



# Diethanolamine and N,N-diethylethanolamine ionic liquids as precatalyst-precursors and reaction media in green Heck reaction protocol

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## ABSTRACT

It was found that Heck reaction with PdCl<sub>2</sub> in diethanolamine and N,N-diethylethanolamine ionic liquids (ILs) is more efficient than analogous reactions performed in classical organic solvents. The used ILs facilitate solubility of the Pd(II) precatalysts, increase catalyst stability during the reaction, and function as reaction media, bases, precatalyst-precursors, good coordinating ligands, and mobile support for active Pd species. Thus, Heck reaction occurs without additional solvents, ligands and bases, that makes experimental procedure much simpler. Our DFT investigation provides mechanistic insight into the formation of the *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex that acts as a precatalyst.

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## 1. Introduction

The palladium-catalyzed arylation of olefines, known as Heck reaction, is one of the most important methods for carbon–carbon bond formation in organic synthesis [1–6]. In the last decade phosphine-free Pd complexes have been introduced as a less complicated and environmentally more desirable alternative to the original Pd–phosphine catalysts [1]. In addition, the applications of ionic liquids as very useful substitutes for hazardous and volatile polluting organic solvents have been put forward [7–17]. Unlike classical salts, whose melting points are not below 800 °C, most of ionic liquids (ILs), which also contain positively and negatively charged ions, are liquids at room temperature. Room temperature ionic liquid (RTIL), molten salt, liquid organic salt, and fused salt—all these terms have been used to describe new class of magical chemicals accepted from chemical industry and academia [18]. As solvents, ILs show several advantages which make them more attractive and ecologically acceptable [19–26]: (1) They are good solvents for a wide range of organic, inorganic and organometallic compounds, (2) They are polar, (3) ILs are immiscible with a number of organic solvents and provide a polar nonaqueous alternative for biphasic catalytic systems, implying that the molecular catalyst is soluble in only one phase, whereas the substrates/products remain in the other, (4) Most of ILs are liquid up to 200 °C, (5) ILs are thermally stable (are not explosive and flammable), and

do not evaporate since they have very low vapour pressures. All these features significantly distinguish ILs from classical volatile and toxic organic solvents, and therefore, ILs are named green solvents.

Ionic liquid as reaction medium for the palladium-catalyzed Heck reaction was for the first-time described in 1996 [27]. But, the process of preparing effective non-phosphine ligands and recyclable catalysts from ordinary ionic liquids was very complex, because of their weak coordinating abilities [28–34]. Recently, some efforts have been made in order to prepare low cost multi-functional ionic liquids that could serve as green solvents, coordinating ligands, as well as recyclable and mobile support for palladium catalyst systems. For this reasons, researchers started to use ionic liquids with additional functional groups in cationic and/or anionic part of ionic liquid molecules. Functional groups that can complex palladium, such as amine, amide, nitrile, ether, alcohol, urea or thiourea [29,35–38] have been introduced into the ILs. Such ionic liquids have been found to demonstrate high solvation capabilities, and low viscosity. These properties made them useful in a broader range of applications.

Here, we wish to report the use of diethanolamine (DEA) and N,N-diethylethanolamine (DEAE) ionic liquids, which act as green solvents, precatalyst-precursors, and mobile support for active Pd species in phosphine-free Heck reaction protocol. In addition, the optimization of the ILs structures, as well as investigation of a possible mechanism for in situ formation of Pd precatalyst, was performed using density functional theory.

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## 2. Experimental

### 2.1. Preparation of ionic liquids

Diethanolammonium acetate [DEA][HAc] (**1**), N,N-diethylethanolammonium acetate [DEAE][HAc] (**2**), diethanolammonium chloride [HDEA][Cl] (**3**), and N,N-diethylethanolammonium chloride [HDEAE][Cl] (**4**) were prepared by dropping the stoichiometric amount of acetic acid or hydrochloric acid to the dichloromethane solution of corresponding amino alcohol (diethanolamine or N,N-diethylethanolamine). The reaction mixture was stirred during 2 h at room temperature. After completion of the reaction, the resulting solution was washed with ethyl acetate ( $2 \times 5 \text{ cm}^3$ ) and ethyl ether ( $2 \times 5 \text{ cm}^3$ ). The organic solvents were evaporated under reduced pressure. The residue was dried *in vacuo* at  $50^\circ\text{C}$  for 4 h to generate the corresponding product. The prepared ionic liquids are colorless viscous liquids.

