



## Theoretical study on the reaction between phosphacyclopropenylidene and ethylene: An alternative approach to the formation of phosphorus-bearing heterocyclic compounds

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**Abstract:** The reaction mechanism between phosphacyclopropenylidene and ethylene has been systematically investigated at the B3LYP/6-311++G(d,p) level of theory in order to better understand the reactivity of unsaturated cyclic phosphorus-bearing carbene. Geometry optimizations and vibrational analyses have been performed for the stationary points on the potential energy surface of the system. Calculations show that the spiro bicyclic intermediate could be produced through the cycloaddition process between phosphacyclopropenylidene and ethylene initially. The reaction mechanism is illustrated with the frontier molecular orbital theory. Introduction of electron-withdrawing group in phosphacyclopropenylidene will better facilitate the addition process. Through subsequent ring-expanding and hydrogen-migrating process, fuse-ring and allene compounds could be produced, respectively. Furthermore, it's easy for spiro bicyclic intermediate and another ethylene to form a spiro tricyclic compound. This study is helps to understand the reactivity of phosphacyclopropenylidene, the evolution of phosphorus-bearing molecules in space, and to offer an alternative approach to the formation of phosphorus-bearing heterocyclic compound.

**Keywords:** phosphacyclopropenylidene; ethylene; reaction mechanism; molecular orbital.

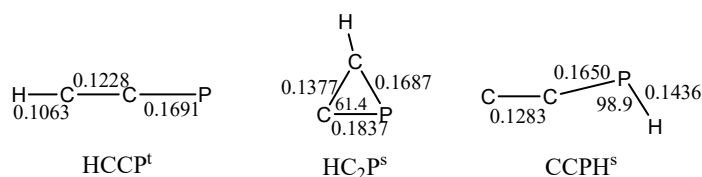
### INTRODUCTION

Approximately 180 molecules have been detected in the interstellar medium (ISM) or in circumstellar envelopes (CSEs) of late-type stars,<sup>1</sup> including six phosphorus-bearing molecules, PN,<sup>2,3</sup> CP,<sup>4</sup> HCP,<sup>5</sup> PO,<sup>6</sup> CCP<sup>7</sup> and PH<sub>3</sub>.<sup>8,9</sup> As a carbon-phosphorus-bearing molecule, HC<sub>2</sub>P might exist in the hot core of star-

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-forming regions.<sup>10</sup> Additionally, HC<sub>2</sub>P is one of the products of reaction between interstellar molecules CP and CH<sub>2</sub>CO theoretically.<sup>11</sup>

There are three isomers of HC<sub>2</sub>P based on the theoretical investigation: triplet linear HCCP (HCCP<sup>t</sup>, phosphapropynylidene), singlet circular HC<sub>2</sub>P (HC<sub>2</sub>P<sup>s</sup>, phosphacyclopropenylidene), and singlet bent CCPH (CCPH<sup>s</sup>, phosphapropadienylidene).<sup>10</sup> Geometrical parameters of three isomers of HC<sub>2</sub>P are shown as Scheme 1. Saito *et al.* detected microwave spectrum of the HC<sub>2</sub>P in the mixture of phosphine and acetylene for the first time using a source-modulated microwave spectrometer. The results show that the structure of HC<sub>2</sub>P is a linear phospho-allenic form, which is somewhat modified by a phosphorene.<sup>12</sup> A detailed and precise measure of line frequencies of HC<sub>2</sub>P is available for its astronomical search in the circumstellar envelopes or dark molecular clouds. Müller and Woon calculated dipole moments of compounds containing silicon and phosphorus, including HC<sub>2</sub>P, for assessing the column density, denoting abundance and predicting reactivity.<sup>13</sup>



Scheme 1. Optimized structures of the HC<sub>2</sub>P (bond length in nm and bond angle in degree) at the B3LYP/cc-pVDZ level of theory.<sup>10</sup>

The order of stability of three HC<sub>2</sub>P isomers is HCCP<sup>t</sup> > HC<sub>2</sub>P<sup>s</sup> > CCPH<sup>s</sup>.<sup>14</sup> For example, based on Boo's results, the relative electronic energy of HCCP<sup>t</sup>, HC<sub>2</sub>P<sup>s</sup>, CCPH<sup>s</sup> is 0, 4.2, and 17.5 kcal\*/mol at the MP2/cc-pVDZ level of theory, respectively.<sup>10</sup> Ding *et al.* investigated the structures and isomerization pathways of HC<sub>2</sub>P isomers in both singlet and triplet states at various levels and drew parallel conclusions from the aforementioned study.<sup>15</sup>

