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Theoretical study of the formation of a spiro-Sn-heterocyclic compound by cycloaddition reaction of $Me_2C{=}Sn$: and ethene

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Abstract: $X_2C{=}Sn$: compounds (X=H, Me, F, Cl, Br, Ph, Ar) are new species. The cycloaddition reactions of $X_2C{=}Sn$: are also a new study field of unsaturated stannylene chemistry. The mechanism of cycloaddition reaction between singlet $Me_2C{=}Sn$: and ethene was investigated for the first time using the MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) method. From the potential energy profile, it was predicted that the reaction has one dominant channel in which the 5p unoccupied orbital of Sn: in $Me_2C{=}Sn$: and the π orbital of ethene form a $\pi \rightarrow p$ donor-acceptor bond in an intermediate product. Instability of the intermediate product results in its isomerization to a four-membered ring of stannylene. The four-membered stannylene further combines with ethene to form another intermediate product that further isomerizes to a spiro-Sn-heterocyclic ring compound.

Keywords: four-membered stannylene; $Me_2C{=}Sn$:; potential energy profile; spiro-Sn-heterocyclic compound.

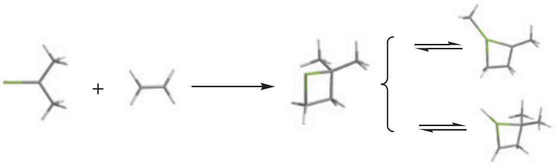
Introduction

In 1997, Clouthier and co-workers [1] analyzed for the first time unsaturated germylidene ($H_2C{=}Ge$:) derivatives. Subsequently, *ab initio* calculations predicted the molecular structure [2, 3], electronic spectrum [2], oscillatory fluorescence decay [2], the ground state structure [3] and stimulated emission pumping (SEP) spectra [4] of the first excited singlet state of germylidene or derivatives. Stogner and Grev have published many papers about *ab initio* calculations [5] on both germylidene and the trans-bent germyne HC≡GeH isomer. We have also been involved in this subject [6–9]. As the studies progressed, research on the analogous species $X_2C{=}Sn$: (X=H, Me, F, Cl, Br, Ph, Ar) has emerged. The stannylene $X_2C{=}Sn$: is a new chemical species [10]. In this report, we have explored theoretically the cycloaddition reactions of $X_2C{=}Sn$: with ethene.

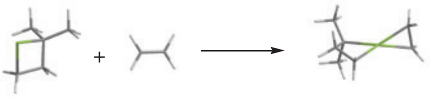
Results and discussion

We used the method of second-order perturbation theory (MP2) and Gaussian 09 package to optimize the structure of $Me_2C{=}Sn$:, and the parameters of cycloaddition reaction with ethene including the transition states and the intermediate products at the MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) [11] theory level. In order to further confirm the correctness of the relevant species, a vibration analysis was included. Finally, the intrinsic reaction coordinate (IRC) [12, 13] was also calculated for all transition states to determine the reaction pathways.

The energies of the singlet and triplet states of $Me_2C{=}Sn$: (R1) calculated by the MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) method are –120.81220 and –120.77967 a.u, respectively. Accordingly, the ground state of $Me_2C{=}Sn$: is a singlet state. Its cycloaddition reaction with ethene (R2) may have two possible outcomes. The geometrical parameters of the intermediate products INT1 and INT2, transition states TS1, TS1.1, TS1.2 and TS2 and products P1, P1.1, P1.2 and P2 which appear in the schematic reactions are given in Figure 1, the energies are listed in Table 1 and the entropy,



(1)



(2)