Spectral characterization of the ionic liquids:

IR (film): [DEA][HAc] (**1**):  $\nu = 3415, 1620, 1560, 1410, 1070, 620 \text{ cm}^{-1}$ ; [DEAE][HAc] (**2**):  $\nu = 3243, 1570, 1400, 1050, 790 \text{ cm}^{-1}$ ; [HDEA][Cl] (**3**):  $\nu = 3344, 1622, 1448, 1063, 939 \text{ cm}^{-1}$ ; [HDEAE][Cl] (**4**):  $\nu = 3361, 1635, 1471, 1076, 798 \text{ cm}^{-1}$ .

$^1\text{H}$  NMR spectrum (200 MHz,  $\text{CDCl}_3$ ): [DEA][HAc] (**1**):  $\delta = 1.962$  (3H,  $\text{CH}_3\text{-CO}$ , s,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.101$  (4H,  $-\text{CH}_2\text{-NH}_2$ , t,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.869$  (4H,  $-\text{CH}_2\text{-OH}$ , t,  $J = 5.0 \text{ Hz}$ ) ppm.

[DEAE][HAc] (**2**):  $\delta = 1.279$  (6H,  $\text{CH}_3\text{-CH}_2\text{-}$ , t,  $J = 5.0 \text{ Hz}$ ) ppm;  $1.989$  (3H,  $\text{CH}_3\text{-CO}$ , s,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.032$  (4H,  $-\text{CH}_2\text{-NH}$ , q,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.105$  (2H,  $-\text{NH-CH}_2$ , t,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.865$  (2H,  $-\text{CH}_2\text{-OH}$ , t,  $J = 5.0 \text{ Hz}$ ) ppm.

[HDEA][Cl] (**3**):  $\delta = 3.266$  (4H,  $-\text{CH}_2\text{-NH}$ , q,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.891$  (2H,  $-\text{NH-CH}_2$ , t,  $J = 5.0 \text{ Hz}$ ) ppm.

[HDEAE][Cl] (**4**):  $\delta = 1.445$  (6H,  $\text{CH}_3\text{-CH}_2\text{-}$ , t,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.22$  (4H,  $-\text{CH}_2\text{-NH}$ , q,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.31$  (2H,  $-\text{NH-CH}_2$ , t,  $J = 5.0 \text{ Hz}$ ) ppm;  $3.77$  (2H,  $-\text{CH}_2\text{-OH}$ , t,  $J = 5.0 \text{ Hz}$ ) ppm.

### 2.2. Preparation of *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] in ionic liquid

The *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex was synthesized starting from PdCl<sub>2</sub> and **1** in molar ratio of 1:2. In the course of 3 h, the reaction of 1 mmol of PdCl<sub>2</sub> in 10 cm<sup>3</sup> of water with 2 mmol of **1**, at  $50\text{--}60^\circ\text{C}$ , afforded an orange solution which was left at room temperature for 2 days. The precipitated yellow-orange crystals were filtered off, washed with ethanol and air-dried. The elemental analyses and  $^1\text{H}$  NMR spectrum of the investigated compound confirmed that its structure corresponds to that of *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex. Calculated for *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] = C<sub>8</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Pd (FW = 387.58): C, 24.77; N, 7.22; H, 5.68%; found: C, 24.83; N, 7.30; H, 5.75%. The monitoring of the Heck reaction in ionic liquid **1** showed that the same complex was formed a few minutes after the heating the reaction mixture.

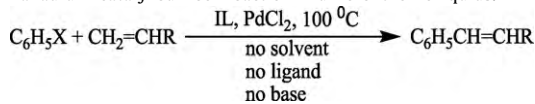
### 2.3. Preparation of [HDEA]<sub>2</sub>[PdCl<sub>4</sub>] in ionic liquid

The [HDEA]<sub>2</sub>[PdCl<sub>4</sub>] complex was synthesized in a similar way, starting from PdCl<sub>2</sub> and **3** in molar ratio of 1:2. In the course of 3 h, the reaction of 1 mmol of PdCl<sub>2</sub> dissolved in 15 cm<sup>3</sup> of water with 2 mmol of **3**, at  $50\text{--}60^\circ\text{C}$ , afforded an orange-brown solution which was left at room temperature for 4 days. The precipitated brown crystals were filtered off, washed with ethanol, air-dried and showed a melting point of  $115\text{--}116^\circ\text{C}$ . Yield 0.446 g (97%). Calculated for [HDEA]<sub>2</sub>[PdCl<sub>4</sub>] = C<sub>8</sub>H<sub>22</sub>O<sub>4</sub>N<sub>2</sub>Cl<sub>4</sub>Pd (FW = 460.42): C, 20.95; N, 6.09; H, 5.21%; found: C, 21.01; N, 6.13; H, 5.18%.