The reaction of azacyclopropenylidene (*c*-C<sub>2</sub>HN) has been investigated, which enriched the azacyclopropenylidene chemistry and provided alternative approaches for synthesizing relevant nitrogen-bearing compounds.<sup>16</sup> Phosphacyclopropenylidene (HC<sub>2</sub>P<sup>s</sup>) is an analogue of azacyclopropenylidene. We believe that further investigation for the reaction mechanism between phosphacyclopropenylidene and unsaturated compounds can stimulate relevant experimental and theoretical studies of HC<sub>2</sub>P. In the present study, we have performed a comprehensive theoretical investigation of the reaction mechanism between phosphacyclopropenylidene and ethylene by employing the popular hybrid density functional B3LYP method with 6-311++G(d,p) basis set. The research results

\* 1 kcal = 4184 J

indicate that three products, fuse-ring, allene and spiro tricyclic compound, are formed. The present results will enrich the existing data for the relevant phosphacycloprenylidene chemistry and discuss the possibility of formation of phosphorus-bearing molecules by means of phosphacycloprenylidene.

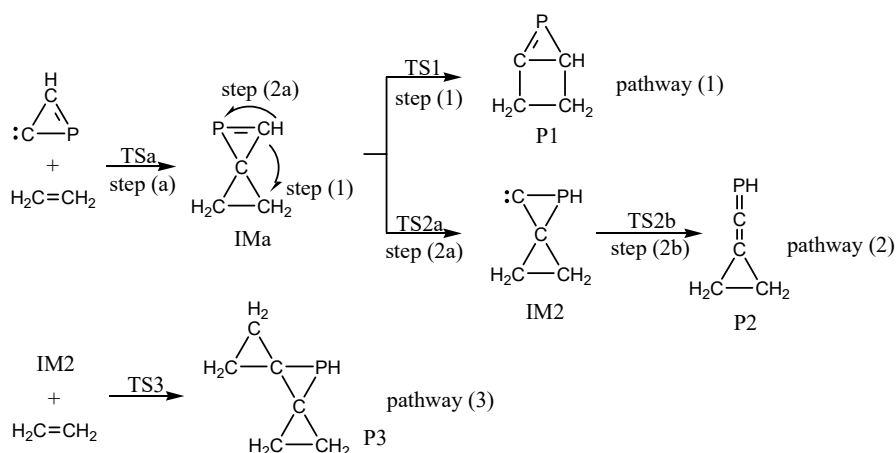
#### CALCULATION METHOD

The popular hybrid density functional B3LYP method, namely Becke's three-parameter non-local exchange functional<sup>17</sup> with the non-local correlation functional of Lee *et al.*<sup>18</sup> and 6-311++G(d,p) basis set including diffuse and polarization functions have been employed to locate all the stationary points along the reaction pathway without imposing any symmetry constraints. The reliability and efficiency of this method in predicting geometries and properties have been verified by a number of investigations.<sup>19-21</sup> Frequency analyses have been conducted to confirm the nature of the minima and transition states. Moreover, intrinsic reaction coordinate (IRC) calculations have also been done to further validate the calculated transition states connecting reactants and products. Additionally, the relevant energy quantity, such as the reaction energies and barrier heights, has been corrected with zero-point vibrational energy (ZPVE) corrections.

All the calculations have been performed using Gaussian 98 program.

#### RESULTS AND DISCUSSION

As displayed in Scheme 2, three possible pathways for the title reaction have been proposed. The geometric parameters for the reactants (R1-phosphacycloprenylidene and R2-ethylene), transition states (TS), intermediates (IM) and products (P) involved in the pathways (1)–(3) are displayed in Fig. 1 (additional data are given in Supplementary material to this paper). The corresponding reaction profile is illustrated in Fig. 2.



Scheme 2. The proposed three pathways for the reaction between phosphacycloprenylidene and ethylene.

