A DFT study on the mechanism of palladium-catalyzed divergent reactions of 1,6-enyne carbonates

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Abstract. The reaction mechanisms of palladium-catalyzed divergent reactions of 1,6-enyne carbonates have been investigated using DFT calculations at the B3LYP/6-31G(d,p) (LanL2DZ for Pd) level. Solvent effects on these reactions have been considered by the polarizable continuum model (PCM) for the solvent (DMF). The formation of vinylidenepyridines and vinylidenepyrrolidines were generated through 5-exo-dig cyclization or 6-endo-dig cyclization. Our calculation results suggested the following: (i) The first step of the whole cycle is the rate-determining step, which causes allenic palladium intermediate through two plausible pathways. This intermediate provides the corresponding products and releases the palladium catalyst by a subsequent hydrogen transfer and elimination process. (ii) For the catalyst CH₃OPdH, the reaction could occur through two possible pathways, but 5-exo-dig cyclization is favoured over 6-endo-dig cyclization. However, when the hydrogen atom is substituted with a phenyl group, the energy barriers for 5-exo-dig cyclization or 6-endo-dig cyclization become relatively high, 18.0–28.5 kcal/mol. The computational results provide good explanation for the experimental observations.

Keywords. 1,6-enyne carbonates; palladium-catalyzed; cyclization; density functional theory.

1. Introduction

Propargylic compounds are one of the most important and useful substrates, which can undergo several types of rearrangement promoted via palladium catalysts to give different kinds of allene, alkyne, enyne and alkene derivatives.^{1,2} Propargylic compounds with various nucleophiles by palladium catalysts have been developed as a powerful tool especially for constructing carbon-carbon and carbon-heteroatom bonds over the past few years.^{3–7} Since the first report of Tsuji in 1985, great progress has been made in developing efficient and selective Pd-catalyzed transformations, as evidenced by the prodigious number of reviews available on various aspects of this growing field.^{8–21} The reactions of allenyl palladium with olefins as nucleophiles are well-known to form carbon-carbon bonds.^{22–25} However, as most of these reactions produce corresponding allenic systems and subsequent rearranged derivatives, much less research interest has been paid to the propargylic substitution reactions of propargylic carbonates with olefins in Pd-catalyzed processes.^{26–28}

Recently, Liang *et al.*²⁹ studied palladium-catalyzed divergent reactions of enyne carbonates by experiments to synthesise six- or five-membered compounds (scheme 1). According to the experimental results, two proposed mechanisms for the palladium-catalyzed cyclization reactions of enyne carbonates are listed in scheme 2. In scheme 2, first 1,6-enyne carbonates undergoes the Pd-catalyzed transformation to generate allenylpalladium intermediate **A** and carbon dioxide. Subsequently, **A** is attacked by an olefin nucleophile to form intermediate **B** or **D**, respectively. The intermediates **B** and **D** provide the corresponding five-membered heterocyclic allenes **C** or six-membered heterocyclic allenes **E** by β -hydrogen elimination, which give the observed products and liberate the palladium catalyst.

To our knowledge, there are no detailed theoretical studies for the palladium-catalyzed divergent reactions reported by Liang group. Here, we present a detailed DFT study on the mechanism of palladium-catalyzed reaction of enyne carbonates to give the corresponding vinylidenepyridines or vinylidenepyrrolidines based on the experiment reported by Liang *et al.* In the experimental studies, Pd(dba)₂ was

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Scheme 1. Palladium-catalyzed synthesis of heterocyclic allenes from 1,6-enyne carbonate.

Scheme 2. Two plausible and more detailed mechanisms are envisioned for this novel palladium -catalyzed transformation.

selected as the catalyst. In order to reduce the computational cost, we have simplified this model catalyst to Pd(OMe)H.

