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Springer

ORIGINAL PAPER

# Triethanolammonium acetate as a multifunctional ionic liquid in the palladium-catalyzed green Heck reaction

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**Abstract** An efficient green Heck reaction protocol was performed using a triethanolammonium acetate ionic liquid–palladium(II) catalytic system. The ionic liquid used acts as a reaction medium, base, precatalyst-precursor, and mobile support for the active Pd species. Our experimental investigation indicates that performing the Heck reaction in ionic liquid is superior to the same procedure carried out in triethanolamine. The mechanism of the reaction of triethanolammonium acetate with $PdCl_2$ was examined using density functional theory (M06 method). It was found that two Pd(II) complexes are formed, one of which acts further as a precatalyst yielding catalytically active Pd(0) complex. The calculated activation energies are in agreement with our experimental findings.

**Keywords** Triethanolamine ionic liquid · Green Heck reaction · Reaction mechanism · Pd(II) precatalyst · Pd(0) catalytically active complex

## Introduction

The palladium-catalyzed arylation of olefins, known as the Heck reaction, is one of the most important methods of carbon–carbon bond formation in organic synthesis [1–4]. Due to its synthetic versatility, the Heck reaction attracts the attention of both experimental [5–9] and theoretical chemists [10–22]. Much effort has been devoted to elucidation of the Heck reaction mechanism [10–12], including catalyst preactivation [13, 14], oxidative addition [15–21], and reductive elimination [22, 23].

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 application of ionic liquids has been put forward as a very useful substitute for hazardous and volatile polluting organic solvents [24–27]. One of the predominant applications of ionic liquids focuses on homogeneous catalysis [24, 28]. Nowadays, multifunctional ionic liquids that can serve as good coordinating ligands, green solvents, as well as recyclable and mobile supports for palladium catalyst systems, are used. Functional groups that can complex palladium, such as amine, amide, nitrile, ether, alcohol, urea or thiourea [29, 30] have been introduced into the cationic and/or anionic moiety of ionic liquids.

Here, we report the use of triethanolammonium acetate [TEA][HOAc] as a multifunctional ionic liquid in a green Heck reaction. The investigated ionic liquid acts as a green solvent, base, precatalyst-precursor, and mobile support for the active Pd species. Our work focused on testing the efficiency of the obtained ionic liquid–palladium catalytic system in the Heck reaction, and on a density functional theory (DFT) investigation of the possible mechanism of in situ formation of the Pd(II) precatalyst. Since very little is known about the mechanism of formation and molecular structure of Pd(0) complexes [13, 14], which are generally accepted as the catalytically active forms, our additional goal was to elucidate the mechanism of reduction of the Pd(II) precatalyst to the catalytically active Pd(0) form.

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## Computational methods

The geometrical parameters of all stationary points and transition states were optimized in vacuum, using Gaussian09 [31]. All calculations were performed using the M06 functional [32]. This hybrid meta functional is a functional with good accuracy "across-the-board" for transition metals, main group thermochemistry, medium-range correlation energy, and barrier heights [32]. The triple split valence basis set 6-311 G(d,p) was used for C, H, O, N, and Cl, whereas LANL2DZ+ECP [33] was employed for the Pd center. All calculated structures were confirmed to be local minima (all positive vibrational frequencies) for ground state structures, or first-order saddle points (one negative vibrational frequency) 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. Natural bond orbital analysis (Gaussian NBO version) was performed for all structures.

## Results and discussion

The structure of ionic liquid triethanolammonium acetate ([TEA][HOAc]) was examined using DFT (Fig. 1). Our investigation revealed that there are no distinguishing cations and anions in [TEA][HOAc]. Bond distances reveal

strong hydrogen bonding in the ionic liquid. The NBO analysis was in accord with this finding, namely there is strong donation of density from the p orbital on N to the $\sigma^*$ antibonding O–H orbital of acetic acid. Owing to hydrogen bonding, it is obvious that molecular association is present. In addition, the molecule is polar (nitrogen and oxygen bear partial negative charge, whereas H1 is partially positively charged). These properties are characteristic of molecular liquids, and generally for ionic liquids. The role of the ionic liquid used and its triethanolamine Pd(II) complexes (Fig. 1) in a green Heck reaction protocol was investigated in this work.

