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$[IL]_2[PdCl_4]$ complexes (IL = imidazolium cation) as efficient catalysts for Suzuki–Miyaura cross-coupling of aryl bromides and aryl chlorides

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ABSTRACT

Palladium complexes of the type $[IL]_2[PdCl_4]$ (IL = imidazolium cation) were found to be very active catalysts for the Suzuki–Miyaura reaction of 2-bromotoluene with phenylboronic acid carried out in 2-propanol or 2-propanol/water at 40 °C using normal heating or microwaves as a heating source. In 2-propanol, the highest yields (89% and 85%) were obtained for $[dmiop]_2[PdCl_4]$ and $[dmdim][PdCl_4]$ (dmiop = 1,2-dimethyl-3-propoxymethyl imidazolium cation, dmdim = 3,3′-[1,7-(2,6-dioxaheptane)]bis(1,2-dimethylimidazolium) cation) containing cations substituted at the C2 carbon with a methyl group. In the presence of water, all $[IL]_2[PdCl_4]$ complexes produced ca. 90% of 2-methylbiphenyl. Very good results were also obtained in the Suzuki–Miyaura reaction of different aryl bromides and chlorides. For example, the conversion of 2-chlorotoluene was 71% at 70 °C. During the catalytic reaction, the formation of Pd(0) nanoparticles was evidenced by TEM. Mechanistic studies, including Hg(0) tests, showed that Pd(0) nanoparticles acted as a source of catalytically active soluble palladium species.

1. Introduction

Palladium-catalyzed cross-coupling reactions of aryl halides have been shown to be highly effective and practical methods for the formation of C–C bonds [1–7]. A special place in this category is occupied by the Suzuki–Miyaura reaction, which is a cross-coupling reaction between aryl (or vinyl) halide and borane or boronic acid to form biaryls [8–11]. There are a number of advantages of the Suzuki–Miyaura reaction: inexpensive substrates (aryl halides and boron compounds), high tolerance toward the presence of functional substituents in the substrates, mild conditions (low temperature, air atmosphere), possible use of water as a solvent, and nontoxic byproducts [12]. Consequently, it is one of the most important methodologies in the synthesis of pharmaceutical agents, organic materials, and natural products [13–15].

When considering catalysts for the Suzuki–Miyaura reaction, palladium complexes with phosphine ligands should be mentioned as the most popular [14–18]. However, the potential toxicity of phosphines and their low stability in the presence of air and water [19–21] has been the cause of an increasing interest in the elaboration of phosphine-free (ligand-free) palladium catalysts. In this context, a high catalytic activity of palladium catalysts bearing N-heterocyclic carbenes (NHC) as ligands has been demonstrated in the literature [22–35]. Also pincer-type ligands [36] and nitrogen ligands [37–41] have found applications in the Suzuki–Miyaura reaction. Palladium nanoparticles, stabilized by polymers or supported on inorganic oxides, have also been used recently [42–47]. Good catalytic performance was noted for palladium nanoparticles formed in situ [48–51].

In contrast, anionic palladium complexes of the type $[IL]_2[PdX_4]$ (IL – imidazolium cation, X = Cl, Br) [52–55] have been explored in catalysis only scarcely [54–58], and there are few examples of their application in the Suzuki–Miyaura reaction [55,56,58].

Complexes of the type $[IL]_2[PdX_4]$ can be easily obtained in reaction of $PdCl_2$ with any ionic liquid [IL]X. Thus, the application of different [IL]X can remarkably influence the properties of the final palladium complexes, in particular their bulkiness. Moreover, under catalytic reaction conditions, the [IL] cation can be deprotonated forming N-heterocyclic carbene (NHC), a potential ligand for palladium. Thus, $[IL]_2[PdX_4]$ used as a catalyst precursor can be transformed in situ into $(NHC)_2PdX_2$ complexes, potential catalysts for the Suzuki–Miyaura reaction [58]. Alternatively, the decomposition of $[IL]_2[PdX_4]$ can result in the formation of Pd(0) nanoparticles stabilized by ionic liquid [IL]X. Such forms can represent the resting state of the catalyst or they can act as a source of soluble palladium species.

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Table 1
Results of Suzuki–Miyaura reaction of 2-bromotoluene with different palladium complexes $[IL]_2[PdCl_4]$.

Complex	Yield (%)[a]				
	2-Propanol			2-Propanol/water	
	1 h	2 h	1 h[b]/MW	1 h	0.5 h[b]/MW
$[HIMes]_2[PdCl_4]$	31	59	59	96	61
$[HSIMes]_2[PdCl_4]$	59	59	63	92	90
$[HIPr]_2[PdCl_4]$	50	75	79	97	89
$[dmiop]_2[PdCl_4]$	74	89	79	91	85
$[mioe]_2[PdCl_4]$	36	49	39	83	85
$[dmdim][PdCl_4]$	77	85	67	69	91
$[mdim][PdCl_4]$	59	82	63	71	64
$[bcpim]_2[PdCl_4]$	50	83	71	80	80
$[bmim]_2[PdCl_4]$	51	73	56	91	80
$PdCl_2(cod)$	28	55	32	58	50
$Pd(OAc)_2$/[mdim]Cl	48	48	23	79	79

Reaction conditions: [Pd] (1 mol%); 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL) or 2-propanol (2.5 mL) + water (2.5 mL), 40 °C.
[a] Estimated as ArX conversion.
[b] Microwave-assisted reaction.

Taking these aspects into account, we decided to test a series of $[IL]_2[PdCl_4]$ complexes in the Suzuki–Miyaura reaction.

2. Results and discussion

2.1. Effect of IL cations on the catalytic activity of $[IL]_2[PdCl_4]$ complexes

A series of palladium complexes of the type $[IL]_2[PdCl_4]$ with imidazolium cations of different steric hindrance (IL) were tested as catalysts for the Suzuki–Miyaura reaction at 40 °C (Figs. 1 and 2).

