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Mechanism of alkene isomerization by bifunctional ruthenium catalyst: A theoretical study

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ABSTRACT

The molecular mechanism of the isomerization of 1-pentene to form (*E*)-2-pentene catalyzed by the bifunctional ruthenium catalyst has been investigated using density functional theory calculations. The reaction is likely to proceed through the following steps: 1) the β-H elimination to generate the ruthenium hydride intermediate; 2) the reductive elimination of the hydride intermediate to generate the nitrogen-protonated allyl intermediate; 3) the transportation of the hydrogen by the dihedral rotation with Ru—P bond acting as axis; 4) the oxidative addition to afford another hydride complex; 5) the reductive elimination of the hydride intermediate to form the C_2-C_3 π-coordinated agostic intermediate; 6) the coordination of the nitrogen to the ruthenium center to give the final product. The rate-determining step is the oxidative addition step (the process of the hydrogen moves to ruthenium center from the nitrogen atom) with the free energy of 31.2 kcal/mol in the acetone solvent. And the N-heterocyclic ligand in the catalyst mainly functions in the two aspects: affords an important internal-basic center (nitrogen atom) and works as a transporter of hydrogen. Our results would be helpful for experimentalists to design more effective bifunctional catalysts for isomerization of a variety of heterofunctionalized alkene derivatives.

1. Introduction

Isomerization of the double bond of an unsaturated compound is an important reaction in organic chemistry [1–10]. And transition-metal-catalyzed isomerization of the carbon—carbon double bond of alkene has been a considerable-interest area [11–17]. Recently, Grotjahn and co-workers reported an attractive ruthenium catalyst to catalyze the extensive isomerization of alkenes [18]. This ruthenium catalyst is a mono-metallic catalyst with an N-heterocyclic ligand (as shown in Scheme 1S), which has been confirmed by NMR. When the N-heterocyclic group on the phosphorus is replaced by phenyl group, the reaction rate of the isomerization of 1-pentene and pent-4-en-1-ol are 330 and 10,000 times slower than using the N-heterocyclic ligand, respectively. Thus, this evidence can elucidate the important role of the heterocycle in the catalyst. Using this catalyst, a variety of heterofunctionalized alkene derivatives can isomerize to the high-purity (*E*)-isomer products (61–97%), just at low loading (2–5%) in many cases. As a bifunctional catalyst, in which the Lewis acid and Lewis base are ruthenium and nitrogen (directly bound to ruthenium), respectively, it can move an alkene double bond over 30 positions along an alkene chain. The possible mechanism of this isomerization process has been proposed by Grotjahn et al (Scheme 1). The catalytic cycle is initiated by the exchange of acetonitrile for alkene. Then, the deprotonation takes place at an allylic position with the assistance of the basic ruthenium-bound nitrogen on the heterocyclic ligand. Finally, the proton goes back to either end of the allyl moiety from the nitrogen atom and promotes isomerization. To our knowledge, no computational study has been carried out to investigate the mechanistic details of alkene isomerization catalyzed by the bifunctional ruthenium catalyst.

In this work, we will perform density functional theory calculations to explore the mechanistic details of alkene isomerization catalyzed by the bifunctional ruthenium catalyst and to find how the catalyst operated in this isomerization process. A prototype reaction, the isomerization of 1-pentene to (*E*)-2-pentene (95%) required only 15 min at room temperature in acetone using 2 mol% catalyst (as shown in Scheme 2), is chosen for study. The results provide a general picture on the mechanism of the isomerization of alkenes, and a molecular level picture on how the bifunctional ruthenium catalyst function in the isomerization process. The information revealed in this study may be useful to experimentalists for inventing more effective bifunctional catalysts for isomerization of alkenes and a variety of heterofunctionalized alkene derivatives.

