A Computational Study of the Mechanism for the Transmetalation of 2-Trimethylstannylbuta-1,3-diene with SnCl$_4$

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Electronic structure calculations were performed at the B3LYP/6-31G** level to identify the stationary structures on the potential energy surfaces for the transmetalation of 2-trimethyl-stannylbuta-1,3-diene with SnCl$_4$. The reaction pathways were characterized by locating the transition states on the intrinsic reaction coordinate. The calculations showed that the reaction between the reactant and SnCl$_4$, which generates 1-trichlorostannylbuta-2,3-diene via transmetalation, has a low energy barrier of 78.1 kJ·mol^{-1}. The following isomerization process is the rate-controlling step. It turned out that the isomerization process from 1-trichlorostannylbuta-2,3-diene to 2-trichloro-stannylbuta-1,3-diene via transmetalation with SnCl$_4$ is more energetically favorable than other possible isomerization processes.

Introduction

Allylic tin is a very important type of reagent in organic synthesis.[1] Such reagents have been extensively studied because of their unique reactivity, ease of preparation, and synthetically useful products. They are powerful for the stereocontrolled construction of organic molecules because the reactions of the allylic tin reagents usually proceed with high regio- and stereoselectivity.[1,2]

The Lewis acid-promoted addition reaction of allylic tin reagents is a popular C—C bond formation method because of its high reactivity and selectivity.[2] On one hand, the Lewis acids can coordinate the electrophiles and enhance their electrophilicity.[3,4] On the other hand, the Lewis acids can react with the allylic tin reagent via transmetalation to generate a more reactive allylic metal reagent.[5,6] If the transmetalation is involved, the product may consist of a mixture of regioisomers due to allylic rearrangement of the allylmetal halide intermediate. Scheme 1 is an example.

Reports about the transmetalation reaction between allylic tins and Lewis acids were published in 1984 on the reaction of crotylin and SnCl$_4$ and TiCl$_4$[7,8] and in 1986 on the reaction of pentadienyltin and SnCl$_4$.[9] Since then,

SCHEME 1
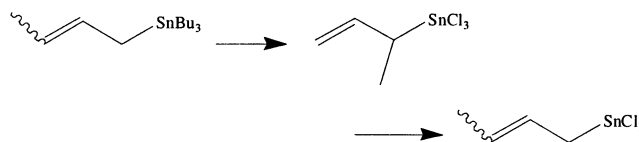
several applications have been applied to the transmetalation of allylic tins with Lewis acids.[10–16] Transmetalation of SnCl$_4$ has also been characterized with NMR spectroscopy.[6,17,18] Recently the reaction of buta-1,3-dienylation with aldehydes via transmetalation of 2-tributyl-stannylbuta-1,3-diene with SnCl$_4$ was reported.[19] Its high regioselectivity presents an interesting and challenging topic for theoretical study.

Compared with the widely experimental studies, the calculations on the transmetalation with the Lewis acid are currently very limited.[20,21] The structural information obtained by theoretical methods based on quantum mechanical calculations of possible intermediates and