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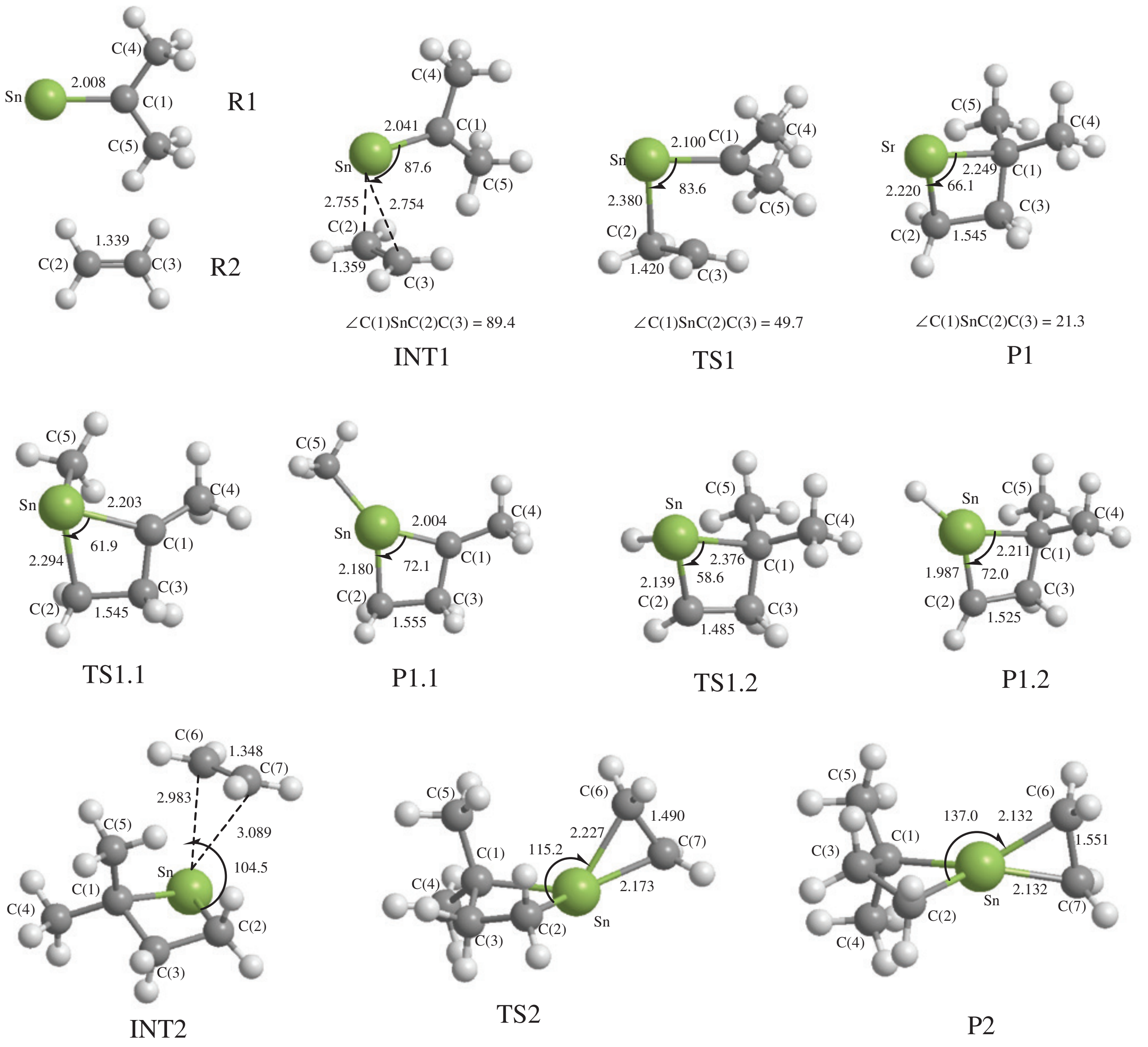

Figure 1 Optimized MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) geometrical parameters and the atomic numbering for the species in cycloaddition reaction between $Me_2C=Sn$: and ethene. Bond lengths are in (Å) and angles in (°).

enthalpy and Gibbs free energy are listed in Table 2. The potential energy profile of the reactions is shown in Figure 2.

The unique imaginary frequencies of the transition states TS1, TS1.1, TS1.2 and TS2 by vibrational analysis are 214.5*i*, 169.1*i*, 828.4*i* and 102.1*i*, respectively. Therefore, these transition states can be affirmed as the real ones. IRC (with the step size of 0.1 $amu^{-1/2}$ bohr) analysis confirms that TS1 connects INT1 and P1, TS1.1 connects P1 and P1.1, TS1.2 connects P1 and P1.2 and TS2 connects INT2 and P2. According to Figure 2, the reaction (1) consists of four steps: in the first step, the two reactants R1 and R2 form an intermediate product INT1. According to Figure 2 and Table 2, the reaction is a barrier-free exothermic process; the 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 −44.1 and −37.3 kJ/mol, and the molar Gibbs free energy of reaction ($\Delta_r G_m$) is −7.5 kJ/mol. In the second step, the intermediate product INT1 undergoes isomerization to a four-membered ring of stannylene P1 via a transition state TS1 with an energy barrier of 37.4 kJ/mol. According to Figure 2 and Table 2, the reaction is exothermic, and the $\Delta_r U_m$ and $\Delta_r H_m$ values at normal temperature and pressure are 124.1 and 120.6 kJ/mol, and the $\Delta_r G_m$ value is −110.6 kJ/mol. In the third and fourth steps, the product P1 undergoes Me-transfer and H-transfer via transition

Table 1 The electronic structure energy (E_{ese}, a.u.) and relative energies (E_R, kJ/mol) for the species from MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) method at 298 K and 101 325 Pa.

