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Original scientific paper

## ***Ab initio* study of the mechanism of formation of a spiro-Sn-heterocyclic ring compound by the cycloaddition reaction of $H_2C=Sn:$ and ethylene**

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**Abstract:**  $X_2C=Sn:$  ( $X = H, Me, F, Cl, Br, Ph, Ar...$ ) are new species of chemistry. The cycloaddition reactions of  $X_2C=Sn:$  is a new study field of stannylene chemistry. The mechanism of cycloaddition reaction of singlet  $H_2C=Sn:$  with ethylene is studied for the first time using the MP2/GENECP (C, H in 6-311++G<sup>\*\*</sup>; Sn in LanL2dz) method in this paper. From the potential energy profile, it could be predicted that the reaction has one dominant reaction channel. The reaction rule presented is that the 5p unoccupied orbital of tin in  $H_2C=Sn:$  sidewise overlaps with the bonding  $\pi$  orbital of ethylene resulting in the formation of an intermediate. The instability of the intermediate makes it isomerise to a four-membered ring stannylene. As the 5p unoccupied orbital of the Sn atom in the four-membered ring stannylene and the  $\pi$  orbital of ethylene form a  $\pi \rightarrow p$  donor–acceptor bond, the four-membered ring stannylene further combines with ethylene to form another intermediate, and this intermediate further isomerises to a spiro-Sn-heterocyclic ring compound. The Sn in the spiro-Sn-heterocyclic ring compound is combined with adjacent atoms by  $sp^3$  hybridization. The results of this study reveal the mechanism of cycloaddition reaction of  $X_2C=Sn:$  with symmetric  $\pi$ -bond compounds.

**Keywords:**  $H_2C=Sn:$ ; four-membered ring stannylene; spiro-Sn-heterocyclic ring compound; potential energy profile.

### INTRODUCTION

The unsaturated olefins of the group IV elements (C, Si, Ge) are all active intermediates,<sup>1–6</sup> Their cycloaddition reaction have been studied<sup>7–13</sup> and with progress of these studies, the study on cycloaddition reactions of unsaturated stannylene should also be put on the agenda. However, there have hitherto been no published reports concerning cycloaddition reactions of unsaturated stan-

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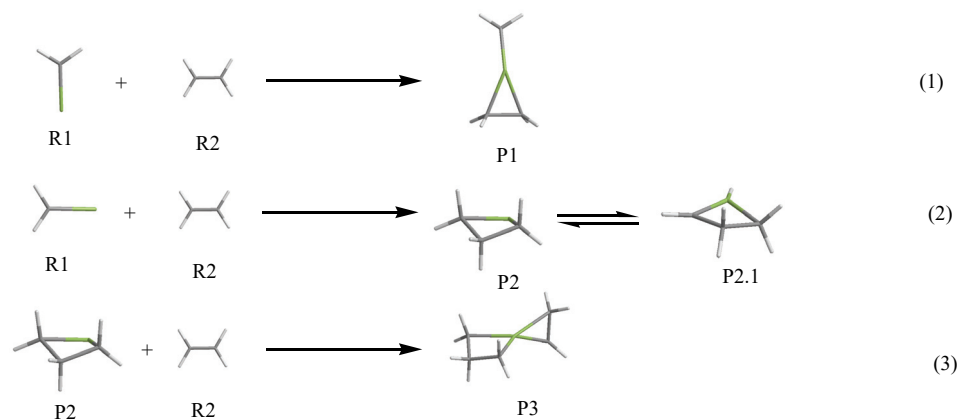
nylene. Unsaturated stannylene (*i.e.*,  $X_2C=Sn:$ ) are a new chemical species and new study field of stannylene chemistry. In particular, the mechanism of their cycloaddition reaction and the rules of cycloaddition reactions between  $X_2C=Sn:$  and symmetric  $\pi$ -bonded compounds should be studied. In this paper  $H_2C=Sn:$  and ethylene were selected as model molecules, and the cycloaddition reaction mechanism (considering H transfer simultaneously) was investigated and analyzed theoretically. The research result indicates the laws of cycloaddition reaction between  $X_2C=Sn:$  and symmetric  $\pi$ -bonded compounds, which are significant for the synthesis of a small-ring containing Sn and spiro-Sn-heterocyclic compounds. The study extended the research area and enriched the research content of stannylene chemistry.

