Density Functional Theory Studies of Ruthenium-Catalyzed Bis-Diels−Alder Cycloaddition of 1,5-Cyclooctadiene with Alkynes

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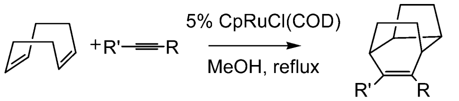
Density functional theory calculations at the B3LYP level have been performed to study the reaction mechanism of the Ru-catalyzed cycloaddition of 1,5-cyclooctadiene (COD) with alkynes. Our calculations point toward the proposed mechanism that the cycloaddition reaction occurs via an intermediate formed by the active species $[CpRu(COD)]^+$ and an alkyne substrate molecule. The first C−C coupling step was found to be the rate-determining step. The active species $[CpRu(COD)]^+$, which is crucial for the catalytic reaction, can be obtained through the ionization of Cl^- from [CpRu(COD)Cl] under the polar solvent of MeOH. The extra $\pi_\perp$ bond of alkynes in comparison to alkenes has been found to play a key role in stabilizing the relevant reaction intermediate as well as lowering the reaction barriers. In the olefin case, the absence of the extra $\pi_\perp$ bond leads to the instability of the corresponding intermediate as well as the high reaction barriers. Reaction mechanisms that are deemed possible on the basis of known fundamental organometallic reactions, such as oxidative coupling, ligand isomerization, and Cp ring slippage, were found to have higher reaction barriers.

Introduction

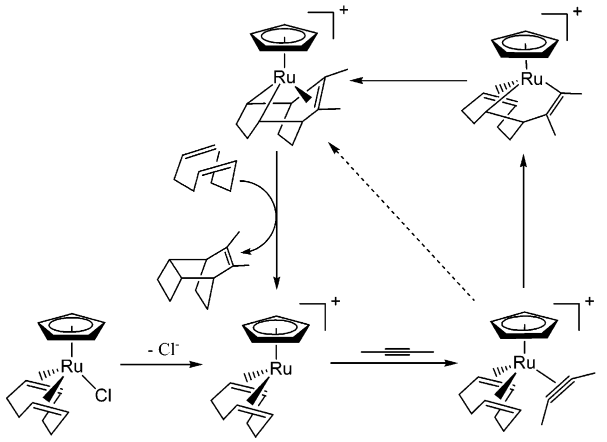
Transition metal-catalyzed cycloaddition reactions have attracted considerable attention in recent years.[1−6] Using a ruthenium catalyst, CpRu(COD)Cl (**1**), Trost and co-workers reported in 1993 the reactions of 1,5-cyclooctadiene (COD) with various alkyne substrates, giving [2+2+2] cycloaddition products (see eq 1).[7] On the basis of the experimental findings, they proposed the reaction mechanism shown in Scheme 1. The proposed mechanism starts with the formation of the active $[CpRu(COD)]^+$ cation by the ionization of Cl^- under the reaction conditions having the polar solvent MeOH. Then, the active 16-electron cationic species takes an alkyne substrate molecule to form an alkyne complex intermediate. The intermediate undergoes either a stepwise carbon−carbon coupling or a concerted one, giving a precursor complex for the formation of the [2+2+2] cycloaddition products upon a reductive elimination step. The proposed mechanism is apparently very convincing. In view of the fact that there are relatively few theoretical calculations[8−11] on the type of carbon−carbon coupling reactions and the importance of metal-catalyzed cycloaddition reactions, we feel it is necessary to theoretically study the proposed mechanism in more



(1)

R' = H, Me, Et, CH_2OR''; R = CH_2OR'', COOMe, CH_2CH_2OR'', C_3H_6COOMe

Scheme 1



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detail in order to understand the intermediate and the corresponding transition states. We hope to answer the following questions. Is the stepwise mechanism or the concerted one operative in the reaction? If the stepwise mechanism is operative, which step is rate-determining? In addition, the experiments also showed that the Ru complex did not catalyze cycloaddition of COD with alkene substrates.[6,7] Through our studies, we hope to understand the inactivity toward alkenes. In this work, we also want to examine other mechanisms, which are deemed possible on the basis of known fundamental organometallic reactions.[12–14] To answer these questions, theoretical calculations based on the B3LYP density functional theory have been carried out to examine the structural and energetic aspects related to the possible reaction pathways.