Spectral characterization of the complex [HDEA]<sub>2</sub>[PdCl<sub>4</sub>]:  $^1\text{H}$  NMR spectrum (200 MHz, D<sub>2</sub>O):  $\delta =$ , t,  $3.24$  (4H,  $-\text{CH}_2\text{-NH}$ ,  $J = 5.2 \text{ Hz}$ ),  $3.86$  (4H,  $-\text{CH}_2\text{-OH}$ , t,  $J = 5.2 \text{ Hz}$ ) ppm; IR (KBr):  $\nu = 323, 698, 958, 1065, 1088, 1405, 1574, 2874, 3299, 3343 \text{ cm}^{-1}$ .

**Table 1**

Palladium-catalyzed Heck reaction in different ionic liquids.



Entry	C <sub>6</sub> H <sub>5</sub> X	R	Ionic liquid	Time (h)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> I	COOCH <sub>3</sub>	<b>1</b>	12	96
2	C <sub>6</sub> H <sub>5</sub> Br	COOCH <sub>3</sub>	<b>1</b>	16	94
3	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>2</sub> H <sub>5</sub>	<b>1</b>	12	95
4	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>2</sub> H <sub>5</sub>	<b>1</b>	16	93
5	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>4</sub> H <sub>9</sub>	<b>1</b>	12	96
6	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>4</sub> H <sub>9</sub>	<b>1</b>	17	91
7	C <sub>6</sub> H <sub>5</sub> I	COOCH <sub>3</sub>	<b>2</b>	13	95
8	C <sub>6</sub> H <sub>5</sub> Br	COOCH <sub>3</sub>	<b>2</b>	17	92
9	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>2</sub> H <sub>5</sub>	<b>2</b>	13	95
10	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>2</sub> H <sub>5</sub>	<b>2</b>	17	91
11	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>4</sub> H <sub>9</sub>	<b>2</b>	13	95
12	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>4</sub> H <sub>9</sub>	<b>2</b>	18	90
13	C <sub>6</sub> H <sub>5</sub> I	COOCH <sub>3</sub>	<b>3</b>	12	90
14	C <sub>6</sub> H <sub>5</sub> Br	COOCH <sub>3</sub>	<b>3</b>	16	88
15	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>2</sub> H <sub>5</sub>	<b>3</b>	12	90
16	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>2</sub> H <sub>5</sub>	<b>3</b>	16	87
17	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>4</sub> H <sub>9</sub>	<b>3</b>	12	90
18	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>4</sub> H <sub>9</sub>	<b>3</b>	17	86
19	C <sub>6</sub> H <sub>5</sub> I	COOCH <sub>3</sub>	<b>4</b>	13	89
20	C <sub>6</sub> H <sub>5</sub> Br	COOCH <sub>3</sub>	<b>4</b>	17	85
21	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>2</sub> H <sub>5</sub>	<b>4</b>	13	88
22	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>2</sub> H <sub>5</sub>	<b>4</b>	17	87
23	C <sub>6</sub> H <sub>5</sub> I	COOC <sub>4</sub> H <sub>9</sub>	<b>4</b>	13	88
24	C <sub>6</sub> H <sub>5</sub> Br	COOC <sub>4</sub> H <sub>9</sub>	<b>4</b>	18	86

<sup>a</sup> Isolated yield; only the *trans* product was detected by  $^1\text{H}$  NMR.

### 2.4. General procedure for green Heck reaction

Corresponding aryl halide (1 mmol), olefin (1 mmol), ionic liquid (1.5 cm<sup>3</sup>), and PdCl<sub>2</sub> (1.5 mol.%) (Table 1) were placed in 25-cm<sup>3</sup> flask, and stirred at  $100^\circ\text{C}$  for 12–18 h. The mixture was cooled to room temperature. The products (*trans*-methyl cinnamate, *trans*-ethyl cinnamate, and *trans*-butyl cinnamate) were separated from the reaction mixture by extraction and decantation with diethyl ether/hexane (5:1). The combined organic layer was washed with water and brine, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The reactions were monitored and analyzed with GC chromatography and  $^1\text{H}$  NMR spectroscopy. Reaction products were purified by column chromatography (silica gel; ethylacetate:dichloromethane = 1:1). The known coupling products were analyzed and characterized on the basis of their spectroscopic data and by comparing these data to the spectra of the commercially available compounds. The  $^1\text{H}$  NMR spectra of these products are presented in Supplementary Data.