Bearing in mind that the trans-[PdCl$_2$(DEA)$_2$] complex acts as a precatalyst in the Heck reaction in [DEA][HOAc] as reaction medium [34], we assumed that [TEA][HOAc] would be good reaction medium, and that the triethanolamine Pd(II) complex would also yield a catalytically active species in the Heck reaction. Thus, we decided to investigate the efficiency of the ionic liquid–palladium ([TEA][HOAc]/ Pd(II) complex) catalytic system. Above all we were interested in the mechanisms of in situ formation of the Pd(II) precatalyst and the catalytically active Pd(0) complex.

The Heck reaction was performed with the corresponding aryl halide (iodobenzene and bromobenzene) and activated olefine (methyl, ethyl, and butyl acrylate) in the investigated ionic liquid at 110°C, and with 2 mol% PdCl$_2$. A 100% conversion of acrylates to the trans cross-coupling products was achieved, with 99% selectivity. The yield of products



**Fig. 1** Optimized geometries of triethanolammonium acetate ([TEA][HOAc]), and trans-[PdCl$_2$(TEA)$_2$] (Pd-N,N and Pd-N,O) complexes)
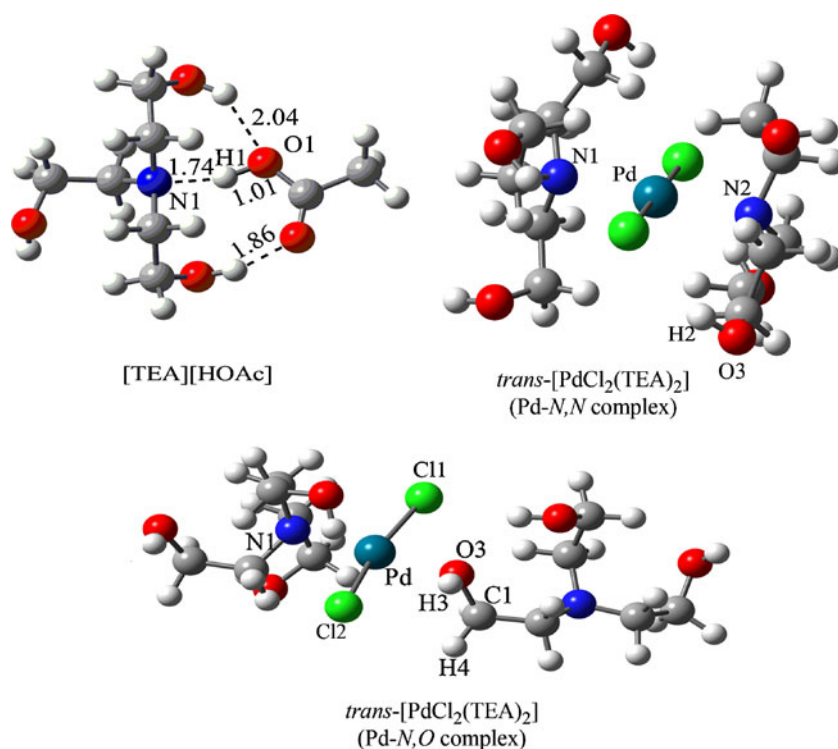
obtained in this reaction was very good (90–93%, Table 1). Next, we wished to compare the experimental procedure and yield of the ionic liquid–Pd(II) catalyzed reaction with the same reaction performed in the absence of ionic liquid, where TEA was used as a reaction medium (Table 1).

When the Heck reaction was performed in TEA, the yield was lower (75–81%). The lower yield of these reactions can be attributed to a competitive polymerization reaction. Our results indicate that the Heck reaction performed in the ionic liquid is superior compared to the procedure carried out in TEA. The ionic liquid used facilitates solubility of $PdCl_2$ and the appropriate Pd(II) catalyst precursor. It seems that the nature of the ionic liquid used increases the stability of the palladium catalyst, extending its lifetime. In addition, this catalytic system remains unchanged during the reaction. The reaction products can be separated via simple extraction, and ionic liquid–palladium catalytic system can be recycled easily.