Computational Details

Molecular geometries of the model complexes ([CpRu(COD)]$^+$ + HC≡CH) and ([CpRu(COD)]$^+$ + $H_2C{=}CH_2$) were optimized at the Becke 3LYP (B3LYP) level of density functional theory.[15] Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). The Stuttgart/Dresden effective core potentials and basis sets[16] were used to describe Ru and Cl, while the standard 6-31G basis set was used for C and H atoms. Polarization functions ($\zeta(d) = 0.6$)[17] were added for the two carbons of the alkyne ligand (or the alkene ligand) and the olefinic carbons of the COD ligand, and ($\zeta(d) = 0.514$)[17] for the chloride ligand. All the calculations were performed with the Gaussian 98 software package.[18]

Results and Discussion

Other Possible Reaction Mechanisms. Before we discuss the mechanism proposed by Trost and coworkers, it is interesting to investigate other mechanistic possibilities on the basis of known fundamental organometallic reactions.[12–14]

Oxidative Coupling Process. It is well known that transition metal complexes can mediate oxidative coupling reactions between two multiple bond units in the manner shown in Scheme 2, giving metallacycle complexes.[13] Such types of coupling reactions have been successfully applied to the synthesis of various interesting metallacyclic compounds using diynes or polyynes.[19] Therefore, it is reasonable to assume that an oxidative coupling could occur between the two coordinated double bond units of the COD ligand, generating an intermediate species that has a vacant coordination site available for the alkyne substrate. The oxidative coupling changes the oxidation state of Ru formally from +2 to +4. In terms of electron counting, the intermediate generated is a 16-electron species. In such a mechanism, the chloride ligand is not necessary to ionize before the coordination of the alkyne substrate.

Calculations show that the alkyne complex **2** derived from the oxidatively coupled intermediate is very unstable with respect to the reactants (Figure 1). The free energy change was calculated to be as high as 49.8 kcal/

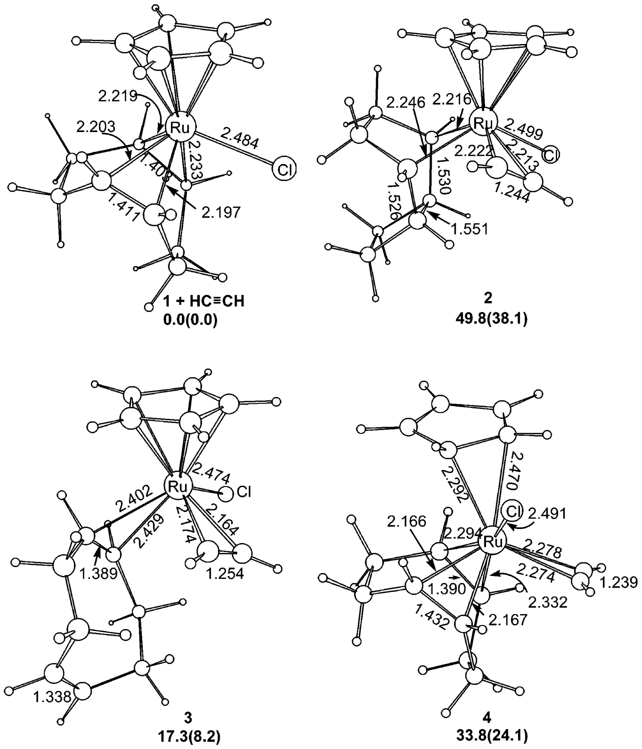
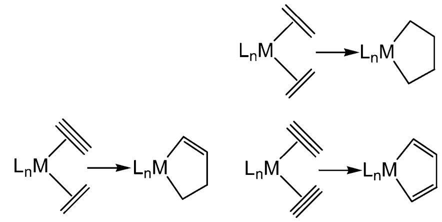


Figure 1. Selected structural parameters (Å) calculated for complexes **1**–**4** shown in Scheme 3. The relative free energies and relative energies (in parentheses) are given in kcal/mol.