It should be pointed out that all anionic complexes gave better results than $PdCl_2(cod)$, although in the case of $[HIMes]_2[PdCl_4]$ and $[HSIMes]_2[PdCl_4]$ the difference in yield was rather small (Table 1).

Two of the IL cations, dmiop and dmdim, were substituted with a methyl group at the C2 carbon, whereas all the remaining cations contained a proton at the C2 carbon. Interestingly, the highest productivity in reactions performed in 2-propanol was observed for $[dmiop]_2[PdCl_4]$ and $[dmdim][PdCl_4]$, after 1 h as well as after 2 h. A lower yield of the product was obtained with $[mdim][PdCl_4]$ containing a di-imidazolium cation analogous to dmdim but not substituted at the C2 carbon. Thus, the presence of the methyl substituent at the C2 carbon positively influenced the catalytic process, probably because the formation of N-heterocyclic carbene was retarded in that case. In agreement with that hypothesis was a relatively low yield of the cross-coupling product (48%) found in the reaction catalyzed by $Pd(OAc)_2$ + [mdim]Cl, in which the formation of a palladium carbene complex was very plausible. Positive effect of C2 protection on the yield of Suzuki–Miyaura product was also earlier reported [35].

Attempts to correlate the steric hindrance of the imidazolium cation present in the $[IL]_2[PdCl_4]$ complex with the reaction yield failed. In particular, the presence of bulky substituents at nitrogen atoms of the imidazole ring (HIMes, HSIMes, HIPr) did not result in an increase in 2-methylbiphenyl yield in comparison with smaller ligands (dmiop, bmim). A positive effect in the palladium-catalyzed Suzuki–Miyaura reaction of sterically hindered NHC ligands has been mentioned in the literature [24–26] and, therefore, we expected to find a similar trend also for anionic complexes. However, that was not the case, and, for example, very similar yields of 2-methylbiphenyl were obtained with the complexes $[bmim]_2[PdCl_4]$ (73%) and $[HIPr]_2[PdCl_4]$ (75%), which contain respectively small alkyl and bulky aryl substituents at nitrogen atoms (Table 1).

Similar results were also obtained under the same conditions with microwaves (MW) [59,60] as an alternative energy source. After 1 h under MW, the yield of the product was in most cases close to that obtained after 2 h with conventional heating (Table 1). Interestingly, a positive effect of MW was observed at temperatures as low as 40 °C.

2.2. Effect of the solvent on the catalytic activity of $[IL]_2[PdCl_4]$ complexes

The second series of Suzuki–Miyaura reactions were performed in 2-propanol/water mixture instead of 2-propanol only. The data collected in Table 1 indicate a very positive effect of that change on the product yield, which increased to 80–90% after 1 h of conventional heating or, alternatively, after 30 min of MW heating. Interestingly, the reaction yield was practically not affected by the structure of the imidazolium cation (IL) in $[IL]_2[PdCl_4]$ complexes when water was present in the reaction mixture.

The optimal ratio of 2-propanol to water was 1:1; at all other proportions, the conversion of 2-bromotoluene was lower. When the reaction was performed in pure water, only 30% of 2-methylbiphenyl was formed, remarkably less than in 2-propanol (Fig. 3).

An effect of the solvent was also noted when the reaction rate was analyzed. Fig. 4 shows the kinetic profile for reaction catalyzed by $[HIPr]_2[PdCl_4]$. Reaction in a 2-propanol/water mixture started immediately without any induction period and reached 70% conversion already after 5 min. A similar yield was obtained in 2-propanol after ca. 40 min. Clearly, the formation of a catalytically active palladium form was facilitated in the presence of water. Alternatively, better solubility of reaction substrates in water than in 2-propanol can positively influence the reaction course.

2.3. Suzuki–Miyaura reactions of different aryl bromides and chlorides

To widen the range of substrates, we carried out Suzuki–Miyaura reactions with different aryl halides using conventional as well as MW heating. In most cases the presence of substituents at the aromatic ring positively influenced substrate conversion in comparison with bromobenzene. In particular, electron-withdrawing groups such as NO_2 facilitated a higher yield of the product, and for 1-bromo-4-nitrobenzene, 100% conversion was obtained. Interestingly, very good results were obtained also for less active bromoanisoles. A steric hindrance effect was noted for bromoanisoles and better results were obtained for 4-bromoanisole than for 2-bromoanisole. Similarly, the conversion of 2-bromo-4-methylbenzonitrile was slightly higher than that of 3-bromo-4-methylbenzonitrile (Table 2).

The activation of aryl chlorides is a challenge for catalysis, in particular in cross-coupling reactions; however, in most cases, harsher conditions are needed than those used for the activation of aryl bromides. Using $[dmiop]_2[PdCl_4]$, it was possible to obtain up to 30% of the cross-coupling product from 1-chloro-2-nitrobenzene after 1 h using MW and 23% after 3 h at 40 °C. Under the same conditions, other chloronitroarenes did not form any products. However, increasing the temperature to 70 °C and extending the time to 24 h allowed us to react different aryl chlorides with good yield. The best result was obtained for 2-chlorotoluene (71%) in a 2-propanol/water mixture. Interestingly, for chlorobenzene 56% of coupling product was formed while slightly lower yield was noted for nitrochlorobenzenes. In fact, in all the experiments the yield of the product was higher in this solvent than in 2-propanol only, similarly as found for aryl bromides. For example, 4-chloro-2-nitrotoluene formed 20% of the cross-coupling product, whereas no