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

Mechanism of formation of Pd(II) complexes

In order to elucidate the mechanism of formation and structure of the Pd(II) precatalyst and catalytically active Pd (0) species, we investigated the possible mechanism of reaction of [TEA][HOAc] with $PdCl_2$. It turned out that two complexes can be formed in this reaction: Pd-N,N and Pd-N,

O complexes (Figs. 1, 2). The selected bond distances of transition states and intermediates are given in Table 2, whereas the relative total energies, enthalpies, and free energies of all relevant species are provided in Table S1 in the Electronic Supplementary Material.

NBO analysis of $PdCl_2$ reveals that palladium is electron deficient, as it bears only four lone pairs in the d orbitals. On the other hand, the HOMO map of [TEA][HOAc] (Fig. S3) delineates the area in the molecule that is most electron sufficient (N1). In addition, the NBO charges of Pd (0.750), and N1 in [TEA][HOAc] (−0.582) indicate that palladium will perform an electrophilic attack on the nitrogen of the ionic liquid.

Our assumption was confirmed by revealing transition state TS1 (Fig. 2), which requires an activation energy of 127.0 kJ mol$^{-1}$ (Table S1). In TS1, the Pd–N1 bond is being formed, whereas the hydrogen N1–H1 bond is being broken (Table 2). The O1–H1 bond is completely formed, implying that the acetic acid molecule leaves the reaction system as a solvent molecule. In this way, the tricoordinated intermediate I1 is formed (Fig. 2). Tricoordinated Pd complexes are known from the literature [12, 18–21]. NBO analysis of the intermediate shows that the p orbitals of the ligating atoms participate with over 80% in the bonds around palladium. Each Pd–Cl bond delocalizes into the adjacent σ* antibonding Pd–Cl orbital, whereas the Pd–N1 bond delocalizes into both σ* antibonding Pd–Cl orbitals. Palladium still bears only four lone electron pairs and, thus, it is electron deficient. The LUMO map of the intermediate (Fig. S4) is in accord with NBO analysis, and indicates Pd as a possible electrophilic site.

**Table 1** Palladium-catalyzed Heck reaction in different reaction media. *[TEA][HOAc]* Triethanolammonium acetate, *TEA* triethanolamine

$$\text{ArX} + CH_2=CHR \xrightarrow[\text{[TEA][HOAc] or TEA}]{\text{2 mol.\% } PdCl_2, \; 110\ ^0C} \text{ArCH}=CHR$$

| Entry | ArX | R | Reaction medium | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | $C_6H_5I$ | $COOCH_3$ | [TEA][HOAc] | 12 | 93 |
| 2 | $C_6H_5Br$ | $COOCH_3$ | [TEA][HOAc] | 14 | 90 |
| 3 | $C_6H_5I$ | $COOC_2H_5$ | [TEA][HOAc] | 12 | 93 |
| 4 | $C_6H_5Br$ | $COOC_2H_5$ | [TEA][HOAc] | 14 | 91 |
| 5 | $C_6H_5I$ | $COOC_4H_9$ | [TEA][HOAc] | 12 | 93 |
| 6 | $C_6H_5Br$ | $COOC_4H_9$ | [TEA][HOAc] | 14 | 90 |
| 7 | $C_6H_5I$ | $COOCH_3$ | TEA | 12 | 81 |
| 8 | $C_6H_5Br$ | $COOCH_3$ | TEA | 14 | 77 |
| 9 | $C_6H_5I$ | $COOC_2H_5$ | TEA | 12 | 80 |
| 10 | $C_6H_5Br$ | $COO\ C_2H_5$ | TEA | 14 | 75 |
| 11 | $C_6H_5I$ | $COOC_4H_9$ | TEA | 12 | 80 |
| 12 | $C_6H_5Br$ | $COOC_4H_9$ | TEA | 14 | 75 |

