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Methoxycarbonylation of Iodobenzene in Ionic Liquids. A Case of Inhibiting Effect of Imidazolium Halides

W. Zawartka,[a] A. M. Trzeciak,[a,*] J. J. Ziółkowski,[a] T. Lis,[a] Z. Ciunik, and J. Pernak[b]

[a] Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50-383 Wrocław, Poland
Fax: (+48)-71–375–7356; e-mail: ania@wchuwr.chem.uni.wroc.pl
[b] Poznań University of Technology, 2 Skłodowskiej-Curie Pl., 60-965 Poznań, Poland

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Abstract: The palladium(II) complexes, $PdCl_2$(cod) (**1**), $PdCl_2[P(OPh)_3]_2$ (**2**), $[bmim]_2[PdCl_4]$ (**3**), and $[bmpy]_2[PdCl_4]$ (**4**) (bmim = 1-butyl-3-methylimidazolium cation, bmpy = 1-butyl-4-methylpyridinium cation), were found to be active catalysts for the methoxycarbonylation of iodobenzene in ionic liquid (IL) media. The best results were obtained in pyridinium salts, [bmpy]X (X = Cl, Br, BF_4, PF_6) (76–100% yield). In methoxycarbonylation reactions carried out in imidazolium salts, [bmim]BF_4 and [bmim]PF_6, the yield of benzoic acid methyl ester was slightly lower (50–78% yield), whereas in [bmim]X (X = Cl, Br) the reaction was totally retarded. The inhibiting effect was not observed when a Me group was present at C-2 (instead of a proton) on the imidazole ring. A palladium-carbene complex, $Pd(bmimy)_2Br_2$ (**5**), obtained in the reaction of a palladium catalyst precursor with [bmim]Cl, presented much lower activity than precursors **1–4**. Its formation may explain the observed inhibition of methoxycarbonylation in a [bmim]Cl medium.

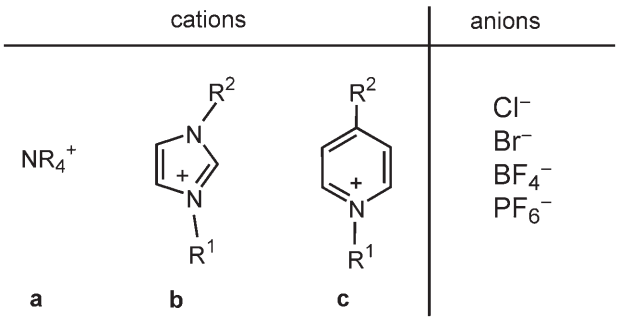
Keywords: ionic liquids; methoxycarbonylation; palladium; palladium carbenes

Introduction

Ionic liquids (IL), regarded as salts with insignificant vapor pressures and melting points much below 100 °C, have recently found widespread use as reaction media for many catalytic processes.[1–10]

Of the large number of ionic liquids, including also tetraalkylammonium halides (**a**), which melt at temperatures below 100 °C, the most frequently used are those with imidazolium cations (**b**) and less often with pyridinium cations (**c**) (Scheme 1).[1–11]

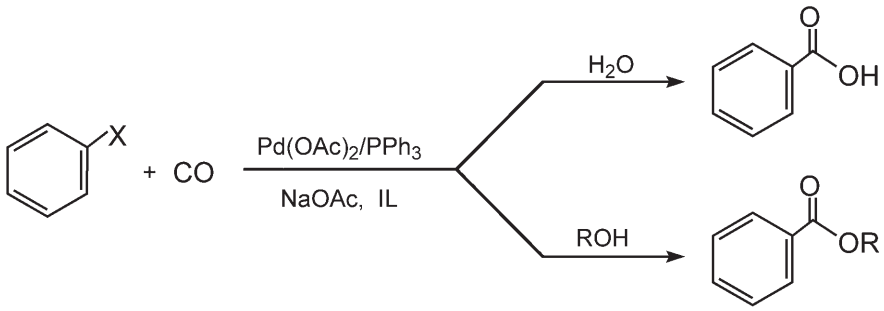
Carbonylation reactions of aryl and benzyl halides in ionic liquids have till now been described in just a few papers.[12–14] To the best of our knowledge, only two examples have been presented of the application of $Pd(OAc)_2$ as a catalyst precursor for the methoxycarbonylation of aryl halides with a 4–20-fold excess of PPh_3 in [bmim]BF_4 and [bmim]PF_6 (bmim = 1-butyl-3-methylimidazolium cation).[12] Ionic liquids used as reaction media significantly enhanced the alkoxycarbonylation of bromobenzene compared with reactions carried out in methanol as solvent.[12] At higher excesses of PPh_3 *versus* palladium quite good results have been obtained in the recyclability of catalysts, both in hydroxycarbonylation and in methoxycarbonylation (Scheme 2).[12,13]



Scheme 1.

The benzothiazole carbene-palladium complex, quite active as a catalyst precursor in the butoxycarbonylation of iodobenzene and 4-bromoacetophenone in molten TBAB (tetrabutylammonium bromide), produced only very low yields of products in reactions carried out in butylpyridinium tosylate and in imidazolium salts.[15]

In our recent paper[16] dealing with the methoxycarbonylation of iodobenzene catalyzed by Pd(0)-colloid dissolved in different ionic liquids, we found that the highest yields of esters were obtained in ionic liquids with pyridinium cations, regardless of the kind of anion present (Cl^-, BF_4^-, or PF_6^-). Slightly worse results were obtained for [bmim]BF_4 and [bmim]PF_6,



Scheme 2.

whereas [bmim]Cl used as the reaction medium acted as a strong inhibitor and caused total retardation of the methoxycarbonylation process.[16]

Those results, which experimentally demonstrate a strong inhibiting behavior of imidazolium chloride, inspired us to undertake more detailed studies to explain this case.

The main goal of the studies presented in this paper was to correlate the molecular structures of ionic liquids with their effect on the activity of palladium catalyst precursors in the methoxycarbonylation of iodobenzene. The role of imidazolium salts of the [bmim]X type ($X = Cl^-$, Br^-, I^-) was of particular interest. It is worth mentioning that [bmim]X-type ionic liquids used in Heck coupling lead to an increase in both the reaction rate and the yield of products.[17]

The results presented in this paper comprise both investigations of methoxycarbonylation reactions as well as identification of palladium complexes formed in reactions with ionic liquids. Two types of palladium catalyst precursors have been studied: phosphane-free and containing a triphenyl phosphite ligand.