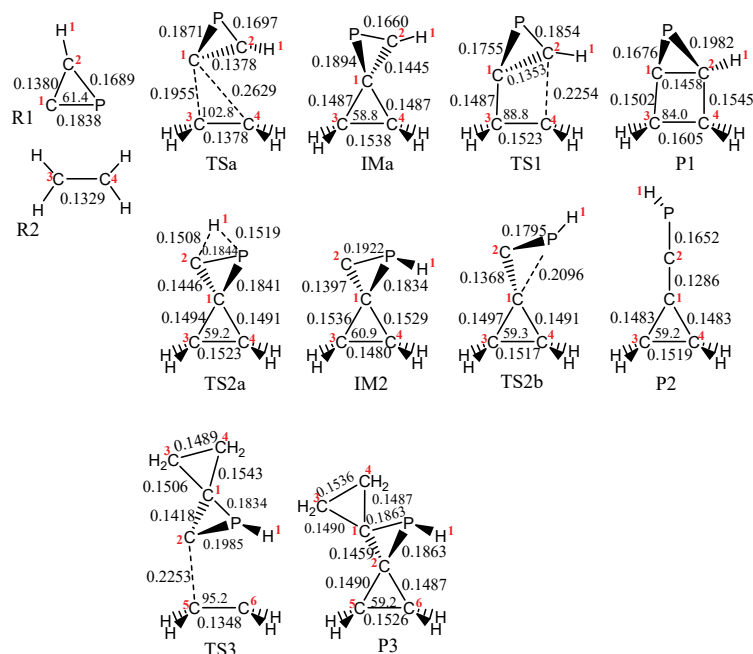


Fig. 1. Optimized structures of the reactants (phosphacyclopropenylidene and ethylene), transition states (TS), intermediates (IM) and products (P) in the reaction pathways (1)–(3) at the B3LYP/6-311++G(d,p) level of theory, where the bond length and bond angle are in nm and degrees, respectively.

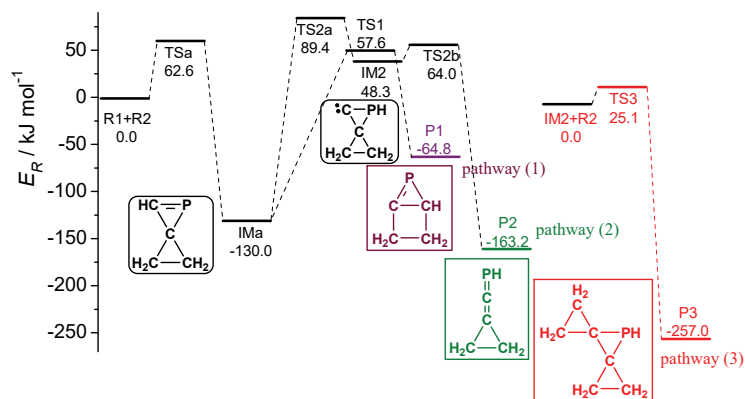


Fig. 2. Reaction profiles for the pathways (1)–(3) between R1 (phosphacyclopropenylidene) and R2 (ethylene) at the B3LYP/6-311++G(d,p) level of theory.

*Step (a): cycloaddition reaction process to form a spiro bicyclic intermediate IMa*

On the pathways (1) and (2), the common intermediate IMa is formed via a cycloaddition reaction process with an energy barrier of 62.6 kJ mol<sup>-1</sup>. The

unique imaginary frequency calculated for the corresponding transition state (TSa) in the step (a) is  $422i \text{ cm}^{-1}$  at the B3LYP/6-311++G(d,p) level of theory.

As shown in Fig. 1, the distance of  $C^1-C^3$  and  $C^1-C^4$  in TSa is 0.1955 and 0.2629 nm, respectively. Thus, in the transition state TSa, two new bonds of  $C^1C^3$  and  $C^1C^4$  are to be formed. At the same time, the distance of  $C^3-C^4$ , in R2 fragment of TSa, is reached to 0.1378 nm, which elongated 0.0049 nm that in ethylene. Therefore, based on the bond length data, the double bond of  $C^3C^4$  in ethylene is transformed into a single bond in IMa *via* TSa. The formation of new  $\sigma$ -bond of  $C^1C^3$  and  $C^1C^4$  and the cleavage of  $\pi$ -bond of  $C^3C^4$  happen simultaneously. Therefore, step (a) is a concerted cycloaddition reaction process. As shown in Fig. 3, those changes can be further validated by the IRC calculations on the basis of TSa.

Qualitatively, the cycloaddition reaction process of step (a) can be realized from the frontier molecular orbital theory. As displayed in Fig. 4, the frontier orbitals for LUMO+1 of R1 (phosphacyclopropenylidene) and HOMO of R2 (ethylene) are symmetrical matching. In addition, the LUMO+1 energy of R1 (0.01333 a.u.) is close to the HOMO of R2 (-0.01081 a.u.). As R1 initially interacts with R2, the unoccupied  $2p$  orbital of  $C^1$  in R1 inserts into the  $\pi$ -orbital of R2 to form a  $\pi$ - $p$  donor-acceptor bond, resulting in the formation of the spiro bicyclic intermediate IMa. The less the electron densities on the  $C^1$  atom in R1, the easier will be the insertion process of formation of a  $\pi$ - $p$  donor-acceptor bond.

