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A Density Functional Theory Study of Rhodium-Catalyzed Hetero-[5+2]-cycloaddition of Cyclopropyl Imine Derivatives and Alkynes

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The intermolecular [5+2]-cycloaddition mechanism of cyclopropyl imines and alkynes catalyzed by $[Rh(CO)_2Cl]_2$ has been studied using density functional theory, comparing this multistep process with the two-step reaction in the absence of catalyst. Calculations show that a similar mechanism to that found for dihydroazepines could also lead to the formation of oxepines by replacing the imine nitrogen by oxygen. The results indicate that the formation of the oxepine can proceed with smaller barriers than those found for dihydroazepines. In fact, energy barriers are even smaller than those for other reactions employed for oxepine production, exhibiting values similar to those obtained for the reactions between acetilene and vinylcyclopropanes. Several substituted alkynes were tested for the reaction leading to no significant differences among them.

1. Introduction

Among the many transition metal catalysts used in organic synthesis, rhodium has played an increasingly important role in the past years.[1] The discovery of the Wilkinson complex in the 1960s marked the beginning of the development of modern rhodium chemistry.[2] Since that moment, a number of new rhodium-catalyzed reactions, especially several new types of cycloadditions, have been reported,[3] offering synthetic routes that are often complementary to those of palladium and ruthenium, the other elements of the *noble metal triad*. Rhodium provides exemplary levels of regio- and stereoselectivity for [*m*+*n*]-cycloadditions. The most common oxidation states for rhodium complexes are Rh(I) and Rh(II). Some popular catalyst of Rh(I) are, for example, $RhCl(PPh)_3$ (the Wilkinson catalyst) or the $[RhCl(BINAP)_2]_2$, $[RhCl(dppb)]_2$ and $[Rh(CO)_2Cl]_2$ dimers. This last one, the $[Rh(CO)_2Cl]_2$ dimer, is a good catalyst for bi- or multicomponent cycloadditions.[4]

The term *carbocyclization* is used for describing ring-forming processes that involve the formation of new carbon−carbon bonds via carbometalation. The general [5+2] *formal* cycloaddition of alkynes and cyclopropyl imines (CPIs) can be defined as a carbocyclization (see Scheme 1).[5] From a formal point of view, this approach to seven-membered rings is mainly an isoelectronic variant of the Diels−Alder cycloaddition: the alkyne acts as a 2π component, and the CPI acts as a $(2\pi + 2\sigma)$ component. The reactions studied in this work constitute an extension of the studies on [5+2] reaction of vinylcyclopropanes (VCPs) and π-systems such as alkenes and alkynes.[6] Introducing a heteroatom such as nitrogen allows one to obtain a new route to synthetize dihydroazepines.[7] This novel hetero-[5+2]-cycloaddition between CPIs and alkynes was first reported by Paul Wender's group,[8] achieving good yields using the $[Rh(CO)_2Cl]_2$ dimer as a catalyst by adding small amounts of alkyne, which gave as a result a high selectivity in the process.

The possible mechanisms proposed by Wender and coworkers were mainly (see Scheme 2) (a) the formation of a hexametallacycle, which leads to a larger metallacycle where, subsequently, the rhodium catalyst is eliminated to achieve the [5+2] product, or (b) the formation of an azametallacyclopentene between the alkyne and the CPI that leads to the same process as the hexametallacycle of (a) to get the product.[9] Two years later, a theoretical study was reported for the mechanism of [5+2]-cycloaddition between VCPs and alkynes,[6] in which an analogue pathway to the proposed pathway (b) of this reaction was ruled out, so the discussion will be focused on mechanism (a).

In this work, the mechanism of the hetero-[5+2]-cycloaddition between CPIs and alkynes was studied in detail, and the role of the rhodium catalyst in the reaction was analyzed, comparing with the same reaction in the absence of catalyst. Otherwise, it is worth noting that, in the experimental process, the starting reactant is an aldehyde, and then the imine is generated *in situ*.[8] If the imine is not generated by amine addition, keeping the catalyst, it could be possible to obtain an oxepine as product.[10] Therefore, replacing nitrogen by oxygen (see Scheme 3) and studying the corresponding reaction would allow estimating the feasibility of oxepine formation.