Results and Discussion

Methoxycarbonylation in Different Ionic Liquids

The results of the methoxycarbonylation reaction of iodobenzene (PhI) in different ionic liquids (IL) are collected in Table 1. Scheme 3 presents the structures of and the abbreviations for the IL cations used.

The following palladium(II) complexes were tested as catalyst precursors: $PdCl_2$(cod) (**1**), $PdCl_2[P(OPh)_3]_2$ (**2**), $[bmim]_2[PdCl_4]$ (**3**), and $[bmpy]_2[PdCl_4]$ (**4**). The anionic complexes **3** and **4** were obtained from reactions of **1** with [bmim]Cl or [bmpy]Cl as the only palladium-containing products (Scheme 4). The complex $[bmim]_2[PdBr_4]$ (**3a**), an analogue of **3**, was also obtained in the same way. Complex **3** was obtained earlier from the reaction of $PdCl_2$ with [bmim]Cl.[18] The molecular structure of **3a** is presented in Figure 1.

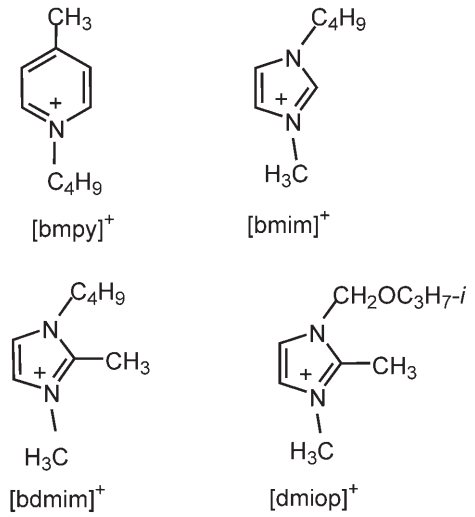
The above results allowed us to assume that complexes **3**, **3a**, and **4** are formed in situ in the catalytic methoxycarbonylation reaction carried out in [bmim]Cl, [bmim]Br, or [bmpy]Cl as the reaction medium with **1** as catalyst precursor. The catalytic activity of both precursors, **3** and **4**, is similar to that of **1**, and in all cases no catalytic activity was observed when [bmim]Cl and [bmim]Br were used as reaction

Table 1. Effect of ionic liquids (IL) on the yield (%) of methoxycarbonylation reaction of iodobenzene with $PdCl_2$(cod) (**1**), $[bmim]_2PdCl_4$ (**3**), $[bmpy]_2PdCl_4$ (**4**), $PdCl_2[P(OPh)_3]_2$ (**2**), and $Pd(Bmimy)_2Br_2$ (**5**) as pre-catalysts.[a]

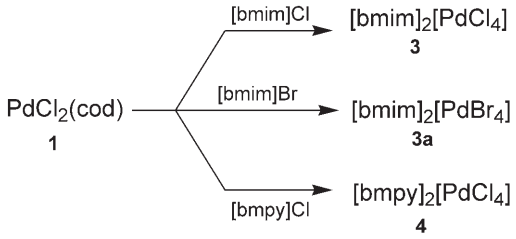
IL	$PdCl_2$(cod) (**1**)	$[bmim]_2PdCl_4$ (**3**)	$[bmpy]_2PdCl_4$ (**4**)	$PdCl_2(P(OPh)_3)_2$ (**2**)	$Pd(bmimy)_2Br_2$ (**5**)
[bmim]Cl	0	0	3	8	0
[bmim]Br	0	0	0	0	0
[dbmim]Br	62	70	74	80	14
[dmiop]Cl	27	30 (29; 18[b])	26		
$[bmim]PF_6$	58	78	78	50	
$[bmim]BF_4$	51	56	71	74	
[bmpy]Cl	60	94	89	100	7
[bmpy]Br	92	96	76		16
$[bmpy]BF_4$	68	89	93	74	22
$[bmpy]PF_6$	92	82	88		55

[a] *Reaction conditions:* [Pd] $5 \cdot 10^{-5}$ mol, [PhI] $8.9 \cdot 10^{-3}$ mol, [NEt_3] $2.1 \cdot 10^{-2}$ mol, [MeOH] $2.4 \cdot 10^{-2}$ mol, 3 h, 5 at, 90 °C, IL 1.5 g.

[b] Reaction yields in 2nd and 3rd runs.



Scheme 3.



Scheme 4.

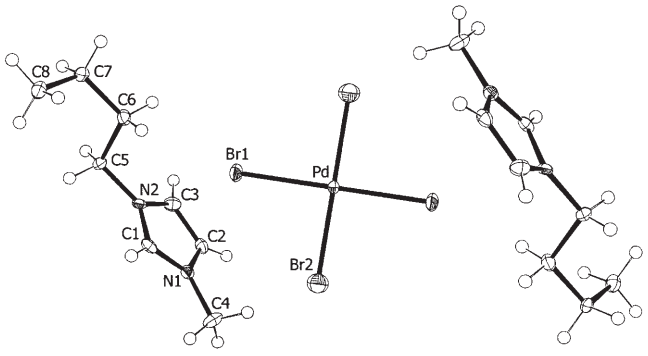


Figure 1. The molecular structure and atom numbering scheme of $[bmim]_2[PdBr_4]$ (**3a**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unnumbered atoms are symmetrically dependent *via* an inversion center. Selected geometric parameters (Å, °): Pd–Br1 2.440(1); Pd–Br2 2.397(1); Br1–Pd–Br2 89.59(3); Br1–Pd–Br2^{i} 90.41(3) (Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*).

media. Contrary to these results, when halide anions in the imidazolium salts were replaced by the weakly coordinating BF_4^- or PF_6^- anions, the methoxycarbonylation reaction proceeded quite well (Table 1). In $[bmpy]BF_4$ and $[bmpy]PF_6$ the yield of ester was *ca.* 90% (Table 1). It is worth noting that high yield of the methoxycarbonylation product was also obtained in reactions proceeding in [bmpy]X ($X = Cl^-$, Br^-), which suggests that the inhibiting effect of some imidazolium salts is not related to the presence of halide anions only.