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SCHEME 2
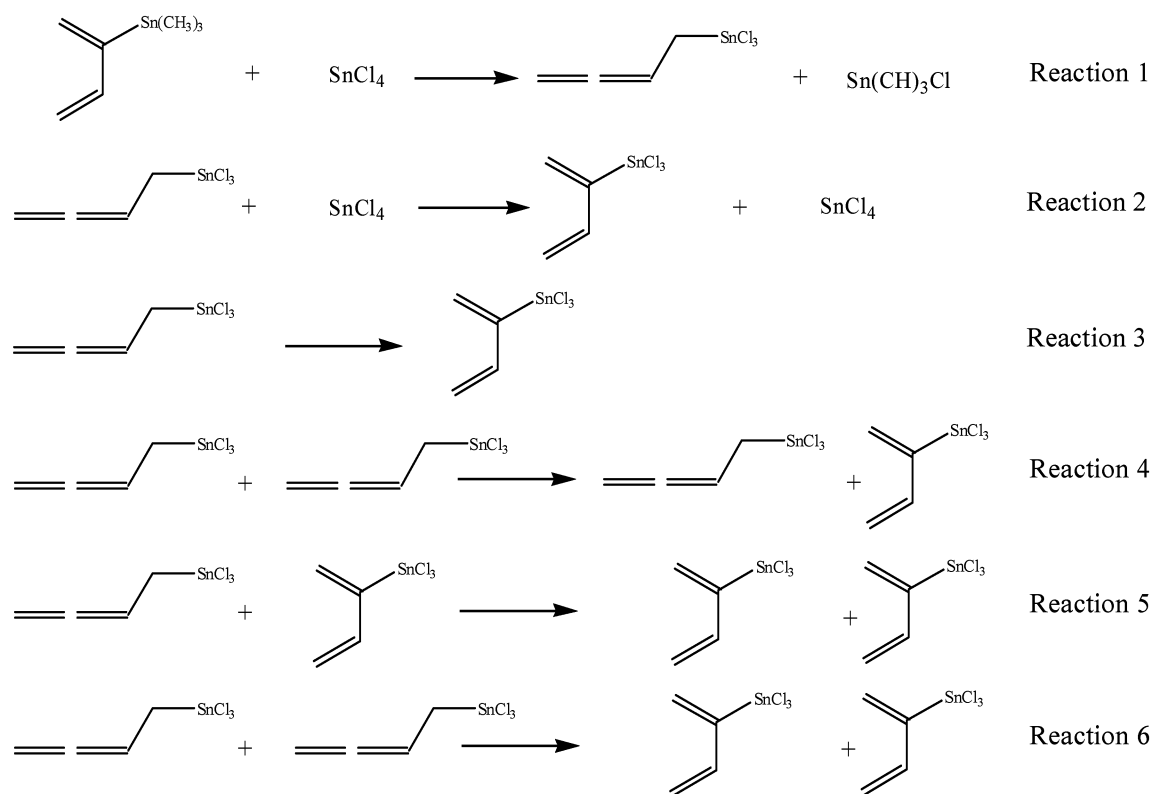
transition structures provides useful assistance for the study of organic reaction mechanisms.[22−24] In this paper, we present density functional calculations on the transmetalation of 2-trimethylstannylbuta-1,3-diene with SnCl$_4$. Although butyl is the most common substituent at tin of allylic tin reagents, we chose 2-trimethylstannylbuta-1,3-diene instead of 2-tributylstannylbuta-1,3-diene because of its small size and homologous properties. The possible reactions for the transmetalation of 2-trimethylstannylbuta-1,3-diene with SnCl$_4$ are given in Scheme 2. In the first reaction, the reactant (2-trimethylstannylbuta-1,3- diene) reacts with SnCl$_4$ to generate the initial product (1-trichlorostannylbuta-2,3-diene). The five reactions followed are the isomerization processes from the initial product to the final product (2-trichlorostannylbuta-1,3-diene). Among these five reactions, reaction 2 is the SnCl$_4$-mediated isomerizatiion. The trichlorotin isomerizes itself in reaction 3. The two initially formed molecules exchange the trichlorotin group in reactions 4 and 6. One initially formed molecule and one finally formed molecule exchange the trichlorotin group in reaction 5. The purpose of this study is to obtain a better understanding of the mechanism of the transmetalation, particularly of the locations and characteristics of all the stationary points involved in the reactions.

Computational Methods

Calculations were carried out with the Gaussian 98 suite of programs.[25] All structures of reactants, transition states, intermediates, and products were fully optimized with the

B3LYP[26] hybrid density functional method and the 6-31G** basis set for all atoms except for Sn for which the CEP-121G[27] basis set was used. The stationary points were identified by frequency calculations to verify that minima and transition structures have zero and one imaginary frequencies, respectively. Zero-point energy corrections (unscaled) were also evaluated from the frequency calculations. Standard Mulliken population analysis[28] was used to analyze electron density. The intrinsic reaction coordinate (IRC[29]) calculations were employed to check the energy profiles connecting each transition structure to the two associated minima of the proposed mechanism.