2. Computational Details

Geometries of all stationary points were fully optimized with the density functional theory (DFT) functional B3LYP and characterized as a minima or saddle points by analytic computation of harmonic vibrational frequencies.[11] 6-31G(d,p) Pople's basis sets were used for C, N, O, H, and Cl atoms, and the *effective core potential* LANL2DZ was used for Rh atom.[12] *Intrinsic reactions paths* (IRCs) were obtained at the same level.[13] All geometry optimizations and subsequent frequency calculations were performed with the Gaussian 03 software package.[14]

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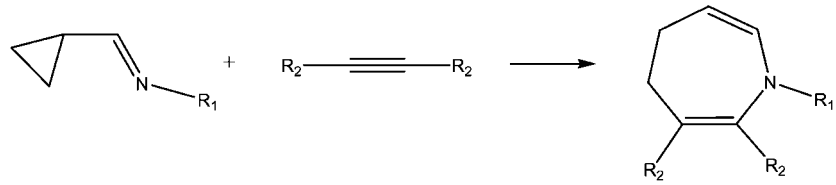
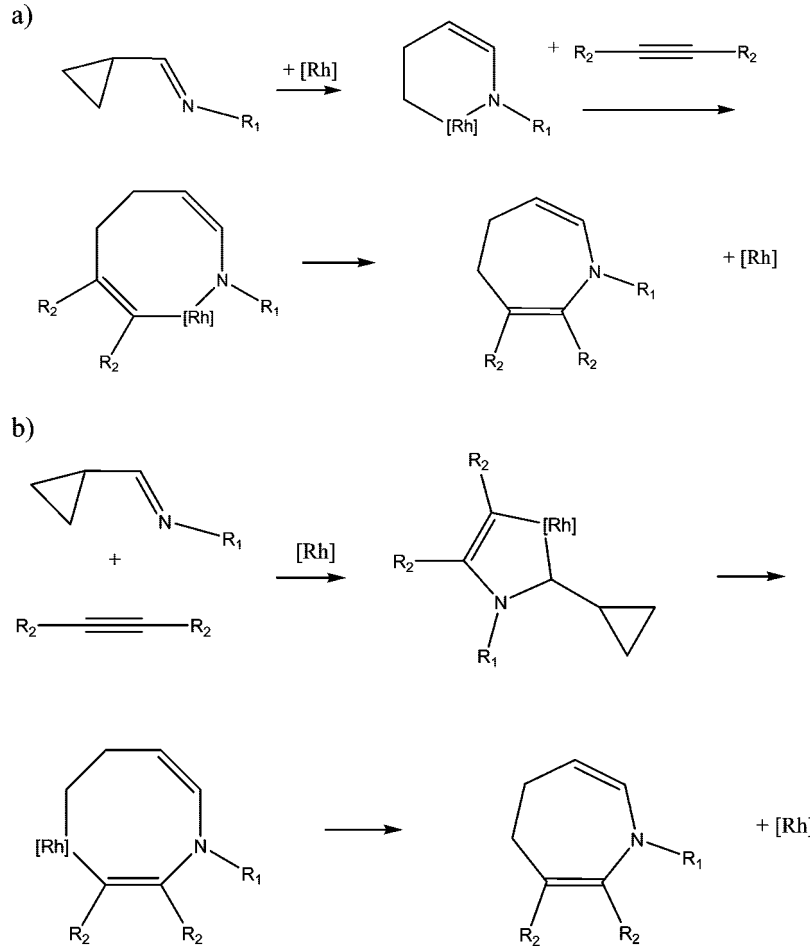
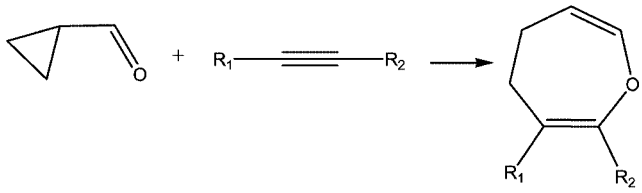
SCHEME 1: General [5+2]-Cycloaddition between Alkynes and CPIs



SCHEME 2: Two Main Mechanisms Have Been Considered: Pathway (a), Which Implies the Formation of an Initial Hexametallacycle, or Pathway (b), Which Implies the Formation of an Azametallacyclopentene between the Alkyne and the CPI



SCHEME 3: A Possible [5+2] Route to Obtain Oxepines



3. Results and Discussion

3.1. Rhodium-Catalyzed Hetero-[5+2]-cycloaddition. In this first section, results obtained for the reaction between CPIs and alkynes are presented. These results are compared to those ones obtained by Yu and co-workers for the reaction between VCPs and acetylene.[6] Also, a comparison with the hypothetical noncatalyzed process is shown as a means of determining the role of the catalyst. In a subsequent section, a possible process leading to oxepines is described based on the CPI route and compared to similar reactions.