Scheme 2



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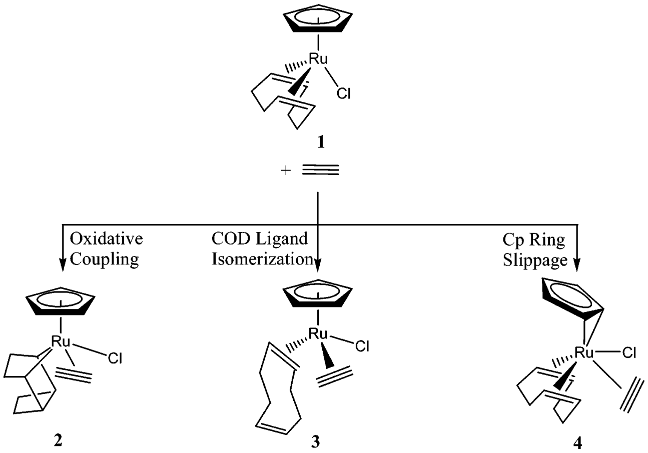
Scheme 3



mol, while the reaction energy change was 38.1 kcal/mol. Clearly, a mechanism starting from an oxidative coupling between the two coordinated double bond units can be ruled out. The instability of **2** can be related to the crowdedness of the ligand environment as well as the ring strain due to the formation of a four-membered ring in the intermediate. The alkyne complex **2** can be described as a four-legged piano-stool structure (see Figure 1).

COD Ligand Isomerization Process. Another possible reaction mechanism, which does not require the ionization of the chloride ligand, is changing the η^4 coordination mode of COD to η^2 so that a vacant coordination site is available for coordination of the alkyne substrate. Our calculations show that it is not possible to have an η^2 coordination mode without the change in the conformation of the COD ligand. We found that a minimum (see **3** in Scheme 3 and Figure 1) corresponding to an η^2 coordinate species has a chair conformation of the COD ligand. The minimum structure (**3**) is found to be 17.3 kcal/mol higher than the reactants. On the basis of the relative energy, it seems possible for such a process that involves the conformation change. However, it is expected that the corresponding carbon−carbon coupling transition states starting from this minimum (**3**) would be even higher. Our calculations, which will be discussed below, show that the reaction barriers in the mechanism proposed by Trost and co-workers are relatively much smaller. Therefore, the reaction pathway starting from **3** was not further investigated because of the expected higher reaction barriers. In addition, we would expect to have [2+2] cycloaddition products, which were not observed experimentally, if the reaction starts with **3**.

Cp Ring Distortion Process. A Cp ring slip process from η^5 to η^3 or lower hapticity also does not require the ionization of the chloride ligand and can release a vacant coordination site in the metal center, allowing coordination of the alkyne substrate for cycloaddition. Various Cp ring slip processes have been extensively studied in the literature.[20−31] Our calculations located a stable η^2-Cp structure **4** having both the chloride and alkyne substrate. **4** can be described as a distorted square-pyramidal structure in which the η^2-Cp ligand occupies the apical position. However, this structure was calculated to be 33.8 kcal/mol higher in energy than the reactants. Again, we can see that a mechanism involving the Cp ring slippage is unlikely in this case. One may be concerned that the use of the 6-31G basis set on the Cp atoms without polarization functions might inflict some imbalance on the relative energies of the η^2-coordination and underestimate the stability of the η^2-Cp species. In view of the significantly high energy of the η^2-Cp species **4**, the error derived from the use of the basis set should become less important.

Summarizing the results discussed above, we conclude that the processes that do not involve ionization of the chloride ligand are expected to have significantly high reaction barriers and are not responsible for the catalytic process observed experimentally. One referee pointed out another possibility of having a direct oxidative coupling of an incoming alkyne with a Ru−olefin bond of [CpRu(COD)Cl] to yield the equivalent of intermediate **IN1-yne** (see below) but with the chloride still coordinated. This path requires that the incoming alkyne attacks the 18-electron species [CpRu(COD)Cl] directly. Such a process is also expected to have high reaction barriers.