Results and Discussions

Total energies (including zero-point correction), relative energies, and Gibbs free energies for the stationary points corresponding to reactions 1−6 are listed in Table 1.

Reaction 1. The optimized geometries of the stationary points for reaction 1 are presented in Figure 1. Our calculations showed that this reaction proceeds via three steps.

In Step 1, the SnCl$_4$ molecule moves toward 2-trimethylstannylbuta-1,3-diene (RE1) to form the molecular complex IN1a, which is 2.7 kJ·mol^{-1} more stable than the reactants. In the complex, atom Sn5 is 4.168 Å away

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TABLE 1. Total Energies (include zero-point correction), Relative Energies, and Gibbs Free Energies for the Stationary Points Corresponding to Reactions 1–6

	E (hartree)	ΔE (kJ·mol^{-1})	G (hartree)	ΔG (kJ·mol^{-1})
reaction 1				
SnCl$_4$	−1844.31993		−1844.35327	
RE1	−278.36489		−278.40705	
SnCl$_4$ + RE1	−2122.68482	0.0	−2122.76032	0.0
IN1a	−2122.68586	−2.7	−2122.74897	29.8
TS1	−2122.65610	75.4	−2122.71163	127.8
IN1b	−2122.71125	−69.4	−2122.77510	−38.8
PR1a	−1539.41035		−1539.45253	
PR1b	−583.29524		−583.33215	
PR1a + PR1b	−2122.70559	−54.5	−2122.78468	−64.0
reaction 2				
PR1a + SnCl$_4$	−3383.73028	0.00	−3383.80580	0.0
IN2a	−3383.73139	−2.9	−3383.79819	20.0
TS2	−3383.69019	105.3	−3383.74490	159.9
IN2b	−3383.74080	−27.6	−3383.80501	2.1
PR2	−1539.41966		−1539.46067	
PR2 + SnCl$_4$	−3383.73958	−24.4	−3383.81394	−21.4
reaction 3				
PR1a	−1539.41035	0.0	−1539.45253	0.0
TS3	−1539.34232	178.6	−1539.38200	185.2
PR2	−1539.41966	−24.4	−1539.46067	−21.4
reaction 4				
PR1a + PR1a	−3078.82070	0.0	−3078.90506	0.0
IN4a	−3078.82399	−8.6	−3078.89331	30.8
TS4	−3078.72287	256.9	−3078.78337	319.5
IN4b	−3078.83379	−34.4	−3078.90176	8.7
PR1a + PR2	−3078.83001	−24.4	−3078.91320	−21.4
reaction 5				
PR1a + PR2	−3078.83001	0.0	−3078.91320	0.0
IN5a	−3078.83398	−10.4	−3078.90233	28.5
TS5	−3078.75264	203.1	−3078.80959	272.0
IN5b	−3078.84281	−33.6	−3078.91071	6.5
PR2 + PR2	−3078.83932	−24.4	−3078.92134	−21.4
reaction 6				
PR1a + PR1a	−3078.82070	0.0	−3078.90506	0.0
IN6a	−3078.82073	−0.1	−3078.89065	37.8
TS6	−3078.74911	188.0	−3078.80713	257.1
IN6b	−3078.83944	−49.2	−3078.90995	−12.8
PR2 + PR2	−3078.83932	−48.9	−3078.92134	−42.7

from atom C4 and atom Cl10 is 5.370 Å away from atom Sn9.

In Step 2, the reaction progresses to form the six-member cyclic chairlike transition state TS1, with a energy barrier height of 78.1 kJ·mol^{-1}. One can see from the analysis of the geometry of TS1 that the transition state is dominated by an asynchronous bond formation. The length of the C4−Sn5 bond at TS1 is 2.243 Å, while the distance between atoms Sn9 and Cl10 is 3.056 Å, indicating that these atoms are not bonded. When complex IN1a becomes the TS1, the Sn9−C2 distance changes from 2.166 Å to 2.520 Å. While the hybridization of C2 is changed from sp^2 to sp, breaking the C2−Sn9 bond, the hybridization of C4 is changed from sp^2 to sp^3, forming the C4−Sn5 bond. Atoms C1 and C3 retain their sp^2 hybridization, consistent with the diene double bond structure.

