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ORIGINAL PAPER

# DFT study on the preactivation reaction of a palladium catalyst precursor in phosphine-free Heck reactions

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**Abstract** The mechanism of the preactivation process of *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex is investigated using density functional theory. The role of diethanolamine (a solvent for the reaction in the absence of a strong base) and acetonitrile (solvent for the reaction in the presence of a strong base) is analyzed by using a discrete model. The Onsager model is applied to assess the effect of the bulk medium. Both models show that diethanolamine activates the complex and thus is a better suited solvent for the Heck reactions of the investigated complex.

**Keywords** Reaction mechanisms · Quantum chemical calculations · *Trans*-[$PdCl_2(DEA)_2$] · Solvent effects

## Introduction

The Heck reaction, i.e., the palladium-catalyzed arylation of olefins, has been attracting much attention [1–8], and a Pd(0) complex has been generally accepted as the catalytically active form [9, 10]. Oxidative addition and reductive elimination, important steps in the Heck reaction mechanism, have been subjects of numerous experimental [11–17] and computational studies [16–22]. On the other hand, the mechanism of the preactivation process, where the Pd cation is reduced to Pd(0), has not been completely elucidated. In addition, very little is known about the molecular structure of the Pd(0) complex.

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In our previous study, the recently synthetized *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[$PdCl_2(DEA)_2$] (**1**)) [23] has been used as a catalyst precursor in phosphine-free Heck reactions [24]. The reactions between different olefins and aryl halides catalyzed with **1** have been carried out in the presence of a weak (diethanolamine) and strong (NaOEt) base, and a mechanistic study of the intramolecular reduction of **1** in the presence of a strong base has been performed. In [24] the mechanism of the preactivation process of **1** in the presence of a weak base as well as the solvent effects on the preactivation reaction performed in the presence of the weak and strong bases have not been studied in detail. The aim of this work is to fill this gap.

## Results and discussion

The first part of our investigation is devoted to the transformations of **1** in the presence of a weak base. The proposed mechanism for the reaction performed in the presence of a weak and strong base is presented in Fig. 1 (pathways A and B).

It is reasonable to expect that polar molecules of diethanolamine (solvent for the reaction in the absence of a strong base [24]) and acetonitrile (solvent for the reaction in the presence of a strong base [24]) form hydrogen bondings with polar groups of the solutes and possibly influence the preactivation reaction course. The second part of our work is devoted to the influence of these two solvents upon the mechanism of the preactivation reaction of **1**. The role of solvents in the energy and geometry of relevant stationary and saddle points is analyzed by using discrete model. The solvent is simulated by adding discrete molecules of diethanolamine and acetonitrile. The Onsager model is used to assess the effect of bulk medium.

*Preactivation reaction in the presence of a weak base*

As expected, the initial abstraction of a proton from an alcoholic OH group in **1** does not occur in the absence of a strong base. Instead, a hydrogen bonded to the carbinol C1 atom (Fig. 2) coordinates to Pd(II) [9, 25], thus forming **4** and an iminium ion, via transition state **6** (Fig. 1). This process requires an activation barrier of 111.8 kJ/mol, which is higher than that observed in the reaction performed in the presence of a strong base by 28.8 kJ/mol [24]. The further course of the reaction is identical to that of the reaction performed in the presence of a strong base and involves reductive elimination of HCl, where the catalytically active anion **5** is formed. The optimized geometries of **1**, **6**, **4**, and **5** are presented in Fig. 2, whereas

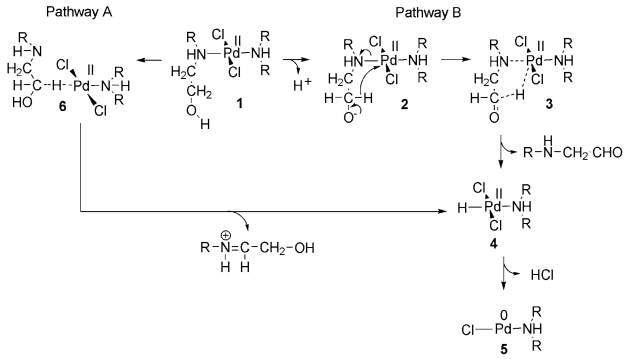


**Fig. 1** Proposed mechanism of the preactivation process of *trans*-[$PdCl_2(DEA)_2$] (**1**). *Pathway A* in the presence of a weak base; *pathway B* in the presence of a strong base. The notation in *pathway B* is identical to that used in [24]. R = $–CH_2CH_2OH$