Reaction Mechanisms of Trost and Co-workers. In the reaction mechanisms proposed by Trost and coworkers, $[CpRu(COD)]^+$ is the active species. $[CpRu(COD)]^+$ is initially formed through ionization of the chloride ligand under the condition of a polar solvent. Theoretically, it is difficult to accurately calculate the ionization energy of the chloride ligand. We employed the polarizable continuum (PCM) models to approximately evaluate the ionization energy. The results of the PCM calculations indicate that the ionization energy is as small as 7.0 kcal/mol. Although the accuracy of the ionization energy calculation is arguable, the calculations, at least, imply that the active species $[CpRu(COD)]^+$ is easily formed under the conditions of a polar solvent. Calculations show that reaction of 1,5-cyclooctadiene with acetylene in the model complex $[CpRu(COD)(C_2H_2)]^+$ proceeds through a stepwise mechanism. When the one-step concerted pathway (Scheme 1) was considered, attempts to locate the transition state were not successful. The failure to locate concerted transition states has been encountered in many other transition metal-mediated hydrogenation reactions of norborna-

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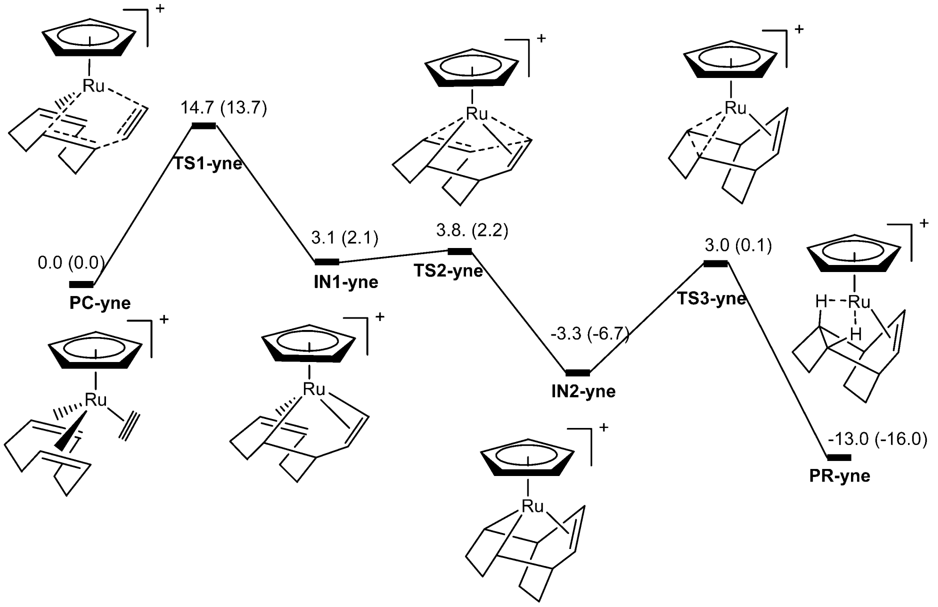

Figure 2. Schematic illustration of the stepwise reaction pathway for ([CpRu(COD)]$^+$ + HC≡CH) together with the calculated relative free energies (kcal/mol) and relative reaction energies (kcal/mol, in parentheses) for species involved in the reaction.

diene (NBD).[32] Thus, we believe that the corresponding concerted process is unlikely.

The energy profile for the reaction is illustrated in Figure 2. In Figure 2, **PC** stands for the precursor model complex; **IN1** and **IN2** represent the intermediate structures; **TS1**, **TS2**, and **TS3** correspond to the transition states of the first, the second, and the third steps in the reaction, respectively; and **PR** is the structure having the cycloadded product molecule as a ligand.

From Figure 2, one can see that the reaction of HC≡CH with COD is energetically very favorable. These results explain the experimental observation that a [2+2+2] cycloaddition occurs easily for the reactions of alkynes with COD with good yields catalyzed by CpRu(COD)Cl. Starting from the alkyne complex (**PC-yne**), the reaction proceeds by having a small barrier (14.7 kcal/mol) to complete the first carbon−carbon coupling step with the formation of the **IN1-yne** intermediate. The second carbon−carbon coupling step, which gives **IN2-yne**, is almost barrierless. The third step involves a reductive elimination, leading to the formation of **PR-yne**. Finally, the dissociation of the [2+2+2] cycloadduct molecule from **PR-yne** generates CpRu$^+$, which can easily take a COD molecule and an alkyne substrate molecule to regenerate **PC-yne** and complete the catalytic circle. Regeneration of **PC-yne** requires a ligand exchange between the cycloadduct molecular ligand and the substrates (COD + alkyne). The ligand exchange is expected to be in equilibrium. Therefore, the rate-determining step in the overall reaction is the first carbon−carbon coupling step. On the basis of the energy profile, we can conclude that the catalytic reaction is favorable both kinetically and thermodynamically.