The value of the imaginary frequency associated with TS1 is calculated to be 129.9i cm^{-1}. Analysis of the atomic motion along this vibrational frequency indicates that this transition state is mainly associated with the motion of the Sn9 and C2 atoms. Moreover, analysis of the

Hessian matrix corresponding to TS1 showed that the transition vector[30] is mainly associated with the Sn9−C2 bond length (the eigenvector is 0.568).

In Step 3, atom Cl10 moves toward atom Sn9 and away from Sn5, and atom Sn9 moves away from C2, forming the intermediate IN1b. The length of Sn9−Cl10 is found to be 2.425 Å. The angle of C1−C2−C3 is 179.6°, indicating that the three atoms are nearly linear. The intermediate IN1b can then be considered as the molecular complex of 1-trichlorostannylbuta-2,3-diene (PR1a) and Sn(CH$_3$)$_3$Cl (PR1b), which lies 69.4 kJ·mol^{-1} below the reactants. The energy of the products is 14.9 kJ·mol^{-1} above that of IN1b, and 54.5 kJ·mol^{-1} below that of the reactants.

Reaction 2. Figure 2 displays the geometry structures of the stationary points for reaction 2. Our studies showed that the two fragments PR1a and SnCl$_4$ move close to form IN2a, with an energy release of 2.9 kJ·mol^{-1}. Atom Sn9 is 4.555 Å away from atom C2 in this complex. While atom Sn5 moves away from C4, and atom Cl12 moves toward atom Sn5, atom Sn9 moves toward atom C2 to form the six-member cyclic chairlike transition state TS2. The energy barrier is 108.2 kJ·mol^{-1}. In the following step, atom Cl12 moves toward Sn5 and away from Sn9, and Sn5 moves away from C4, to form the intermediate IN2b. The hybridization of atom C2 is changed from sp to sp^2, forming the C2−Sn9 bond, while the hybridization of atom C4 is changed from sp^3 to sp^2, breaking the C4−Sn5 bond. While the Sn5−Cl12 length of 2.333 Å presents a well-formed Sn−Cl bond, the Sn9−Cl12 distance of 4.427 Å indicates that the bond is broken. These analyses indicated that IN2b is actually the molecular complex of 2-trichlorostannylbuta-1,3-diene (PR2) and SnCl4, which lies below the reactants with an energy difference of 27.6 kJ·mol^{-1}.

The value of the imaginary frequency associated with TS2 is found to be 122.1i cm^{-1}. Analysis of the atomic motion along this vibrational frequency indicates that this transition state is mainly associated with the Sn5−Cl12 bond formation.

Reaction 3. Figure 3 displays the geometry structures of the stationary points for reaction 3. This reaction is actually the isomerization of 1-trichlorostannylbuta-2,3-diene to 2-trichlorostannylbuta-1,3-diene. Just like the case of reaction 2, the arrangement of the stannic atoms around atoms C2 and C4 indicates that the hybridization of atom C2 is changed from sp to sp^2 along with the formation of the C2−Sn5 bond, while the hybridization of atom C4 is changed from sp^3 to sp^2 along with the C4−Sn5 bond breaking. The barrier height is found to be 178.6 kJ·mol^{-1}. The value of the imaginary frequency associated with TS3 is found to be 530.9i cm^{-1}. This transition state is dominated by the formation of the Sn5−C2 bond.