**Table 1** Selected bond distances for transition state **6**

| | Dist./nm |
|---|---|
| Pd-Cl1 | 0.2367 |
| Pd-Cl2 | 0.2352 |
| Pd-N1 | 0.3491 |
| Pd-N2 | 0.2088 |
| Pd-H2 | 0.1822 |
| C1-H2 | 0.1137 |

The crucial bond distances for **1**, **4**, and **5** are provided in [24]

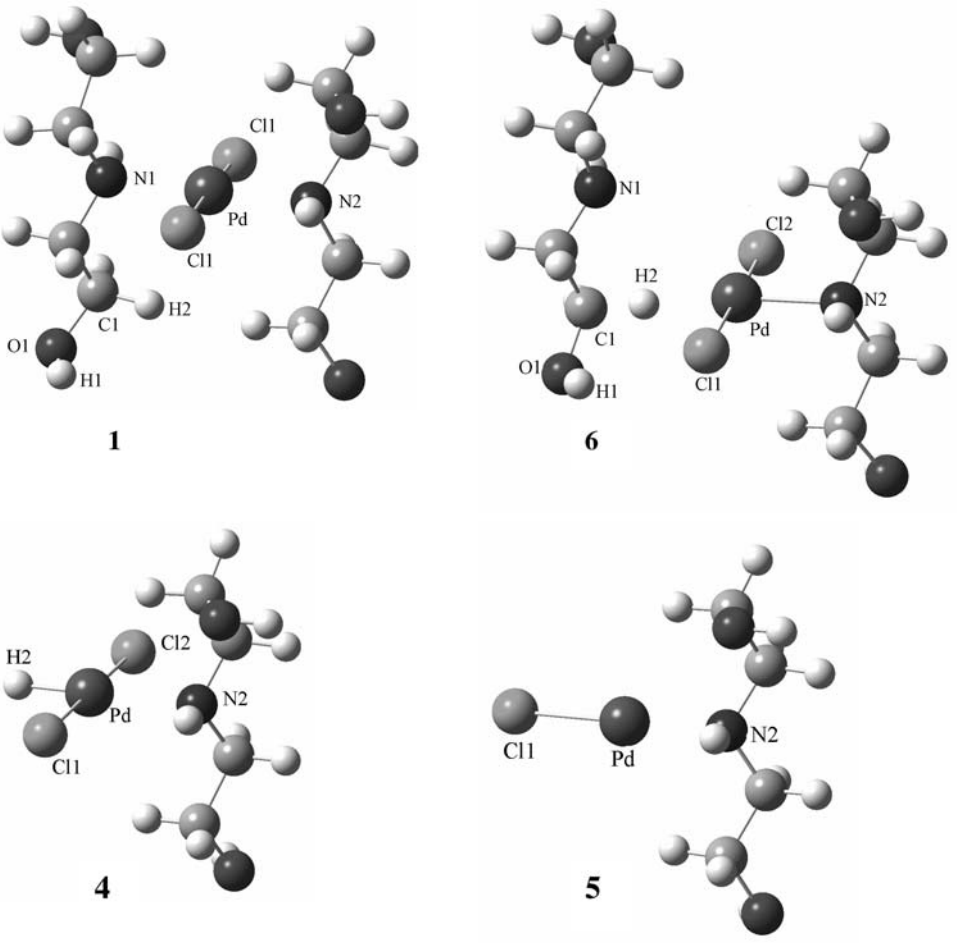


**Fig. 2** Optimized geometries of *trans*-[$PdCl_2(DEA)_2$] (**1**), transition state **6**, and intermediates **4** and **5**

the selected bond distances for **6** are given in Table 1. The values of electronic energies, enthalpies, and free energies for **1** and **4**–**6** are provided in Table 2.

The natural bond orbital (NBO) analysis of **1** reveals covalent bonds between the Pd and Cl atoms, whose hybrid composition is: $0.42(sp^{2.2}d^{1.2})_{Pd} + 0.91(sp^{5})_{Cl}$. A 3-center N1-Pd-N2 hyperbond is observed. There is strong donation of density from the lone pairs on the N atoms to the adjacent $\sigma^*$ antibonding Pd-N orbitals, in accord with the usual chemical picture of 3-center 4-electron hyperbonds. In **6** palladium forms the following covalent bonds: $0.42(sp^{2.6}d^{1.4})_{Pd} + 0.91(sp^{6.2})_{Cl1}$, $0.43(sp^{2.3}d^{1.3})_{Pd} + 0.90(sp^{6.5})_{Cl2}$, and $0.43(sp^{0.1}d^{0.9})_{Pd} + 0.90(sp^{5.3})_{N2}$. There is a weak C1-H2 bond with an occupancy of 1.87 and hybrid composition $0.73(sp^{3.7})_{C1} + 0.68(s)_{H2}$. A predominant p character in sp hybridization on C1 with little s mixing is noticeable. This bond delocalizes into the formally empty, almost pure p orbital of palladium. In the further course of the reaction, this electron pair is used for the formation of the Pd-H2 bond in **4**. In **4** palladium forms covalent bonds with the Cl atoms $(0.40(sp^{2.3}d^{1.3})_{Pd} + 0.92(sp^{4.5})_{Cl})$ and with H2 $(0.71(sp^{0.2}d^{1.0})_{Pd} + 0.70(s)_{H2}$. There is no