To study the [5+2]-cycloaddition showed in Scheme 1, one of the experimental cases included in Paul Wender's paper was chosen,[8] in which R_1 = cyclopropyl and R_2 = CO_2Me (so the alkyne is dimethyl acetylenecarboxylate (DMAD)).

Taking as a reference the VCPs and alkyne cycloaddition,[6] the pathway for the hetero-[5+2]-cycloaddition with an easier substituent for the alkyne (R_2 = F) was first studied, and then, the definitive structures with DMAD were optimized using it as a starting point. The intermediate and transition state structures thus obtained at the B3LYP/6-31G(d,p)+LANL2DZ level in gas phase using the $[Rh(CO)_2Cl]_2$ dimer as a catalyst are shown in Figure 1.

The $[Rh(CO)_2Cl]_2$ dimer is in equilibrium with two monomeric units, in which the rhodium atom, bonded to CO and Cl ligands, is the active species.[15] The hetero-[5+2]-cycloaddition between CPI and DMAD can be divided in two parts: the first one, from **I1** to **I5**, mainly corresponds to a geometry change in the rhodium complex; in the second one, from **I5** to **I10**, the

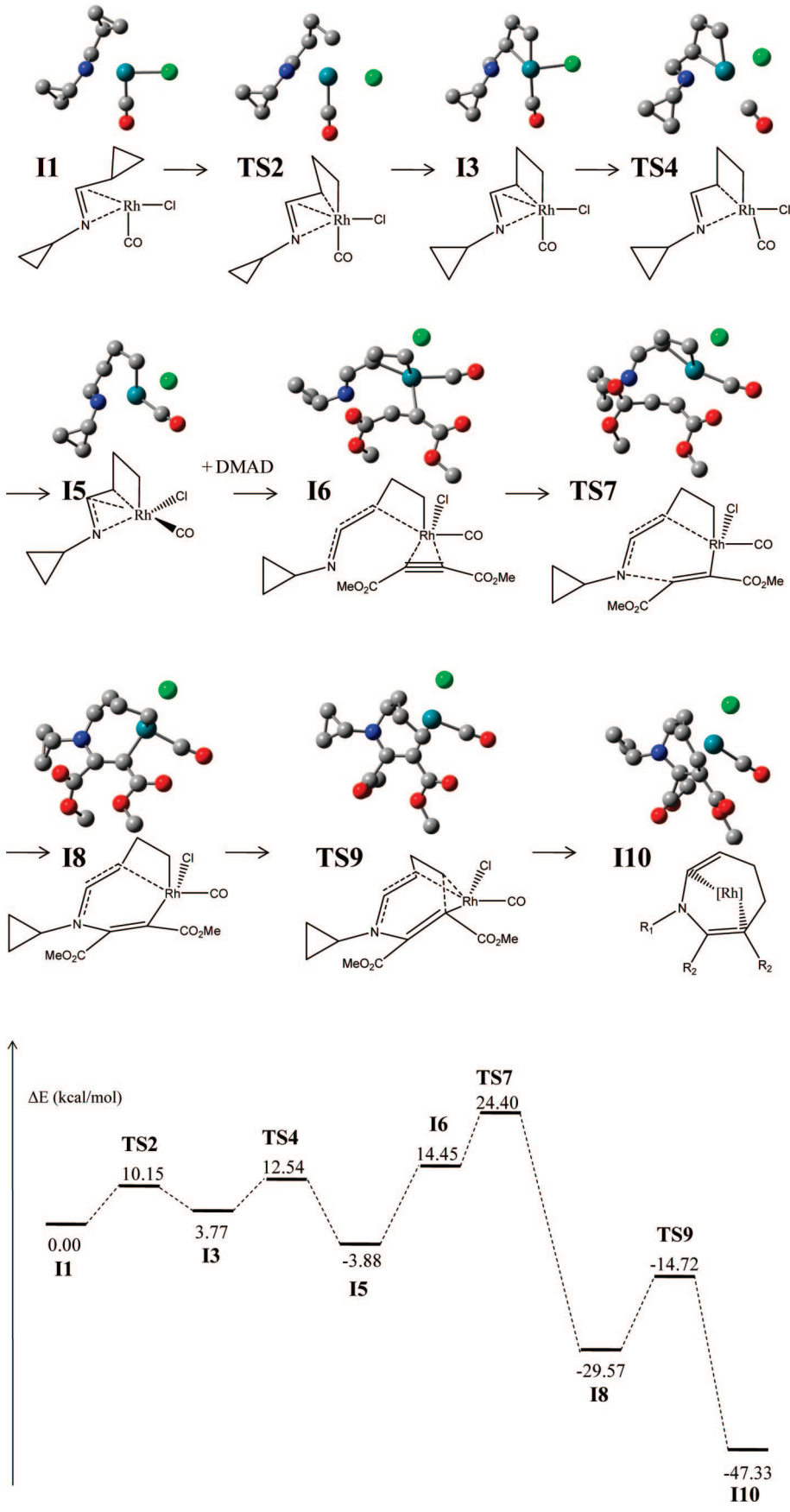


Figure 1. Intermediate and transition state geometries of the Rhodium-catalyzed hetero-[5+2]-cycloaddition between CPI and the alkyne DMAD in gas-phase at the B3LYP/6-31G(d,p)+LANL2DZ level. Also shown is an energy profile for the reaction with energies in kcal/mol.

insertion of DMAD and the formation of the final seven-membered ring takes place.

I1 is a 16 e^- complex where the metal adopts a square-planar geometry, acting as the cyclopropyl group ligand. The transition

TABLE 1: Absolute and Relative Electronic Energies in Atomic Units and kcal/mol for the Rhodium-Catalyzed CPI+DMAD Cycloaddition in Gas Phase at the B3LYP/6-31G(d,p)+LANL2DZ Level[a]

	E (a.u.)	E + ZPE (a.u.)	ΔE_{ZPE} (kcal/mol)	imaginary frequencies (cm^{-1})