#### CALCULATION METHOD

The method of the second-order perturbation theory (MP2)<sup>14</sup> and Gaussian 09 package were used to optimize the structure of  $H_2C=Sn:$  and its cycloaddition reaction with ethylene, its transition state form at the MP2/GENECP (C, H in 6-311++G\*\*, Sn in LanL2dz level) of theory. In order to further confirm the correctness of the relevant species and obtain the thermodynamic function for the species, vibration analysis was included. Finally, the intrinsic reaction coordinate (IRC)<sup>15,16</sup> was also calculated for all the transition states to determine the reaction paths and directions.

#### RESULTS AND DISCUSSION

As theoretical research shows that the ground state of  $H_2C=Sn:$  (R1) is a singlet state, its cycloaddition reaction with ethylene (R2) has the following three possible routes:



The geometrical parameters of the intermediates (INT1 and INT3), transition states (TS1, TS2, TS2.1 and TS3) and products (P1, P2, P2.1 and P3) that appear in the above three reactions are given in Fig. 1, the energies are listed in Table I and the entropy, enthalpy and Gibbs energy values are listed in Table II. The potential energy profile of the above three reactions are shown in Fig. 2.

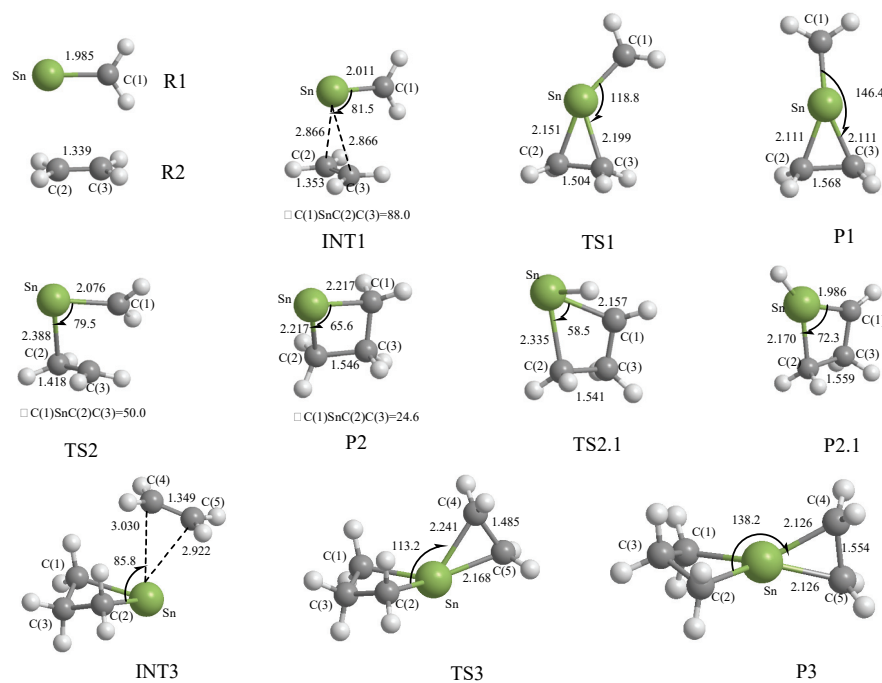


Fig. 1. Optimized MP2/GENECP (C, H in 6-311++G\*\*; Sn in LanL2dz) geometrical parameters and the atomic numbering for the species in cycloaddition reaction between  $\text{H}_2\text{C}=\text{Sn}$ : and ethylene. Bond lengths and bond angles are in angstrom and degree, respectively.