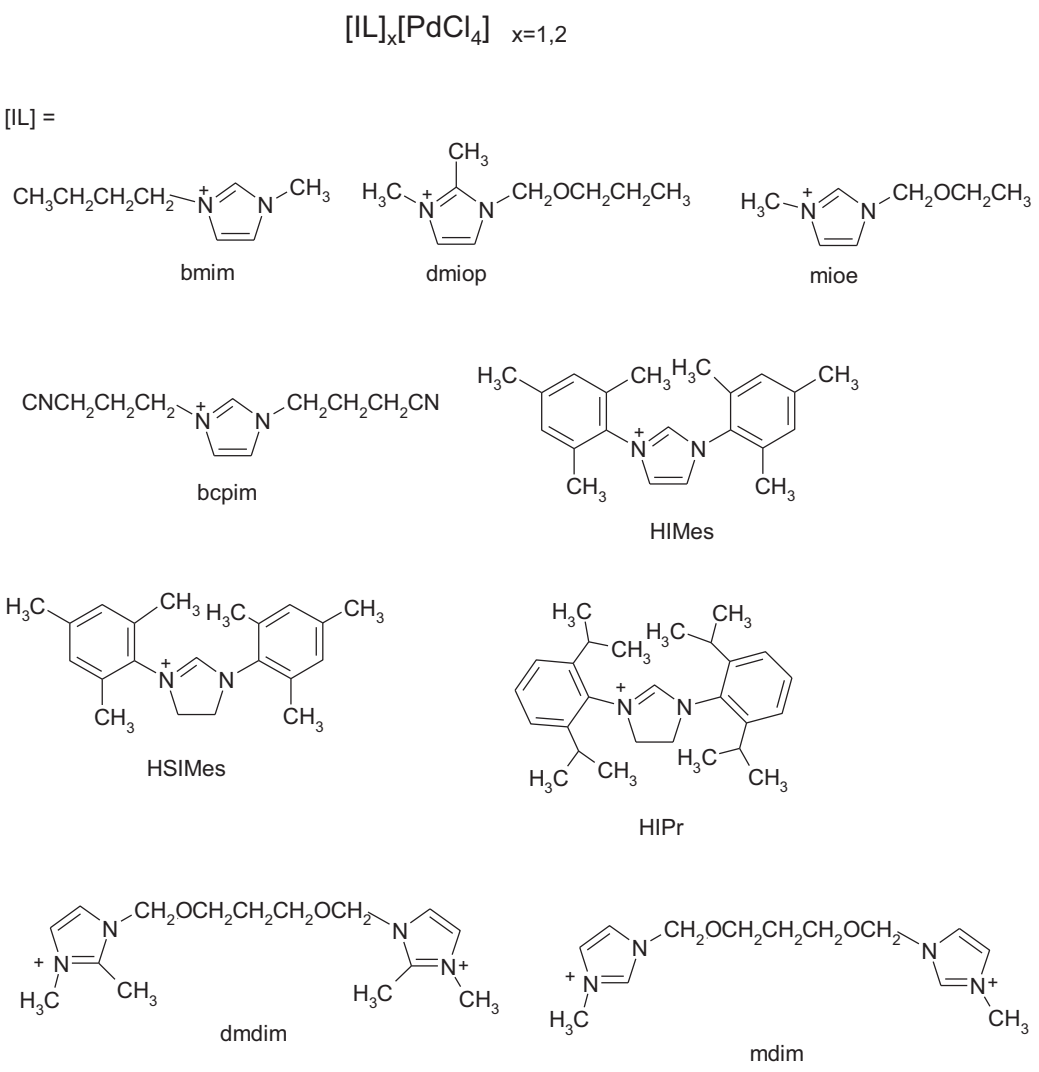

Fig. 1. $[IL]_2[PdCl_4]$ complexes studied as Pd-catalyst precursors. [bmim], 1-methyl-3-butylimidazolium cation; [mioe], 1-methyl-3-ethoxymethylimidazolium cation; [dmiop], 1,2-dimethyl-3-propoxymethylimidazolium cation; [bcpim], 1,3-bis(3-cyanopropyl)imidazolium cation; [HIMes], 1,3-bis(2,4,6-trimethylphenyl)imidazolium cation; [HSIMes], 1,3-bis(2,4,6-trimethylphenyl)imidazolinium cation; [HIPr], 1,3-bis(2,6-diisopropylphenyl)imidazolinium cation; [dmdim], 3,3′-[1,7-(2,6-dioxaheptane)]bis(1,2-dimethylimidazolium) cation; [mdim], 3,3′-[1,7-(2,6-dioxaheptane)]bis(1-methylimidazolium) cation.

product was obtained after 24 h in 2-propanol (Table 3). In contrast to nitrochlorobenzenes, 4-chloroanisole did not react, as expected for the substrate containing electron-donor substituent.

2.4. Effect of palladium concentration

The effect of catalyst concentration is illustrated in Fig. 5 for the representative complex $[dmiop]_2[PdCl_4]$. In the 0.25–3 mol% range, the yield differs by a maximum of 12%, presenting non-linear dependence on catalyst amount. Thus, when the amount of palladium was higher than 1 mol%, the yield of the product decreased, which can be an indication of the participation of Pd(0) nanoparticles in the reaction course [46]. Consequently, further studies were undertaken to get a closer insight into the mechanism of the catalytic function of the palladium complexes under study.

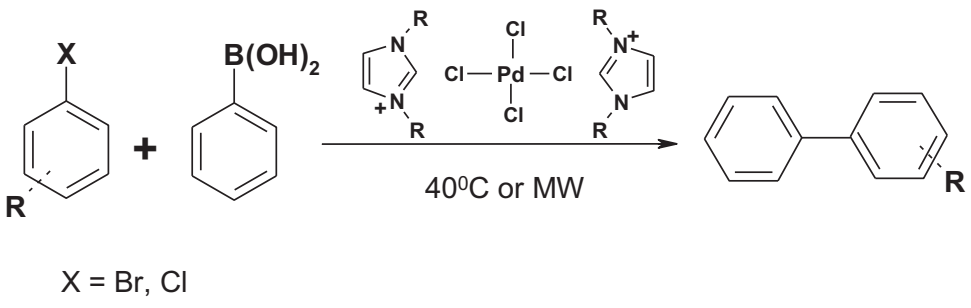

Fig. 2. Suzuki–Miyaura reaction.

Table 2
Results of Suzuki–Miyaura reaction of different aryl halides.