Figure 3 shows the optimized structures with selected structural parameters for all the species involved in the reaction pathway. **PC-yne** is a typical three-legged piano-stool complex. The intermediate formed after the first C−C bond formation corresponds to an unusual η^2-alkenyl structure (**IN1-yne**), which will be discussed in more detail below. **IN2-yne** is again a three-legged piano-stool structure. **PR-yne** has two agostic bonds.

As mentioned in the Introduction, the CpRu(COD)Cl (**1**) complex did not catalyze cycloaddition of COD with alkene substrates. To understand the origin of the inactivity, we also calculated the corresponding structures in the reaction of [CpRu(COD)]$^+$ + $H_2C{=}CH_2$. The results of calculations are shown in Figure 4. All the structures shown in Figure 4 can find analogous counterparts in Figure 3 for the reaction with alkyne. Here, we did not calculate the corresponding **TS3-ene** and **PR-ene** for the reaction with $H_2C{=}CH_2$. The two structures are not important for our understanding of the origin of the inactivity mentioned above. In addition, the catalytic reactions with alkene substrates were not observed experimentally.

Remarkably, the results of calculations (Figure 4) well explain the inactivity of [CpRu(COD)]$^+$ toward alkene substrates. In comparison with that in the reaction of [CpRu(COD)]$^+$ + HC≡CH, the first carbon−carbon coupling step in the reaction of [CpRu(COD)]$^+$ + $H_2C{=}CH_2$ has only a slightly higher energy barrier (17.7 vs 14.7 kcal/mol). However, the reaction barrier for the second carbon−carbon coupling step is significant in contrast to the barrierless step found in the reaction with HC≡CH. Both steps of the carbon−carbon coupling are important for the overall reaction. The results also show that the reaction of [CpRu(COD)]$^+$ + $H_2C{=}CH_2$ is both kinetically and thermodynamically unfavorable.

Thermodynamically, **IN2-yne** in the reaction of [CpRu(COD)]$^+$ with HC≡CH is more favorable than the corresponding **IN2-ene** in the reaction of [CpRu(COD)]$^+$ with $H_2C{=}CH_2$. Apparently, the strong Ru−olefin interaction in **IN2-yne** (Figure 3) makes the crucial contribution to its high stability. In **IN2-ene** (Figure 4), the two Ru−agostic bonds are relatively weak.