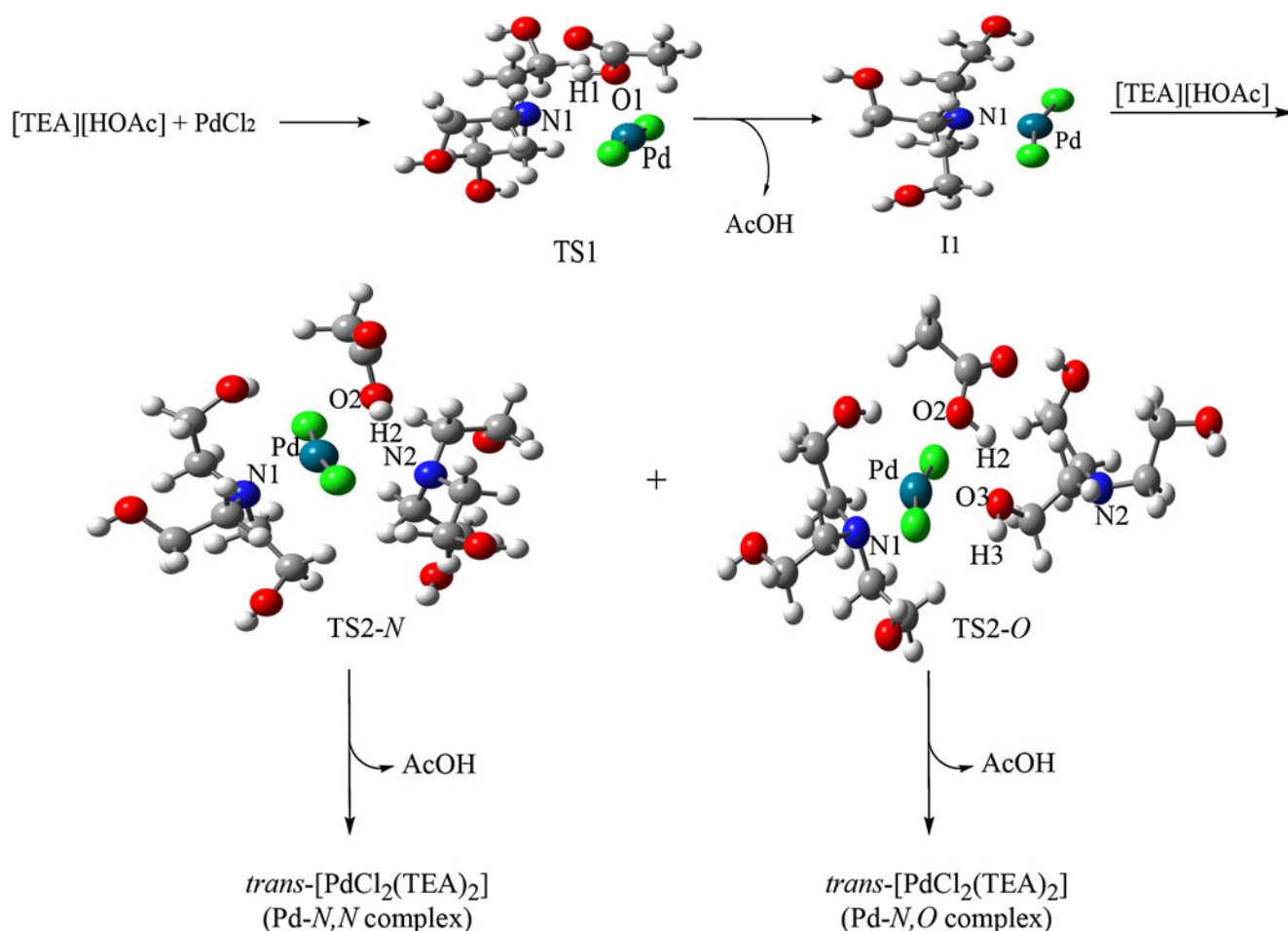[a] Isolated yield; only the *trans* product was detected by ${}^1$H NMR

**Fig. 2** Proposed mechanism for the formation of Pd-N,N and Pd-N,O complexes

Our investigations revealed two pathways for the electrophilic attack of Pd of I1 on another molecule of [TEA][HOAc]. The first pathway, in which Pd attacks nitrogen, occurs via transition state TS2-N (Fig. 2). An energy barrier of 139.7 kJ mol$^{-1}$ is required for the formation of this transition state (Table S1). 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. 2, Table 2), again implying that acetic acid leaves the reaction system as a solvent molecule. In this way, a Pd-N,N complex is yielded (Figs. 1, 2). Our experiments confirm that the Pd–N,N complex is formed during the course of the Heck reaction, as it was identified in the reaction mixture by means of NMR spectroscopy. This identification was achieved by comparing the NMR spectrum of the reaction mixture to the NMR spectrum of the separately prepared Pd–N,N complex. Indeed, this complex was formed upon mixing of PdCl$_2$ with [TEA][HOAc] in molar ratio 1:2, at 100°C. The Pd-N,N complex exhibits a square planar coordination. According to NBO analysis, palladium is sp$^2$d

