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Quantum mechanical study on the mechanism and kinetics of the *cis*-to-*trans* isomerization of $[Pd(C_6Cl_2F_3)I(PH_3)_2]$

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ABSTRACT

In this work, mechanism and kinetics of the *cis*-to *trans* isomerization of $[Pd(C_6Cl_2F_3)I(PH_3)_2]$, has been theoretically investigated in detail. Using quantum mechanical approach, different pathways were investigated. Experimentally, a four-pathways mechanism had been proposed for *cis*-to-*trans* isomerization of $[Pd(C_6Cl_2F_3)I(PH_3)_2]$ which consists of two PPh_3-sensitive (k_3,k_4) and two PPh_3-insensitive (k_1,k_2). For PH_3-sensitive pathways, a complex is initially formed in the shape of a square pyramidal following which a process through a trigonal bipyramidal transition state occurs. Our proposal for PH_3-insensitive pathway is a dissociative reaction with a fast equilibrium step following which the slow process occurs. Considering the solvent effects, the activation energy, activation enthalpy and activation Gibbs free energy for different pathways were calculated. Using Gibbs free energies and the transition state theory, the rate constants have been evaluated. k_3 Pathway (solvent-assisted) has the main contribution in this process.

1. Introduction

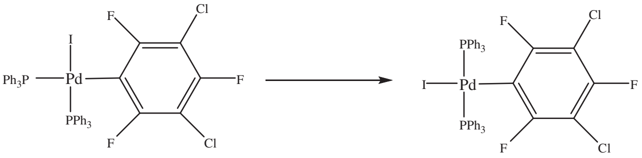
The basic importance of organopalladium intermediates in chemical reactions is their extensive synthetic applications. One of the strongest and most important tools in synthesizing a wide range of different organic compounds is Pd-catalyzed cross-coupling reactions in which carbon–carbon and heteroatom–carbon bonds are formed [1].

These reactions are of such importance that Heck and Negishi were awarded the Nobel prize for chemistry in 2010 for their crucial role in the production of the most complex tools available to chemists, i.e., Pd-catalyzed cross-coupling in organic synthesis [1,2]. A number of chemical reactions, deemed to be impracticable in the past, can now be performed using palladium catalysts [3]. Therefore, understanding of the functional mechanism of palladium in different processes is of paramount importance.

Cross-coupling reactions are an important step in the process of producing complex molecules and these methods are nowadays extensively used in the commercial production of electronic and medical materials, including anti tomural drugs and new antibiotics [1].

Pd-catalyzed cross-coupling mechanism consists mainly of three steps [4–7]: oxidative addition of R–X to palladium (R = Aryl. X = Halid), transmetalation and reductive elimination. Many experimental and theoretical studies have been done on oxidative addition of R–X to zerovalent Pd complexes mechanism. In most of these studies, it was found that in this reaction, at first the *cis* isomer is formed and then ultimately due to more thermodynamic stability, it is converted into the *trans* isomer [4–7].

In 1998, Espinet and Casado [4] studied the *cis* to *trans* isomerization mechanism experimentally. They studied the following reaction (Eq. (1)):



(1)

The reactions followed first-order rate laws $\ln([2]/[2]_0) = k_{iso}t$. The rate dependence on the concentration of added PPh_3 and the starting complex 2 ($[2]_0$) are presented in Eqs. (2) and (3), respectively:

$$k_{iso} = a + \frac{b}{[PPh_3] + c} \tag{2}$$

$$k_{iso} = d + e[2]_0 \tag{3}$$

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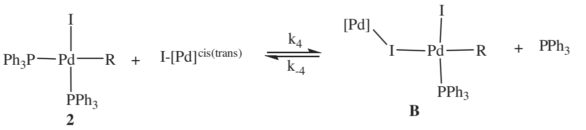
From Eqs. (1) and (2), Casado and Espinet concluded that [4]:

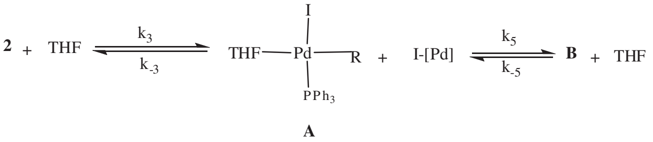
$$k_{iso} = f + g[2]_0 + \frac{h + i[2]_0}{[PPh_3] + j} \tag{4}$$

Considering Eq. (4), they proposed a four-pathway mechanism, shown in Eqs. (5)–(9).

($R = C_6Cl_2F_3$)



(5)



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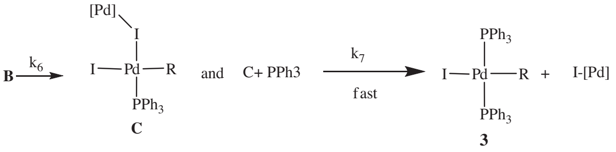
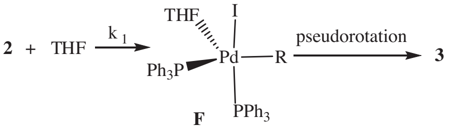


(7)



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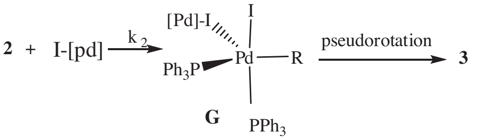

(9)

There are two PPh_3-insensitive (k_1,k_2) and PPh_3-sensitive (k_3,k_4) pathways. By applying the steady state approximation the following equation is obtained:

$$r_{iso} = k_{iso}[2] = \left\{ k_1 + k_2[2]_0 + \frac{k_3k_6 + k_4k_6[2]_0}{k_{-4}[PPh_3] + k_6} \right\}[2] \tag{10}$$

In this work, PPh_3-insensitive and PPh_3-sensitive pathways are studied by using quantum mechanical method.