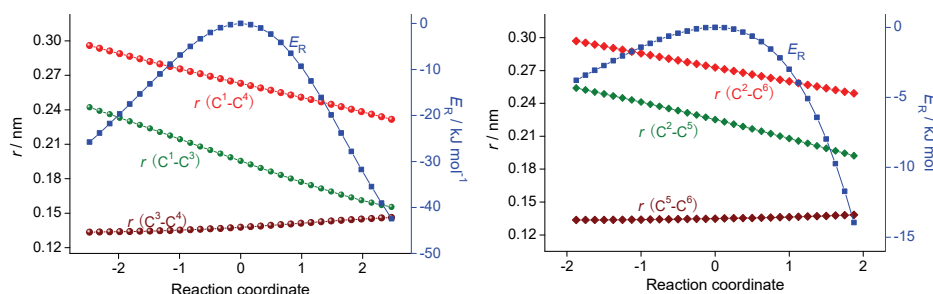


Fig. 3. The relative energy ( $E_R$ ) and selected bond lengths change along the reaction coordinates of the step (a) (left) and step (3) (right).

There are two  $\pi$ -electrons in the R1 ( $C^1$  offers an empty  $p$ -orbital,  $C^2$  and P offers a  $\pi$ -electron, respectively), conforming to the Hückel rule ( $\pi$ -electrons are  $4n+2$ ,  $n = 0$ ). Therefore, R1 represents an aromatic molecule. By the conjugation effect, introduction of electron-withdrawing group at  $C^2$  in R1 will decrease the electron density on  $C^1$ , which will better facilitate the reaction between R1 and R2. Introduction of electron-donating group will result in the opposite effect. As summarized in Table I, introduction of electron-withdrawing group, F,  $CF_3$ , and CN, decreases the electron density at the  $C^1$  atom in R1, by which it can decrease

the barrier of step (a). On the contrary, electron-donating groups, CH<sub>3</sub>, OH and OCH<sub>3</sub>, *etc.*, increase the barrier of step (a).

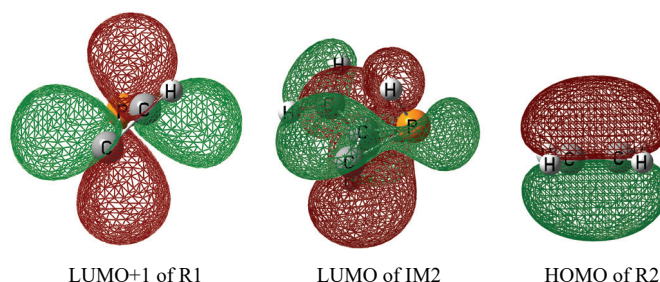


Fig. 4. The calculated MO orbitals for R1 (phosphacyclopropenylidene), R2 (ethylene) and IM2.

TABLE I. The barrier in step (a) of the cycloaddition reaction process between XC<sub>2</sub>P<sup>s</sup> and ethylene at the B3LYP/6-311++G(d,p) level of theory

X (electron-withdrawing group)	Barrier, kJ mol <sup>-1</sup>	X (electron-donating group)	Barrier, kJ mol <sup>-1</sup>
H	62.6	CH <sub>3</sub>	65.8
F	60.3	OH	69.5
CF <sub>3</sub>	58.6	OCH <sub>3</sub>	71.4
CN	57.3	NH <sub>2</sub>	69.8
		NHCH <sub>3</sub>	67.7
		N(CH <sub>3</sub> ) <sub>2</sub>	71.6

IMa is a spiro bicyclic compound. Two three-membered rings, C<sup>1</sup>C<sup>2</sup>P and C<sup>1</sup>C<sup>3</sup>C<sup>4</sup>, share C<sup>1</sup> atom. IMa can transfer to P1 through ring expansion process (step (1)) and to IM2 through H migration process (step (2)).

*Step (1): ring-expanding process to form a fuse-ring compound P1*

On the pathway (1), the product P1 is formed via a ring-expanding process of IMa. The unique imaginary frequency calculated for the corresponding transition state TS1 in the step (1) is 601i cm<sup>-1</sup>.