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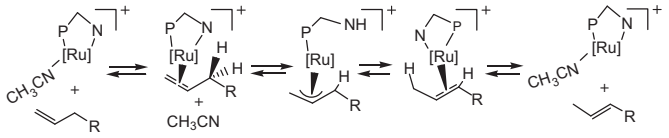


Scheme 1. Mechanistic hypothesis proposed by Grotjahn et al.

2. Computational methods

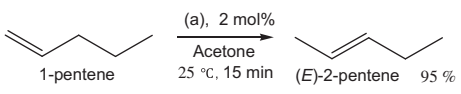
All calculations are carried out using the Gaussian03 package [19]. Two basis sets are used. The geometries of all stationary points are fully optimized with the B3LYP density functional [20,21] with the basis set 1 (BS1). In BS1, relativistic effective core potential (ECP) [22,23] is employed for ruthenium and phosphorus. The basis set for Ru is a modified LANL2DZ plus an f-type polarization function [24], in which the two 5p functions of the standard LANL2DZ are replaced by the optimized 5p functions from Couty and Hall [25]. For phosphorus, the standard LANL2DZ augmented by a d-type function with the exponent of 0.387 is used [26]. For the catalyst **1**, the five-membered N-heterocyclic atoms, a 6-31G (d, p) basis set is employed, and all of the other atoms in the ligands (heterocyclic ligand and cyclopentadienyl group) are described with the 3-21G basis set. For all atoms in 1-pentene, a 6-31G (d, p) basis set is used. For each stationary point, vibrational frequencies are calculated to obtain zero-point vibrational energies (ZPVE) and verify whether it is a minimum or a transition state. Intrinsic reaction coordinates (IRC) [27,28] calculations are performed from each transition state to verify whether the reactant and the product are really connected by the transition state.

More accurate relative energies of all species are obtained by subsequent single point calculations with a larger basis set (BS2) at the geometries optimized with BS1, denoted as B3LYP/BS2//B3LYP/BS1. In BS2, for the catalyst **1**, a 6-311++G(d,p) basis set is employed for the phosphorus and the five-membered N-heterocyclic atoms, a 6-31G(d, p) basis set is employed for all of the other atoms in the ligands (heterocyclic ligand and cyclopentadienyl group). For all atoms in 1-pentene, a 6-311++G (d,p) basis set is used. For all stationary points, free energies of solvation are computed as the energy difference between single point B3LYP/BS2 calculations in acetone calculated with the PCM model [29] and those in the gas phase at the B3LYP/BS1 gas-phase geometries.

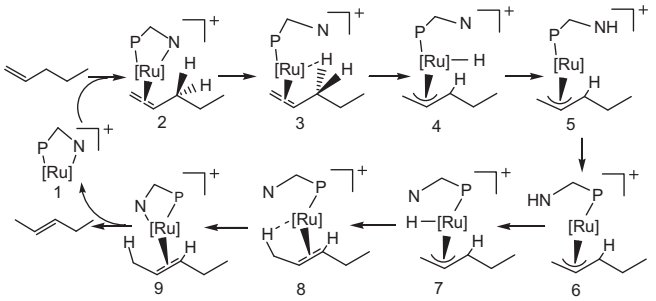
3. Results and discussion

In this section, we will explore the potential energy surface of the isomerization of 1-pentene catalyzed by the bifunctional cationic ruthenium catalyst **1** (as shown in Scheme 3), and in the next subsection, how this catalyst function in the isomerization process will be elucidated. The optimized structures of all stationary points are collected in Figs. 1 and 2, and their relative free energies are provided in Fig. 3.

Due to two possible geometric isomers for 2-pentene, *E* or *Z*, there should be two possible reaction pathways to generate the products of (*E*)-2-pentene and (*Z*)-2-pentene, respectively. The reaction pathway for producing the 2-pentene with *E* or *Z* configuration should be similar. In the experiments with the ruthenium catalyst, the main product is of *E* configuration. Thus, only the process for the formation of the (*E*)-2-pentene is discussed in this work.



Scheme 2. The isomerization of 1-pentene.