Reaction 4. Figure 4 displays the geometry structures of the stationary points for reaction 4. First, two PR1a molecules move close to form IN4a with an energy release of 8.6 kJ·mol^{-1}. Atom Sn9 is 4.437 Å away from atom C2. Then atom Sn5 moves away from C4, and atom C13 moves toward atom Sn5. Atom Sn9 moves toward atom C2 to form a six-member cyclic chairlike transition state TS4 with an energy barrier of 265.5 kJ·mol^{-1}. In the

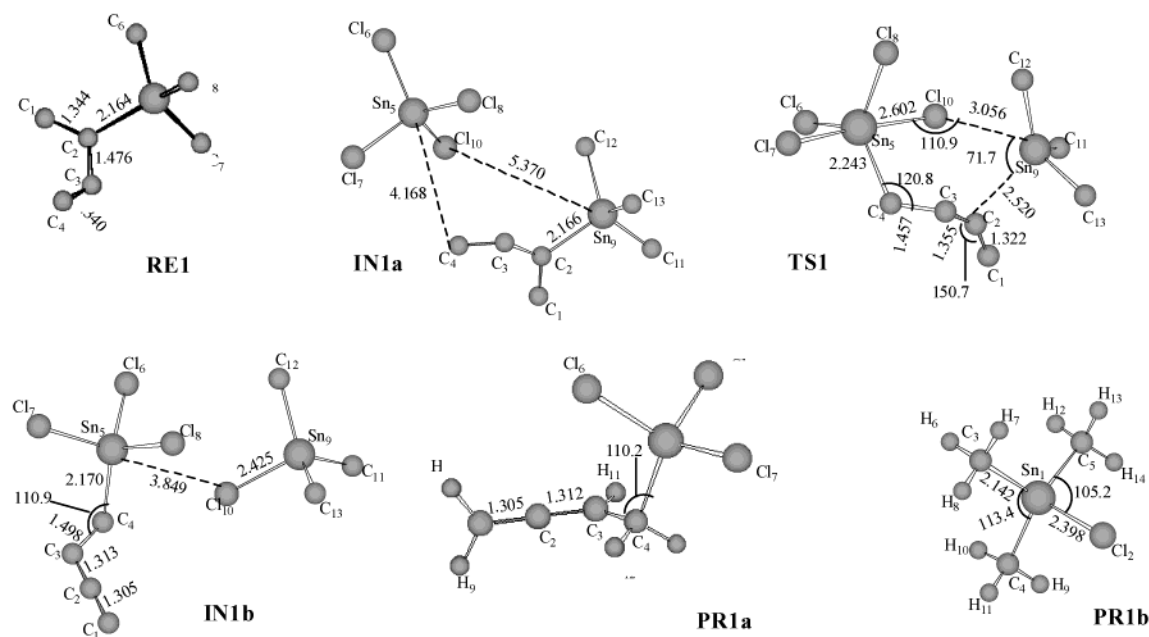(30) McIver, J. W. *Acc. Chem. Res.* **1974**, *7*, 72.

FIGURE 1. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 1. All distances are in Å, and all angles are in deg. Hydrogen atoms have been removed for clarity except PR1a and PR1b.
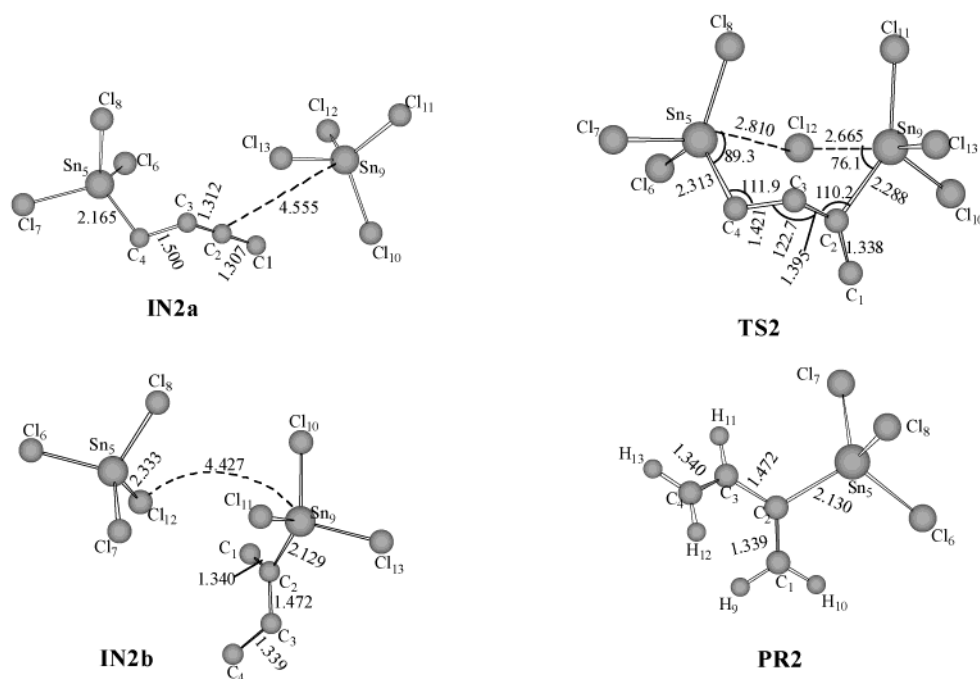