In TS1, cleavage of π bond of C<sup>2</sup>P formed single electron on C<sup>2</sup> and P, the cleavage of σ-bond of C<sup>1</sup>C<sup>4</sup> formed single electron on C<sup>1</sup> and C<sup>4</sup>, respectively. In the meanwhile, two single electrons on C<sup>2</sup> and C<sup>4</sup> formed a new σ-bond, the other two single electrons on C<sup>1</sup> and P formed a new π-bond. The distance of C<sup>2</sup>-C<sup>4</sup> in TS1 is 0.2254 nm, denoting the formation of a new σ-bond between C<sup>2</sup> and C<sup>4</sup>. The distance of C<sup>1</sup>-P in TS1 is 0.1755 nm, which is between the length of a single bond (C<sup>1</sup>P in IMa) and double bond (C<sup>1</sup>P in P1), denoting the transformation of C<sup>1</sup>P bond from a single bond to a double bond. P1 is a fuse-ring compound, which is exothermic with the value of 64.8 kJ mol<sup>-1</sup> higher than that of the reactants.

*Step (2a): H-migrating process to form a spiro intermediate IM2*

Step (2a) in pathway (2) is the hydrogen ( $H^1$ ) migration from  $C^2$  to the adjacent P, resulting in the isomerization of IMA into IM2 via TS2a. Here, calculated energy is  $89.4 \text{ kJ mol}^{-1}$ , the imaginary frequency of TS2a is  $894i \text{ cm}^{-1}$ . In details, as shown in Fig. 1, the distance of  $C^2-H^1$  in TS2a has been elongated to  $0.1508 \text{ nm}$ , and the distance of  $P-H^1$  reached to  $0.1519 \text{ nm}$ , indicating that the  $H^1$  atom can migrate from  $C^2$  to P. In the meantime, the bond length of  $C^2P$  in TS2a increased to  $0.1844 \text{ nm}$  (the bond length of  $C^2P$  in IMA is  $0.1660 \text{ nm}$ ), suggesting the double bond of  $C^2P$  in IMA will be transferred into the single bond of  $C^2P$  in IM2.

Similar to IMA, IM2 is also a spiro intermediate. The difference between IM2 and IMA is that the former has a pair of lone electrons on  $C^2$  atom. That is, IM2 is characterized by unstable carbene structure. Along the reaction profile, IM2 is endothermic with the value of  $48.3 \text{ kJ mol}^{-1}$  higher than that of the reactants. In general, carbene will isomerize to the stable species by bonding its lone electrons. Therefore, IM2 can isomerize to P2 through a ring-opening process of  $C^1C^2P$ , or react with ethylene to form P3.

*Step (2b): ring-opening process to form an allene product P2*

As noted above, IM2 can isomerize to P2 through a ring-opening process of  $C^1C^2P$  via TS2b, which is named as step (2b). Here, the calculated energy of TS2b is  $64.0 \text{ kJ mol}^{-1}$  and the imaginary frequency of TS2b is  $374i \text{ cm}^{-1}$ . As shown in Fig. 1, the distance of  $C^1-P$  in TS2b has been elongated to  $0.2096 \text{ nm}$ , indicating the break-up of the  $C^1P$  bond and the open-up of  $C^1C^2P$  ring. In P2, the bond length of  $C^1C^2$  is  $0.1286 \text{ nm}$ , which fall in the range of the intermediate between  $C=C$  double bond and  $C\equiv C$  triple bond length. Analogously, the bond length of  $C^2P$  ( $0.1652 \text{ nm}$ ) in P2 is similar to CP double bond ( $C^2P$  double bond is  $0.1689 \text{ nm}$  in R1), and is quite shorter than CP single bond ( $C^2P$  single bond is  $0.1922 \text{ nm}$  in IM2). The three atoms,  $C^1$ ,  $C^2$ , and P, are approaching to the same line ( $\angle C^1C^2P$  is  $173.1^\circ$ ). Therefore, P2 has the allenes structure. Along the reaction profile, P2 is exothermic with the value of  $163.2 \text{ kJ mol}^{-1}$  higher than that of the reactants. As shown in Fig. 5, those changes in bond length and angle can be further validated by the IRC calculations on the basis of TS2b.

IM2 is similar to R1, both of them have carbene characteristic. IM2 can react with ethylene to form P3 via TS3. Reaction of IM2 and ethylene is similar to the reaction of R1 and ethylene. As displayed in Fig. 4, the frontier orbitals for LUMO of IM2 and HOMO of R2 are symmetrical matching.