### 2.5. Recycling experiment after Heck reaction

After the extraction of the product of the first-time reaction, the solvent residue of the Heck reaction (ionic liquid + Pd catalyst) was washed with C<sub>2</sub>H<sub>5</sub>OH (3 cm<sup>3</sup>) and Et<sub>2</sub>O (3 × 3 cm<sup>3</sup>), and dried under reduced pressure. After this treatment, catalyst–ionic liquid system can be reused directly without further purification.

### 2.6. Computational method

The geometrical parameters of all stationary points and transition states were optimized in vacuum, using Gaussian03 [39] with the B3LYP hybrid functional [40–42]. The triple split valence basis set 6-311G(d,p) was used for C, H, O, N, and Cl, whereas LANL2DZ + ECP [43] was employed for the Pd centre. All calculated structures were confirmed to be local minima (all positive eigenvalues) for ground state structures, or first-order saddle points (one

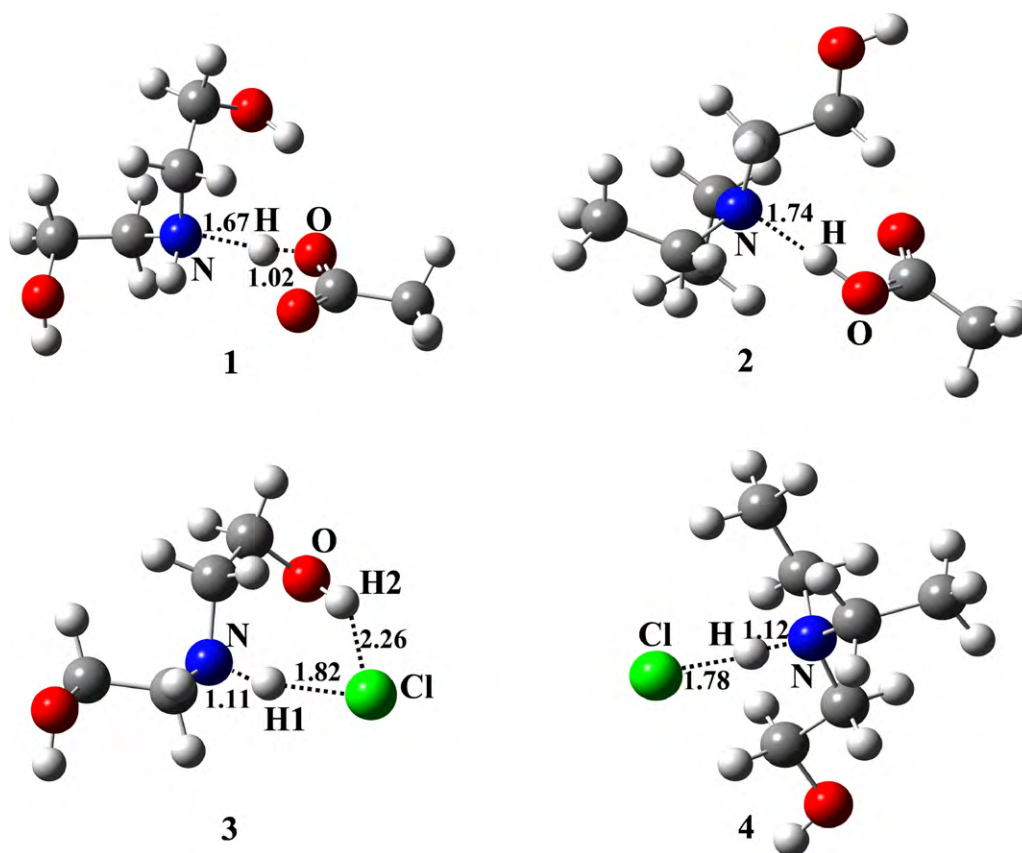
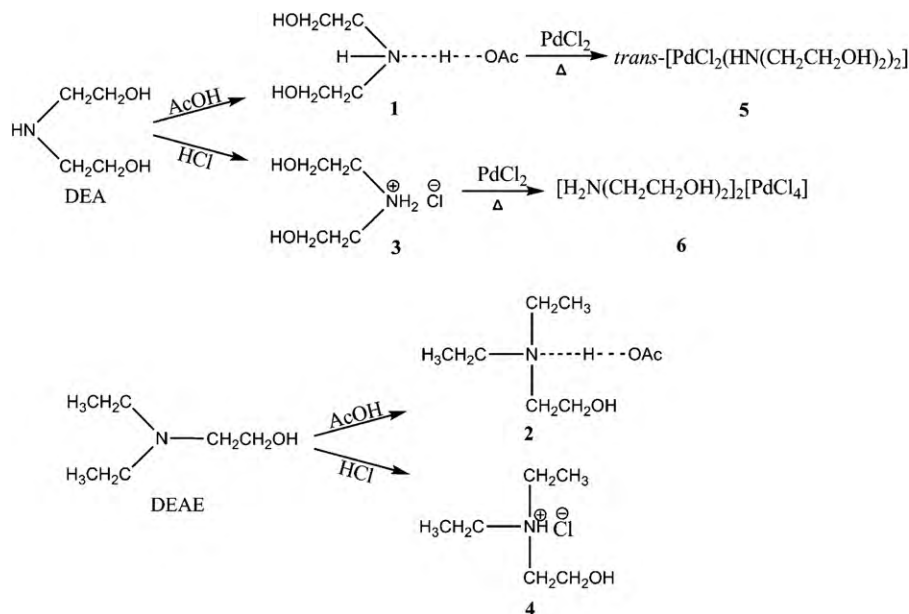