hybridized, and builds covalent bonds with both nitrogens and both chlorines. The sp$^3$ orbitals of the Cl atoms and almost pure p orbitals of the N atoms participate with about 85% in the bonds around palladium. There is strong donation of density from each Pd–N bond to the adjacent σ* antibonding Pd–N orbital. As a consequence, the occupancies in the Pd–N orbitals are noticeable low (1.86).

The second pathway, in which Pd of I1 attacks the oxygen of [TEA][HOAc], proceeds via transition state TS2-O (Fig. 2), which has an activation barrier of 85.8 kJ mol$^{-1}$ (Table S1). In TS2-O the Pd–O3 bond is being formed, whereas the hydrogen bond between N2 and H2 is completely broken (Fig. 2, Table 2). In this way the Pd–N,O complex is formed (Fig. 1). Our finding is supported by previously reported experimental results [35] that showed that oxygen coordination to Pd(II) and proton abstraction from the alcoholic group is possible, even in weak acidic medium. It is worth pointing out that acetate buffer is formed during our Heck reaction (AcOH/[TEA][HOAc], measured pH≈6).

**Table 2** Selected bond distances (Å) in the investigated species for the mechanism of formation of Pd(II) complexes

| Ionic liquid + PdCl$_2$ | |
|---|---|
| N1-H1 | 1.05 |
| O1-H1 | 1.61 |
| Pd-Cl | 2.31, 2.35 |
| TS1 | |
| N1-H1 | 2.11 |
| O1-H1 | 0.98 |
| Pd-N1 | 2.89 |
| I1 | |
| Pd-N1 | 2.08 |
| Pd-Cl | 2.32, 2.35 |
| TS2-*N* | |
| Pd-N1 | 2.15 |
| Pd-Cl | 2.36, 2.38 |
| N2-H2 | 3.40 |
| O2-H2 | 0.98 |
| Pd-N2 | 2.88 |
| TS2-*O* | |
| Pd-N1 | 2.17 |
| Pd-Cl | 2.36, 2.38 |
| N2-H2 | 4.42 |
| O2-H2 | 0.98 |
| Pd-N2 | 5.75 |
| Pd-O3 | 2.59 |
| Pd-*N,N* complex | |
| Pd-N1 | 2.17 |
| Pd-Cl | 2.38, 2.42 |
| Pd-N2 | 2.17 |
| Pd-*N,O* complex | |
| Pd-N1 | 2.13 |
| Pd-N2 | 5.08 |
| Pd-Cl | 2.36, 2.40 |
| Pd-O3 | 2.12 |

It should be emphasized that, in the Heck reaction with TEA, instead of [TEA][HOAc], a competitive polymerization reaction occurred, and formation of the Pd-N,N complex was not observed during the course of the reaction. In agreement with this experimental finding, our attempts to reveal a transition state for an electrophilic attack of Pd on the nitrogen or oxygen of TEA were unsuccessful.

Mechanism of formation of the Pd(0) complex

Analysis of the stability of the complexes obtained showed that the Pd–N,O complex is less stable than the Pd–N,N complex by 31.4 kJ mol$^{-1}$. This instability is a probable reason why it has not been identified in the reaction mixture. Thus we assume that it undergoes further transformation, yielding catalytically active Pd(0) complex.

The proposed mechanism is presented in Fig. 3. All relevant bond distances in transition states and intermediates are given in Table 3, whereas the relative total energies, enthalpies, and free energies of all relevant species are provided in Table S2.