Substrate	Yield (%)[a]		
	1 h	2 h	1 h[b]/MW
4-iodoanisole	65	83	75
4-bromoanisole	87	90	99
2-bromoanisole	78	81	72
2-bromo-4-methylbenzonitrile	97	99	100
3-bromo-4-methylbenzonitrile	93	93	94
bromobenzene	70	89	77
4-bromotoluene	79	81	85
1,4-dibromobenzene	65(10)[c]	67(11)[c]	64(24)[c]
2-bromo-4-nitrotoluene	93	94	96
2-bromo-5-nitrotoluene	82	87	91
4-bromo-benzaldehyde	90	96	100
1-bromo-4-nitrobenzene	100	100	100

Reaction conditions: $[dmiop]_2[PdCl_4]$ (1 mol%); PhX (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL), 40 °C, 1 h.
[a] Estimated as ArX conversion.
[b] Microwave-assisted reaction.
[c] 1,4-diphenylbenzene.

Table 3
Results of Suzuki–Miyaura reaction of different aryl chlorides.

Substrate	Yield (%)[a]		
	$[dmiop]_2[PdCl_4]$	$[dmiop]_2[PdCl_4]$[b]	$[dmiop]_2[PdCl_4]$[c]
chlorobenzene	30	56	43
1-chloro-2-nitrobenzene	23	55	30
1-chloro-3-nitrobenzene	44	50	40
2-chloro-6-nitrotoluene	15	26	6
4-chloro-2-nitrotoluene	0	20	0
2-chlorotoluene	66	71	58
4-chlorotoluene	49	58	55
4-chloroanisole	0	0	0

Reaction conditions: [Pd] (1 mol%); PhX (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL), 70 °C, 24 h.
[a] Estimated as ArX conversion.
[b] 2-propanol (2.5 mL) + water/(2.5 mL), 70 °C, 24 h.
[c] 6 h, 70 °C, microwaves, 2-propanol.

2.5. Mechanistic studies

A set of experiments were performed, including TEM analyses and the Hg(0) poisoning test. The TEM analysis (Fig. 6) of the post-reaction mixture with $[HIPr]_2[PdCl_4]$ as catalyst evidenced the presence of 4–6 nm Pd(0) nanoparticles forming bigger aggregates, 60–80 nm, composed from individual nanoparticles. Interestingly,

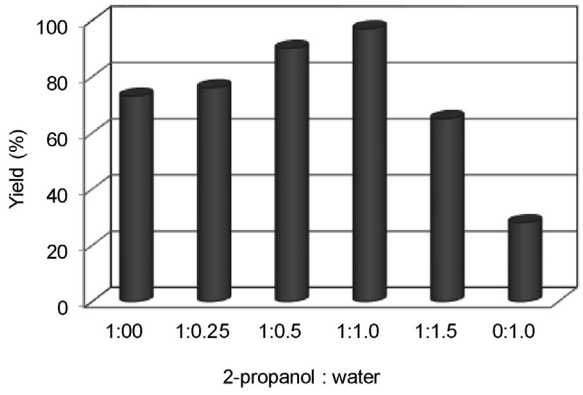

Fig. 3. Results of Suzuki–Miyaura reaction with $[HIPr]_2[PdCl_4]$ in 2-propanol/water mixtures. Reaction conditions: $[HIPr]_2[PdCl_4]$ (1 mol%); 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL) or 2-propanol/water (2.5 mL + 2.5 mL); 40 °C.

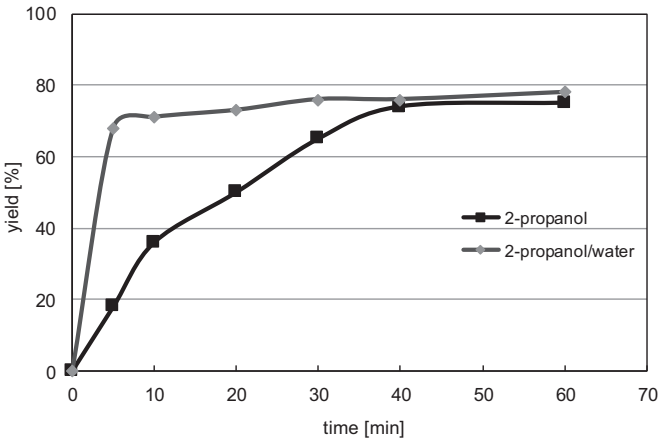

Fig. 4. Kinetic profile of Suzuki–Miyaura reaction in different solvents. Reaction conditions: $[dmiop]_2[PdCl_4]$; 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL); 40 °C, 2 h.

bigger nanoparticles were formed under MW heating. In this case, the size distribution of nanoparticles was wider and the elongated shape dominated over the round shape. A similar observation has been reported in the literature [61–63].

The formation of Pd(0) nanoparticles is to be expected in the absence of strongly coordinating ligands such as phosphines [45–47]. However, the presence of Pd(0) colloid did not necessarily indicate its dominating role as the catalytically active form, as it can also be the resting state of the catalyst. The role of colloidal palladium in the catalytic reaction can be estimated by the so-called Hg(0) test [48,64–66], in which a reaction catalyzed by nanoparticles or underligated Pd(0) species is retarded. In the case of $[HIPr]_2[PdCl_4]$ and $[bmim]_2[PdCl_4]$, the yield of the product decreased from ca. 50% to ca. 20% in the presence of Hg(0).