I1 + DMAD	−1544.22307	−1543.93151	0.00 (0.00)	
TS2 + DMAD	−1544.20500	−1543.91534	10.15 (9.64)	i225.03
I3 + DMAD	−1544.21087	−1543.92550	3.77 (6.35)	
TS4 + DMAD	−1544.20040	−1543.91153	12.54 (13.27)	i232.07
I5 + DMAD	−1544.22878	−1543.93769	−3.88 (−2.06)	
I6	−1544.20077	−1543.90849	14.45 (−3.79)	
TS7	−1544.18470	−1543.89265	24.40 (10.27)	i112.87
I8	−1544.27571	−1543.97863	−29.57 (−35.57)	
TS9	−1544.25053	−1543.95497	−14.72 (−21.81)	i391.79
I10	−1544.30488	−1544.00693	−47.33 (−68.75)	

[a] The values of the cycloaddition between VCP and alkyne are given in parentheses.[16]

state **TS2** involves the ring opening of the cyclopropyl group to get **I3**, where the rhodium complex has a trigonal bipyramidal form, with a coordination number equal to five. In **TS4**, the CO ligand is moving from an axial position to the plane which contains the double bond, the chlorine ligand, and the rhodium atom. A square-based pyramid is the geometry of the rhodium complex in the intermediate **I5**. So, essentially, from **I1** to **I5**, a transformation from a square-planar to a square-based pyramid geometry takes place.

The intermediate **I6** has the DMAD molecule bonded to the rhodium atom, and now the double bond N=C is not interacting with the metal. So, formally, a 18 e^- complex is not formed. It seems that, with the alkyne insertion, we have just changed one ligand to another.

In **TS7**, the alkyne is bonded to rhodium through just one carbon, while the other one is near the nitrogen of the CPI. An eight-membered ring is formed in **I8**. Through **TS9**, the rhodium catalyst is eliminated from the ring, and in **I10** the dihydroazepine is formed. The catalyst is over the ring, interacting with the two double bonds of the product. When a new reactant molecule interacts with the rhodium, the catalytic cycle begins one more time.