Fig. 1. Optimized geometries of ILs under investigation, with selected bond distances.

negative eigenvalue) for transition state structures, by frequency calculations. The intrinsic reaction coordinates (IRCs), from the transition states down to the two lower energy structures, were traced using the IRC routine in Gaussian in order to verify that each saddle point is linked with two putative minima. The natural bond orbital analysis (Gaussian NBO version) was performed for all structures.

### 3. Results and discussion

In our previous study, the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>]) has been used as a precatalyst in Heck reaction [44]. The reactions between different olefins and aryl halides with this complex have been carried out in the presence of strong base NaOEt, in CH<sub>3</sub>CN as solvent, and in



Scheme 1. Preparation of ionic liquids [DEA][HAc] (1), [DEAE][HAc] (2), [HDEA][Cl] (3), [HDEAE][Cl] (4), *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex, and [HDEA]<sub>2</sub>[PdCl<sub>4</sub>].

the presence of diethanolamine (DEA) as a weak base and solvent. The mechanism of the preactivation reaction, i.e., the formation of the Pd(0) complex, was examined using density functional theory [44,45]. Our results showed that the yield of the cross-coupling products was lower for the reactions performed with NaOEt. The reason for this is a partial decomposition of active palladium species, which was demonstrated by a small amount of palladium black precipitate remained in the reaction flask. In the reaction with DEA, a polymerization reaction was observed as a competitive reaction. In order to advance this protocol, as well as to avoid the use of toxic CH<sub>3</sub>CN and mentioned undesirable side reactions, we decided to employ DEA and DEAE ionic liquids **1–4** in Heck reaction. We assumed that using the investigated ionic liquids, all essential requirements for the Heck reaction (including solvent, base, ligand for formation of Pd precatalyst, and mobile support for Pd catalyst) would be accomplished.

There are many studies on Heck reaction performed in the presence of palladium bulky phosphine complexes in ionic liquids (for example [27,46–49]). In comparison to these reactions, phosphine-free Heck reaction in ionic liquids has shown numerous advantages [16,50–52]. Therefore, the phosphine-free Heck reaction in the ionic liquids and in the presence of PdCl<sub>2</sub> was studied herein. The structures of the investigated ILs were optimized using density functional theory (Fig. 1). Our investigation shows that there are no distinguished cations and anions in **1** and **2**, but owing to hydrogen bonding, molecular association is present. In addition, these molecules are polar (nitrogen and oxygen bear partial negative charge, whereas hydrogen is partially positively charged). These properties are characteristic for molecular liquids, and generally for ionic liquids. On the other hand, the NBO analysis reveals the N–H1 bond in **3** and N–H bond in **4**, implying that **3** and **4** consist of chloride anion and diethanolammonium and N,N-diethylethanammonium cations, respectively. This can be explained with the fact that chloride anion is weaker, whereas acetate anion is stronger base than DEA and DEAE. Bond distances reveal strong hydrogen bonding in all ILs. The NBO analysis is in accord with this finding. Namely, there is strong donation of density from the p orbitals on N to the σ\* antibonding O–H1 orbital of **1**, and O–H orbital of **2**. Similarly, the p orbitals on Cl delocalize into the σ\* antibonding N–H1 orbital of **3**, and N–H orbital of **4**.