Reaction	Species	MP2/GENECP	
		E_{ese}	E_R
[a]Reaction (1)	R1 + R2	−199.15872	0.0
	INT1	−199.17551	−44.1
	TS1 (INT1-P1)	−199.16128	−6.7
	P1	−199.22277	−168.2
	TS1.1 (P1-P1.1)	−199.13260	68.6
	P1.1	−199.16449	−15.1
	TS1.2 (P1-P1.2)	−199.11668	110.4
	P1.2	−199.15446	11.2
[b]Reaction (2)	P1 + R2	−277.56930	0.0
	INT2	−277.58145	−31.9
	TS2 (INT2-P2)	−277.56187	19.5
	P2	−277.56594	8.8

[a]$E_R = E_{ese} — E_{ese}$, (R1 + R2), [b]$E_R = E_{ese} — E_{ese}$(P1 + R2).

states TS1.1 and TS1.2 with energy barriers of 236.8 and 278.6 kJ/mol, respectively. The products of Me-transfer and H-transfer are P1.1 and P1.2. According to Figure 2 and Table 2, both reactions are endothermic, and the $\Delta_r U_m$ and $\Delta_r H_m$ values at normal temperature and pressure are 153.1, 179.4 and 147.1, 166.5 kJ/mol, respectively. The $\Delta_r G_m$ values are 138.9 and 165.1 kJ/mol, respectively. Accordingly, the transitions P1→P1.1 and P1→P1.2 are thermodynamically prohibited at normal temperature and pressure, and the product of reaction (1) will be P1.

In reaction (2), the four-membered ring stannylene P1 undergoes a further reaction with ethene R2 to form a spiro-Sn-heterocyclic compound P2. According to Figure 2, in the reaction (2), the product P1 formed in reaction (1) undergoes a subsequent reaction with ethene R2 to form an intermediate INT2. According to Figure 2 and Table 2, the reaction is a barrier-free exothermic process with the $\Delta_r U_m$ and $\Delta_r H_m$ values at normal temperature and pressure of 31.9 and 24.8 kJ/mol, and the $\Delta_r G_m$ value is −14.6 kJ/mol. Then, the intermediate INT2 undergoes isomerization to a spiro-Sn-heterocyclic compound P2 via a transition state TS2 with an energy barrier of 51.4 kJ/mol. According to Figure 2 and Table 2, this reaction is an endothermic process with the $\Delta_r U_m$ and $\Delta_r H_m$ values at normal temperature and pressure of 40.7 and 39.9 kJ/mol, and the $\Delta_r G_m$ value is 63.8 kJ/mol. According to Figure 2, reaction (2) and the transformations P1→P1.1 and P1→P1.2 in reaction (1) are competitive processes. As the transitions P1→P1.1 and P1→P1.2 are thermodynamically forbidden, reaction (2) is the dominant reaction pathway. Considering that the $\Delta_r G_m$ value of INT2→P2 is 63.8 kJ/mol and the $\Delta_r G_m$ value of P1 + R2→P2 is 49.2 kJ/mol, the transition P1 + R2→INT2→P2 is a continuous reaction. Analysis of the following thermodynamic function shows that if the reaction is carried out under liquid phase conditions,

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

$\Delta V \approx -1$ and $P_2 \approx \Delta G(P_1) + P_1 = 165\ 125$ Pa. Accordingly, at the temperature of 298 K in liquid phase, for the reaction P1 + R2→P2, the pressure of the reaction system must be greater than 165 125 Pa (1.6 atm).

According to all analyses, reaction (2) should be the dominant pathway of the cycloaddition between singlet Me_2C=Sn: and ethene. It can be formulated as follows:

Table 2 Entropy (S, a.u.), enthalpy (*H*, a.u.) and Gibbs free energy (G, a.u.) for the species from MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) methods at 298 K and 101 325 Pa.