Table 1 shows the electronic energies for the CPI+DMAD cycloaddition. The values of the electronic energies for the VCP and acetylene reaction are shown in parentheses. The transformation from **I1** to **I5** is a slightly exothermic process in two steps whose energy barriers are very close to the VCP ones.[6] Therefore, for the first part of the reaction leading to the formation of the complex between rhodium and the CPI, no differences are found with respect to the same reaction with VCP. However, the second part of the reaction shows an interesting difference with the VCP and alkyne case. Here the DMAD insertion is a much more expensive step. Moreover, with nitrogen instead of carbon, the rhodium−heteroatom interaction of **I5** does not continue in **I6**.

Then, the coordination of the alkyne to the Rhodium atom displacing other C=N requires more than 18 kcal/mol from **I5**. However, the complete transformation to **I10** is very exothermic (approximately −47 kcal/mol), and the relative barriers **I6**−**TS7** and **I8**−**TS9** are below 11 and 15 kcal/mol, respectively, so the relative barriers for transformation from **I6** to **I10** are similar for both VCP and CPI reactions.

Summarizing, both cycloaddition reactions proceed by means or fairly similar mechanisms, the only significant difference being the greater energetic cost of the coordination of the alkyne to the rhodium atom (**I5** to **I6**) and the subsequent formation of the eight atom metallacycle in the case of CPIs. Therefore, substitution by nitrogen makes the second part of the reaction more difficult compared to the VCP case though following the same steps.

3.2. Noncatalyzed Hetero-[5+2]-cycloaddition. As a way of measuring the influence of the catalyst on the reaction mechanism, the same process was studied in the absence of rhodium. In practice, the formation of the dihydroazepine in the absence of catalyst is not feasible. The reaction pathway in the absence of catalyst was studied in order to compare it with the rhodium-catalyzed cycloaddition. Calculations were carried out at the B3LYP/6-31G(d,p) level.

Figure 2 shows the intermediate and transtion state structures for the noncatalyzed pathway. It was not possible to find any transition state that allows one to get to dihydroazepine from DMAD and CPI in only one step. The noncatalyzed cycloaddition has a two-step mechanism. In the first transition state, **TS2′**, one of the carbons of the triple bond of the DMAD interacts with the CPI nitrogen, giving then a zwitterionic intermediate **I3′**. The cyclopropyl group opens in **TS4′**, forming a bond with the other carbon of the alkyne. The final product is formed in **I5′**.

Table 2 shows the electronic energies for the noncatalyzed cycloaddition. The rate-limiting step has a barrier of ∼31 kcal/mol, corresponding with the second transition state, **TS4′**. The cyclopropyl opening is a very difficult step in the absence of catalyst, while in presence of rhodium it occurs with a barrier of only ∼10 kcal/mol during the first step of the reaction. So the presence of the catalyst transforms a two-step process into a multistep process with much lower activation energies.

3.3. Oxepine Formation. As commented above, the same reaction with oxygen instead of nitrogen (see Scheme 3) to obtain an oxepine as product was also studied. The rearrangement of divinyloxirane to 4,5-dihydrooxepine is a very studied reaction since the oxepine nucleus is present in a number of important biological products.[17] The mechanism of this reaction consists of a concerted electrocyclic closure of the reactant. The process requires a temperature of about 60 °C. The Cope rearrangement of 2,3-divinyloxirane to 4,5-dihydrooxepine has a activation barrier of 24.8 kcal/mol, and the formation of the product is exothermic by −21.6 kcal/mol. A rhodium-catalyzed cycloaddition could be a different way to obtain oxepines; the only difference with the experimental process to obtain dihydroazepines would be that the amine is not added.

As commented in the preceding section, the first part of the reaction shows no significant differences between VCP and CPI addition, and so is the case when imine nitrogen is replaced by oxygen. For brevity, the discussion will be focused on the insertion part (see Figure 3) from the square-based pyramid geometry of the reactant complexed with the catalyst **I5** to the product **I10**, although values for the first part are available as Supporting Information.

The reaction is completely similar to the dihydroazepine case. The alkyne insertion is a slightly endothermic process that leads to the complex **I6**. Through the transition-state **TS7**, one of the carbons of the alkyne triple bond interacts with the heteroatom (oxygen in this case), and an eight-membered metallacycle is formed in the intermediate **I8**. The carbocyclization occurs in **TS9**, giving a new carbon−carbon bond in the final product **I10**, where the rhodium atom has a square planar disposition.