Scheme 3. The reaction pathway supposed for the catalyzed isomerization.

3.1. The formation of the active catalyst

In experiment, $[CpRu(II)(CH_3CN)_3]^+$ PF_6^- (217.1 mg,0.49 mmol) and the required phosphine ligand (125.9 mg, 0.51 mmol) were mixed in acetone to generate the yellowish brown powder. Finally, the 18e precatalyst $[CpRu(II)(CH_3CN)L]^+$ PF_6^- (*a*, Scheme 1S) was confirmed by the NMR and elemental analysis. And the initial dissociation of an acetonitrile (CH_3CN) ligand is found to be much more facile, with the free energy change of 6.9 and -0.2 kcal/mol, in gas phase and in the solution phase, respectively.

$$[CpRu(CH_3CN)L]^+ \rightarrow [CpRuL]^+ + CH_3CN$$

Therefore, a 16e complex, $[CpRu(II)L]^+$ PF_6^-, is to be formed. And in this work, the cation $[CpRu(II)L]^+$ (*c*, Scheme 1S) is the active catalyst.

3.2. The allyl mechanism

According to the pathway shown in Scheme 3, the initial step of the reaction is the coordination of 1-pentene to the ruthenium center to produce the π-bound intermediate **2**. Then, the agostic intermediate **3** is obtained by the positional adjustment of 1-pentene on the metal. Thus, the C—H bond, at the activated allylic position (i.e. β-H) of the 1-pentene, is oxidatively added to generate the η^3-allyl hydride **4**. Next, the Ru-bound hydrogen moves to the basic nitrogen to produce the intermediate **5**. Subsequently, the N-bound hydrogen is transported to the side of the terminal allylic carbon to give **6**. And another η^3-allyl hydride **7** is obtained by an oxidative addition reaction. Then, the agostic species **8** is formed by the reductive elimination. Finally, the final product dissociates from the π-bound intermediate **9**, and the active catalyst is regenerated.

3.2.1. The formation of the η^3-allyl hydride

Initially, 1-pentene is Л-coordinated to the ruthenium to form an 18e complex **2**. In **2**, the C_1—C_2 bond is elongated to 1.396 Å (from 1.333 Å in free 1-pentene), indicating that the C—C double bond activation by ruthenium has been significantly achieved. The free energy change of this coordination step is 10.8 kcal/mol above the reactants (as shown in Fig. 3). Next, there will be two possible modes for the allylic-positional hydrogen transfer. The first one is that the proton directly moves to the basic nitrogen (N_1) from the allylic position (C_3). Much endeavor has been done to find the transition state of this β-H elimination step, but none of the corresponding structure could be located. The second one is that the β-H adds to the ruthenium center to produce the η^3-allyl hydride. Initially, the agostic intermediate **3** is formed via the transition state **TS1**. In **TS1**, the Ru—H distance is getting shorter (from 3.370 Å in **2** to 2.372 Å), but the Ru—N_1 bond is breaking (from 2.324 Å in **2** to 3.123 Å). The free energy barrier of this agostic intermediate-formation step is 11.0 kcal/mol. Subsequently, the β-H elimination affords the η^3-allyl hydride **4** via the transition state