The ILs **1–4** were prepared starting from amino alcohols DEA and DEAE (Scheme 1). When PdCl<sub>2</sub> was heated in ionic liquid **1** ([DEA][HAc]) at 55 °C an orange solution was obtained, from which, after 2 days, a yellow-orange substance crystallized. The NMR and IR spectra, as well as elemental analysis, showed that the structure of the obtained ionic liquid-coordinated complex corresponds to that of (*trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>]) complex (**5** in Scheme 1). The crystal structure of *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>], as well as selected bond distances, bond angles and hydrogen bonds, were provided in [53], whereas its electronic structure was presented in [45]. However, when the reaction of PdCl<sub>2</sub> was performed with ionic liquid **3** ([HDEA][Cl]), the [HDEA]<sub>2</sub>[PdCl<sub>4</sub>] complex (**6**) was obtained. Despite the potential of the diethanolammonium cation of **3** to coordinate to palladium, in this case palladium(II) reacts exclusively with the chloride counteranion yielding complex **6**.

Our finding that ionic liquids **1** and **3** coordinated well with PdCl<sub>2</sub> motivated us to investigate the efficiency of such ionic liquid–palladium catalytic system in green Heck reaction protocol. Heck reaction was also performed with PdCl<sub>2</sub> in ILs **2–4**. All these reactions were carried out in the absence of any additives. Usually, some bases (CH<sub>3</sub>ONa, CH<sub>3</sub>COONa, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Et<sub>3</sub>N, etc.) and salt additives (phosphonium or ammonium chlorides and bromides) have been used in Heck reaction with or without phosphines [54–57] in order to stabilize Pd<sup>0</sup> halide species and accelerate the olefination reaction of aryl halides. In our case ionic liquids **1–4** are themselves bases and ammonium salts, and we

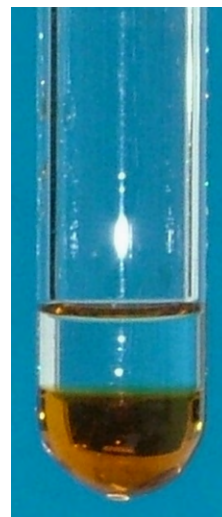


Fig. 2. Biphasic mixture of IL–Pd catalyst system (bottom layer) and diethyl ether/hexane (top layer).

believed that they could act as stabilizing and immobilizing agents for palladium active species. Some results with ionic liquids having aliphatic tertiary amine pendants [58,59], substantiated our assumption because DEAE is also a tertiary amine.

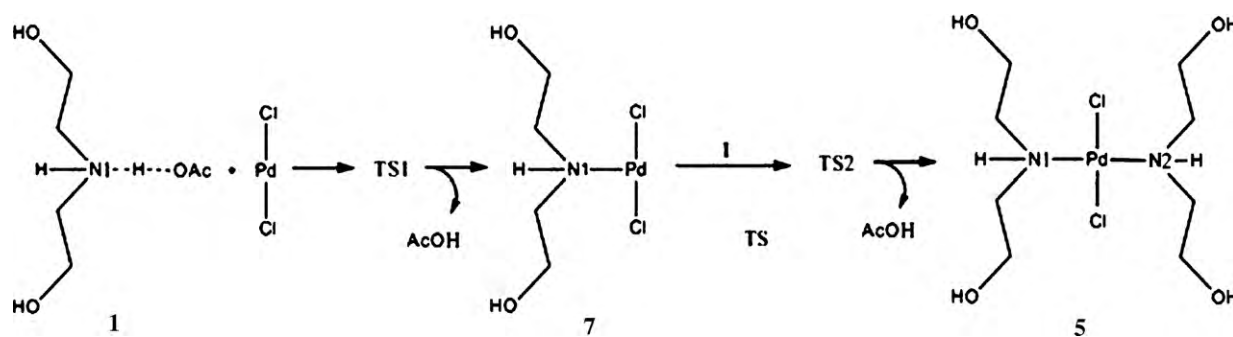
During the course of the improvement of reaction protocol, a reaction temperature of 100 °C and 1.5 mol.% of PdCl<sub>2</sub> in ILs **1–4** were found to be optimal. Iodobenzene and bromobenzene were used in the investigated reactions. A 100% conversion of the aryl halide was reached with 99% selectivity to *trans* cross-coupling products. With all used ionic liquids, a homogeneous yellow-orange solution was formed during the reaction. The desired products were then purified by column chromatography and isolated. The yield of products obtained in Heck reaction performed in acetate ionic liquids **1** and **2** was excellent (>94%), while the yield of the products obtained in chloride liquids **3** and **4** was lower (Table 1). We assume that precatalyst **6**, obtained in situ during the reaction, less readily converts to the active catalyst, since it is coordinatively saturated by chloride ligands.