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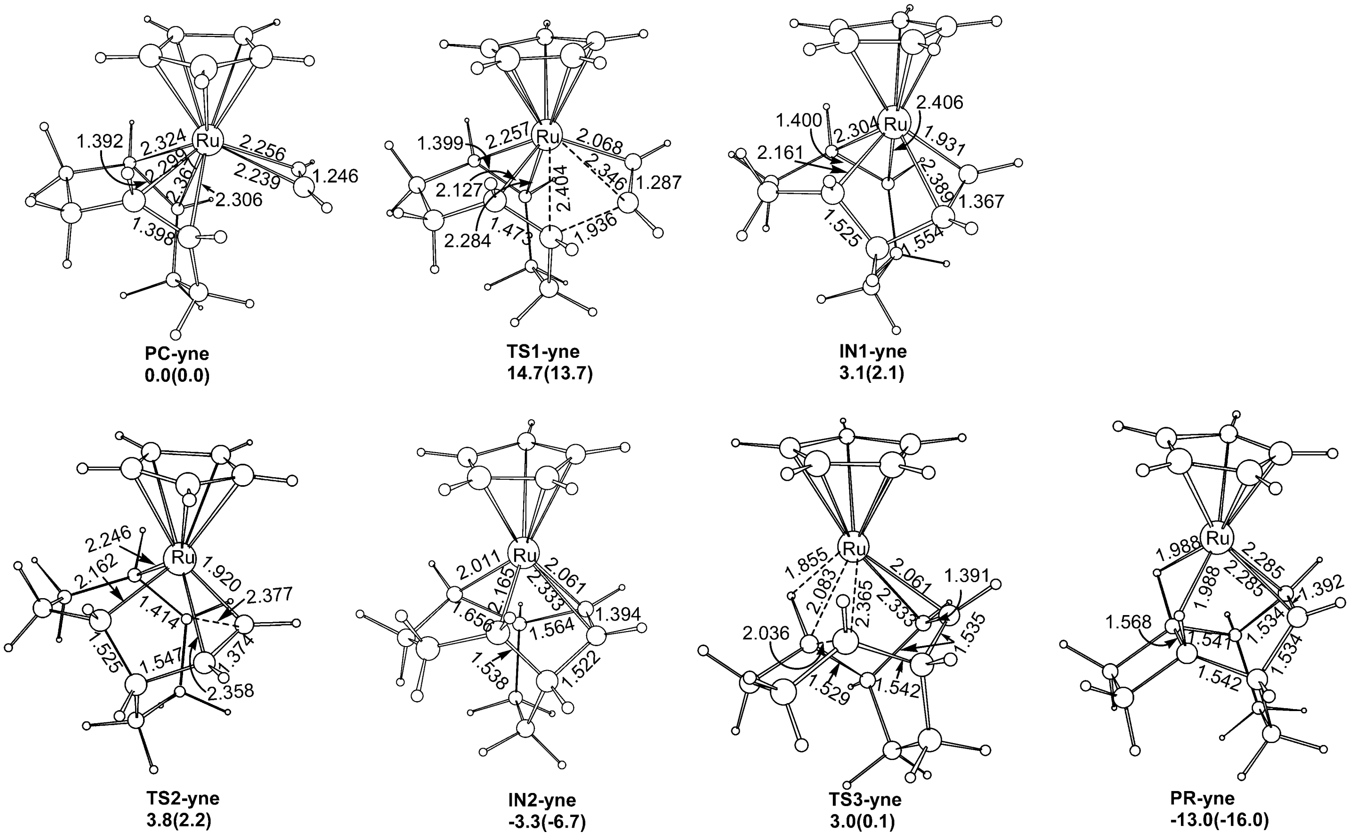
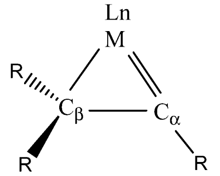


Figure 3. B3LYP-optimized structures for species involved in the Ru-catalyzed cycloaddition of COD with HC≡CH. The relative free energies and relative reaction energies (in parentheses) are given in kcal/mol. Selected bond distance are given in angstroms.

Because of the two agostic interactions, the two agostic carbons are pushed away from the metal center and the COD + $H_2C{=}CH_2$ organic moiety is structurally rotated in such a way that there is a significant repulsive interaction between the Cp ring and the $-CH_2CH_2-$ unit directly linked with the two metal σ-bonded carbons. The repulsive interaction in turn weakens the two Ru−C σ-bonding interactions. The two Ru−C σ bond distances in **IN2-ene** (2.178 and 2.179 Å, see Figure 4) are longer than the two corresponding distances in **IN2-yne** (2.011 and 2.165 Å, see Figure 3). In **IN2-yne** (Figure 3), the corresponding structural rotation of the organic moiety is not necessary because of the strong Ru−olefin bonding interaction, which keeps the two olefinic carbons close to the metal center. The $-CH_2$-CH_2- unit linked directly to the two metal σ-bonded carbons is clearly farther away from the Cp ring in the calculated structure. Summarizing the arguments above, we can see that the stability of **IN2-yne** is related to the strong Ru−olefin interaction and small Cp···CH_2-CH_2- repulsion, while the instability of **IN2-ene** is a result of weaker Ru−C(σ) and Ru−agostic interactions and significant Cp···CH_2CH_2- repulsion.