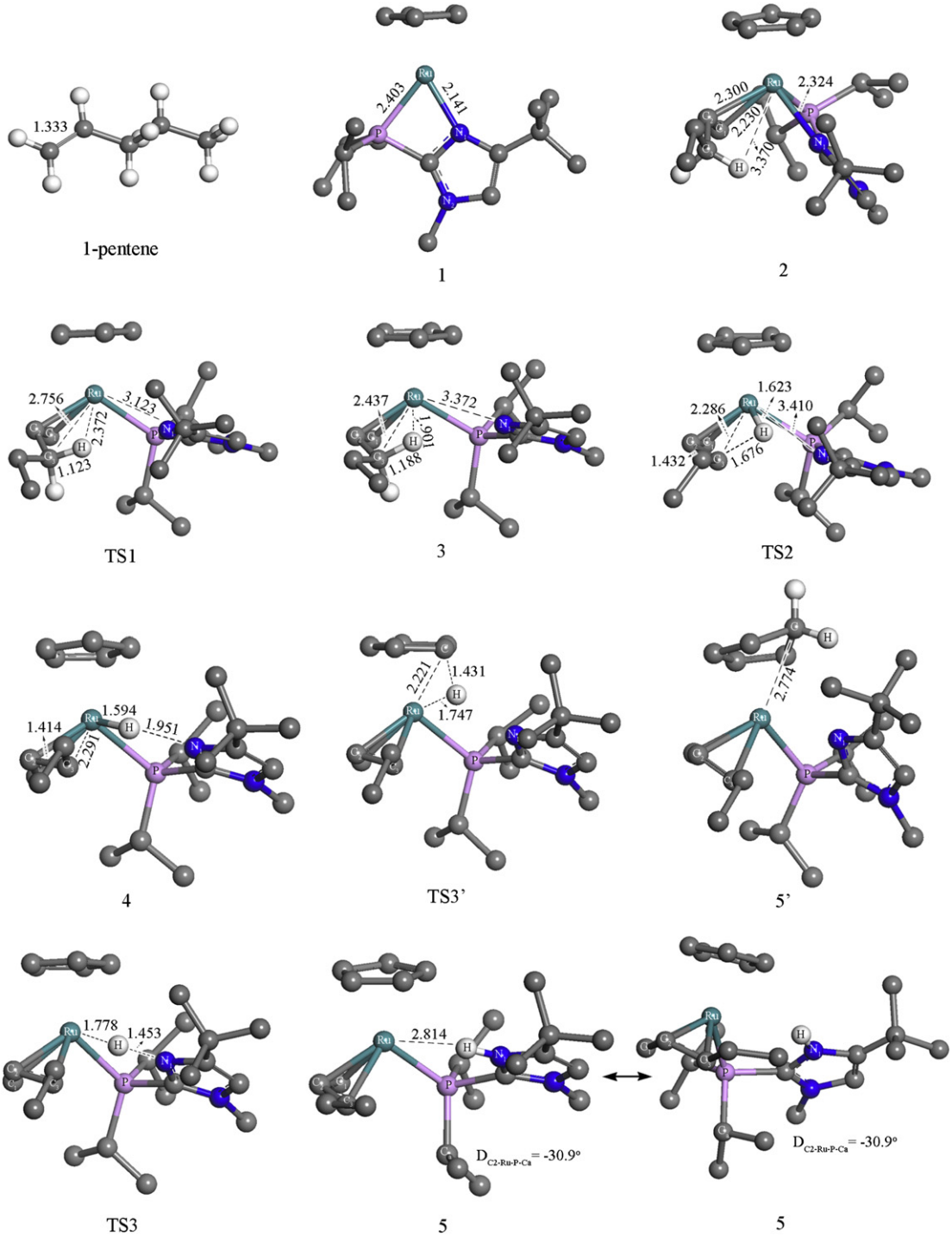


Fig. 1. Optimized geometries of the stationary points along the reaction pathway of isomerization. All H atoms (except those involved in isomerization process) are omitted for clarity.

TS2. In **TS2**, the Ru—H bond is forming (from 1.901 Å in **3** to 1.623 Å), and the C_3—H bond is breaking (from 1.188 Å in **3** to 1.676 Å). The free energy barrier of this β-H elimination step is 3.0 kcal/mol with respect to **3**.

3.2.2. The reductive elimination

In order to achieve the isomerization, the Ru-bound hydrogen must migrate to the terminal allyl carbon (C_1). For the intermediate **4**, there will be three modes for the hydrogen transfer.

