck reaction.







Fig. 7. Pd(0) NPs size distribution of 1C after Heck reaction.

Fig. 8. SEM image of 1C surface after Heck reaction. Pd weight %: 1-2.1, 2-1.7, 3-2.9, 4-10.8, 5-12.4, 6-19.0.



Fig. 9. SEM image of 1C cross-section. Pd weight %: 1-1.1, 2-0.9, 3-1.6, 4-1.3, 5-1.7, 6-0.8, 7-0.



Fig. 10. SEM image of 1C surface after Heck reaction with Hg(0). Pd/Hg: 1-1.77, 2-1.65, 3-1.30, 4-0.99, 5-0.77.



Fig. 11. SEM image of 1 surface after Heck reaction with Hg(0). Pd/Hg: 1-0.84, 2-0.88, 3-0.57, 4-0.49, 5-0.66, 6-0.46, 7-0.73.



Fig. 12. SEM image of 1C surface after Heck reaction with Hg heated at 80 °C. Pd/Hg: 1-2.73, 2-1.71, 3-0.56, 4-0.39, 5-0.51, 6-1.32.



Fig. 13. SEM image of 1 surface after Heck reaction with Hg heated at 80°C. Pd/Hg: 1-1.31, 2-1.23, 3-1.00, 4-0.92, 5-0.59, 6-0.52, 7-0.57, 8-0.58.



Fig. 14. SEM image of 2C surface after Heck reaction with Hg(0) heated at 150 °C. Pd/Hg: 1-0.68, 2-1.04, 3-1.53, 4-2.86, 5-4.32, 6-4.10.



Fig. 15. SEM image of 1 surface after Heck reaction with Hg(0) heated at 150 °C. Pd/Hg: 1-0.61, 2-0.62, 3-0.80, 4-0.80, 5-1.42, 6-1.24.



Fig. 16. SEM image of 1C surface after Heck reaction with Hg(0) heated at 200 °C. Pd/Hg: 1-3.74, 2- 5.58, 3-4.62, 4-3.37.



Fig. 17. SEM image of 1 surface after Heck reaction with Hg(0) heated at 200 $^{\circ}$ C. Pd/Hg: 1-5.41, 2-3.12, 3-3.02, 4-2.15.



Table 1. Results of the Heck coupling of iodobenzene with cyclohexene catalyzed by $Pd(OAc)_2/Al_2O_3 + IL.$

Catalyst	PhI conversion (%)	I + III (%)	Selectivity to III (%)	Biphenyl (%)
1 (Pd/Al ₂ O ₃)	62	59	90	2
$IA (Pd/Al_2O_3 + A)$	91	81	82	9
$1B \left(Pd/Al_2O_3 + B \right)$	87	82	87	5
$1C \left(\frac{Pd}{Al_2O_3} + C\right)$	90	84	87	6

Reaction conditions: 2.68 10⁻³ mol PhI; 8.77 10⁻³ mol cyclohexene; 2 mol% Pd (0.22 g Pd/Al₂O₃); 2.5 10⁻³ mol KOH; 100°C; 4h; Pd/IL=1/2; DMF (5 cm³).

Catalyst	PhI conversion (%)	Yield I+III (%)	Selectivity to III (%)	Biphenyl (%)
PdCl ₂ (PhCN) ₂	62	62	94	-
$PdCl_2(PhCN)_2 + A$	54	47	81	7
$PdCl_2(PhCN)_2 + B$	71	68	90	3
$PdCl_2(PhCN)_2 + C$	52	48	87	4
$Pd(OAc)_2$	45	45	96	-
$Pd(OAc)_2 + A$	58	51	81	7
$Pd(OAc)_2 + B$	58	54	86	4
$Pd(OAc)_2 + C$	46	46	96	-
$2 \left(Pd(OAc)_2 + Al_2O_3^a \right)$	72	62	81	10
$2A (Pd(OAc)_2 + A + Al_2O_3^a)$	70	64	86	5
$2B (Pd(OAc)_2 + B + Al_2O_3^a)$	70	65	86	5
$2C \left(Pd(OAc)_2 + C + Al_2O_3^a \right)$	82	76	88	6

Table 2. Effect of ILs and Al₂O₃ on the Heck arylation of cyclohexene with iodobenzene.

Reaction conditions: $2.68 \cdot 10^{-3}$ mol PhI; $8.77 \cdot 10^{-3}$ mol cyclohexene; $2.5 \cdot 10^{-3}$ mol KOH; 2 mol% Pd; Pd/IL=1/2; 100 °C; 4 h; ^a 0.25 g of Al₂O₃ added to the reaction mixture.

	PhI	I+III	Selectivity to	Biphenyl
catalyst	conversion	(%)	III	(%)
	(%)		(%)	
<i>1C</i>	90	84	87	6
1C + Hg	18	13	67	5
1	62	59	90	2
1 + Hg	17	12	65	4

Table 3. Results of Hg(0) addition in reactions catalyzed by 1 and 1C.

Reaction conditions: $2.68 \cdot 10^{-3}$ mol PhI; $8.77 \cdot 10^{-3}$ mol cyclohexene; $2.5 \cdot 10^{-3}$ mol KOH; $100 \text{ }^{\circ}\text{C}$; Hg was added after 1 h; 2% mol Pd; Hg/Pd = 500

catalyst 1C after Heck reaction with		catalyst 1 after Heck reaction with		
Hg(0)		Hg(0)		
point	Pd/Hg	point	Pd/Hg	
1	2.2	1	0.8	
2	5.0	2	1.4	
3	6.4	3	0.7	
4	2.5	4	1.7	
5	5.0	5	1.4	
6	3.5	6	0.4	
7	4.0	7	1.2	
8	4.3	8	0.4	
9	2.2	9	1.3	
10	3.9	10	0.6	

Table 4.: Pd/Hg ratios determined in cross-sections of 1C and 1 after Heck reaction performed at the presence of Hg(0).

Table 5. Surface analysis of Al₂O₃ support and Pd catalysts after Heck reaction.

Sample	Surface area [m ² /g]	Pore volume [cm ³ /g]	Pore size [Å]
Al_2O_3	257.9	0.39	24.5
1C	235.2	0.36	24.7
1	233.4	0.34	47.4
2C	217.0	0.32	23.6
2	219.7	0.33	47.7