**Table 2** Total energies ($E$), enthalpies ($H^{298}$), and free energies ($G^{298}$) of the participants in the preactivation reaction of *trans*-$[PdCl_2(DEA)_2]$ (**1**) in the absence of a strong base

| Species | **1** | **6** | **4** | **5** |
|---|---|---|---|---|
| $-E$/a.u. | 1,775.343703 | 1,775.298281 | 1,411.935525 | 951.081853 |
| $-H^{298}$/a.u. | 1,775.318838 | 1,775.273562 | 1,411.919756 | 951.068273 |
| $-G^{298}$/a.u. | 1,775.400576 | 1,775.357981 | 1,411.980620 | 951.123487 |

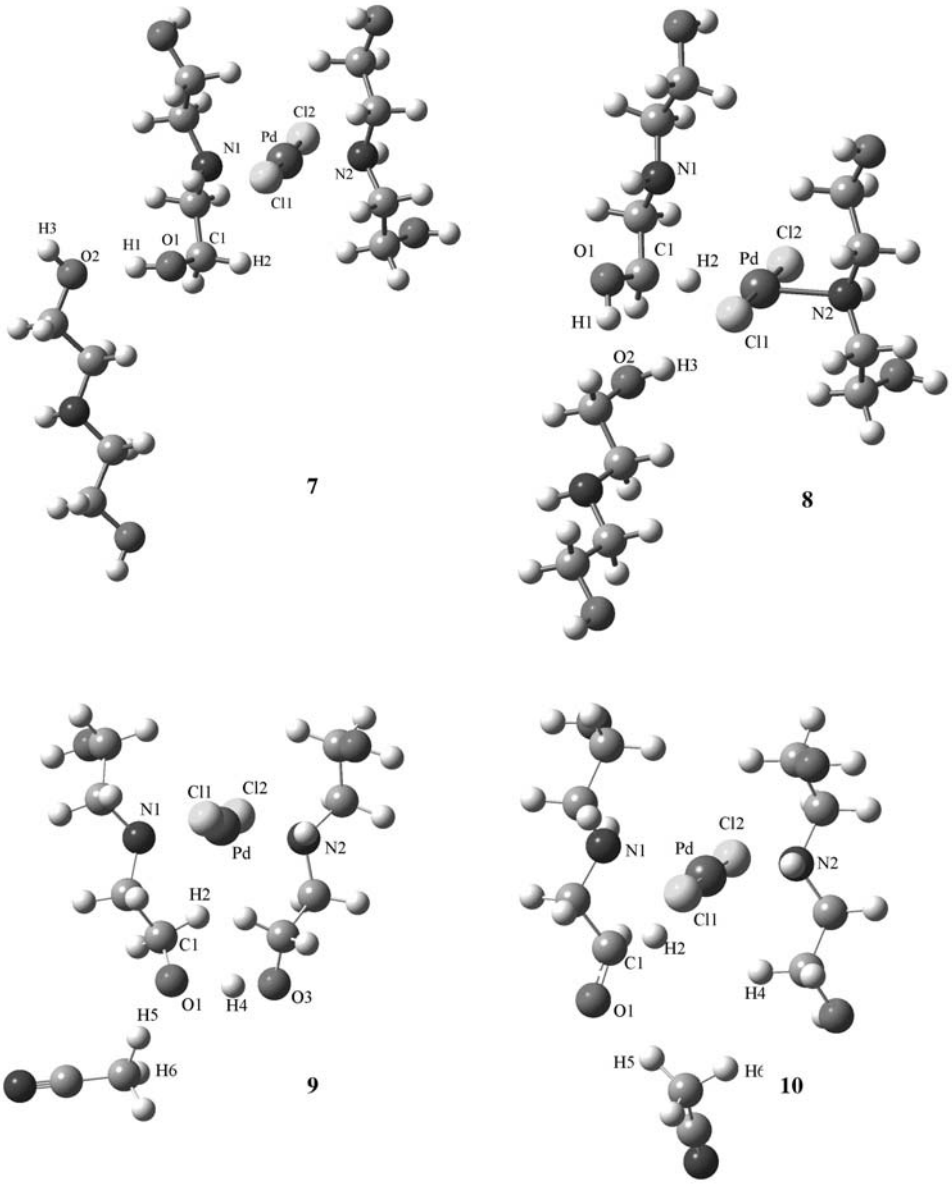


**Fig. 3** Optimized geometries of the solvated *trans*-$[PdCl_2(DEA)_2]$ complex (**7**), deprotonated *trans*-$[PdCl_2(DEA)_2]$ complex (**9**), and corresponding transition states (**8** and **10**)

covalency between the Pd and N2 atoms. Instead, the lone pair on N4 ($sp^{5.1}$ orbital with an occupancy of 1.80) donates density to the formaly empty, almost pure p orbital on palladium, and to the $\sigma^*$ antibonding Pd-H2 bond. In **5** palladium is approximately sp hybridized and forms covalent bonds with nitrogen and chlorine. $\sigma$ bonding Pd-Cl1 orbital is delocalized to $\sigma^*$ antibonding Pd-N2 orbital, and $\sigma$ bonding Pd-N2 is delocalized to $\sigma^*$ antibonding Pd-Cl1 orbital.

*Solvation models*

To examine the solvent effects on the preactivation reaction of **1**, a discrete diethanolamine molecule is added to both **1** and **6**, so that it is placed next to the reactive center. The so-obtained structures are fully optimized without any movement restriction (**7** and **8** in Fig. 3). Following the same procedure, a molecule of acetonitrile is added to **2** and **3**. In this way, the structures **9** and **10** are obtained, and they are also depicted in Fig. 3. Selected bond distances for **7**–**10** are presented in Table 3, whereas the values of electronic energies, enthalpies, and free energies are provided in Table 4.