Our results indicate that this Heck protocol is advanced in comparison to the previous procedures performed in classical organic reaction media [44,60]. At first, the used ILs facilitate solubility of PdCl<sub>2</sub> and appropriate Pd(II) precatalyst. In addition, this catalytic system remains unchanged during the reaction (no palladium black). It seems that the nature of the used ILs increases the stability of the palladium catalyst extending its lifetime. IL–Pd catalytic system can be easily recycled, also, and products separated via simple extraction (diethyl ether/hexane) and decantation from the reaction mixture. Fig. 2 demonstrates the biphasic mixture of IL–Pd catalyst system (bottom layer), and diethyl ether/hexane (top layer), where the solubility of the yellow-orange palladium catalyst in the ionic liquid is clearly visible.

After extraction of the products from the reaction mixture, the ionic liquid–palladium catalyst system was recovered and fresh reactants were charged. IL–Pd catalytic system was recycled three times without significant loss in activity (the yields of coupling products were up to 5% lower).

Although it is clear that ionic liquids are useful for the green Heck protocol, and other homogeneous catalyses, to make them more effective, very little is known about mechanistic details of these reactions, and their role in the precatalyst formation. For this reason, we investigated the reaction between diethanolammonium acetate as an ionic liquid and palladium(II) chloride using density functional theory.





**Scheme 2.** Mechanism of formation of the precatalyst  $trans$ -[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex from diethanolammonium acetate (**1**) and PdCl<sub>2</sub>.

**Table 2**

Selected bond distances (in Å) for the participants in the reaction between diethanolammonium acetate and palladium(II) chloride.

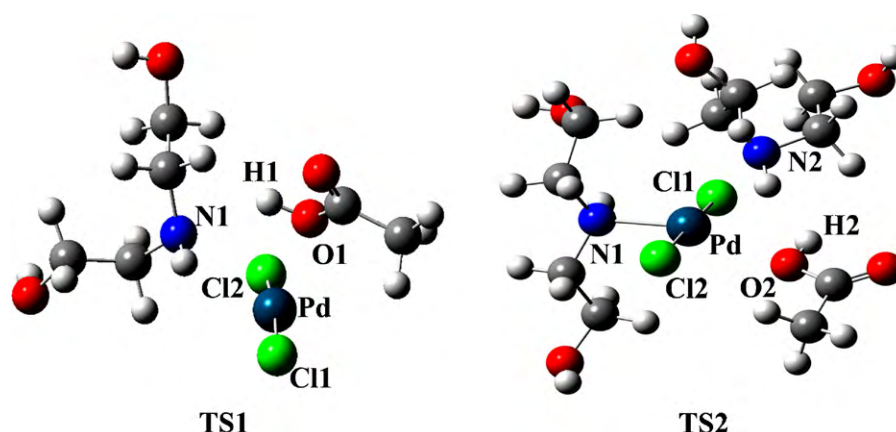
PdCl <sub>2</sub>	
Pd–Cl	2.32
TS1	
Pd–N1	2.92
Pd–Cl1	2.32
Pd–Cl2	2.34
N1–H1	2.16
O1–H1	0.98
<b>7</b>	
Pd–N1	2.06
Pd–Cl1	2.33
Pd–Cl2	2.35
TS2	
Pd–N1	2.09
Pd–Cl1	2.38
Pd–Cl2	2.36
Pd–N2	2.91
N2–H2	3.37
O2–H2	0.97

The proposed mechanism is depicted in Scheme 2. The reaction begins with an electrophilic attack of palladium on electron rich nitrogen atom of **1**, affording a three-coordinated intermediate **7** via transition state TS1. In the second step of the reaction palladium of **7** performs an electrophilic attack on nitrogen of another ionic liquid molecule, yielding the  $trans$ -[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex, via transition state TS2. The optimized geometries of transition states and intermediates are presented in Fig. 3. The selected bond distances of transition states and intermediates are given in Table 2. The total energies, enthalpies, and free energies of all relevant species are provided in Table 1 of Supplementary Data.