TABLE I. The electronic structure energy ( $E_{\text{ese}}$ ) and relative energies ( $E_{\text{R}}$ ) for the species from the MP2/GENECP (C, H in 6-311++G\*\*; Sn in LanL2dz) method at 298 K and 101325 Pa

Reaction	Species	MP2/GENECP	
		$E_{\text{ese}} / \text{Ha}$	$E_{\text{R}} / \text{kJ mol}^{-1}$
(1) <sup>a</sup>	R1+R2	-120.76486	0.0
	INT1	-120.78058	-41.3
	TS1 (INT1-P1)	-120.72718	98.9
	P1	-120.73150	87.6
(2) <sup>a</sup>	R1+R2	-120.76486	0.0
	INT1	-120.78058	-41.3
	TS2(INT1-P2)	-120.76248	6.2
	P2	-120.82512	-158.2
	TS2.1(P2-P2.1)	-120.71765	123.9
(3) <sup>b</sup>	P2.1	-120.75656	21.8
	P2+R2	-199.17164	0.0
	INT3	-199.18360	-31.4
	TS3(INT3-P3)	-199.16216	24.9
	P3	-199.16806	9.4

<sup>a</sup> $E_{\text{R}} = E_{\text{ese}} - E_{\text{ese}}(\text{R1}+\text{R2})$ , <sup>b</sup> $E_{\text{R}} = E_{\text{ese}} - E_{\text{ese}}(\text{P2}+\text{R2})$

TABLE II. Entropy, enthalpy and Gibbs free energy for the species from MP2/GENECP (C, H in 6-311++G\*\* ; Sn in LanL2dz) methods at the 298 K and 101325 Pa

Reaction	Species	$H / \text{Ha}$	$S \times 10^4 / \text{Ha}$	$G / \text{Ha}$
(1)	R1+R2	-120.68436	1.83010	-120.73895
	INT1	-120.69667	1.31074	-120.73577
	TS1 (INT1-P1)	-120.64511	1.19512	-120.68076
	P1	-120.64842	1.23904	-120.68538
(2)	TS2(INT1-P2)	-120.67918	1.18527	-120.71454
	P2	-120.73864	1.17524	-120.77369
	TS2.1(P2-P2.1)	-120.63781	1.17213	-120.67277
	P2.1	-120.67517	1.20096	-120.71099
(3)	P2+R2	-199.03032	2.01150	-199.09031
	INT3	-199.03946	1.52138	-199.08484
	TS3(INT3-P3)	-199.01940	1.35050	-199.05968
	P3	-199.02440	1.40081	-199.06618