2. Computational Methods

Gaussian 03 program³⁰ was used for all the calculations, and all geometries reported were fully optimized at the B3LYP level of the density functional theory (DFT).³¹ This hybrid DFT method has been successfully applied in the mechanistic studies of transition-metal-catalyzed reaction systems.^{32,33} In calculations, the effective core potentials (ECPs) of Hay and Wadt with the double- ζ valence basis set (LanL2DZ) were selected to describe Pd atom,^{34,35} while the 6-31G basis set with polarization

(d) and (p)³⁶ were chosen for H, C, N, O and S atoms. Natural bond orbital (NBO) analysis was used at the same level. Frequency analyses were calculated in order to ensure that the transition state has only one imaginary frequency, and stable intermediates have no imaginary frequency. The total energies and free energies were calculated at 298.15 K and 1atm, and the relative energies are corrected by zero-point energies (ZPE, not scaled). In several significant cases, IRC calculations³⁷ were carried out to confirm the connectivity between the transition states and minima (reactants, intermediate and products). To further consider the solvation effects, we calculated single-point solvation energy for all of the species calculated at the B3LYP/PCM/6-311++G(d,p) (LanL2DZ for Pd) level, using UAHF sets of radii on the polarizable continuum model (PCM).^{38,39} Agreeing

with the experimental conditions DMF ($\epsilon = 38.3$) was used as the solvent.

3. Results and Discussion

The energy profiles for the possible paths a–d of reaction systems are shown in figures 1 and 2. The optimized structures for the reactants (R1 and R2), transition states, intermediates and products of the reaction pathways are shown in figures 3 and 4. Free energies and the relative energies including zero-point energies of the reaction systems in the gas and solution phases are listed in table 1. Unless otherwise noted, free energies are discussed in DMF solvent.

3.1 Divergent reaction of 1,6-enyne carbonate ($R_1 = R_2 = H$) using CH_3OPdH catalyst

3.1a 6-Endo-dig cyclization: The energy profile for pathways a and b of this reaction process is represented

in figure 1. The structures of the various critical points located on the potential surface along with the values of the most relevant geometry parameters are shown in figure 4. As we know, the C–C triple bond functional group is characterized via two orthogonal π bonds, which has higher energy and easily interact with the d orbitals of transition metals (electrophiles). Meanwhile, the LUMO of alkynes has lower energy, which is easily attacked by strong nucleophiles. Once the alkyne is activated by coordination with the electrophilic metal complex, the alkyne becomes susceptible allenic to be attacked by weaker nucleophiles. Thus, the interaction of the C–C triple bond of enyne carbonates with the palladium atom would give the preliminary intermediate **R1**. From the energy profile it is evident that the first step of pathway indeed involves the preliminary intermediate **R1** stabilized by the coordination of the Pd atom to the carbon atom of olefin and the π -bond of the allenic moiety. In **R1**, this is a polarized complex with distances between Pd and two sp^2 -hybridized carbon atoms of 2.146 and 2.111 Å, respectively.

Figure 1. Energy profiles for pathways a (in red) and b (in black). Relative energies are given in kcal/mol.

Figure 2. Energy profiles for pathways 'c' (in red) and d (in black). Relative energies are given in kcal/mol.

Furthermore, the C¹–C² bond has lost a little of its double bond character and is now 1.269 Å. Meanwhile, the Pd–O¹, N–C³, C³–C⁴ and C⁴–C⁵ bond lengths are 1.937, 1.480, 1.506 and 1.343 Å, respectively. Once in **R1**, the coordination of the double bond with the palladium atom enhances the electrophilicity and induces a cyclization of the alkenyl carbon (C⁵) onto the double bond (C¹). A new and stable intermediate structure **1a** is formed through a six-membered ring transition structure **TSa1** (**TSa1** has only one imaginary frequency of 312.7 i cm^{−1} and IRC calculations confirmed that this TS connects the corresponding reactants and intermediate). Inspection of figure 1 shows that the palladium atom is completely connected with the C² atom of the allenic group (the bond distance Pd–C² is 2.897 Å) in **TSa1** and the bond of the C¹–C² and C⁴–C⁵ changes from 1.269 to 1.506 and from 1.343 to 1.446 Å, respectively. At the same time, palladium atom gradually transferred to the C⁴ atom, and the bond length of Pd–C⁴ is 2.073 in **TSa1**. Moreover, the transition vector obtained from the frequency