The first mode is the positional adjustment of the Ru-bound hydrogen. In this way, the hydrogen can shift to the side of the terminal allyl carbon (C_1). However, this adjustment must overcome a very high free energy barrier (45.1 kcal/mol, relative to **1** and 1-pentene). Hence, it is impossible for the isomerization to go along in this mode.

For the second mode, the Ru-bound hydrogen may initially add to the carbon of the cyclopentadienyl (Cp) ligand (the corresponding transition state is **TS3′**) to generate the intermediate **5′**,

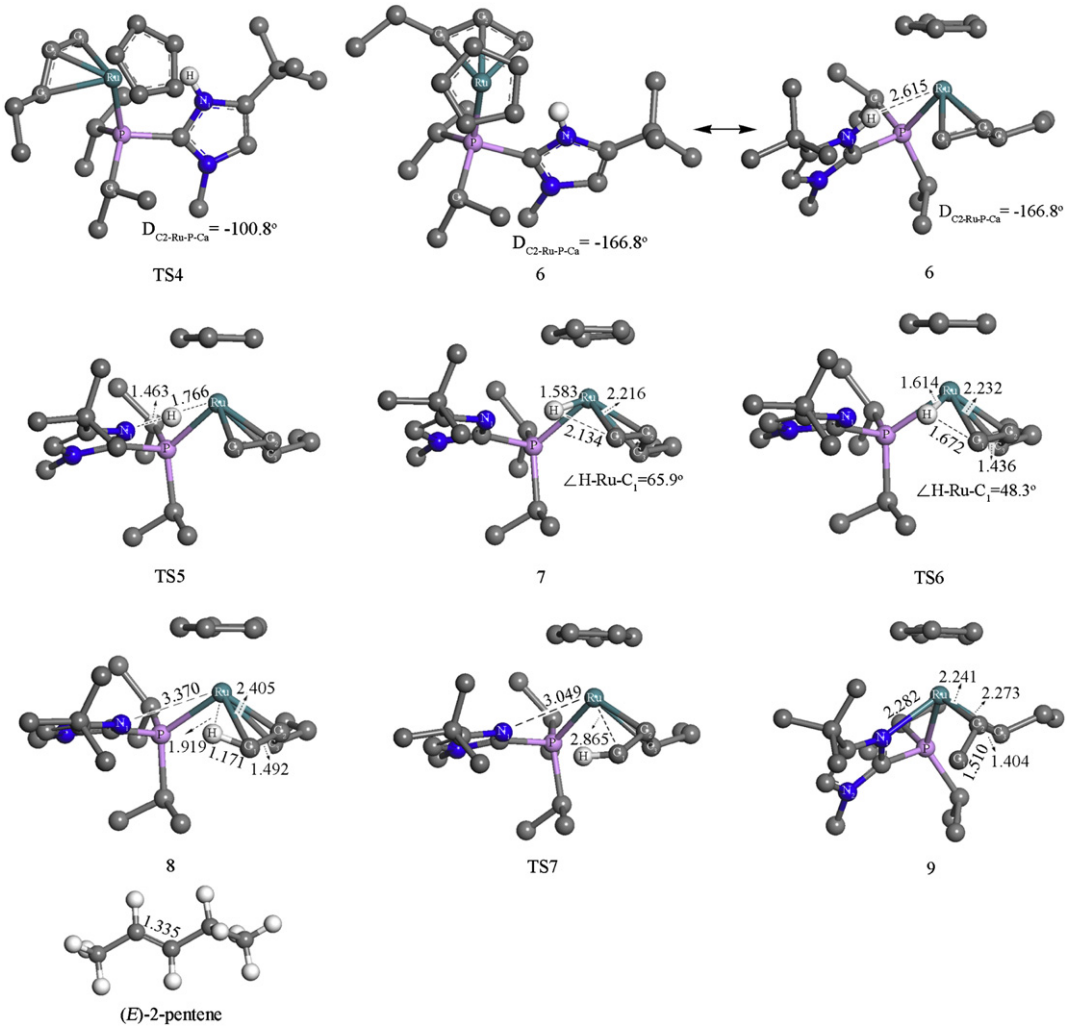


Fig. 2. Optimized geometries of the stationary points along the reaction pathway of isomerization. All H atoms (except those involved in isomerization process) are omitted for clarity.