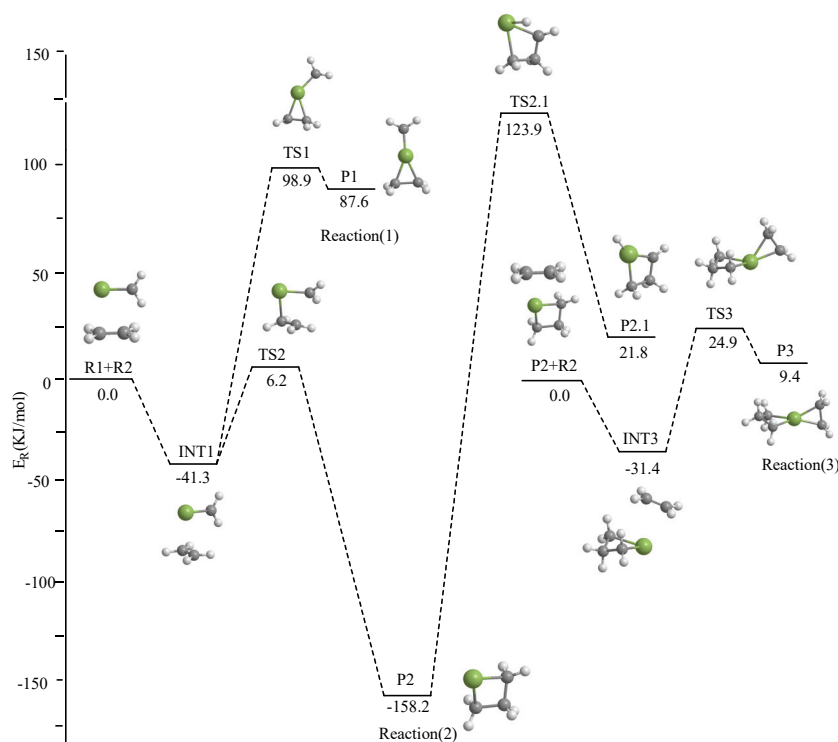


Fig. 2. The potential energy surface for the cycloaddition reactions between  $\text{H}_2\text{C}=\text{Sn}$ : and ethylene as calculated with MP2/GENECP (C, H in 6-311++G\*\* ; Sn in LanL2dz).

The unique imaginary frequency of the transition states TS1, TS2, TS2.1, and TS3 obtained through vibrational analysis are  $220.7i$ ,  $419.7i$ ,  $784.5i$  and  $120.8i$ , respectively, and therefore, these transition states could be affirmed as the

genuine ones. IRC (with a step-size of  $0.1 \text{ amu}^{-1/2} \text{ Bohr}$ ) analysis confirmed that TS1 connects INT1 and P1, TS2 connects INT1 and P2, TS2.1 connects P2 and P2.1, and TS3 connects INT3 and P3.

According to Fig. 2, it could be seen that reaction (1) consists of two steps: the first one is that the two reactants (R1 and R2) form an intermediate (INT1). According to Fig. 2 and Table II, the reaction is a barrier-free exothermic reaction, and the changes of molar constant volume heat of reaction ( $\Delta_r U_m$ ) and molar heat of reaction ( $\Delta_r H_m$ ) at normal temperature and pressure are  $-41.3$  and  $-32.3 \text{ kJ mol}^{-1}$ , respectively, and the change of molar Gibbs energy of the reaction ( $\Delta_r G_m$ ) is  $-8.3 \text{ kJ mol}^{-1}$ . The second is that INT1 isomerises to a three-membered Sn-heterocyclic ring product P1 *via* transition state TS1 with an energy barrier of  $140.2 \text{ kJ mol}^{-1}$ . According to Fig. 2 and Table II, the reaction is endothermic, and the  $\Delta_r U_m$  and  $\Delta_r H_m$  values at normal temperature and pressure are  $128.9$  and  $126.7 \text{ kJ mol}^{-1}$ , respectively, and the  $\Delta_r G_m$  value is  $140.6 \text{ kJ mol}^{-1}$ . Hence, INT1→P1 is thermodynamically forbidden at normal temperature and pressure, and reaction (1) will end in INT1.

According to Fig. 2, it could be seen that reaction (2) consists of three steps: the first one is that the two reactants (R1 and R2) form an intermediate (INT1) (the situation is the same as reaction (1)). The second is that the INT1 isomerizes to a four-membered ring stannylene (P2) *via* transition state TS2 with an energy barrier of  $47.5 \text{ kJ mol}^{-1}$ . According to Fig. 2 and Table II, the reaction is exothermic, and  $\Delta_r U_m$  and  $\Delta_r H_m$  the values at normal temperature and pressure are  $-116.9$  and  $-110.2 \text{ kJ mol}^{-1}$ , respectively, and the  $\Delta_r G_m$  value is  $-91.2 \text{ kJ mol}^{-1}$ . The third is that the P2 undergoes H transfer *via* transition state TS2.1 with an energy barrier of  $282.1 \text{ kJ mol}^{-1}$ , resulting in the formation of product P2.1. According to Fig. 2 and Table II, the reaction is an endothermic reaction, and the  $\Delta_r U_m$  and  $\Delta_r H_m$  values at normal temperature and pressure are  $180.0$  and  $166.6 \text{ kJ mol}^{-1}$ , respectively, and the  $\Delta_r G_m$  value is  $164.6 \text{ kJ mol}^{-1}$ . Thus, P2→P2.1 is thermodynamically forbidden at normal temperature and pressure, and reaction (2) will end in P2. Comparing reaction (2) with reaction (1), INT1→P1 is thermodynamically forbidden, and thus, reaction (2) will be the dominant reaction channel.