computations on **TSa1** is dominated by the C¹–C⁵ bond and the bond distance C¹–C⁵ is 2.184 Å. Table 1 and figure 1 show that the free energy of activation for this step is calculated to be 22.6 kcal/mol for **TSa1** and −18.7 kcal/mol for **1a** with respect to **R1**. In **1a**, it is evident that the C⁴–C⁵ double bond completes its change from a double bond to a single bond (1.531 Å) and the C¹–C⁵ bond becomes completely formed (1.554 Å). The Pd–C¹ bond also becomes almost broken and is now 2.253 Å. The palladium catalyst has completed the transfer process from C¹ to C⁴ atom. Due to the ring strain of six-membered ring, β-hydrogen in the intermediate structure **1a** is then eliminated to intermediate **2a** by a hydrogen transfer transition structure **TSa2**. In **TSa2**; the hydrogen of C³ atom connected in **1a** is transferred to Pd atom, and the lengths of breaking bond C³–H is 1.604 Å and the that of forming Pd–H bond is 1.573 Å. The Pd–C⁴ and the C³–C⁴ bonds in **TSa2** are now 2.105 and 1.430 Å, respectively. The C³–C⁴ single bond almost completes its change from a single bond to a double bond. The activation of free energy of the

Figure 3. Optimized structures for path 'a' and 'b' are shown in figure 1 with selected structural parameters (hydrogen atoms are omitted for clarity and bond lengths are presented in Å).

second step was 19.6 kcal/mol, and the formation of **2a** is an exergonic process (the free energy of reaction for the **2a** is -2.6 kcal/mol with respect to **1a**). This step for migration of the hydrogen atom results in the formation of the final product (**2a**) and regeneration of the catalyst (CH_3OPdH). The total reaction barrier of pathway 'a' is 22.6 kcal/mol, which indicates that the first step is the rate determining one. In total, the whole catalytic process was exothermic by -21.3 kcal/mol, lower than the reactant **R1**.

3.1b 5-Exo-dig cyclization: Apart from 6-endo-dig cyclization, a reaction between the alkenyl carbon (C^4) and the double bond (C^1) would give rise to another possible reaction pathway b in **R1**. The energy profile for this process is shown in figure 1. The structures of the various critical points located on the potential surface along with the values of the most relevant geometry parameters are presented in figure 4. Inspection of figure 4 shows that the first step for pathway 'b' of cyclization would give the new and

Figure 4. Optimized structures for path **c** and **d** are shown with selected structural parameters (hydrogen atoms are omitted for clarity and bond lengths are presented in Å).

stable structure **1b** through the five-membered-ring transition structure **TSb1** (**TSb1** has only one imaginary frequency of 304.8i cm⁻¹ and IRC calculations confirmed that this TS connects the corresponding reactants and intermediate). The C¹ atom is completely

connected with the C⁴ atom of the alkene (the C¹–C⁴ bond distance is 1.996 Å) in **TSb1** and the Pd–C¹ bond length changes from 2.111 to 2.143 Å. In **TSb1**, the Pd–C⁵, Pd–O¹ and C⁴–C⁵ distances are 2.073, 1.979 and 1.464 Å, respectively. Table 1 and figure 1 show that

Table 1. Thermodynamic properties (the relative free energy and activation free energy in gas phase and in solution) of the structures in figures 1 and 2.^a