Reaction	Species	*H*, a.u.	*S*, a.u.	*G*, a.u.
Reaction (1)	R1 + R2	−199.01703	2.09768×10^{-4}	−199.07675
	INT1	−199.03122	1.52654×10^{-4}	−199.07959
	TS1 (INT1-P1)	−199.01826	1.38714×10^{-4}	−199.05964
	P1	−199.07715	1.39870×10^{-4}	−199.11887
	TS1.1 (P1-P1.1)	−198.99180	1.42594×10^{-4}	−199.03433
	P1.1	−199.02112	1.50390×10^{-4}	−199.06597
	TS1.2 (P1-P1.2)	−198.97773	1.39018×10^{-4}	−199.01920
	P1.2	−199.01375	1.41544×10^{-4}	−199.05597
Reaction (2)	P1 + R2	−277.36883	2.23496×10^{-4}	−277.42993
	INT2	−277.37829	1.73142×10^{-4}	−277.43549
	TS2 (INT2-P2)	−277.36003	1.54895×10^{-4}	−277.40622
	P2	−277.36310	1.61220×10^{-4}	−277.41119

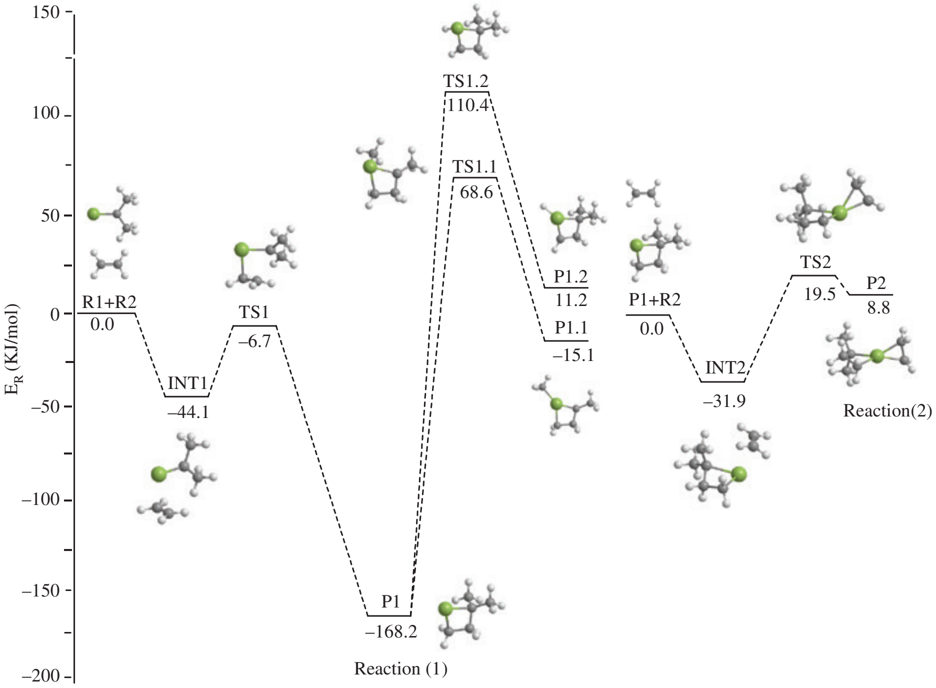

Figure 2 The potential energy surface for the cycloaddition reaction between Me_2C=Sn: and ethene with MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz).

$$R1+R2 \longrightarrow INT1 \xrightarrow{TS1} P1 \xrightarrow{+R2} INT2 \xrightarrow{TS2} P2$$

The frontier molecular orbitals of R1, R2 and P1 are shown in Figure 3. As can be seen, the mechanism of the transformation can be explained by analysis of the frontier molecular orbital diagrams (Figures 4 and 5). Briefly (Figures 1 and 4), when Me_2C=Sn: (R1) initially interacts with ethene (R2), the 5p unoccupied orbital of the Sn atom in Me_2C=Sn: (R1) undergoes insertion of the π orbital of ethene to form a $\pi \rightarrow p$ donor-acceptor bond, leading to the formation of the intermediate product INT1. As the reaction progresses, INT1 isomerizes to a four-membered stannylene P1 via the transition state TS1. Because P1 is still an active molecule, it may further react with ethene to form a spiro-Sn-heterocyclic compound P2 through the intermediary of INT2 and TS2. The mechanism of this reaction can be explained by analysis of Figures 1 and 5. Before the transition state TS2, the covalent bonds are formed between Sn and C(6), and Sn and C(7). After the transition state TS2, the Sn atom hybridization changes to a *sp*3 hybrid orbital. Overall, the intermediate product INT2 undergoes isomerization to a spiro-Sn-heterocyclic compound P2 via the transition state TS2.