The catalytic activity of **2** was found to be similar to that observed for the phosphane-free palladium precursor **1** and also to those of **3** and **4**. Application of imidazolium halides as the reaction medium practically totally inhibited the catalytic activity of **2**, whereas in pyridinium ionic liquids, [bmpy]X ($X = Cl^-$, Br^-), the methoxycarbonylation proceeded smoothly.

It is well known that imidazolium salts may react with palladium complexes to form N-heterocyclic carbene species that have been found to be good catalysts for Heck, Suzuki, and amination reactions,[18–23] but which have never been tested in methoxycarbonylation.

Methoxycarbonylation with an N-Heterocyclic Carbene-Palladium Complex

To learn about the possible contribution of N-heterocyclic carbene-palladium species in the methoxycarbonylation, special test reactions were performed in imidazolium halides substituted at C-2 with a Me group, in [dmiop]Cl and [bdmim]Cl (Scheme 3). Such imidazolium cations are unable to form carbene complexes with Pd–C–2 bonds. As expected, the presence of a Me group at C-2 did not affect the reactivity of these ILs towards the precursor **1**, and a **3**-type complex, $[dmiop]_2[PdCl_4]$ **(3b)** (Figure 2), was obtained.

The methoxycarbonylation of iodobenzene in both media, [dbmim]Cl as well as [dmiop]Cl, proceeded more effectively than in the corresponding non-substituted analogues, i.e., [bmim]Cl. Particularly good results, *ca.* 70% of ester, were obtained in [bdmim]Cl (Table 1). It was also seen that, in spite of a rather low yield of the methoxycarbonylation reaction in [dmiop]Cl (*ca.* 30% for precursors **1**, **3**, and **4**), the palladium catalyst was still reasonably active in two subsequent experiments producing 29% and 18% of ester, respectively (Table 1).

A further test reaction of methoxycarbonylation was studied with a carbene complex, $Pd(bmim\text{-}y)_2Br_2$ (**5**), as the catalyst precursor, synthesized according to the Scheme 5, following a modified procedure described in the literature.[17]

Complex **5** was found to be less active than the other palladium precursors (Table 1). This is well illustrated by the results obtained in pyridinium salts, [bmpy]X ($X = Br^-$, BF_4^-, PF_6^-). In these media the yield of ester ranged from 7% to 55% when **5** was used as a catalyst precursor, whereas all other precursors produced from 60% to 100% of the ester. A low

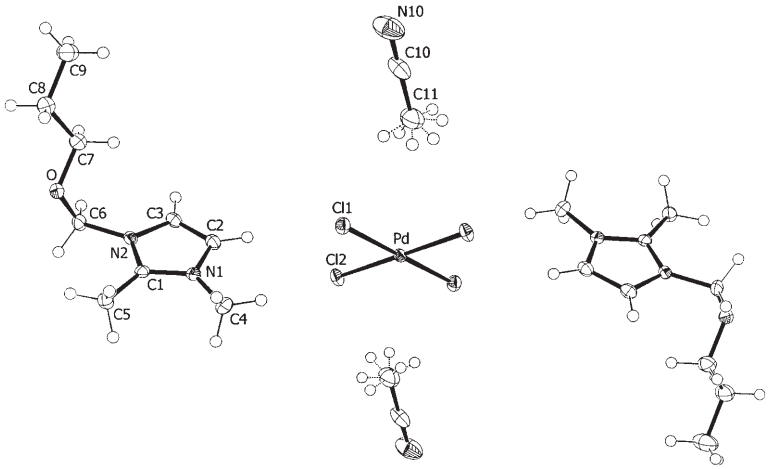
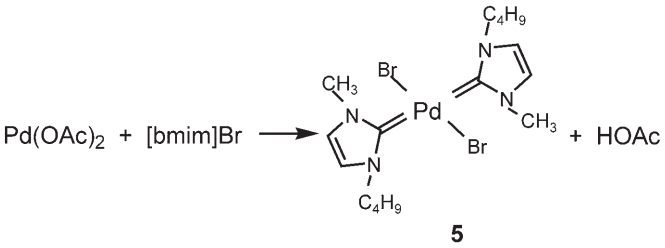


Figure 2. The molecular structure and atom numbering scheme of $[dmiop]_2[PdCl_4]\cdot 2MeCN$ (**3b**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unnumbered atoms are symmetrically dependent *via* an inversion center. Selected geometric parameters (Å, °): Pd–Cl1 2.3111(7); Pd–Cl2 2.3089(9); O–C6 1.389(3); O–C7 1.441(3); Cl1–Pd–Cl2 89.14(3); Cl1–Pd–Cl2^{i} 90.86(3); C6-O-C7 112.7(2) (Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*). Disordered parts (50% occupancy) in the acetonitrile molecules are represented by dashed lines.



Scheme 5.