System	$\Delta E_{\text{gas}}^{\text{rel}}$	$\Delta E_{\text{gas}}^{\ddagger}$	$\Delta G_{\text{gas}}^{\text{rel}}$	$\Delta G_{\text{gas}}^{\ddagger}$	$\Delta E_{\text{sol}}^{\text{rel}}$	$\Delta E_{\text{sol}}^{\ddagger}$	$\Delta G_{\text{sol}}^{\text{rel}}$	$\Delta G_{\text{sol}}^{\ddagger}$
R1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TSa1	18.9	18.9	22.5	22.5	19.4	19.4	22.6	22.6
1a	−12.9		−8.7		−24.5		−18.7	
TSa2	0.4	13.3	2.8	11.5	0.5	25.0	0.9	19.6
2a+CH ₃ OPdH	−10.2		−19.5		−9.7		−21.3	
TSb1	4.5	4.5	7.8	7.8	9.6	9.6	12.7	12.7
1b	−18.0		−15.0		−15.0		−10.9	
TSb2	3.2	21.2	5.3	20.3	4.2	19.2	4.3	15.2
2b+CH ₃ OPdH	−3.5		−13.6		−0.4		−13.3	
R2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TSa1	18.9	18.9	21.6	21.6	26.0	26.0	28.5	28.5
1c	−11.8		−8.8		3.1		3.5	
TSa2	1.6	13.4	3.2	12.0	8.2	5.1	8.4	4.9
2c+CH ₃ OPdH	−11.8		−22.8		−1.0		−14.5	
TSd1	4.5	4.5	6.6	6.6	16.3	16.3	18.0	18.0
1d	−17.2		−15.7		−7.7		−5.2	
TSd2	3.1	20.3	4.9	20.6	12.6	20.3	12.7	17.9
2d+CH ₃ OPdH	−4.2		−15.9		−4.1		−18.3	

^aThese values, in kcal/mol, were calculated at the B3LYP/6-31G(d,p) (LANL2DZ for Pd) level of theory and included the zero-point energy correction, using single-point PCM calculations at the B3LYP/PCM/6-311++G(d,p)//B3LYP/6-31G(d,p) (LanL2DZ for Pd) level of theory to model the effect of the solvent (DMF)

the free energy of activation for this step is calculated to be 12.7 kcal/mol for **TSb1** and the free energy of reaction for the **1b** intermediates is −10.9 kcal/mol with respect to **R1**. The lower barriers found for **TSb1** in comparison to those of **TSa1** can be mainly attributed to the following reasons. The NBO charges for the C¹, C⁴ and C⁵ atoms of **R1** are 0.099, −0.117 and 0.972 au, respectively. A positive charge found for the C¹ atom makes the nucleophilic attack of C⁴ on the positively charged C¹ more feasible than that of the C⁵ atom. Just as is exhibited by the structure of **1a**, the C¹–C⁴ and the Pd–C⁵ bonds in **1b** also become completely formed and are now 1.549 and 2.092 Å, respectively. Furthermore, the C⁴–C⁵ bond also accomplished the conversion of the double bond to a single bond, and now the bond distance is 1.540 Å. The subsequent step for migration of the hydrogen atom results in the formation of the final product (**2b**) and regeneration of the catalyst (CH₃OPdH) through **TSb2**. Figure 2 shows that the C⁶–H and Pd–H distances are 1.541 and 1.569 Å in **TSb2**, respectively. Meanwhile, the C⁵–C⁶ and Pd–C⁵ bond lengths changed from 1.521 to 1.430 Å and from 2.092 to 2.147 Å, respectively. The activation free energy of the step is 15.2 kcal/mol, and the formation of product **2b** is an exothermic process (the free energy of reaction for the **2b** is −2.4 kcal/mol with respect to **1b**), and the whole catalytic process is exothermic by −13.3 kcal/mol. Comparison of the structure of **TSa2**,

the activation free energy of this step for **TSb2** is lower than that for **TSa2** by 4.4 kcal/mol. It is therefore obvious that the first step of the two pathways is rate determining for the whole catalytic process. The relatively high barriers found for both of the two different pathways. The higher barriers found for **TSa1** indicate that the reaction pathway for 5-exo-dig cyclization is more feasible than that of 6-endo-dig cyclization. Our calculated results are also consistent with the experimental observations of Liang *et al.* for the palladium-catalyzed divergent reactions of 1,6-enyne carbonate.