Further experiments with Hg(0) were performed using $[dmiop]_2[PdCl_4]$ as the catalyst precursor. The complex was stirred in 2-propanol containing KOH and a 625-fold excess of Hg(0) for a certain time prior to the introduction of the Suzuki–Miyaura substrates. Next, the Suzuki–Miyaura reaction proceeded for 2 h, and the products were analyzed. The results, presented in Fig. 7, confirmed a decrease in catalytic activity when treatment with Hg(0) was prolonged. However, it can also be stated that the deactivation of the catalyst was only partial. For instance, the catalyst stirred with Hg(0) for 30 min before the Suzuki–Miyaura reaction was still active and produced 60% of 2-methylbiphenyl. Most probably, the presence of Suzuki–Miyaura reactants facilitated the formation of Pd(0) nanoparticles and therefore the inhibiting effect of Hg(0) was stronger in the real catalytic process. The next

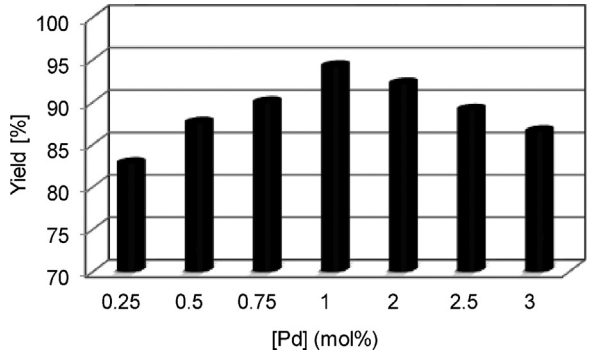

Fig. 5. Effect of palladium amount on Suzuki–Miyaura reaction yield. Reaction conditions: $[dmiop]_2[PdCl_4]$ (1 mol%); 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL), 40 °C, 2 h.

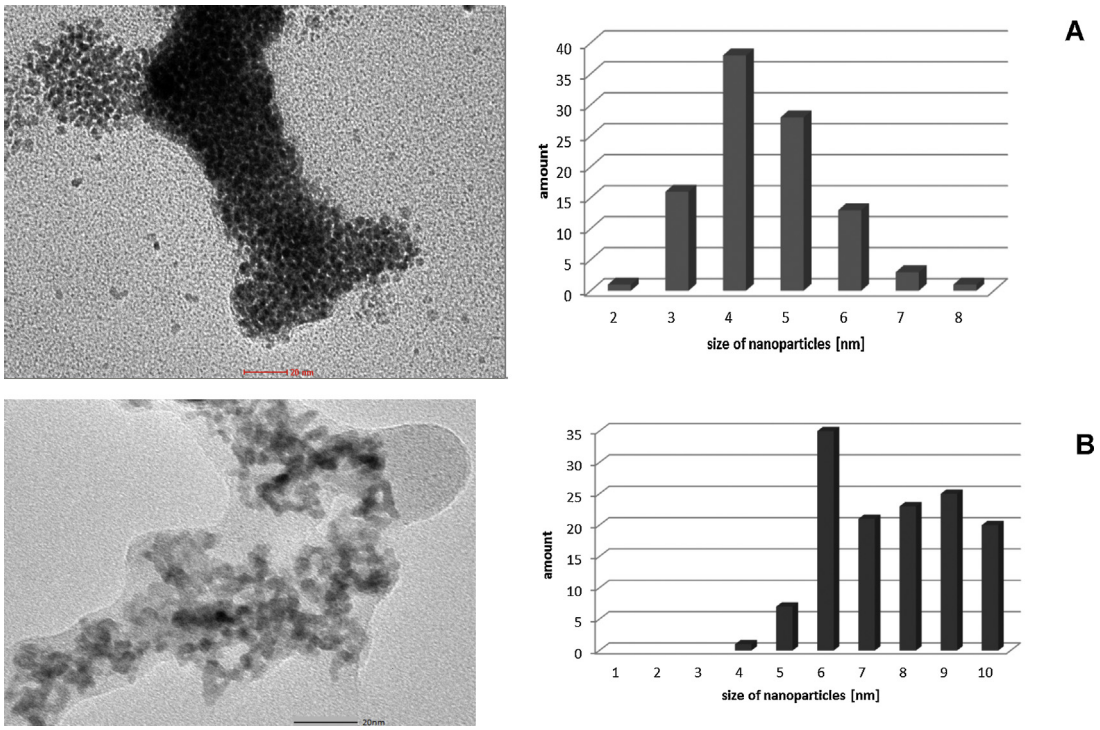

Fig. 6. TEM micrograph of $[HIPr]_2[PdCl_4]$ after Suzuki–Miyaura reaction: (A) normal heating and (B) microwaves. Reaction conditions: $[HIPr]_2[PdCl_4]$ (1 mol%); 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol (5 mL); 40 °C, 1 h, [Hg/Pd] = 625.

experiment with Hg(0) was performed according to the typical procedure [64–66]. Thus, after 20 min of reaction between 2-bromotoluene and phenylboronic acid, when conversion reached 49%, Hg(0) was added and reaction was continued for 40 min. The final yield of 2-methylbiphenyl was 70%, whereas 74% was formed in analogous experiment without Hg(0).

Consequently, the catalytic activity of soluble palladium complexes should be considered in the system under study. That conclusion is in agreement with the effect of catalyst concentration, whereby yield increases with an increase in the amount of solvent. This effect is shown in Fig. 8, which presents product yield obtained in the Suzuki–Miyaura reaction performed in 3, 5 and 10 mL of 2-propanol.

In these experiments, $[dmiop]_2[PdCl_4]$ was stirred for 10–60 min in 2-propanol in the presence of KOH before the addition of 2-bromotoluene and phenylboronic acid. In 3 mL, the palladium complex was quickly deactivated and in the last reaction only 11% of the product was formed. In contrast, in an analogous reaction in 10 mL, the yield of 2-methylbiphenyl was 63%. Most probably, at the lower concentration, Pd(0) nanoparticles are formed more slowly and their agglomeration is less plausible. Therefore, the catalyst is more stable and remains active for a longer time.