FIGURE 2. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 2. All distances are in Å, and all angles are in deg. Hydrogen atoms have been removed for clarity except PR2.

following step, atom C13 moves toward Sn5 and away from Sn9, and Sn5 moves away from C4 to reach an intermediate IN4b. The hybridization of atom C2 is changed from sp to sp^2, while the hybridization of atom C4 is changed from sp^3 to sp^2. Sn5 and C13 form a bond with a bond length of 2.167 Å. The Sn9−C13 distance is 5.529 Å, indicating this bond is broken. So IN4b is actually the molecular complex of 2-trichlorostannylbuta-1,3-diene (PR2) and 1-trichlorostannylbuta-2,3-diene (PR1a). The value of the imaginary frequency associated with TS4 is found to be 291.5i cm^{-1}. This transition state is mainly associated with the Sn9−C2 bond formation.

Reaction 5. Figure 5 displays the geometry structures of the stationary points for reaction 5. Our studies showed that the two molecules PR1a and PR2 move close to form IN5a, which is 10.4 kJ·mol^{-1} more stable than the reactants. In this complex, the length of Sn9−C2 is 5.796 Å, and the length of Sn5−C14 is 5.565 Å. Similar to reaction 4, the six atoms (Sn5, C4, C14, Sn9, C2, C3) move to form the six-member cyclic chairlike transition
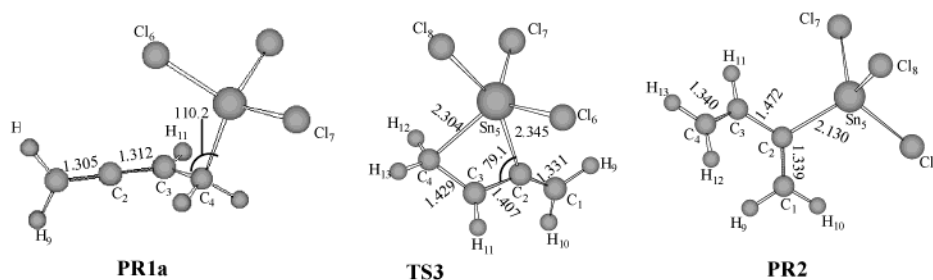
FIGURE 3. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 3. All distances are in Å, and all angles are in deg.
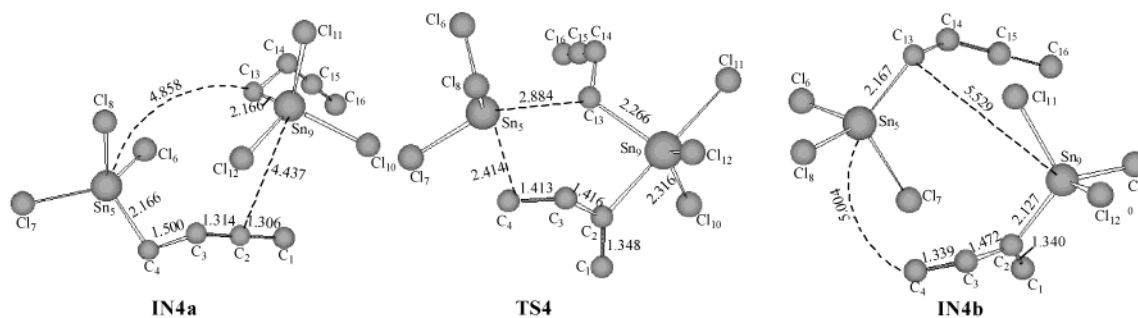