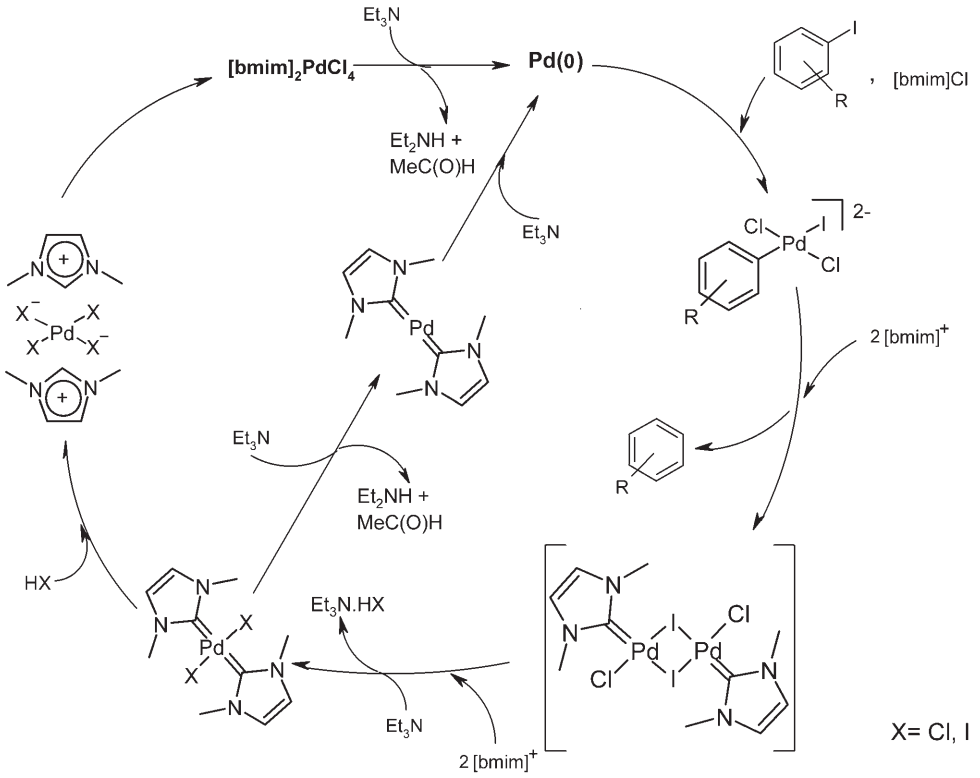
yield of ester, just 14%, was obtained in [bdmim]Br, a very good reaction medium for all other precursors (Table 1).

Keeping in mind the mechanism of the methoxycarbonylation reaction, in which Pd(0) plays an essential role, one may suppose that a Pd(II)-carbene complex is less reactive because it does not easily transform into catalytically active Pd(0) species. To test this hypothesis we carried out a reduction of Pd(II) to Pd(0) in complexes **1** and **5** with NEt_3 in methanol at 40 °C. Complex **1** underwent reduction within a few minutes and after 1 h practically all Pd(II) had been reduced to palladium black. Under the same reaction conditions, complex **5** remained stable after 1 h, and only traces of Pd(0) appeared after 1 h of heating at 60 °C. Complex **5** was also quite stable in a dihydrogen atmosphere (1 atm); however after 1 h heating at 60 °C it decomposed partially to palladium black. The ^{1}H NMR spectra of the post-reaction solution showed the presence of an imidazolium cation with a proton at the C-2 carbon. This points to the possibility of transformation of the carbene complex **5** to a cationic one like **3**, as proposed in Scheme 6. Protonation of the C-2 carbon in complex **5** was also confirmed when **5** was treated with HCl. Also in this case, the ^{1}H NMR spectrum presented three proton signals characteristic of imidazolium cations ($\delta = 7.36$, 7.48, 9.89).

According to literature data,[23,24] reduction of **5** can lead to a bis-carbene Pd(0) complex, but until now we have not been able to confirm the formation of a bis-carbene species when **5** is reacted with NEt_3 (Scheme 6).

The Mechanism of Catalyst Deactivation in the Presence of Imidazolium Halides: The Case of Phosphane-Free Catalyst Precursors 1, 3, 4, and 5

The results of the catalytic reactions collected in Table 1 show that the anionic palladium complexes, **3** and **4**, are very good precursors of methoxycarbonylation catalysts. Therefore, the formation of complex **3** in the first stage of a reaction catalyzed by **1** in a [bmim]Cl medium does not explain the lack of activity of that system. Due to the better understanding of the nature of interactions between imidazolium halides and palladium catalyst precursors, the reactions of complexes **3** and **4** with iodobenzene and iodotoluene in the presence of NEt_3 were studied. It was expected that Pd(II) in **3** and **4** would undergo in situ reduction with NEt_3 to Pd(0), which would then interact *via* oxidative addition with aryl halide to form a new Pd(II) species containing an X–Pd(II)–Ph fragment. Instead, the formation of benzene was identified in the reaction mixture, and in the ^{13}C NMR spectrum two signals appeared, at $\delta = 167.9$ and 166.4, indicating the existence of palladium-carbene complexes. These results enabled us to propose a mecha-



Scheme 6. Transformations of a phosphane-free Pd(II) catalyst precursor under methoxycarbonylation reaction conditions in [bmim]Cl as the reaction medium.

nism (Scheme 6) in which the key stage is a reaction of the proton of the imidazolium cation with the aryl ligand leading to its elimination as benzene (or toluene). This means that an intermediate complex of Pd(II), formed as the product of oxidative addition of iodobenzene to Pd(0), is decomposed under the influence of [bmim]Cl and therefore the methoxycarbonylation reaction is inhibited. Reactions of complex **3** with iodotoluene (at **[(3)]**:[RI] = 1) in the presence of NEt_3 were repeated using 5- and 10-fold excesses of NEt_3 in relation to complex **3**. After 6 h, 10% and 17% of toluene were obtained, respectively. When complex **4** was used in reactions carried out under the same conditions, the formation of toluene was not observed; however, when $[dmiop]_2[PdCl_4]$ **3c** was used, *ca.* 4% of toluene was found.

Conclusions from the above observations are taken into account in the mechanism proposed in Scheme 6, which presents a possible pathway for the transformation of an I–Pd(II)–Ph intermediate species to a less active carbene complex with simultaneous loss of the aryl ligand. Both these processes cause a decrease in the catalytic activity of the system (Table 1).