Taking into account that imidazolium cations containing a proton at the C2 carbon can be transformed into NHC carbenes under the catalytic reaction conditions, it was interesting to compare the activity of anionic and carbene palladium complexes. According to our previous results [34], $(NHC)_2PdX_2$ complexes are very good catalysts for the Suzuki–Miyaura reaction in ethylene glycol and consequently that solvent was selected for the test. It was found that $[IL]_2[PdCl_4]$ complexes are active in the presence of both bases, KOH and $NaHCO_3$ (Table S1), whereas carbene complexes catalyzed the Suzuki–Miyaura reaction only when $NaHCO_3$ was present. Therefore, one cannot rule out the possibility that $(NHC)_2PdX_2$ complexes participated in reactions with $[IL]_2[PdX_4]$ complexes as catalyst precursors, although such an effect seems to be base-controlled. In fact, as all reactions with $[IL]_2[PdCl_4]$

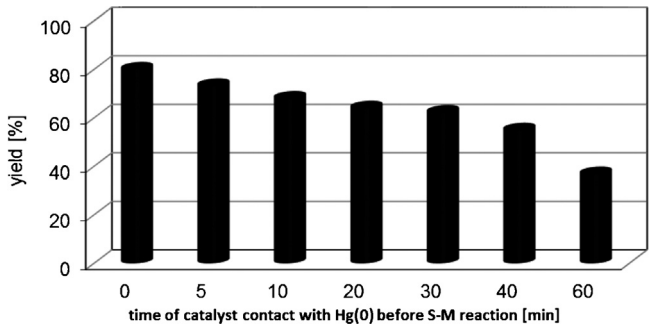

Fig. 7. Effect of Hg(0) on the conversion of 2-bromotoluene. Reaction conditions: $[dmiop]_2[PdCl_4]$ (1 mol%); 2-MePhBr (1 mmol); $PhB(OH)_2$ (1.5 mmol); KOH (1.2 mmol); 2-propanol, 2 h.

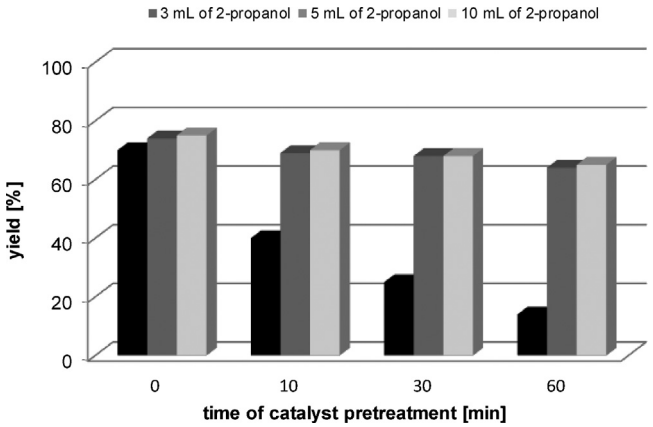

Fig. 8. Effect of solvent volume on the Suzuki–Miyaura reaction with $[dmiop]_2[PdCl_4]$.

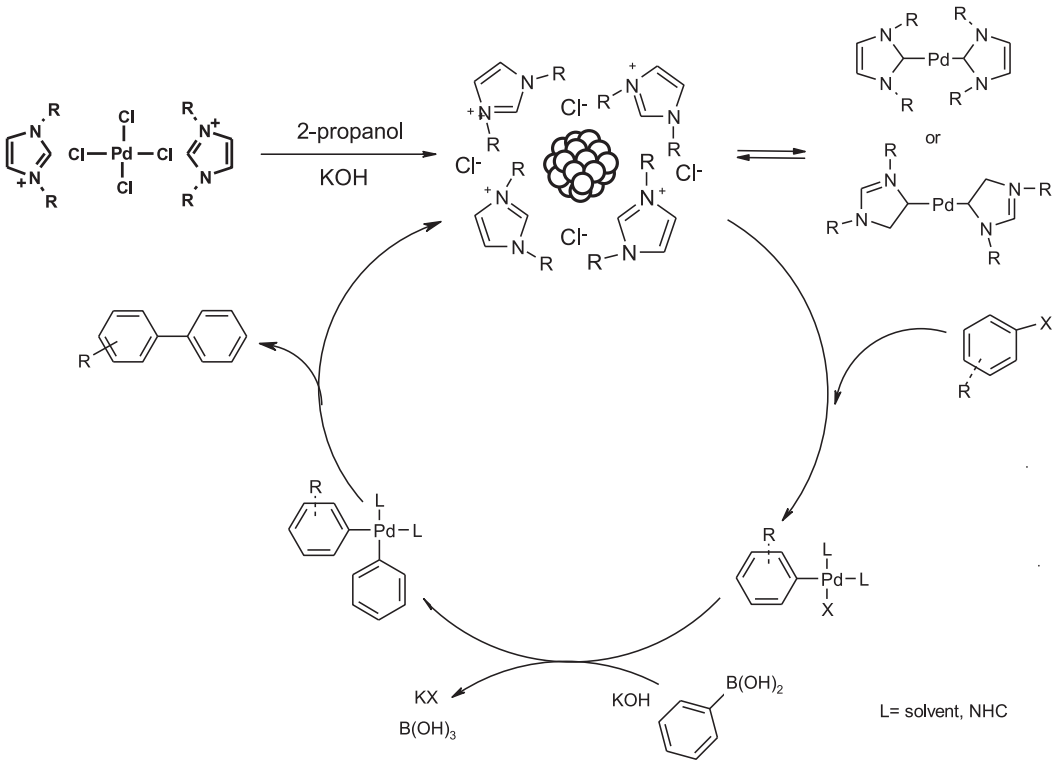

Fig. 9. Proposed mechanism of Suzuki–Miyaura reaction.

reported in this paper were performed in the presence of KOH, the participation of carbene complexes in these reactions seems to be unimportant.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.06.046.

It should be mentioned that in ethylene glycol participation of $(NHC)_2PdX_2$ complexes in the catalytic reaction could be considered as more important than in 2-propanol. Such conclusion is based on the fact that $Pd(OAc)_2$/[mdim]Cl system, in which formation of carbene complex in highly probable, produced 59% of 2-methylbiphenyl (Table S1). On the other hand, formation of palladium carbene complexes in reaction of $Pd(OAc)_2$ with [IL]X is well documented [67] while transformation of $[IL]_2[PdX_4]$ to $(NHC)_2PdX_2$ can be performed in the presence of Ag salt [58].