In reaction (3), the four-membered ring stannylene (P2) further reacts with ethylene (R2) to form a spiro-Sn-heterocyclic ring, compound (P3). According to Fig. 2, it could be seen that the process of reaction (3) is based on the P2 formed in reaction (2) reacting further with ethylene (R2) to form an intermediate (INT3). According to Fig. 2 and Table II, the reaction is a barrierless exothermic reaction, and the  $\Delta_r U_m$  and  $\Delta_r H_m$  values at normal temperature and pressure are  $-31.4$  and  $-24.0 \text{ kJ mol}^{-1}$ , respectively, and the  $\Delta_r G_m$  value is  $-14.4 \text{ kJ mol}^{-1}$ . Then intermediate (INT3) isomerizes to a spiro-Sn-heterocyclic ring compound (P3) *via* a transition state (TS3) with an energy barrier of  $56.3 \text{ kJ mol}^{-1}$ . Accord-

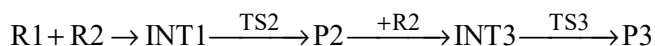
ing to Fig. 2 and Table II, the reaction is an endothermic reaction, and the  $\Delta_r U_m$  and  $\Delta_r H_m$  values at normal temperature and pressure are 40.8 and 39.5 kJ mol<sup>-1</sup>, respectively, and the  $\Delta_r G_m$  value is 63.4 kJ mol<sup>-1</sup>. According to Fig. 2, reaction (3) and P2→P2.1 in reaction (2) are competitive reactions. As P2→P2.1 is thermodynamically forbidden, reaction (3) will be the dominant reaction channel.

In reaction (3), since  $\Delta_r G_m$  value of P2+R2→P3 is 49.0 kJ mol<sup>-1</sup>, it is a thermodynamically forbidden reaction at normal temperature and normal pressure. In order to realize the reaction, according to the following thermodynamic formula:

$$\Delta G(p_2) - \Delta G(p_1) = \int_{p_1}^{p_2} \Delta V dp$$

At a temperature of 298 K, P2+R2→P3 is allowed to proceed, and the pressure of the reaction system must be greater than 150325 Pa (1.5 atm).

According to all the analyses, reaction (3) should be the dominant reaction channel of the cycloaddition reaction between singlet H<sub>2</sub>C=Sn: and ethylene, namely:



In this reaction, the frontier molecular orbitals of R1, R2 and P2 are shown in Fig. 3. According to Fig. 3, the mechanism of reaction (3) could be explained with the frontier molecular orbital diagrams (see Figs. 4 and 5). According to Figs. 1 and 4, when H<sub>2</sub>C=Sn: (R1) initially interacts with ethylene, the 5p unoccupied orbital of tin sidewise overlaps with the bonding  $\pi$ -orbital of ethylene, leading to the formation of an intermediate (INT1). As the reaction proceeds, the Sn–C(2) bond (INT1: 2.886 Å, TS2: 2.388 Å, P2: 2.217 Å),  $\angle C(1)SnC(2)C(3)$  (INT1: 88.0°, TS2: 50.0°, P2: 24.6°) and  $\angle C(1)SnC(2)$  (INT1: 81.5°, TS2: 79.5°, P2: 65.6°) gradually decrease, and the C(1)–Sn and C(2)–C(3) bond (INT1: 2.011 and 1.353 Å; TS2: 2.076 and 1.418 Å; P2: 2.217 and 1.546 Å) gradually lengthen. Before the transition state TS2, Sn and C(2) form a covalent bond. After the transition state TS2, C(1) and C(3) form a covalent bond. Thus, INT1 isomerizes to a four-membered ring stannylene (P2) *via* transition state TS2. As