Table 3 contains the results for the reaction between cyclopropanecarbaldehyde plus acetylene to give the oxepine (R_1=R_2=H, Scheme 3), compared with the analogue reaction of CPI (R_1=R_2=H, Scheme 1). It can be observed from the

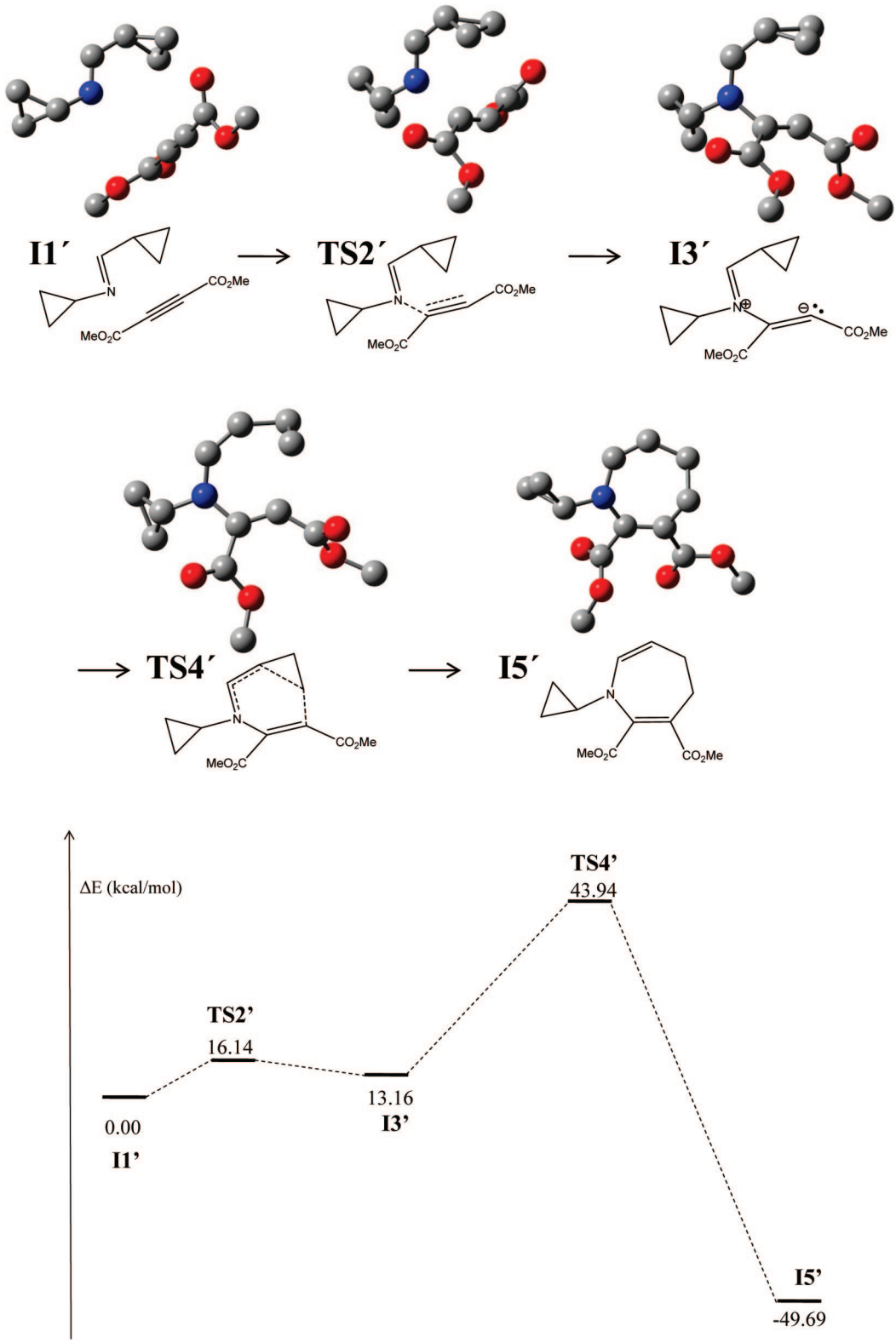


Figure 2. Intermediate and transition state geometries of the noncatalyzed hetero-[5+2]-cycloaddition between CPI and DMAD in gas-phase at the B3LYP/6-31G(d,p) level. Also shown is an energy profile for the reaction with energies in kcal/mol.

data in Table 3 that both reactions perform similarly overall, but significant differences can be appreciated. As commented in the previous section, the presence of nitrogen in the imine makes the coordination of acetylene much more difficult that in the case of VCP, as reflected in the energy differences between **I5** and **I6**. In the case of the oxepine route, the process is also slightly exothermic by −1.38 kcal/mol, and much more favorable than the CPI coordination.