Figure 3 and Table 3 show that in all cases the formed arrangements are controlled with hydrogen bonds between the solute and solvent molecules (O2-H1 in **7** and **8**; O1-H5 in **9** and **10**; O3-H6 in **10**). The sum of the free energy values of **2** and acetonitrile is higher than that of **9** by 18.1 kJ/mol. This fact implies that on solvation in acetonitrile, the deprotonated complex becomes stabilized, and thus slightly deactivated for the reaction. On the other hand, the sum of the free energy values of the complex **1** and diethanolamine are lower than that of **7** by 26.7 kJ/mol. This indicates that on solvation in diethanolamine **1** becomes activated for the reaction. In accord with this consideration, the activation barriers required for the formation of **8** and **10** amount to 102.2 kJ/mol (lowered in comparison with **6**) and 91.6 kJ/mol (elevated in comparison with **2** [24]).

**Table 3** Selected bond distances in the solvated *trans*-[$PdCl_2(DEA)_2$] complex (**7**), deprotonated complex (**9**), and corresponding transition states (**8** and **10**)

| | Dist./nm | | | |
|---|---|---|---|---|
| | **7** | **8** | **9** | **10** |
| Pd-Cl1 | 0.2378 | 0.2387 | 0.2399 | 0.2386 |
| Pd-Cl2 | 0.2378 | 0.2342 | 0.2400 | 0.2388 |
| Pd-N1 | 0.2112 | 0.3666 | 0.2114 | 0.2542 |
| Pd-N2 | 0.2120 | 0.3155 | 0.2125 | 0.2234 |
| Pd-H2 | 0.3049 | 0.1807 | 0.2627 | 0.1943 |
| C1-O1 | 0.1418 | 0.1370 | 0.1365 | 0.1301 |
| C1-H2 | 0.1094 | 0.1166 | 0.1115 | 0.1212 |
| O1-H1 | 0.0981 | 0.0992 | | |
| O2-H1 | 0.1844 | 0.1731 | | |
| O2-H3 | 0.0969 | 0.0982 | | |
| O1-H4 | | | 0.1543 | 0.1942 |
| O3-H4 | | | 0.1038 | 0.0970 |
| O1-H5 | | | 0.1785 | 0.1942 |
| O3-H6 | | | 0.2931 | 0.4639 |