2. Computational details

All of the present calculations have been performed with the B3LYP [8–10] hybrid density functional level using the GAUSSIAN 03 package [11]. The 6-31G(d,p)basis sets were employed except for Pd and I where the LANL2DZ basis set [5,12,13] was used with effective core potential (ECP) functions.

The solvent has an important role (implicit or explicit) in chemical reactions. For example, it was demonstrated that a chain of water molecules play an important role in the Wacker process (explicit solvent effects) [14–16]. One group of approaches to study the solute–solvent interactions is referenced to as self-consistent reaction field (SCRF) methods (Implicit solvent effects). In this work, we used polarized continuum model (PCM) [17–19]. In the PCM method, the molecular cavity is made up of the union of interlocking atomic spheres.

First, all degrees of freedom for all geometries were optimized. The transition states obtained were confirmed to have only one imaginary frequency of the Hessian. Then, the gas-phase-optimized geometries were used to perform frequency calculations in gas phase and solvent (using PCM model). We assumed that the change of the molecular geometry upon solvation has a negligible effect on the thermodynamic parameters. Thus, the optimized geometries calculated in gas phase were used. To reduce computational cost, PPh_3 ligand has been replaced by PH_3 [20].

3. Results and discussion

3.1. PH_3-sensitive pathways

First, we investigated PH_3-sensitive pathways (k_3 and k_4). These pathways correspond to an associative substitution of PH_3 from complex [*cis*-$Pd(C_6Cl_2F_3)I(PH_3)_2$] (**2**) by an iodide ligand coordinated to either **2** or **3** (both represented by I-[Pd] in Eqs. (5) and (6)) to give a mono-bridged dimer **B**. The ligand substitution can be THF-assisted (step k_3, intermediate **A** is considered) or direct (step k_4) [4].

3.1.1. k_4 Pathway

In order to find the transition state of step k_4 (Eq. (5)), the I-[Pd] molecule in the vicinity of the species 2 should be optimized:

$$2 + I-[Pd] \underset{}{\overset{K'_4}{\rightleftarrows}} 2 \cdots I-[Pd] \underset{}{\overset{k'_4}{\rightleftarrows}} B \cdots PH_3 \underset{}{\overset{K'_{-4}}{\rightleftarrows}} B + PH_3 \tag{11}$$

where $K'_4(K'_{-4})$ and $k'_4(k'_{-4})$ are equilibrium constants and rate constants, respectively. Our investigations showed that a complex is formed in the shape of a square pyramidal, naming it $2 \cdots I—[Pd]$. By transiting through a trigonal bipyramidal transition state (TS_{2B}), this complex is converted into complex $B \cdots PH_3$, being also in the form of a square pyramidal. It should be noted that compound I-[Pd] could exist in both *cis* (**2**) and *trans* (**3**) forms. Considering reactant $2 \cdots I—[Pd]^{cis}$ and product $B^{cis} \cdots PH_3$, a transition state is obtained which we call TS_{2B}^{cis}. Fig. 1 presents the optimized structures of $2 \cdots I—[Pd]^{cis}$, $B^{cis} \cdots PH_3$ and TS_{2B}^{cis}. TS_{2B} is trigonal bipyramidal with I and PH_3 at the apical positions and R, the leaving PH_3 and the incoming I–[Pd] in the trigonal plane.

The I–Pd bond length decreases from 4.690 Å for $2 \cdots I—[Pd]^{cis}$ to 3.086 Å for TS_{2B}^{cis} and the P–Pd bond length increases from 2.399 Å for $2 \cdots I—[Pd]^{cis}$ to 3.090 Å for TS_{2B}^{cis}.

In the same manner the similar figures are obtained for $2 \cdots I—[Pd]^{trans}$, $B^{trans} \cdots PH_3$ and TS_{2B}^{trans} (Supplementary material). Relative energies for different structures have been presented in Table 1. The evaluated energy barriers (E_a) for the *cis*-to-*trans* isomerization of $[Pd(C_6Cl_2F_3)I(PH_3)_2]$ complexes have been shown in Fig. 2 (PCM model).

According to the proposed mechanism (Eq. (11)), $k_4 = k'_4K'_4$, therefore, the activation parameters related to step k_4 including total activation energy (E_a), total activation enthalpy ($\Delta H^{\ddagger}$) and total activation Gibbs energy ($\Delta G^{\ddagger}$).

For *cis* (*trans*) path, in gas phase, the values of $E_{a,2B}$ $\Delta H_{2B}^{\ddagger}$ and $\Delta G_{2B}^{\ddagger}$ are 10.55 (28.31), 14.37 (33.00) and 60.52 (72.10) kJ/mol, respectively. From Table 1, it is observed that solvent has an important effect on the values of energies. Using PCM model For *cis* (*trans*) path, the values of $E_{a,2B}$, $\Delta H_{2B}^{\ddagger}$ and $\Delta G_{2B}^{\ddagger}$ are 38.22 (68.71), 41.10 (84.93) and 77.85 (97.63) kJ/mol, respectively, which are higher than the gas phase values. This means that the reactant is more stabilized by the solvent than is the transition state (Supporting material).

As shown in Table 1 and Fig. 2, the values of activation parameters (E_a, $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$) for TS_{2B}^{trans} are higher than TS_{2B}^{cis} but $2 \cdots I—[Pd]^{trans}$, $B^{trans} \cdots PH_3$ are more stable than $2 \cdots I—[Pd]^{cis}$, $B^{cis} \cdots PH_3$, therefore, kinetically, the *cis* isomer has the main contribution in this step.