The significant kinetic difference between the two reactions ($[CpRu(COD)]^+$ with HC≡CH and $H_2C{=}CH_2$) becomes evident in the second carbon−carbon coupling step. In the reaction with alkyne, the step is almost barrierless (see Figures 2 and 3). It has, however, a significant barrier in the reaction with alkene. A careful examination of the structural features of **IN1-yne** provides us some clues regarding the barrierless feature in the reaction with HC≡CH. **IN1-yne** (Figure 3) shows an unusual η^2-alkenyl coordination mode in which the metal center strongly interacts with the π electrons of the alkenyl unit as a result of achieving an 18-electron configuration. A normal metal−η^2-alkenyl complex is usually described as a metallacyclopropene (**5**) in which the α-carbon has a planar geometry.[33] In **IN1-yne**, however, the α-carbon of the η^2-alkenyl unit shows a pyramidal geometry (see Scheme 4). The pyramidal geometry allows us to formally sketch the bonding interaction between the metal center and the η^2-alkenyl unit, shown in Scheme 4. The sp^2-hybridized orbital, which is available for σ-bonding interaction with the metal center, at the α-carbon is expected to be perpendicular to the π-bonding orbital of the alkenyl unit. Therefore, a bent Ru−C_α σ bond can be envisaged in view of the pyramidal geometry at the σ-carbon (Scheme 4). Here, one can see that the Ru−C σ bond bends toward the adjacent olefinic carbon that is ready to form a new carbon−carbon bond in the second C−C coupling step. Apparently, the bent Ru−C_α σ bond facilitates the orbital overlap between C_α and the adjacent olefinic carbon and thus favors the C−C bond formation and lowers the reaction barrier from **IN1-yne** to **IN2-yne**.



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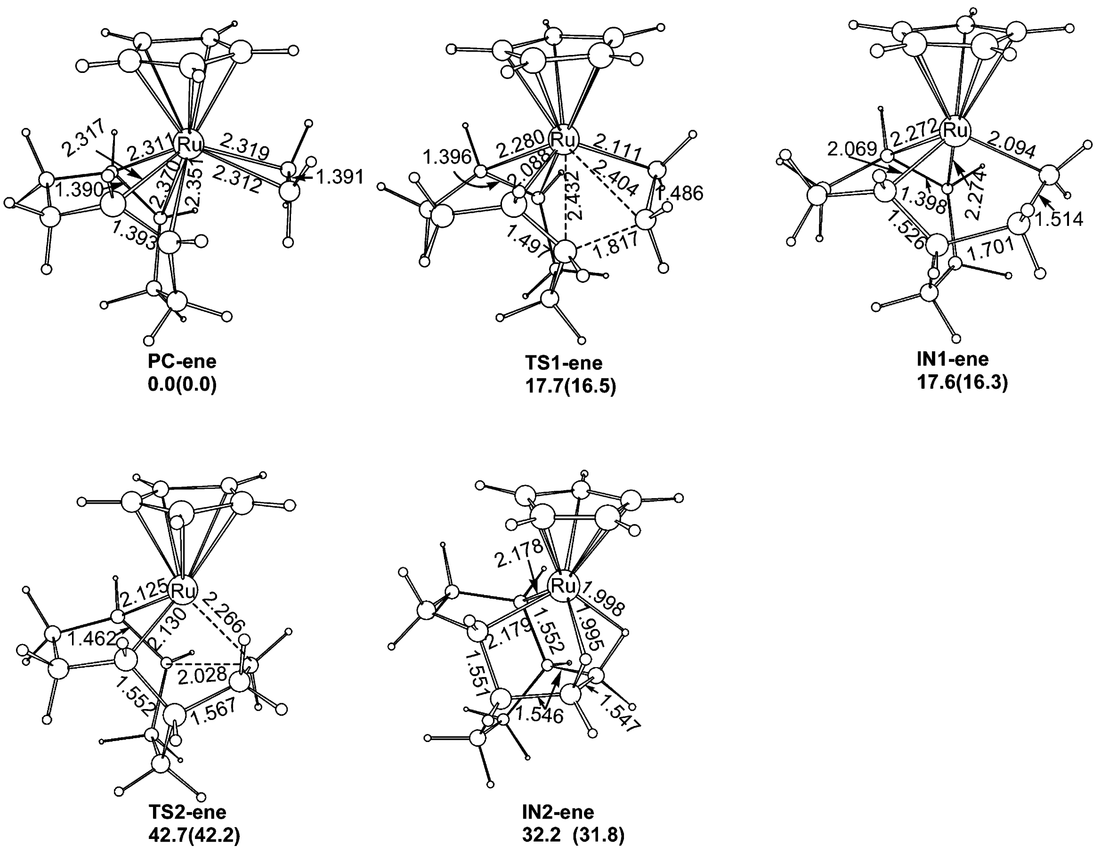