The Mechanism of Catalyst Deactivation in the Presence of Imidazolium Halides: The Case of a Catalyst Precursor Containing a Phosphorus Ligand (2)

To elucidate the essence of the impact of the imidazolium halide on a catalytic system with the precursor **2**, we synthesized and isolated two palladium-aryl complexes with the formulas $PdI(Ph)[P(OPh)_3]_2$ (**6**) and $[PdI(Ph)P(OPh)_3)]_2$ (**7**), which may contribute to the catalytic cycle. Complex **6** is the product of oxidative addition of iodobenzene (PhI) to Pd in a monomolecular complex of the formula $Pd[P(OPh)_3]_4$:

$$Pd[P(OPh)_3]_4 + PhI \longrightarrow \underset{\mathbf{6}}{Pd(I)(Ph)[P(OPh)_3]}$$

The dimeric complex **7** was obtained in the reaction of **2** with PhI in the presence of NEt_3, i.e., under reaction conditions close to those in the real methoxycarbonylation process:

$$PdCl_2[P(OPh)_3]_2 + PhI \xrightarrow{NEt_3} \underset{\mathbf{7}}{\{Pd(I)(Ph)[P(OPh)_3]\}_2}$$

The formation of **7** was expected on the basis of our earlier studies[25] and the analogous synthesis of $[Pd(Br)(CH_2Ph)P(OPh)_3]_2$. It may be assumed that the Pd(II) complex **2** is reduced with NEt_3 in the presence of traces of water to a Pd(0) species of the composition $Pd[P(OPh)_3]_x(NEt_3)_{4-x}$. Oxidative addition of PhI to that complex leads to the formation of the dimeric complex **7**. A similar dimeric complex with a P(3-Me-$OC_6H_4)_3$ ligand instead of $P(OPh)_3$, of the formula $\{PdI(Ph)[P(3\text{-Me-}OC_6H_4)_3]\}_2$ (**7a**), was also synthesized in an analogous reaction:

$$PdCl_2[P(3\text{-Me-}OC_6H_4)_3]_2 \ (\mathbf{2a}) + PhI \xrightarrow{NEt_3} \{Pd(I)(Ph)[P(3\text{-Me-}OC_6H_4)_3]\}_2 \ (\mathbf{7a})$$

The molecular structure of **7a** was determined by X-ray crystallographic analysis (Figure 3).

Reactions of the palladium-aryl complexes **6**, **7** and **7a** with [bmim]Cl were monitored by means of ^{31}P NMR measurements. After the addition of [bmim]Cl to the solution of **6** in $CDCl_3$, besides the main signal at $\delta = 94.2$ from the starting complex **6**, two new signals appeared, at $\delta = 96.4$ and 12.1, which could be assigned to two products. One was isolated and identified by X-ray crystallography as an anionic complex of the formula $[bmim]\{Pd(I)_2Cl[P(OPh)_3]\}$ (**8**) (Figure 4), and the other one, characterized by means of ^{31}P NMR (signal at $\delta = 12.1$) and by MS (peak at $m/z = 387.9$), was identified as the phosphonium salt $[P(Ph)(OPh)_3]X$. The product of the hydrolysis of the phosphonium salt was analyzed by GC-MS and assigned as $OP(Ph)(OPh)_3$.

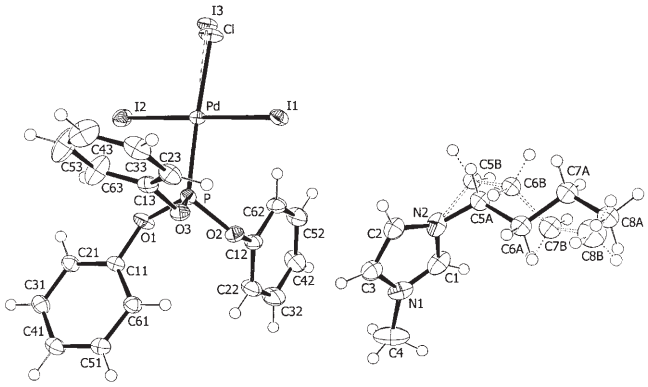


Figure 4. Molecular structure and atom numbering scheme of $[bmim]\{Pd(I)_2(Cl)[P(OPh)_3]\}$ (**8**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres with arbitrary radii. Disordered parts with lower occupancy (40%) are represented by dashed lines. Selected geometric parameters (Å, °): Pd–I1 2.624(1); Pd–I2 2.613(1); Pd–I3 2.626(2); Pd–Cl 2.351(4); Pd–P 2.211(1); P–Pd–I1 87.14(3); P–Pd -I2 93.49(3); P–Pd–I3 176.98(7); P–Pd–Cl 176.7(2); I1–Pd–I3 91.49(7); I2–Pd–I3 87.98(7); I1–Pd–Cl 89.6(2); I2–Pd–Cl 89.8(2); I1–Pd–P–O1 −175.81(9); I2–Pd–P–O3 −122.41(9); I1–Pd–P–O2 −52.70(9); Pd–P–O1–C11 −159.4(2); I1–Pd–P–O3 59.80(9); Pd–P–O2–C12 −63.9(2); I2–Pd–P–O1 1.99(9); Pd–P–O3–C13 40.3(2); I2–Pd–P–O2 125.10(9).

Interaction of **6** with [bmim]Cl according to the reaction pattern below leads to the elimination of both aryl (Ph) and $P(OPh)_3$ ligands from the palladium co-

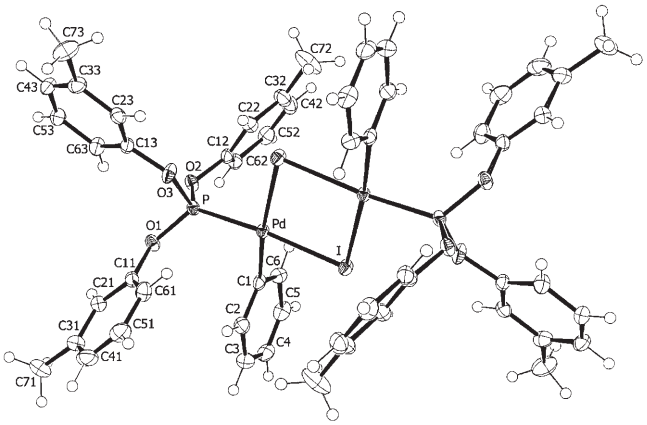


Figure 3. Molecular structure and atom numbering scheme of $\{PdI(Ph)[P(O\text{-}3\text{-}Me\text{-}C_6H_4)_3]\}_2$ (**7a**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres with arbitrary radii. Unnumbered atoms are symmetrically dependent *via* an inversion center. Selected geometric parameters (Å, °): Pd–I 2.6661(9); Pd–I^i 2.7303(6); Pd–P 2.212(1); Pd–C1 2.025(3); Pd–I–Pd^i 93.31(3); I–Pd–I^i 86.69(3); I–Pd–P 98.28(3); I–Pd–C1 88.34(8); P–Pd–C1 86.85(9); I–Pd–C1–C2 83.1(2); Pd–P–O1–C11 51.1(3); I^i–Pd–P–O1 −143.6(1); Pd–P–O2–C12 −30.0(3); I^i–Pd–P–O2 100.8(1); Pd–P–O3–C13 173.9(2); I^i–Pd–P–O3 −21.4(1) (Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*)

ordination sphere and the formation of **8** and phosphonium salt:

$$\underset{\mathbf{6}}{Pd(I)(Ph)[P(OPh)_3]_2} + [bmim]Cl \longrightarrow [bmim]\{Pd(I)_2Cl[P(OPh)_3]\}_{\mathbf{8}} + [P(Ph)(OPh)_3]X + \ldots$$