and then the hydrogen was migrated to the side of the terminal allyl carbon (C_1) by the rotation of Cp group. And the subsequent steps will be the oxidative addition following the reductive elimination. The free energy of **TS3′** is 35.3 kcal/mol (relative to **1** and 1-pentene). Therefore, it is difficult for this mode to take place under the experimental conditions.

For the last mode, the hydrogen migrates to the nitrogen atom (N_1) to generate the intermediate **5** via the transition state **TS3**. In **TS3**, the Ru-H bond is breaking (from 1.594 Å in **4** to 1.778 Å), but the H—N_1 bond is forming (from 1.951 Å in **4** to 1.453 Å). The free energy of **TS3** is 25.0 kcal/mol (relative to **1** and 1-pentene).

Comparison of the above three modes, one can find that the third one is the most possible pathway for the isomerization reaction to undergo through. The subsequent steps, after the formation of **5** by the reductive elimination step, will be discussed in the next subsection in detail.

3.2.3. The transportation of the hydrogen

To ensure the successful progress of the isomerization reaction, the hydrogen on the nitrogen atom (N_1) must be transported to the side of the terminal allyl carbon (C_1). For **5**, the most possible mode for the transportation of the hydrogen (on the N_1 atom) is the dihedral rotation with the Ru—P bond acting as axis, the corresponding transition state is **TS4** (Fig. 2). The free energy barrier of this rotational step is only 3.6 kcal/mol. Therefore, the rotation is facile under the experimental environment to generate the intermediate **6**.

3.2.4. The oxidative addition and the subsequent steps to produce the final product

After the formation of **6**, the hydrogen will migrate to the terminal carbon (C_1) to generate the final product. Firstly, the directly transfer of the hydrogen from the N_1 atom to the C_1 atom is taken into account. But it is similar to the above mentioned that none of the transition state is to be located. Herein, the oxidative addition initially takes place to generate the η^3-allyl hydride **7** via the transition state **TS5**. In **TS5**, the Ru—H bond is forming (from 2.615 Å in **6** to 1.766 Å), but the H—N_1 bond is breaking (from 1.032 Å in **6** to 1.463 Å). And this oxidative addition step is the rate-determining step with the free energy of 27.2 kcal/mol (relative to **1** and 1-pentene). Subsequently, the hydrogen adds to the terminal allyl carbon (C_1) via the transition state **TS6**. In **TS6**, the Ru—H bond is breaking (from 1.583 Å in **7** to 1.614 Å), but the H—C_1 bond is forming (from 2.134 Å in **7** to 1.6723 Å). And the C_1—C_2 bond is elongated to 1.436 Å (from 1.419 Å in **7**). The free energy barrier of this reductive elimination step is only 0.3 kcal/mol with respect to **7**. Hence, another agostic intermediate **8**, in which the Ru—N_1 bond distance is 3.370 Å, is afforded. Next, the basic nitrogen (N_1) will