**Table 4** Total energies ($E$), enthalpies ($H^{298}$), and free energies ($G^{298}$) of the solvated *trans*-[$PdCl_2(DEA)_2$] complex (**7**), deprotonated complex (**9**), and corresponding transition states (**8** and **10**)

| Species | **7** | **8** | **9** | **10** |
|---|---|---|---|---|
| $-E$/a.u. | 2,139.390285 | 2,139.352544 | 1,907.512421 | 1,907.475549 |
| $-H^{298}$/a.u. | 2,139.354639 | 2,139.317575 | 1,907.483935 | 1,907.446154 |
| $-G^{298}$/a.u. | 2,139.465219 | 2,139.426286 | 1,907.575815 | 1,907.540919 |

The Onsager model also indicates that diethanolamine decreases, whereas acetonitrile increases the energy of activation. Namely, the activation energies needed for the formation of **8** and **10** are equal to 108.9 and 101.5 kJ/mol. The computed activation energies are in accord with our experimental results, which showed that the presence of a strong base accelerated the rate of the examined Heck reactions, though it slightly decreased the yields [24].

These findings indicate that diethanolamine may be a more suitable solvent for the Heck reaction, where **1** is used as a precatalyst, than acetonitrile. The Heck reactions in the presence of a strong base and diethanolamine as solvent are under experimental and computational investigations.

## Method

To provide the compatibility of the results of this work with the findings of our previous investigation [24], we use the same computational method. Thus, the density functional theory calculations are carried out with the Gaussian 03 package of programs [26]. The minima and transition states are fully optimized with the B3LYP hybrid functional [27, 28]. The 6-31G(d) basis set is used for C, H, O, N, and Cl, and LANL2DZ + ECP [29] is employed for the Pd center. Natural bond orbital [30] (Gaussian NBO version) and vibrational analyses are performed for all structures. To describe solvent effects to the key step in the preactivation process of **1**, the microsolvated and Onsager models are used.

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## References


1. Heck R (1979) Acc Chem Res 12:146
2. Alonso DA, Nájera C, Pácheco MC (2000) Org Lett 2:1823
3. Beletskaya IP, Cheprakov AV (2000) Chem Rev 100:3009
4. De Vries JG (2001) Can J Chem 79:1086
5. Consorti CS, Zanini ML, Leal S, Ebeling G, Dupont J (2003) Org Lett 5:983
6. Jin CM, Twamley B, Shreeve JM (2005) Organometallics 24:3020
7. Wang R, Twamley B, Shreeve JM (2006) J Org Chem 71:426
8. Cui X, Li J, Zhang ZP, Fu Y, Liu L, Guo QX (2007) J Org Chem 72:9342
9. Cabri W, Candiani I (1995) Acc Chem Res 28:2
10. Amatore C, Jutand A (2000) Acc Chem Res 33:314
11. Stille JK, Lau KSY (1977) Acc Chem Res 10:434
12. Stang PJ, Kowalski MH (1989) J Am Chem Soc 111:3356
13. Stang PJ, Kowalski MH, Schiavelli MD, Longford D (1989) J Am Chem Soc 111:3347
14. Amatore C, Pflüger F (1990) Organometallics 9:2276
15. Jutand A, Mosleh A (1995) Organometallics 14:1810
16. Hii KK, Claridge TDW, Brown JM, Smith A, Deeth RJ (2001) Helv Chim Acta 84:3043
17. Amatore C, Jutand A, Khalil F (2006) ARKIVOC 4:38
18. Deeth RJ, Smith A, Hii KK, Brown JM (1998) Tetrahedron Lett 39:3229
19. Goossen LJ, Koley D, Hermann H, Thiel W (2004) Chem Commun 19:2141
20. Goossen LJ, Koley D, Hermann HL, Thiel W (2005) Organometallics 24:2398
21. Green JC, Herbert BJ, Lonsdale R (2005) J Organomet Chem 690:6054
22. Cui X, Li Z, Tao CZ, Xu Y, Li J, Liu L, Guo QX (2006) Org Lett 8:2467
23. Petrović ZD, Djuran MI, Heinemann FW, Rajković S, Trifunović S (2006) Bioorg Chem 34:225
24. Petrović ZD, Marković S, Simijonović D, Petrović V, Monatsh Chem. Published on Web September 17, 2008
25. Jensen DR, Schultz MJ, Mueller JA, Sigman MS (2003) Angew Chem Int Ed Engl 42:3810
26. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick AD, Rabuck KD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (2003) Gaussian 03, revision E.01-SMP, Gaussian Inc., Pittsburgh
27. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
28. Becke AD (1993) J Chem Phys 98:5648
29. Hay PJ, Wadt WR (1985) J Chem Phys 82:270
30. Reed AE, Weinstock RB, Weinhold F (1985) J Chem Phys 83:735