The elimination of the aryl ligand may explain the effect of methoxycarbonylation retardation caused by [bmim]Cl. Partial elimination of $P(OPh)_3$ ligands from **6** brings this system closer to the phosphane-free system discussed above.

It is worth stressing that the imidazolium cation in this case facilitates the Ph ligand transfer from the I–Pd–Ph fragment to $P(OPh)_3$. A similar reaction of phosphonium salt formation was observed during the thermal decomposition of the $[Pd(I)(Ph)(PPh_3)_2]$ complex.[26]

The dimeric complexes **7** and **7a** react with [bmim]Cl in a similar way as complex **6**, and in both reactions phosphonium salts, $[PPh(OPh)_3]X$ and $[PPh(3\text{-Me-}OC_6H_4)_3]X$ ($m/z = 430$), respectively, were obtained. Besides signals of the phosphonium salts, the ^{31}P NMR spectra of the reaction mixture showed two signals of palladium complexes with phosphite ligands: at $\delta = 96.4$ (less intensive) due to the cationic complex **8** and at $\delta = 94.1$ due to the other species. The same products were also formed in the reaction of **2** with [bmim]I, and the most reasonable formula that can be proposed for the product that shows a signal at $\delta = 94.1$ is $[bmim]\{PdI_xCl_{3-x}[P(OPh)_3]\}$ **8a**, analogous to **8**. However, we were not able to isolate that complex from this reaction mixture.

$$\underset{\mathbf{7}}{\{Pd(I)(Ph)[P(OPh)_3]\}_2} + [bmim]Cl \longrightarrow [bmim]\{Pd(I)_2Cl[P(OPh)_3]\}_{\mathbf{8}} + [bmim]\{Pd(I)_xCl_{3-x}[P(OPh)_3]\}_{\mathbf{8a}} + [P(Ph)(OPh)_3]X$$

Our efforts to obtain the cationic complexes **8** and **8a** in other reactions described below were unsuccessful. In the reaction of **2** with [bmim]Cl no new products were obtained, and in the reaction of $[bmim]_2[PdCl_4]$ with $P(OPh)_3$ only complex **2** was formed.

The reaction of the Pd-aryl phosphito complexes **6**, **7**, and **7a** with [bmim]X, leading to transfer of the aryl ligand to the phosphito one has a negative impact on the yield of methoxycarbonylation. We cannot also rule out the possibility that Pd-aryl complexes react with [bmim]Cl with the formation of benzene and carbene complexes, like it was found in the phosphane-free system. However, careful analysis of the ^1H NMR spectra did not confirm the presence of a carbene ligand when phosphite was present in the system.

Conclusions

Imidazolium halides inhibit the methoxycarbonylation reaction with all the palladium precursors used, both phosphane-free, **1**, **3**, **4**, and **5**, and containing a $P(OPh)_3$ ligand, **2**. However, when a proton at the C-2 carbon was substituted with a Me group, the inhibiting effect of [bmim]Cl was practically not observed and reaction yields were similar to those in imidazolium salts with weakly-coordinating anions (BF_4^-, PF_6^-).

In phosphane-free systems, it was indirectly shown that imidazolium halide participates in the decomposition of the aryl-palladium complex, an important intermediate in the catalytic process (Scheme 6). Aryl-palladium complexes with phosphito ligands are also decomposed by imidazolium halides, which facilitates the formation of phosphonium salts. The low catalytic activity of the carbene-palladium complex indicates that the formation of this species in a catalytic system, very probable in the presence of imidazolium halide, leads to a decrease in methoxycarbonylation reaction yield. Scheme 7 summarizes the inhibiting action of [bmim]X ionic liquids observed in the catalytic systems under study (Scheme 7).

Experimental Section

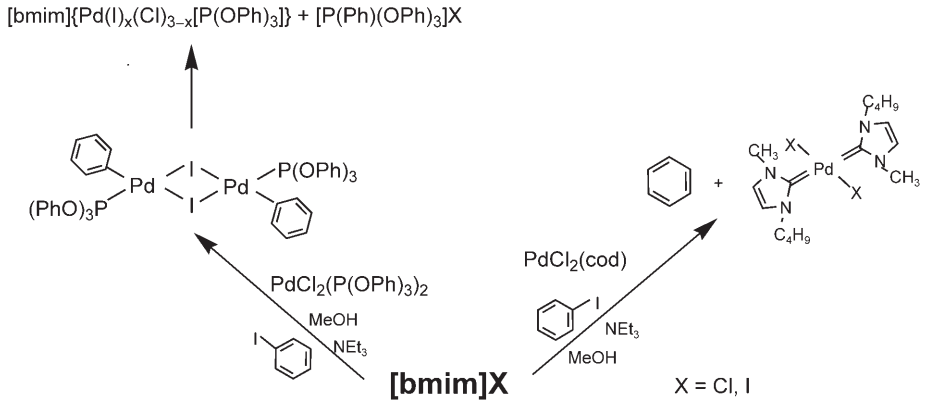
Methanol, Et_3N and diethyl ether were purified using standard procedures.[27] Iodobenzene and mesitylene (POCh, Gliwice, Poland) were used without purification. Ionic liquids were purchased from Fluka or synthesized[28] and used as obtained.

Palladium complexes **1**[29] and **2**[30] were obtained according to methods described in the literature.