3.2 Divergent reaction of 1,6-enyne carbonate (R₁ = H, R₂ = Ph) using CH₃OPdH catalyst

To further improve our understanding of the palladium-promoted reactions for different unsaturated substrates as proposed in scheme 1, we have done additional calculations to begin to study the reactivity via a ligand exchange of hydrogen atom (the group is marked as R₂ in scheme 1 and 2) in **R1** with phenyl group. Following the originally proposed mechanism and the model studies, the detailed mechanism of formation is displayed in figure 3 and similar reaction pathways have been determined for the reaction systems. The structures of the various critical points located on the potential surface along with the values of the most relevant geometry parameters are presented in figure 3.

3.2a 6-Endo-dig cyclization: Examination of figure 2 shows that the first step for pathway 'c' also involves the preliminary intermediate **R2**, stabilized by the coordination of the Pd atom to the π bond of the allene moiety. In **R2**, the Pd–C¹ distance is 2.101 Å and the lengths of the C¹–C² bond is 1.270 Å. Structure **R2** causes a cyclization of the C¹ atom of allene onto the double bond (C⁵) and gives the new and stable structure **1c** through the six-membered-ring transition structure **TSc1**. In **TSc1**, the new C¹–C⁵ bond is 2.171 Å. Figure 2 and table 1 shows that the activation free energy for this step is calculated to be 28.5 kcal/mol for **TSc1** and the free energy of the reaction for the intermediate **1c** is -3.5 kcal/mol with respect to **R2**. The higher activation free energy found for this step indicates that it is also the rate-determining step. The higher barrier found for **TSc1** in comparison to that for **Tsa1** indicated that an iodine group would greatly reduce the positive charge of C⁵ (0.855 and 0.714 au for **R1** and **R2** respectively). The next step for a hydrogen transfer and elimination reaction process produces the formation of the final product (**2c**) and regeneration of the catalyst (**CH₃OPdH**) through **TSc2**. The activation free energy of the step is 4.9 kcal/mol, and the formation of **2a** is an exothermic process (the free energy of reaction for **2c** is 18.0 kcal/mol with respect to **1c**). These total catalytic cycle steps are exothermic by -14.5 kcal/mol.

3.2b 5-Exo-dig cyclization: As we mentioned above, attack between the C¹ and the C⁴ atom of the double bond would also give rise to another possible reaction pathway 'd' through **R2**. Examination of figure 2 shows that the first step for pathway 'd' also involves the preliminary intermediate **R2**. Cyclization of the C¹ atom onto the double bond (C⁴) would give the new and stable structure **1d** through the five-membered-ring transition structure **TSd1**. According to our calculated results, figure 4 shows that the C¹–C⁴ bond distance is 1.994 Å in **TSd1**. In **TSd1**, palladium complex has migrated from the C² to the C⁵ atom, and the Pd–C⁵ distance in **TSd1** is 2.073 Å. Table 1 shows that the activation free energy for this step is calculated to be 18.0 kcal/mol for **TSd1** and the free energy of the reaction for the intermediate **1d** is -5.2 kcal/mol with respect to **R2**. The relatively lower barriers are found for **TSd1** in comparison to those for **TSc1** (28.5 kcal/mol). It is important to point out that this step is also the rate-determining step for the pathway. However the reaction pathway via **TSb1** only needs to overcome a barrier of 12.7 kcal/mol, some 5.3 kcal/mol lower than that for **TSd1**. The C¹–C⁴ and Pd–C⁵ bonds are 1.550 and 2.097 Å in **1d**, respectively. The subsequent step for migration of the hydrogen

atom to palladium atom results in the product (**2d**) and regeneration of the catalyst (**CH₃OPdH**) via **TSd2**. Furthermore, the C⁵–C⁶ bond also accomplished the conversion of the single bond to a double bond and now the bond distance is 1.337 Å in **TSd2**. The final barrier of 17.9 kcal/mol is required to release the product and regenerate the catalyst. This final step is exothermic by -13.1 kcal/mol. The lower barrier found for **TSd1** in comparison to that for **TSc1** indicates that 5-exo-dig cyclization of the nucleophile onto the internal carbon of the alkyne with a phenyl group is favoured.