Fig. 1 in Supplementary Data shows the LUMO map of PdCl<sub>2</sub> and HOMO map of **1**. The LUMO map delineates the area in PdCl<sub>2</sub> that is most electron-deficient (Pd), and agrees with the NBO analysis of PdCl<sub>2</sub> which shows that palladium bears only four lone electron pairs in the d orbitals. On the other hand, the HOMO map delineates the area in **1** that is most electron-sufficient (N1). In addition, the NBO charges of Pd in PdCl<sub>2</sub> (0.792) and N1 in **1** (–0.702) indicate that palladium will perform an electrophilic attack on the nitrogen of **1**. Our assumption was confirmed by revealing transition state TS1 (Fig. 3) that requires activation energy of 75.2 kJ/mol (Table 1 of Supplementary Data). The results of the IRC calculation for this transition state are presented in Fig. 2 of Supplementary Data. In TS1, the Pd–N1 bond is being formed, whereas the hydrogen N1–H1 bond is completely broken (Table 2). This implies that the acetic acid molecule leaves the reaction system as a solvent molecule.

In this way the three-coordinated intermediate **7** is formed (Scheme 2). The NBO analysis of **7** shows that the lone electron pairs in the p orbitals of ligating atoms participate with over 80% in the bonds around palladium. There is strong donation of density from each Pd–Cl bond to the adjacent  $\sigma^*$  antibonding Pd–Cl orbital, and from the Pd–N1 bond to both  $\sigma^*$  antibonding Pd–Cl orbitals. As a consequence, the occupancies in the bonding orbitals around Pd are noticeable low (around 1.87). Palladium still bears only four lone electron pairs, and thus, it is electron-deficient. The LUMO map of **7** (Fig. 1 in Supplementary Data) is in accord with the NBO analysis, and indicates Pd as a possible electrophilic site.

Our investigation shows that the electrophilic attack of Pd of **7** on the nitrogen of another molecule of ionic liquid **1** occurs via transition state TS2 (Scheme 2), requiring an activation barrier of 120.6 kJ/mol (Table 1 of Supplementary Data). Similarly to the case of transition state TS1, the Pd–N2 bond is being formed, whereas the hydrogen N2–H2 bond is completely broken (Fig. 3 and Table 2),



**Fig. 3.** Optimized geometries of TS1 and TS2.

implying again that the acetic acid leaves the reaction system. In this way the *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex is yielded.

It is worth noting that the activation energy for the formation of TS1 was calculated as a difference between the free energy of TS1 and the structure obtained by optimizing **1** and PdCl<sub>2</sub> together. In a similar way, the activation energy for the formation of TS2 was calculated as a difference between the free energy of TS2 and the structure obtained by optimizing **1** and **7** together (**8** and **9** in Fig. 3 of Supplementary Data). We suppose that the activation barrier for the formation of TS2 is higher than that for the formation of TS1 because of numerous hydrogen bonds in the structure **9**. Relatively high calculated activation energies can be attributed to the fact that the calculations were performed in vacuum. We assume that in practice, in the presence of the solvent, the activation barriers are lowered.

#### 4. Conclusion

It was found that the reaction of PdCl<sub>2</sub> with diethanolamine and *N,N*-diethylethanolamine ionic liquids provides the ionic liquid–palladium catalytic systems for green Heck reaction. Our DFT investigation presented herein provides mechanistic insight into the formation of the *trans*-[PdCl<sub>2</sub>(DEA)<sub>2</sub>] complex that acts as a precatalyst. The used ILs facilitate solubility of the Pd(II) precatalysts, increase catalyst stability during the reaction, and function as reaction media, bases, precatalyst-precursors, good coordinating ligands, and mobile support for active Pd species. Thus, Heck reaction occurs without additional solvents, ligands and bases, that makes experimental procedure much simpler. This used IL–Pd catalytic system is ecological friendly and can be recovered and recycled what make it attractive and economically acceptable.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.05.010.

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