3. Conclusion

In conclusion, the general procedure involving the use of $[IL]_2[PdCl_4]$ as a catalyst precursor, 2-propanol/water as solvent, and microwave heating was shown to be suitable for the Suzuki–Miyaura reaction of activated aryl bromides and unactivated aryl chlorides. Under such conditions, all reactions proceeded with high yields at low temperatures, 40–70 °C. It should be pointed out that easily obtained and air-stable $[IL]_2[PdCl_4]$ complexes exhibited similar or even higher catalytic activity than less-stable carbene complexes of the type $(NHC)_2PdX_2$.

The results of mechanistic studies are summarized in Fig. 9. We propose a homogeneous pathway of the Suzuki–Miyaura reaction with the participation of palladium species bearing imidazolium cations or N-heterocyclic carbenes as key intermediates. The Pd(0) nanoparticles that are formed in these systems under the Suzuki–Miyaura reaction conditions act mainly as a source of soluble palladium species.

In our opinion $(NHC)_2PdX_2$ complexes formed in situ during catalytic reaction do not present the main catalytically active form of palladium. However contribution of palladium carbene complexes in the catalytic process is not excluded and it depends on the reaction conditions, mainly on the kind of base and solvent.

During the catalytic process, Pd(II) was reduced to Pd(0), forming nanoparticles identified by TEM. Pd(0) nanoparticles act mainly as a source of catalytically active soluble palladium species.

4. Experimental

All reactants were obtained from Aldrich, Fluka, or Merck in "for synthesis" quality or higher, and were used as received without further purification or drying. Imidazolium salts: [dmiop]Cl, [mioe]Cl, [dmdim]Cl and [mdim]Cl were synthetized according to methods described in the literature [68].

The palladium complexes $[bmim]_2[PdCl_4]$, $[mioe]_2[PdCl_4]$, $[dmiop]_2[PdCl_4]$ and $[bmpy]_2[PdCl_4]$ were obtained according to methods described in the literature [55,57].

4.1. General procedure for the Suzuki–Miyaura reaction

The Suzuki–Miyaura reaction was carried out in a 50 mL Schlenk tube. The solid substrates: base (1.2 mmol), phenylboronic acid (1.5 mmol, 0.184 g), aryl halide (1.0 mmol) and the palladium complex (0.01 mmol) were weighted and placed in the Schlenk tube. Next, 5 mL of the solvent (2-propanol or 2-propanol (2.5 mL)/water (2.5 mL)) was added with a pipette. The tube was closed with a rubber plug and the reaction mixture was stirred at 40 °C. After the specified reaction time, the tube was cooled down and the organic products were extracted with 10 mL of *n*-hexane. For better phase separation, 1 mL of water was added. The upper *n*-hexane layer was taken and 0.076 mL of dodecane was added as an internal standard. The organic products were analyzed using the GC–MS method (instrument HP 5890 II with capillary column).

4.2. General procedure for the Suzuki–Miyaura coupling of aryl chlorides

In a 50 mL Schlenk tube phenylboronic acid (1.0 mmol) was mixed with aryl chloride (1.0 mmol). Then base (1.2 mmol), palladium complex (0.01 mmol) and 2-propanol (5 mL) were added. The Schlenk tube was placed in an 70 °C oil bath and stirred for 24 h. The mixture was then cooled to room temperature. The organic products were extracted with 10 mL of *n*-hexane (15 min with stirring). For better phase separation, 1 mL of water was added and the upper *n*-hexane layer was taken for GC analysis.

4.3. General procedure for Hg(0) test

The Suzuki–Miyaura reaction was carried out in a 50 mL Schlenk tube. The base (1.2 mmol) and the palladium complex (0.01 mmol) were weighted and placed in the Schlenk tube. Next, 5 mL of 2-propanol and 6.25 mmol of Hg(0) were added. The reactor was closed with a rubber plug and the reaction mixture was stirred at 40 °C. After the specified reaction time, phenylboronic acid (1.5 mmol, 0.184 g) and 2-bromotoluene (1.0 mmol) were added to the Schlenk tube and the mixture was stirred at 40 °C. After 2 h, the reactor was cooled down and the organic products were extracted with 10 mL of *n*-hexane. The organic products were analyzed using the GC–MS method.

4.4. Synthesis of palladium complexes:

[HIPr]$_2$[PdCl$_4$]: 0.45 g (1.0 mmol) of [HIPr]Cl was added to the solution of 0.14 g (0.48 mmol) $PdCl_2$(cod) in hot CH_3CN (5 mL). The mixture was heated for 15 min, until the yellow solution became red. The solution was cooled to room temperature and solvent was removed under reduced pressure. The product was precipitated by addition of diethyl ether (2–3 mL). Product yield: 85%; elemental analysis calcd. (%) for $PdCl_4C_{54}H_{78}N_4$: C 62.88, H 7.62, N 5.46; found: C 62.37, H 7.46, N 5.40. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS): δ = 8.49 (s, 2H, N—CH═N); 7.57 (t, J(H,H) = 7.8 Hz, 4H, Ar); 7.42 (d, J(H,H) = 7.8 Hz, 8H, Ar); 4.48 (s, 8H, CH_2—CH_2); 3.10 (m, J(H,H) = 6.9 Hz, 8H, CH); 1.40 (d, J(H,H) = 6.9 Hz, 24H, CH_3); 1.26 (d, J(H,H) = 6.9 Hz, 24H, CH_3,); ^{13}C NMR (125.75 MHz, CD_3CN, 25 °C, TMS): δ = 160.0 (N—CH═N); 147.2 (Ar); 131.0 (Ar); 125.5 (Ar); 53.7 (CH_2—CH_2); 28.5 (CH); 24.0 (CH_3); 23.5 (CH_3).