*Pathway (3): addition reaction process to form a spiro tricyclic compound P3*

As IM2 initially interacts with ethylene, the unoccupied  $2p$  orbital of  $C^2$  in IM2 inserts into the  $\pi$ -orbital of ethylene to form a  $\pi$ -p donor-acceptor bond,

resulting in the formation of the spiro tricyclic compound P3. Unlike the R1, IM2 has no aromatic characteristic. Therefore, it is easier for the reaction of IM2 and ethylene than that of R1 and ethylene, which can be demonstrated through the barrier in step (3) ( $25.1 \text{ kJ mol}^{-1}$ ) and step (a) ( $62.6 \text{ kJ mol}^{-1}$ ). As shown the IRC calculation in Fig. 3, changes in the relative energy and selected bond lengths in step (3) are very similar to that in step (a).

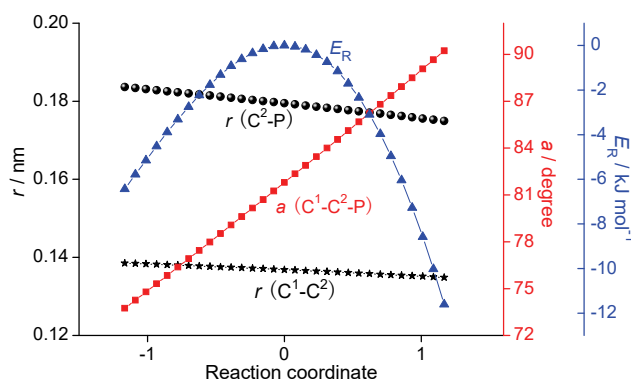


Fig. 5. The selected bond lengths, bond angle and relative energy ( $E_R$ ) change along the reaction coordinates of the step (2b).

## CONCLUSION

In this study, the reaction mechanism between phosphacyclopropenylidene and ethylene has been systematically investigated employing the B3LYP/6-311++G(d,p) level of theory. The reaction involves three pathways: (1)–(3). The spiro bicyclic compound is the common intermediate for three pathways through cycloaddition process. Introduction of electron-withdrawing group in phosphacyclopropenylidene will better facilitate the cycloaddition process. Introduction of electron-donating group will result in the opposite effect. Pathway (1) is the process of formation of phosphorus-bearing fuse-ring compound *via* a ring expansion. Pathway (2) is the process of formation of phosphorus-bearing allene compound through hydrogen migration and ring-opening. Pathway (3) is to form a phosphorus-bearing spiro tricyclic compound. This study is useful to understand the reactivity of phosphacyclopropenylidene, the evolution of phosphorus-bearing molecules in space, and to offer an alternative approach to the formation of phosphorus-bearing heterocyclic compound.

## SUPPLEMENTARY MATERIAL

Matrixes of whole optimized structures (Table S-I) are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/index>, or from the corresponding author on request.



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## ИЗВОД

## ТЕОРИЈСКО ИСТРАЖИВАЊЕ РЕАКЦИЈЕ ИЗМЕЂУ ФОСФАЦИКЛОПРОПЕНИЛИДЕНА И ЕТИЛЕНА: АЛТЕРНАТИВНИ ПРИСТУП ФОРМИРАЊУ ФОСФОР-НОСЕЋИХ ХЕТЕРОЦИКЛИЧНИХ ЈЕДИЊЕЊА

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Механизам реакције између фосфациклопропенилидена и етилена је систематски изучаван на ВЗЛР/6-311++G(d,p) нивоу теорије како би се боље разумела реактивност незасићених цикличних карбена који носе фосфор. Оптимизације геомерије и вибрационе анализе су извршене за стационарне тачке на површини потенцијалне енергије система. Израчунавања показују да спиро бициклични интермедијери могу да се произведу процесом циклоадисије иницијално између фосфациклопропенилидена и етилена. Реакциони механизам је илустрован теоријом граничних молекулских орбитала. Увођење електрон-привлачних група у фосфациклопропенилиден ће олакшати процес адисије. Накнадним процесима проширивања прстена и миграције водоника, могу бити произведена једињења са кондензованим прстеновима, односно аленска једињења. Надаље, спиро бициклични интермедијер и други етилен лако формирају spiro трициклично једињење. Ова студија је од помоћи за разумевање реактивност фосфациклопропенилидена, еволуције фосфор-носећих молекула у међузвезданом простору, као понуда алтернативног приступа за формирање фосфор-носећих хетероцикличних једињења.

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