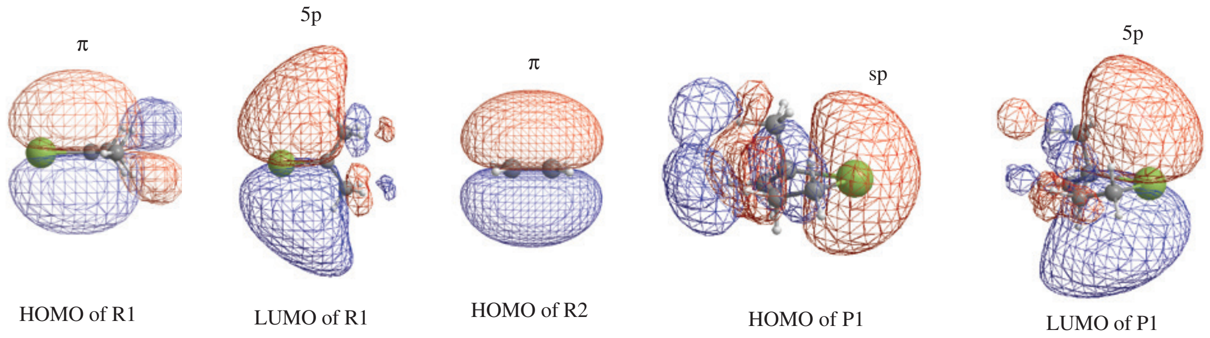

Figure 3 The frontier molecular orbitals of R1, R2 and P1.

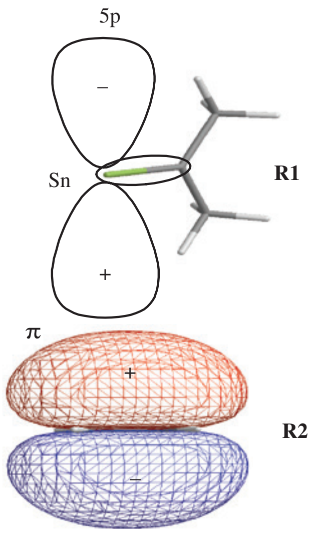

Figure 4 A schematic interaction diagram for the frontier orbitals of Me_2C=Sn: (R1) and C_2H_4 (R2).

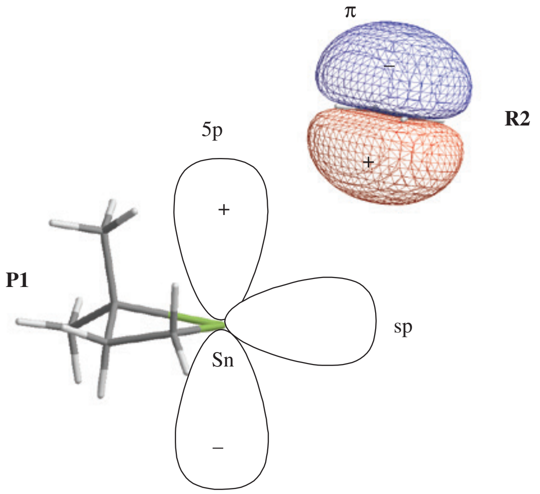

Figure 5 A schematic diagram for the frontier orbitals of P1 and C_2H_4 (R2).

Conclusion

On the basis of the potential energy profile, the cycloaddition reaction between singlet species Me_2C=Sn: and ethene obtained with the MP2/GENECP (C, H in 6-311++G**; Sn in LanL2dz) method was predicted. This reaction has one dominant channel that consists of four steps: (1) the two reactants first form an intermediate INT1 through a barrier-free exothermic reaction of 44.1 kJ/mol; (2) the intermediate INT1 isomerizes to a four-membered stannylene P1 via the transition state TS1 with an energy barrier of 37.4 kJ/mol; (3) the four-membered stannylene P1 further reacts with ethene R2 to form another intermediate product INT2 through a barrier-free exothermic reaction of 31.9 kJ/mol; and (4) the intermediate product INT2 undergoes isomerization to a spiro-Sn-heterocyclic compound P2 via the transition state TS2 with an energy barrier of 51.4 kJ/mol. At the temperature of 298 K in liquid phase, the pressure of the reaction system needs to be greater than 165 125 Pa (1.6 atm).

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