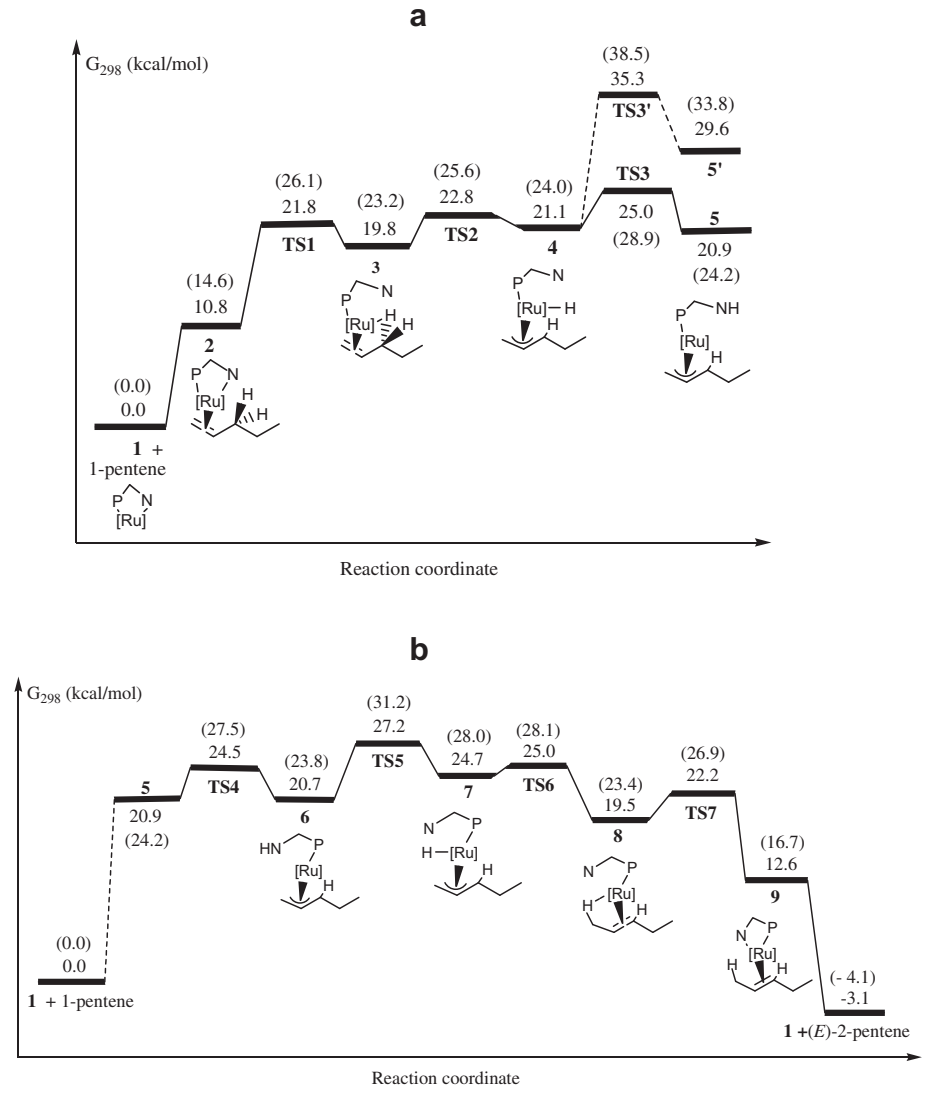


Fig. 3. Free energy profiles of the isomerization of 1-pentene in gas phase and in the solution phase (values in parentheses).

coordinate to the ruthenium accompanying the elimination of the agostic structure, the corresponding transition state is **TS7**. In **TS7**, the Ru—N_1 bond distance is shortened to 3.049 Å, and the Ru—H bond distance is elongated to 2.622 Å (from 1.919 Å in **8**). The free energy barrier of this coordination step is 2.7 kcal/mol (relative to **8**). Therefore, the intermediate **8** can easily convert into **9**, in which the C_2—C_3 double bond π-coordinated to the ruthenium. Ultimately, the product, (*E*)-2-pentene, can be released from the species **9**, and the active catalyst **1** is regenerated.

3.3. The solvent effect on the reaction

In the preceding subsections, the free energy profiles of the whole reaction in gas phase have been discussed. When the solvent effect is taken into account, the relative energies of the intermediates and transition states are increased to different extent (as shown in Fig. 3), but the qualitative trend of the free energy profile remains the same (as in gas phase).

For example, the rate-determining step on the whole reaction pathway is the oxidative addition step from **6** to **7** in both gas phase and the solution phase, which with the free energies of 27.2 (gas phase) and 31.2 kcal/mol (solvent), respectively.