NBO analysis of the Pd–N,O complex shows that Pd forms covalent bonds with both chlorines and nitrogen (Fig. 1). The p orbitals of the ligating atoms participate with over 80% in the bonds around palladium. The O3–H3 orbital and lone pair on O3 (sp$^3$ orbital) delocalize into formally empty p orbital (with little s and d mixing) on Pd, thus forming a coordinative Pd–O3 bond. Density is also donated from the sp$^3$ orbital of O3 to the σ* antibonding Pd–N1 orbital. The Pd–N1 bond delocalizes into both σ* antibonding Pd–Cl orbitals. Due to this, the occupancies of all palladium bonds are low (about 1.90). NBO analysis also reveals that the O3–H3 bond is particularly polar (NBO charges of O3 and H3 amount −0.697 and 0.517). Taking into account that O3 is engaged in the coordinative bond with Pd, and that H3 is acidic, we supposed that this H3 can be abstracted by the acetate buffer. Our assumption was confirmed by successful optimization of the intermediate I2 (Fig. 3). NBO analysis of I2 shows that p orbitals of the ligating atoms participate with over 80% in the bonds around palladium. Each Pd–Cl bond delocalizes into the adjacent σ* antibonding Pd-Cl orbital, whereas the Pd–O3 bond delocalizes into both σ* antibonding Pd–Cl orbitals. The lone pair on N1 delocalizes into σ* antibonding Pd–O3.

Our experience with the preactivation process of trans-[PdCl$_2$(DEA)$_2$] [13, 14] shows that β hydrogens (with respect to Pd) have affinity to coordinate to Pd. As H4 has the most favorable position, we supposed a nucleophilic attack of H4 to palladium(II) to be a plausible next step of the reaction. Our assumption was confirmed by revealing transition state TS3 (Fig. 3). The results of the IRC calculation for TS3 are presented in Fig. S5. The formation of TS3 has an energy barrier of 141.9 kJ mol$^{-1}$ (Table S2). In TS3, Pd–O3 and C1–H4 bonds are being broken, while a Pd–H4 bond is being formed (Table 3). It is worth pointing out that hydrogen is transferred from carbon to palladium as a hydride ion. This transfer leads to the formation of the intermediate I3a (Fig. S2). The structure of I3a shows that it contains a completely separated molecule [N,N-bis(2-hydroxyethyl)amino-acetaldehyde] that probably acts further as a solvent molecule. For this reason we excluded the N,N-bis(2-hydroxyethyl)amino-acetaldehyde molecule (C$_6$H$_{13}$NO$_3$) from further consideration (I3 in Fig. 3). NBO analysis of I3 reveals that the intermediate complex exhibits a square planar coordination, where Pd forms covalent bonds with both chlorines and hydrogen. As for nitrogen, its almost pure p orbital donates density to the formally empty p orbital (with little s and d mixing) on Pd.
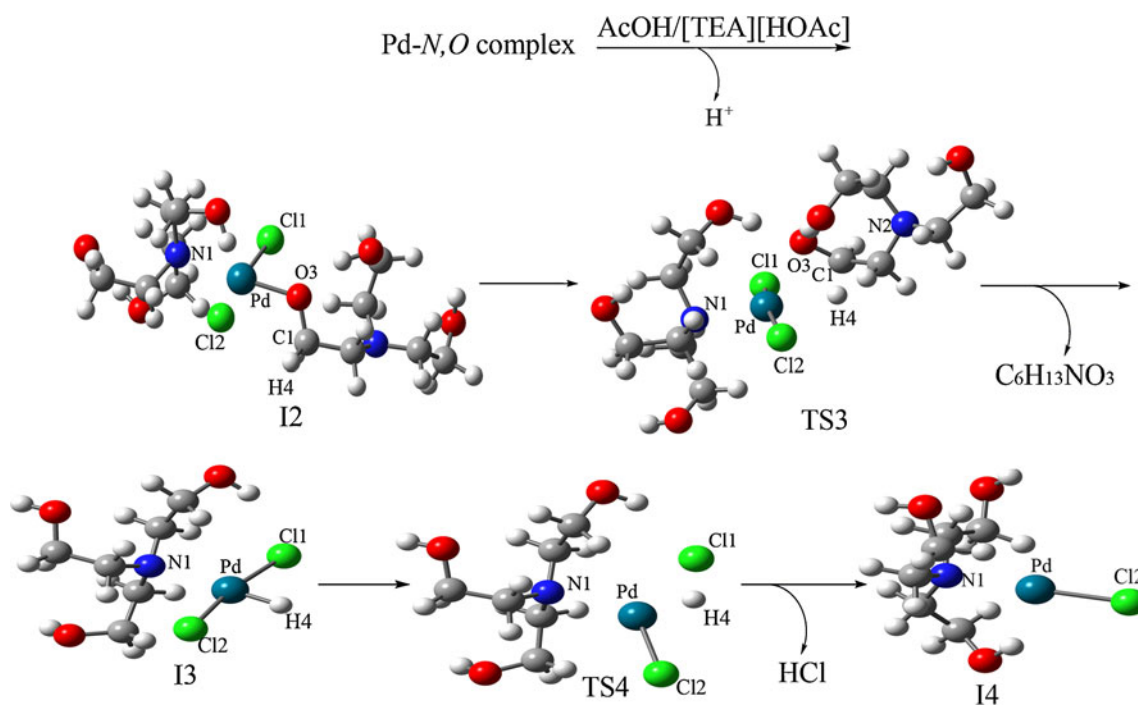
**Fig. 3** Proposed mechanism for the formation of the Pd(0) complex