As shown in table 1, for the consideration of the solvent effect of the reaction systems the activation free energies of the first steps (**Tsa1**, **TSb1**, **TSc1** and **TSd1**) are increased than that of the gas phase. However, the activation free energies of the subsequent steps (**Tsa2**, **TSb2**, **TSc2** and **TSd2**) in solution are decreased compared to those of the gas phase, indicating that the CC bond cyclization process of the solvent DMF is disadvantageous, and the solvent DMF is more favourable for the hydrogen transfer process.

3.3 5-Exo-dig Cyclization vs 6-Endo-dig Cyclization

According to the experimental results, palladium-catalyzed divergent cyclizations of 1,6-enyne carbonates can be combined with Suzuki coupling to prepare highly functionalized 3-vinylidene-1-tosylpyrrolidines. Two general mechanisms have been postulated to explain the formation of 5-exodig cyclization and 6-endo-dig cyclization (scheme 1). Our calculated results clearly suggest that the hydrogen migration process has lower activation energies for the catalytic reaction systems, and the first step of 5-exodig cyclization and 6-endo-dig cyclization is the rate-limiting step for 1,6-enyne carbonates. The results show that in the reaction of 1,6-enyne carbonate (R₁ = R₂ = H) with **CH₃OPdH** both 5-exodig cyclization and 6-endo-dig cyclization (pathways 'a' and 'b') are feasible, with a barrier height of 22.6 and 12.7 kcal/mol, respectively. While the reaction for the pathway 'b' takes place more easily. They can also promote divergent reactions of 1,6-enyne carbonate at experimental temperatures due to their relatively low activation energies. For 1,6-enyne carbonate (R₁ = H R₂ = Ph), it is widely favoured that the 5-exodig cyclization over 6-endo-dig cyclization represents the reaction reality, the reaction barriers of the pathway 'c' (28.5 kcal/mol) are much higher than those of the pathway d (18.0 kcal/mol). However, the reaction for **R2** (phenyl group substitution of the hydrogen atom of **R1**) have relatively higher activation barriers of 18.0–28.5 kcal/mol and the reactions produce products of 5-exodig cyclization at relatively high temperatures. The

above comparison is qualitatively consistent with the experimental reaction and helps to provide a reasonable explanation for understanding some basic factors that determine the reactivity of these types of unsaturated substrates and their reaction pathways for the divergent reaction promoted by palladium catalyst.

4. Conclusions

In summary, this work has provided the first theoretical study for the reaction of the palladium-catalyzed divergent reactions of 1,6-enyne carbonates. According to our calculations, the reaction proceeds through two possible channels. The first step of the catalytic cycle is the addition of the vinyl carbon atom onto the triple bond to form an allenic palladium intermediate through 5-exo-dig cyclization or 6-endo-dig cyclization. Subsequently, allenic palladium intermediate undergoes hydrogen transfer and elimination reactions to produce the observed products and liberate the palladium catalyst. For the two different reaction pathways, the first step is the rate-determining step. For the catalyst CH_3OPdH , this reaction could occur through two possible pathways where 5-exo-dig cyclization is easier than 6-endo-dig cyclization. On the other hand, when the hydrogen atom is substituted with a phenyl group, the energy barriers for 5-exo-dig cyclization or 6-endo-dig cyclization are relatively higher, 18.0–28.5 kcal/mol and the reactions occur at relatively higher temperatures. Our computational results provide explanation for the experimental observations of Liang group for the palladium-catalyzed divergent reaction of 1,6-enyne carbonates.

Supporting Information

The Cartesian coordinates for the calculated stationary structures and the sum of the electronic and zero-point energies for the transition and ground states obtained from the DFT calculations are available at www.ias.ac.in/chemsci.

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