$[bmim]_2[PdCl_4]$ (3)

Method 1:[18] $PdCl_2$ (0.5 g, 0.003 mol) and 1.0 g (0.006 mol) [bmim]Cl were refluxed 24 h at 110 °C in CH_3CN and **3** precipitated when solution was cooled down; yield: 1.01 g (67 %).

Method 2: $PdCl_2$(cod) (0.1 g, 0.00035 mol) and 0.10 g (0.0007 mol) [bmim]CI were dissolved in 4.5 mL of warm CH_3CN and stirred for *ca.* 15 min, during which time the color of the solution changed from yellow to red-brown.



Scheme 7. Deactivation mechanism of palladium catalyst precursors containing phosphorus ligand (left part) and phosphorus-free (right part) in imidazolium halide, [bmim]X, as methoxycarbonylation reaction medium.

The solution was cooled to room temperature and a solvent was removed under reduced pressure. Crystallization of the resultant powder from CH_3CN/toluene solution afforded **3** as dark red crystals; yield: 1.7 g, (90 %); anal. calcd. for $C_{16}H_{30}Cl_4N_4Pd$: C 36.5, H 5.7, N 10.6 %; found: C 36.6, H 5.6, N 10.5 %; ^{1}H NMR (CD_3CN): δ = 8.81 (s, 1 H, -N-CH-N-), 7.36; 7.39 (s, 2 H, -CH=CH-), 4.17 (t, 2 H, N-CH_2-, $J_{H,H}$ = 7.27 Hz), 3.85 (s, 3 H, N-CH_3), 1.80 (qi, 2 H, -CH_2-, $J_{H,H}$ = 7.47 Hz), 1.31 (sx, 2 H, -CH_2-, $J_{H,H}$ = 7.27 Hz), 0.92 (t, 3 H, -CH_3);^{13}C NMR (CD_3CN): δ = 137.5 (d, -N-CH-N-, J = 55.8 Hz), 124.5, 122.0 (d, -CH=CH-, J = 21.9 Hz), 50.1 (t, N-CH_3, J = 21.66 Hz), 39.9 (s, N-CH_2-), 32.6, 19.9 (s, -CH_2-), 13.6 (d, -CH_3, J = 18.21 Hz); UV-Vis (CD_3CN): λ = 220, 250 nm; IR (KBr): ν = 3133, 3098, 3064 (= C-H), 2935, 1462, 1440, 1097, 864, 764 (C-H), 1632 (C=C), 1561 cm^{-1} (C=N).

[bmim]$_2$[PdBr$_4$] (3a)

The complex was obtained according to the procedure given for **3**, using 0.38 g (0.0007 mol) of $PdBr_2$(cod) and 0.8 g (0.0036 mol) of [bmim]Br; yield: 0.47 g, (95 %); anal. calcd. for $C_{16}H_{30}Br_4N_4Pd$: C 27.3, H 4.3, N 7.9 %; found: C 27.4, H 4.1, N 8.1 %; ^{1}H NMR (CD_3CN): δ = 9.1 (s, 1 H, -*N*-CH-*N*-), 7.43, 7.38 (s, 2 H, -CH=CH-), 4.23(t, 2 H, N-CH_2-, $J_{H,H}$ = 7.27 Hz), 3.9 (s, 3 H, N-CH_3), 1.9 (qi, 2 H, -CH_2-, $J_{H,H}$ = 7.47 Hz), 1.38 (sx, 2 H, -CH_2-, $J_{H,H}$ = 7.27 Hz), 0.93 (t, 3 H, -CH_3); ^{13}C NMR (CD_3CN): δ = 137.5 (d, -*N*-CH-*N*-, J = 55.8 Hz), 124.5, 122.0 (d, -CH=CH-, J = 21.9 Hz), 50.1 (t, N-CH_3, J = 21.66 Hz), 39.9 (N-CH_2-), 32.6, 19.9 (s, -CH_2-), 13.6 (d, -CH_3, J = 18.21 Hz); UV-VIS (CD_3CN): λ = 222, 272 nm; IR (KBr): ν = 3098, 3064 (= C-H), 2940, 1464, 1362, 1167, 860, 768 (C-H), 1640 (C=C), 1560 cm^{-1} (C=N).

[dmiop]$_2$[PdCl$_4$] (3c)

The complex was obtained according to the procedure given for **3** using 0.17 g (0.0006 mol) of $PdCl_2$(cod) and 0.2 g (0.0012 mol) of [dmiop]Cl; yield: 0.47 g (95 %); anal. calcd. for $C_{18}H_{34}Cl_4N_4Pd$: C 38.9, H 6.0, N 10.1 %; found: C 35.8, H 5.4, N 11.2 %; ^{1}H NMR (CD_3CN): δ = 7.5, 7.4 (d, 2 H, -CH=CH-, $J_{H,H}$ = 2.09 Hz), 5.5 (s, 2 H, N-CH_2-O-), 3.8 (s, 3 H, N-CH_3), 3.4 (t, 2 H, -CH_2-O-, $J_{H,H}$ = 6.69 Hz), 2.6 (s, 3 H, = C-CH_3), 1.5 (sx, 2 H, -CH_2-, $J_{H,H}$ = 7.32 Hz), 0.8 (t, 3 H, -CH_3); ^{13}C NMR($CDCl_3$): δ = 146.5 (s, -*N*-C-*N*-), 123.3, 122 (d, -CH=CH-, J = 16.28 Hz), 118 (s, -*N*-CH_3), 78.9 (t, -*N*-CH_2-O-, J = 9.15 Hz), 71.9 (s, -*N*-CH_3), 35.9 (t, -O-*C*H_2-CH_2-, J = 6.10 Hz), 23.1 (s, -O-CH_2-*C*H_2-), 10.6 (s, -CH_2-*C*H_3).