**Table 3** Selected bond distances (Å) in the investigated species for the mechanism of formation of Pd(0) complex

| I2 | |
| --- | --- |
| Pd-N1 | 2.25 |
| Pd-N2 | 4.87 |
| Pd-Cl1 | 2.40 |
| Pd-Cl2 | 2.43 |
| Pd-O3 | 1.99 |
| C1-H4 | 1.10 |
| Pd-H4 | 3.15 |
| **TS3** | |
| Pd-N1 | 2.15 |
| Pd-Cl1 | 2.38 |
| Pd-Cl2 | 2.37 |
| Pd-O3 | 2.42 |
| C1-H4 | 1.15 |
| Pd-H4 | 2.11 |
| **I3** | |
| Pd-N1 | 2.42 |
| Pd-Cl1 | 2.39 |
| Pd-Cl2 | 2.42 |
| Pd-H4 | 1.52 |
| **TS4** | |
| Pd-N1 | 2.55 |
| Pd-Cl1 | 2.81 |
| Pd-Cl2 | 2.39 |
| Pd-H4 | 1.56 |
| Cl1-H4 | 1.71 |
| **I4** | |
| Pd-N1 | 2.28 |
| Pd-Cl2 | 2.38 |

The Pd–H4 orbital delocalizes into both σ* antibonding Pd–Cl orbitals, and vice versa.

In the further course of the reaction, I3 undergoes reductive elimination of HCl. Our investigation shows that this step of the reaction proceeds via transition state TS4, which requires an activation energy of 78.9 kJ mol$^{-1}$ (Table S2). The results of the IRC calculation for TS4 are presented in Fig. S6. In TS4, the Pd–H4 and Pd–Cl1 bonds are being cleaved, whereas the Cl1–H4 bond is being formed, implying that HCl leaves the reaction system. This process leads to the formation of the catalytically active Pd(0) complex, the final product of preactivation reaction (I4 in Fig. 3). NBO analysis reveals that palladium bears five lone pairs in the d orbitals, implying that the oxidative number of Pd is 0. Ligating atoms (chlorine and nitrogen) participate in bonds around palladium with more than 90%. The Pd–Cl bond delocalizes into the σ* antibonding Pd-N1 orbital, and vice versa.

## Summary

The structure of the ionic liquid [TEA][HOAc] was examined using DFT. It was shown that [TEA][HOAc] acts as multifunctional ionic liquid providing a good reaction medium, base, precatalyst-precursor, and mobile support for the active Pd species in a phosphine-free Heck reaction. The mechanism of the reaction of [TEA][HOAc] with PdCl$_2$ was examined using DFT. It was found that two

Pd(II) complexes, Pd–N,N and Pd–N,O, are formed where the Pd–N,O complex further acts as a precatalyst, yielding the catalytically active Pd(0) species. The calculated activation energies are in agreement with our experimental findings.

The reaction of $PdCl_2$ with [TEA][HOAc] provides an effective ionic liquid–palladium catalytic system for the Heck reaction. The catalytic system used is ecologically friendly and can be recovered and recycled.

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