PC-ene
0.0(0.0)

TS1-ene
17.7(16.5)

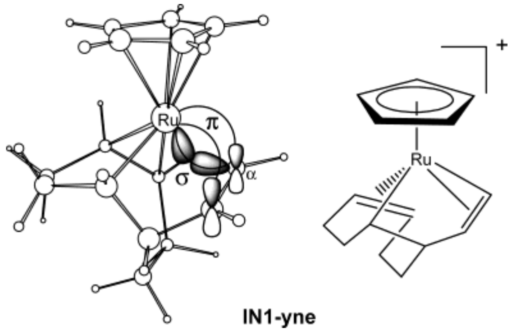
IN1-ene
17.6(16.3)

TS2-ene
42.7(42.2)

IN2-ene
32.2 (31.8)

Figure 4. B3LYP-optimized structures for species involved in the Ru-catalyzed cycloaddition of COD with $H_2C{=}CH_2$. The relative free energies and relative reaction energies (in parentheses) are given in kcal/mol. Selected bond distance are given in angstroms.

Scheme 4



The possibility of having the unusal metal–η^2-alkenyl interaction in **IN1-yne** results from the fact that an alkyne substrate molecule has an extra $\pi_\perp$ bonding orbital in comparison to an alkene substrate molecule. The unusal Ru–η^2-alkenyl bonding interaction is expected to make an important contribution to the stability of **IN1-yne**. The reason for the adoption of an unusual Ru–η^2-alkenyl coordination mode in **IN1-yne** instead of the normal one (**5**) could be related to the complicated ring structure in the intermediate.

In the reaction with an alkene substrate molecule, the second step starts from an intermediate **IN1-ene**, where the two carbons originated from the alkene are saturated. Thus, there are not enough available electrons to form a new C–C bond and at the same time provide for the electronic needs of the metal center. Therefore, the reaction follows a less favorable path than in the case of alkyne addition. In addition, the absence of an extra $\pi_\perp$ orbital destabilizes the intermediate **IN1-ene** (Figure 4), and it is not possible to have a bent Ru–C_α σ bond to facilitate the C–C bond formation in the second step.

Conclusions

In this paper, the reaction mechanism of the Ru-catalyzed cycloaddition of 1,5-cyclooctadiene (COD) with alkynes has been theoretically investigated. Our calculations point toward the proposed mechanism that the cycloaddition reaction occurs via an intermediate formed by the active species $[CpRu(COD)]^+$, which is derived from the ionization of Cl^- from CpRu(COD)Cl, under the polar solvent MeOH, and an alkyne substrate molecule. The intermediate undergoes a stepwise C–C coupling mechanism leading to the formation of cycloaddition products. The first C–C coupling step was found to be the rate-determining step. A parallel study on the Ru-catalyzed cycloaddition of COD with alkene showed that it is both kinetically and thermodynamically unfavorable, consistent with the experimental observation that CpRu(COD)Cl does not catalyze reactions of COD with alkenes.

Structural and energetic analyses indicate that in the reactions of COD with alkynes the extra $\pi_\perp$ orbital of an alkyne substrate molecule in comparison to an alkene substrate plays crucial roles in stabilizing the relevant reaction intermediates as well as facilitating the second C–C coupling step in the catalytic reactions.

Other possible reaction pathways that do not involve the ionization of Cl^- in the catalytic reactions have also been examined. These possible reaction pathways include (1) oxidative coupling between the two olefin bonds of the COD ligand, (2) change in the coordination mode of COD from η^4 to η^2, and (3) Cp ring slippage. Calculations of these pathways show that they are not favorable because the intermediates formed are inaccessible. It should be pointed out that ionization of Cl$^-$ becomes the most crucial for the proposed reaction mechanism. When ionization of Cl$^-$ is not possible, more studies seem necessary in order to delineate the actual reaction mechanism.

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Supporting Information Available: Cartesian coordinates of all the calculated structures reported in this article are available free of charge via the Internet at http://pubs.acs.org.

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