[bmpy]$_2$[PdCl$_4$] (4)

The complex was obtained according to the procedure given for **3** using 0.042 g (0.00015 mol) of $PdCl_2$(cod) and 0.072 g (0.0003 mol) of [bmpy]Cl; yield: 0.08 g (97 %); anal. calcd. for $C_{20}H_{32}Cl_4N_2Pd$: C 36.5, H 5.7, N 10.6 %; found: C 36.6, H 5.6, N 10.5 %; ^{1}H NMR (CD_3CN): δ = 8.74, 7.86 (d, 2 H, Ph-H, $J_{H,H}$ = 6.64 Hz), 4.55 (t, 2 H, N-CH_2-, $J_{H,H}$ = 7.47 Hz), 2.60 (s, 3 H, N-CH_3), 1.93 (qi, 2 H, -CH_2-, $J_{H,H}$ = 7.68 Hz), 1.33 (sx, 2 H, -CH_2-, $J_{H,H}$ = 7.47 Hz), 0.92 (t, 3 H, -CH_3); ^{13}C NMR (CD_3CN); δ = 160.5 (s, CH_3-*C*-CH), 144.5 (d, -*N*-*C*H=CH-, J = 83.4 Hz), 129.6 (d, -*N*-CH=*C*H-, J = 32.1 Hz), 61.5 (s, N-CH_2-), 33.8 (s, -C-*C*H_3), 22.3, 19.9 (s, -CH_2-), 13.8 (s, -CH_3); UV-VIS (CD_3CN): λ = 226, 292 nm; IR (KBr): ν = 3137, 3104, 3072 (C-H), 2973, 2960, 2940, 1466, 1447, 873, 768 ,628 (C-H), 1637 (C=C), 1564 cm^{-1} (C=N).

Pd(bmimy)$_2$Br$_2$ (5)

The complex was obtained according to modified procedure reported in ref.[17] To the solution of 0.051 g of $Pd(OAc)_2$ in 10 mL of THF 0.106 g of [bmim]Br were added and the mixture was stirred at 70 °C for 3 h. During that time the color changed from red to yellow and two phases were formed. The upper yellow phase containing **5** was separated and THF was removed under reduced pressure to give yellow product which was washed with hexane (9 mL), water (2 × 10 mL), diethyl ether (5 mL) and dried; yield: 54 %; anal. calcd. for $C_{16}H_{28}Br_2N_4Pd$: C 35.4, H 5.2, N 10.3 %; found: C 34.1, H 5.0, N 10.25 %; ^{1}H NMR ($CDCl_3$): δ = 6.79 (s, 4 H, -CH=CH-), 4.41 (m, 4 H, N-CH_2-), 4.06 (s, 6 H, N-CH_3), 2.03 (m, 4 H, -CH_2-), 1.43 (m, 4 H, -CH_2-), 0.98 (t, 6 H, -CH_3); ^{13}C NMR ($CDCl_3$): δ = 169.0 (-*N*-CH-*N*-), 121.9, 120.8 (-CH=CH-), 50.7 (N-CH_3), 37.9 (N-CH_2-), 32.8, 20.1 (-CH_2-), 13.8 (-CH_3).

PdI(Ph)[P(OPh)$_3$]$_2$ (6)

To 0.13 g of Pd[P(OPh)$_3$]$_4$[25] in 1 mL of benzene 0.1 mL of PhI was added and the resultant red-brown solution was stirred for 1 h. Next, the solution was condensed in vacuum and after addition of 1 mK of ethanol product **6** precipitated as an orange powder. Anal. calcd. for $C_{42}H_{35}O_6P_2IPd$: C 54.2, H 3.8%; found: C 52.8, H 3.6%; ^{31}P NMR ($CDCl_3$): $\delta =$ 94.2.

{PdI(Ph)[P(OPh)$_3$]}$_2$ (7)

To the suspension of 0.114 g of PdCl$_2$[P(OPh)$_3$]$_2$[30] in 2 mL of benzene 0.15 mL of NEt_3 were added and the resultant mixture was stirred for 10 min under dinitrogen. Next, 0.15 mL of PhI were added. After 30 min 1 mL of ethanol was added to precipitate compound **7**. Anal. calcd. for $C_{24}H_{19}O_3PIPd$: C 46.5, H 3.1%; found: C 46.2, H 3.0%; ^{31}P NMR($CDCl_3$): $\delta = 89.1$.

{PdI(Ph)[P(O-3-Me-C$_6$H$_4$)$_3$]}$_2$ (7a)

This complex was obtained in the similar way as **7** using 0.14 g of PdCl$_2$[P(O-3-Me-C$_6$H$_4$)$_3$]$_2$[30] and 0.15 mL of PhI. The orange crystals of **7a** were isolated next day; yield: 56%. One crystal suitable for X-ray examination was selected. Anal. calcd. for $C_{27}H_{26}O_3PIPd$: C 48.9, H 4.0%; found: C 49.0, H 3.8%; ^{31}P NMR ($CDCl_3$): $\delta = 88.32$.

X-Ray Diffraction

CCDC-602492 (complex **8**), CCDC-602493 (complex **7**), CCDC-602494 (complex **3b**), CCDC-602495 (complex **3a**) contain the supplementary crystallographic data for these compounds. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/deposit.

Measurements

^{1}H and ^{31}P NMR spectra were recorded on Bruker 300 and Bruker 500 spectrometers. For ^{31}P NMR at 300 MHz 85% H_3PO_4 was used as an external standard and at 500 MHz methylenediphosphonic acid was used as an external standard. FT-IR spectra were measured on Nicolet Impact 400 spectrometer. GC-MS an GC analyses were made on Hewlett Packard 8452 A instrument.

Catalytic Reactions

The reactions were carried out in a 130 mL thermostatted steel autoclave with magnetic stirring. Reagents: PhI 1.0 mL ($8.93\cdot10^{-3}$ mol), NEt_3 3.0 cm^3 ($2.15\cdot10^{-2}$ mol), mesitylene – internal standard, 0.64 cm^3 ($4.6\cdot10^{-3}$ mol), methanol 1.0 mL ($2.4\cdot10^{-2}$ mol), and ionic liquid (1.5 g) and catalyst ($5\cdot10^{-5}$ mol), were introduced to the autoclave in an N_2 atmosphere. Next, the N_2 atmosphere was replaced by CO. The reaction was carried out at 90 °C for 3 h. Afterwards, the autoclave was cooled down and organic products were separated by extraction with diethyl ether (3 times with 3 mL) and analyzed by GC-MS (Hewlett Packard 8452 A).

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