The acetylene insertion step to give the metallacyle also shows these differences. Energy barriers are smaller for the aldehyde cases, whereas for the imines the process is more penalized. Nevertheless, as stated above, the relative barriers for the transformation between **I6** and **I8** are similar in all cases. After formation of the metallacycle, the remaining processes are similar in all cases, leading to a greatly exothermic process.

TABLE 2: Absolute and Relative Electronic Energies in Atomic Units and kcal/mol for the Noncatalyzed CPI+DMAD Cycloaddition in Gas Phase at the B3LYP/6-31G(d,p) Level

	E (a.u.)	E + ZPE (a.u.)	ΔE_{ZPE} (kcal/mol)	imaginary frequencies (cm^{-1})
I1′	−861.13758	−860.85572	0.00	
TS2′	−861.11274	−860.82999	16.14	i225.81
I3′	−861.11961	−860.83474	13.16	
TS4′	−861.06901	−860.78570	43.94	i572.59
I5′	−861.22333	−860.93940	−49.69	

TABLE 3: Relative Electronic Energies in kcal/mol for the Catalyzed [5+2]-Cycloaddition to Obtain Oxepine at the B3LYP/6-31G(d,p)+ LANL2DZ Level with R_1=R_2=H (See Figure 3)[a]

	ΔE_{ZPE} (kcal/mol)	imaginary frequencies (cm^{-1})
I5 + C_2H_2	0.00 (0.00)	
I6	−1.38 (10.56)	
TS7	13.05 (27.35)	i287.23
I8	−25.90 (−32.75)	
TS9	−9.69 (−17.10)	i435.33
I10	−52.73 (−59.86)	

[a] The values of the same cycloaddition but with N (R_1=H, R_2=H in Scheme 1) are given in parentheses as a reference.

Finally, calculations were performed for the oxepine formation reaction for estimating the effect of the substituents on the alkyne. The results listed in Table 4 indicate that no significant effect can be ascribed to any of the substituents tested, which lead to similar energetic profiles in all cases, with only slight differences due obviously to the increasing size of the alkyne in the insertion process.

TABLE 4: Relative Electronic Energies (ZPE Included) in kcal/mol for the Catalyzed [5+2]-Cycloaddition to Obtaine Oxepine at the B3LYP/6-31G(d,p)+ LANL2DZ Level with Different Substituents

	ΔE_{ZPE} (kcal/mol)		
	R_1=R_2=COH	R_1=R_2=CH_2OH	R_1=R_2=CH_2OCH_3
I5 + R_1CCR_2	0.00	0.00	0.00
I6	2.54	4.14	4.67
TS7	15.47	17.92	18.56
I8	−32.90	−24.85	−24.40
TS9	−10.63	−6.84	−6.42
I10	−51.75	−51.00	−50.22

Therefore, taking into account the results presented in Table 3, it can be stated that acetylene insertion is the key step of the processes studied in this work. In the case of imines, it constitutes the rate limiting step presenting the largest barrier. However, in the case of VCP or aldehydes, the barriers for insertion are much smaller, and even less significant than the barriers that must be overcome in the first part of the reaction. As shown by the calculations, the formation of the oxepine would be as energetically feasible as the reaction between VCP and alkynes.