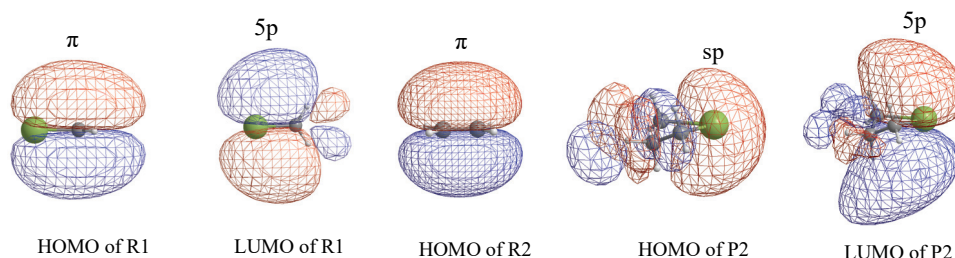


Fig. 3. The frontier molecular orbitals of R1, R2, P2.

P2 is still an active molecular species, P2 may further react with ethylene to form a spiro-Sn-heterocyclic ring compound (P3). The mechanism of this reaction could be explained with Figs. 1 and 5. According to the rule of molecular orbital symmetry adaptation, when P2 interacts with ethylene (R2), the 5p unoccupied orbital of the Sn atom in P2 insert the p orbital of ethylene forming a  $\pi \rightarrow p$  donor-acceptor bond, leading to the formation of an intermediate (INT3). As the reaction proceeds, the Sn–C(4) and Sn–C(5) bond lengths gradually decrease (INT3: 3.030 and 2.922 Å; TS3: 2.241 and 2.168 Å; P3: 2.126 and 2.126 Å), the  $\angle C(2)SnC(4)$  angle (INT3: 85.8°, TS3: 113.2°, P3: 138.2°) gradually increases, the C(4)–C(5) bond gradually lengthens (INT3: 1.349 Å, TS3: 1.485 Å, P3: 1.554 Å). Before the transition state TS3, a covalent bond is formed between Sn and C(4) and between Sn and C(5). After the transition state TS3, INT3 further isomerizes to a *spiro*-Sn-heterocyclic ring compound (P3) *via* transition state TS3. Sn in the *spiro*-Sn-heterocyclic ring compound is combined with adjacent atoms by  $sp^3$  hybridization.

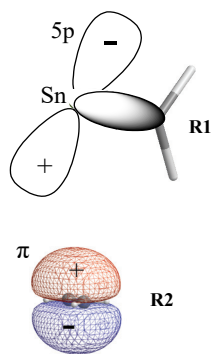


Fig. 4. A schematic interaction diagram for the frontier orbitals of  $H_2C=Sn$ : (R1) and  $C_2H_4$  (R2).

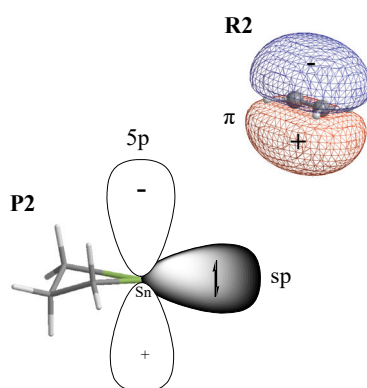


Fig. 5. A schematic diagram for the frontier orbitals of P2 and  $C_2H_4$  (R2).