3.4. The role of the N-heterocyclic ligand in the ruthenium catalyst

As mentioned above, for the intermediate **4**, when the nitrogen atom on heterocyclic ligand does not operate in the catalyst cycle, there are mainly two channels for the reaction to progress. The first one is the positional adjustment of the hydrogen on the ruthenium center, but with a very high free energy (45.1 kcal/mol, relative to **1** and 1-pentene). For the second, the hydrogen initially adds to the carbon of cyclopentadienyl (Cp) ligand (the corresponding transition state is **TS3′**), and then undergoes through the rotation of Cp group to transfer the hydrogen to the same side of the terminal allyl carbon (C_1). The free energy of **TS3′** is 35.3 kcal/mol (relative to **1** and 1-pentene). Therefore, it is difficult for the isomerization reaction to take place through these two channels under the experimental conditions. And this result is in agreement with the experimental evidence, which is that when the phenyl group is used to substitute for the N-heterocyclic group on the phosphorus, the reaction rate of the isomerization of 1-pentene is 330 times slower than that using the N-heterocyclic ligand. However, when the hydrogen adds to the nitrogen (N_1), the free energy of the elimination step from **4** to **5** is reduced to 25.0 kcal/mol (relative to **1** and 1-pentene). In a similar way, the free energy of the oxidative addition step from **6** to **7**, which

is the rate-determining step, is 27.2 kcal/mol (gas phase). Therefore, this can elucidate that the N-heterocyclic ligand in the catalyst affords an important internal-basic nitrogen atom (act as a Lewis base). Thus, the nitrogen atom (as the Lewis base) and the ruthenium atom (as the Lewis acid) in this bifunctional catalyst can work cooperatively to promote the isomerization reaction.

After the formation of **5**, it is the dihedral rotation with the Ru—P bond acting as axis that transport the hydrogen (on the N_1 atom) to the side of the terminal allyl carbon, the corresponding transition state is **TS4**. The free energy barrier of this rotational step is only 3.6 kcal/mol. Therefore, the N-heterocyclic ligand in the catalyst also works as a transporter of hydrogen.

In general, the N-heterocyclic ligand in the bifunctional catalyst mainly functions in the two aspects: affords an important internal-basic center (nitrogen atom) and works as a transporter of hydrogen.

4. Conclusions

In this paper, we have carried out detailed density function calculations to investigate the possible mechanism of the isomerization of 1-pentene catalyzed by the bifunctional ruthenium catalyst. According to our calculations, the isomerization reaction of 1-pentene to generate (*E*)-2-pentene is likely to proceed through the following steps: 1) the β-H elimination to generate the ruthenium hydride intermediate; 2) the reductive elimination of the hydride intermediate to generate the nitrogen-protonated allyl intermediate; 3) the transportation of the hydrogen by the dihedral rotation with Ru—P bond acting as axis; 4) the oxidative addition to afford another hydride complex; 5) the reductive elimination of the hydride intermediate to form the C_2—C_3 π-coordinated agostic intermediate; 6) the coordination of the nitrogen to the ruthenium center to produce the final product. For the whole reaction, the rate-determining step is the oxidative addition step (the process of the hydrogen moves to ruthenium atom from the nitrogen atom) with the free energy of 31.2 kcal/mol in the acetone solvent. And the N-heterocyclic ligand in the bifunctional ruthenium catalyst mainly functions in the two aspects: affords an important internal-basic center (nitrogen atom) and works as a transporter of hydrogen. The mechanism proposed here for the isomerization of 1-pentene is expected to be general for isomerization of many other alkene derivatives, and thus would be helpful for experimentalists to design more effective bifunctional catalysts for isomerization of a variety of heterofunctionalized alkene derivatives.

Acknowledgments

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Appendix. Supplementary Information

Supplementary Information associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.08.034.

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