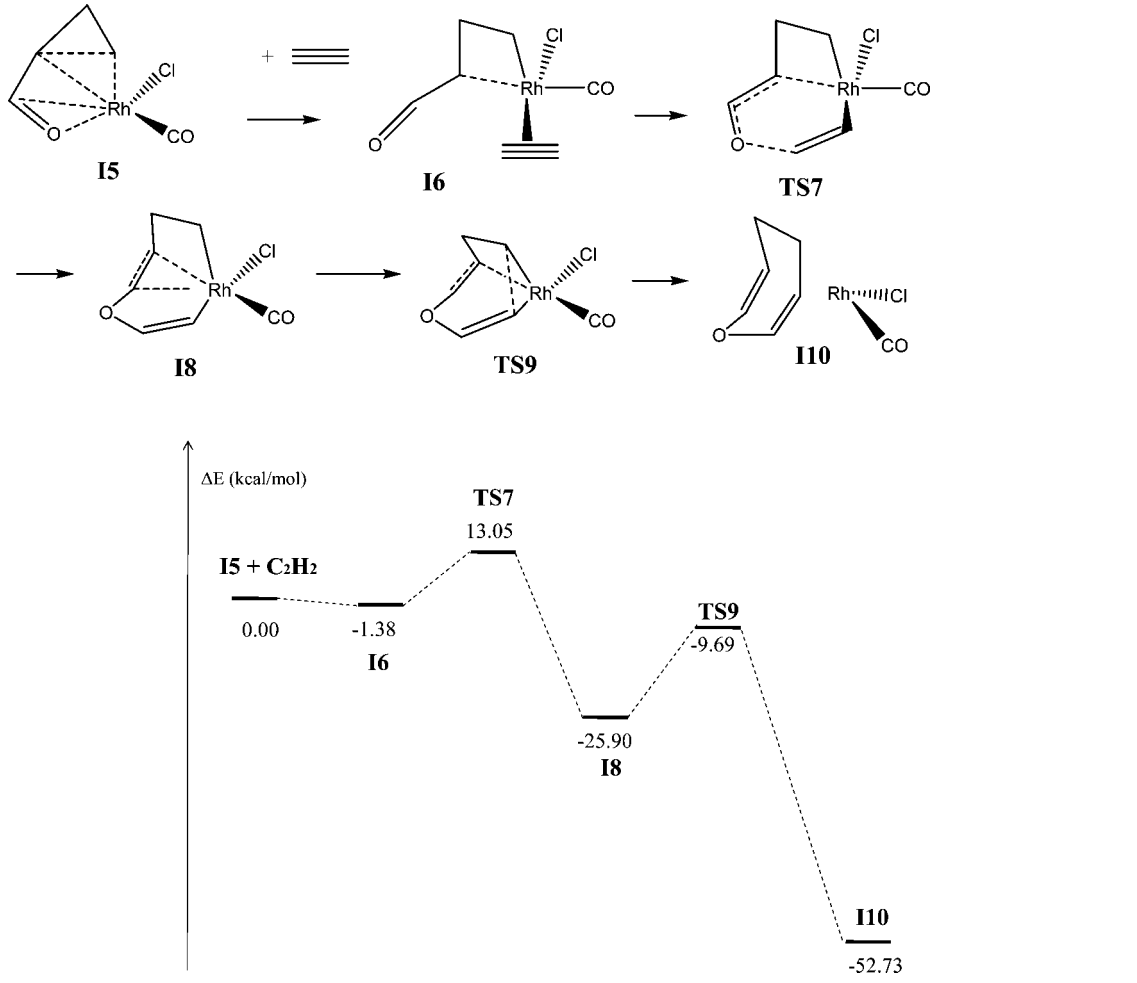


Figure 3. Intermediate and transition-state structures for the catalyzed [5+2]-cycloaddition to obtain oxepine at the B3LYP/6-31G(d,p)+LANL2DZ level. Also shown is an energy profile for the reaction with energies in kcal/mol.

4. Conclusions

Two different hetero-[5+2]-cycloadditions to obtain dihydroazepines and oxepines catalyzed by rhodium were studied with DFT, identifying the intermediate and transition state structures. As indicated by the calculations, the only differences among the cases studied are related with the process of alkyne insertion. This insertion step is much more costly for imines than for aldehydes. In the latter case, barriers are even lower than for other reactions employed to produce oxepines, as it is the Cope rearrangement route. The comparison with the noncatalyzed cycloaddition allows seeing how the rhodium catalyst transforms a two-step process with high barriers into a multistep process with lower activation energies.

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Supporting Information Available: Tables containing Cartesian coordinates for all structures as well as energetic information for the oxepine route. This material is available free of charge via the Internet at http://pubs.acs.org.

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