## CONCLUSIONS

According to the potential energy profile, the cycloaddition reaction between singlet  $\text{H}_2\text{C}=\text{Sn}:$  and ethylene obtained with the MP2/GENECP (C, H in 6-311++G\*\*; Sn in LanL2dz) method can be predicted. This reaction has one dominant channel. It consists of four steps: 1) the two reactants first form an intermediate (INT1) through a barrier-free exothermic reaction of  $41.3 \text{ kJ mol}^{-1}$ ; 2) the intermediate (INT1) isomerizes to a four-membered ring stannylene (P2) via transition state TS2 with an energy barrier of  $47.5 \text{ kJ mol}^{-1}$ ; 3) the four-membered ring stannylene (P2) further reacts with ethylene (R2) to form another intermediate INT3 through a barrier-free exothermic reaction of  $31.4 \text{ kJ mol}^{-1}$ ; 4) intermediate (INT3) isomerizes to a spiro-Sn-heterocyclic ring compound (P3) via transition state TS3 with an energy barrier of  $56.3 \text{ kJ mol}^{-1}$ . At a temperature of 298 K, the reaction is carried out, and the pressure of the reaction system needs to be greater than 150325 Pa (1.5 atm).

The 5p unoccupied orbital of Sn in  $\text{X}_2\text{C}=\text{Sn}:$  is involved in cycloaddition reaction of  $\text{X}_2\text{C}=\text{Sn}:$  and the symmetric  $\pi$ -bonded compounds. The 5p unoccupied orbital of tin in  $\text{H}_2\text{C}=\text{Sn}:$  sidewise overlaps with bonding  $\pi$ -orbital of ethylene resulting in the formation of an intermediate. The instability of the intermediate makes it isomerise to a four-membered ring stannylene. As the 5p unoccupied orbital of the Sn atom in the four-membered ring stannylene and the  $\pi$ -orbital of symmetric  $\pi$ -bonded compounds forms a  $\pi \rightarrow p$  donor-acceptor bond, the four-membered ring stannylene further combines with symmetric  $\pi$ -bonded compounds to form another intermediate, and this intermediate further isomerises to a spiro-Sn-heterocyclic ring compound. Sn in the spiro-Sn-heterocyclic ring compound is combined with adjacent  $\text{sp}^3$  hybridized atoms.

## ИЗВОД

*Ab initio* ПРОУЧАВАЊЕ МЕХАНИЗМА НАСТАЈАЊА СПИРО-Sn-ХЕТЕРОЦИКЛИЧНИХ ЈЕДИЊЕЊА ЦИКЛОАДИЦИОНОМ РЕАКЦИЈОМ  $\text{H}_2\text{C}=\text{Sn}:$  И ЕТИЛЕНА

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$\text{X}_2\text{C}=\text{Sn}:$  (X = H, Me, F, Cl, Br, Ph, Ar...) су нове хемијске врсте. Циклоадиционе реакције врста  $\text{X}_2\text{C}=\text{Sn}:$  су ново поље у хемији станилена. Механизам циклоадиционе реакције синглетног  $\text{H}_2\text{C}=\text{Sn}:$  са етиленом је у овом чланку по први пут проучаван коришћењем MP2/GENECP (C, H са 6-311++G\*\*; Sn са LanL2dz) метода. Из профила потенцијалне енергије може се предсказати да реакција има један доминантан реакциони пут. Представљено је реакционо правило да се 5p незаузета орбитала калаја у  $\text{H}_2\text{C}=\text{Sn}:$  бочно преклапа са везивном  $\pi$ -орбиталом етилена формирајући одговарајући интермедијер. Нестабилност интермедијера чини да се он изомеризује у четворочлани прстен станилена. Пошто 5p незаузета орбитала Sn атома у четворочланом прстену станилена и  $\pi$ -орбитала етилена формирају  $\pi \rightarrow p$  донорско-акцепторску везу, четворочлани прстен станилена се даље комбинује са етиленом дајући нови интермедијер, а тај се даље изомеризује у СПИРО-Sn-хетероциклично једињење. Sn у СПИРО-Sn-хетеро-



цикличном једињењу се комбинује са суседним  $sp^3$  хибридованим атомима. Резултат ове студије открива механизам циклоадиционе реакције  $X_2C=Sn$ : са симетричним  $\pi$  везивним једињењима.

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