[HIMes]$_2$[PdCl$_4$]: The complex was obtained according to the procedure given for [HIPr]$_2$[PdCl$_4$] using 0.3 g (1.0 mmol) of $PdCl_2$(cod) and 0.72 g (2.1 mmol) of [HIMes]Cl; yield: 87%; elemental analysis calcd. (%) for $PdCl_4C_{42}H_{50}N_4$: C 58.72, H 5.87, N 6.52; found: C 58.20, H 5.44, N 6.38. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS): δ = 8.94 (s, 2H, N—CH═N); 7.75 (s, 4H, CH═CH); 7.19 (s, 8H, Ar); 2.40 (s, 12H, CH_3); 2.16 (s, 24H, CH_3); ^{13}C NMR (125.75 MHz, CD_3CN, 25 °C, TMS): δ = 141.0 (N—CH═N); 134.0 (Ar); 129.6 (Ar); 125.6 (CH═CH); 20.0 (CH_3); 16.0 (CH_3).

[HSIMes]$_2$[PdCl$_4$]: The complex was obtained according to the procedure given for [HIPr]$_2$[PdCl$_4$] using 0.17 g (0.6 mmol) of $PdCl_2$(cod) and 0.4 g (1.2 mmol) of [HSIMes]Cl; yield: 48%; elemental analysis calcd. (%). for $PdCl_4C_{42}H_{54}N_4$: C 58.44, H 6.31, N 6.49; found: C 58.43, H 6.65, N 6.10. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS) δ = 8.18 (s, 2H, N—CH═N); 6.99 (s, 8H, Ar); 4.33 (s, 8H, CH_2—CH_2); 2.26 (s, 24H, CH_3); 2.23 (s, 12H, CH_3); ^{13}C NMR (125.75 MHz, CD_3CN, 25 °C, TMS): δ = 159.8 (N—CH═N); 135.3 (Ar); 129.5 (Ar); 51.0 (CH_2—CH_2); 20.0 (CH_3); 16.6 (CH_3).

[bcpim]$_2$[PdCl$_4$]: The complex was obtained according to the procedure given for [HIPr]$_2$[PdCl$_4$] using 0.32 g (1.1 mmol) of $PdCl_2$(cod) and 0.5 g (2.2 mmol) of [bcpim]Cl; yield: 78%; elemental analysis calcd. (%). $PdCl_4C_{22}H_{30}N_4$: C 40.43, H 4.66, N 17.13; found: C 39.81, H 4.12, N 17.03. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS) δ = 9.96 (s, 2H, N—CH═N); 7.49 (s, 4H, CH═CH); 4.32 (t, J(H,H) = 7.1 Hz, 8H, N—CH_2); 2.55 (t, J(H,H) = 7.3 Hz, 8H, CH_2—CN); 2.24 (m, J(H,H) = 7.1 Hz 8H, CH_2); ^{13}C NMR (125.75 MHz, CD_3CN, 25 °C, TMS): δ = 142.0 (N—CH═N); 122.5 (CH═CH); 119.2 (CN); 48.0 (N—CH_2); 25.0 (CH_2); 13.5 (CH_2).

[dmdim][PdCl$_4$]: The complex was obtained according to the procedure given for [HIPr]$_2$[PdCl$_4$] using 0.4 g (1.4 mmol) of $PdCl_2$(cod) and 0.4 g (1.4 mmol) of [dmdim]Cl; yield: 95%; elemental analysis calcd. (%). $PdCl_4C_{15}H_{26}N_4O_2$: C 33.18, H 4.83, N 10.32; found: C 33.40, H 4.91, N 10.33. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS) δ = 7 78 (s, 2H, CH═); 7.61 (s, 2H, ═CH); 5.54 (s, 4H, CH_2—O); 3.77 (s, 6H, CH_3—N); 3.42 (t, J(H,H) = 6.5, 4H, CH_2—O); 2.53 (s, 6H, –CH_3); 1.70 (m, J(H,H) = 6.5, 2H, –CH_2–); ^{13}C NMR (125.75 MHz, CD_3CN, 25 °C, TMS): δ = 146 0 (N—C═N); 123.4 (C═C); 122.5 (C═C); 77.0 (CH_2—O); 66.8 (N—CH_3); 35.5 (O—CH_2); 27.3 (CH_2); 10.1 (CH_3).

[mdim][PdCl$_4$]: The complex was obtained according to the procedure given for [HIPr]$_2$[PdCl$_4$] using 0.4 g (1.4 mmol) of $PdCl_2$(cod) and 0.4 g (1.4 mmol) of [mdim]Cl; yield: 90%; elemental analysis calcd. (%). $PdCl_4C_{13}H_{22}N_4O_2$: C 30.40, H 4.21, N 10.76; found: C 30.34, H 4.31, N 10.89. ^{1}H NMR(500 MHz, CD_3CN, 25 °C, TMS) δ = 9 62 (s, 2H, –CH–); 7.90 (s, 2H, –CH═); 7.85 (s, 2H, –CH═); 5.64 (s, 4H, –CH_2—O); 3.92 (s, 6H, –CH_3); 3.63 (t, J(H,H) = 6.5, 4H, –CH_2—); 1.80 (t, J(H,H) = 6.5, 2H, –CH_2—); ^{13}C NMR (125.7 5 MHz, CD_3CN, 25 °C, TMS): δ = 138.0 (N—C═N); 124.3 (C═C); 122.2 (C═C); 79.3 (CH_2—O); 66.5 (N—CH_3); 36.2 (O—CH_2); 29.0 (CH_2).

4.5. Measurements

^{1}H and ^{13}C NMR spectra were measured in CD_3CN and C_6D_6 on Bruker 500 spectrometers. Morphology and microstructure were investigated by TEM (Philips CM-20 SuperTwin operating at 200 kV and providing 0.25 nm resolution). The products of the catalytic experiments were analyzed with a GC–MS (Hewlett Packard 8452A instrument). Experiments with microwaves heating were performed in microwave oven (Plazmatronika RM-800, 256 W).

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