FIGURE 4. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 4. All distances are in Å, and all angles are in deg. Hydrogen atoms have been removed for clarity.
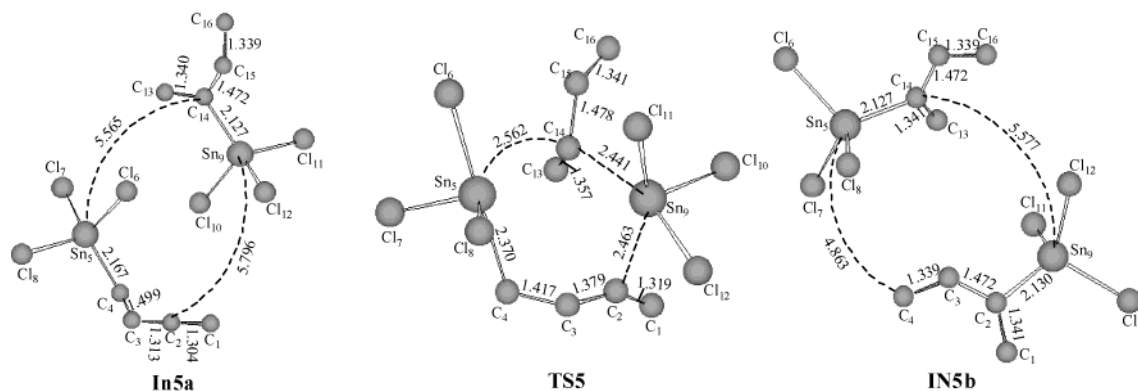

FIGURE 5. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 5. All distances are in Å, and all angles are in deg. Hydrogen atoms have been removed for clarity.

state TS5 with the energy barrier of 213.5 kJ·mol^{-1} above the IN5a. The atom C14 moves toward Sn5 and away from Sn9, and Sn5 moves away from C4 to form an intermediate IN5b. The hybridization of atom C2 is changed from sp to sp^2 along with the formation of the C2–Sn9 bond, while the hybridization of atom C4 is changed from sp^3 to sp^2 along with the breaking of the C4–Sn5 bond. The length of Sn5–C14 is 2.127 Å, and the Sn9–C14 distance is 5.577 Å. The analysis showed that the IN5b is actually the molecular complex of two 2-trichlorostannylbuta-1,3-diene (PR2) molecules. The value of the imaginary frequency associated with TS4 is found to be 243.7i cm^{-1}. Analysis of the atomic motion along this vibrational frequency indicated that this transition state is mainly associated with the Sn9–C2 bond formation.

Reaction 6. Figure 6 displays the geometry structures of the stationary points for reaction 6. At first, IN6a is formed by the two PR1a molecules with an energy release

of 0.1 kJ·mol^{-1}. Atom Sn5 moves away from C4, and atom C15 moves toward atom Sn5, meanwhile, and atom Sn9 moves toward atom C2 to form the eight-member cyclic transition state TS6 with a energy barrier height 188.1 kJ·mol^{-1} above that of the IN6a. In the following step, atom C15 moves toward Sn5 and away from Sn9, and Sn5 moves away from C4 to form a stable intermediate IN6b. The hybridization of atom C2 is changed from sp to sp^2 along with the formation of the C2–Sn9 bond, as is atom C15 along with the formation of the Sn5–C15 bond. The hybridization of atom C4 is changed from sp^3 to sp^2 along with the breaking of the C4–Sn5 bond, as is atom C13 along with the breaking of the Sn9–C13 bond. The length of the formed bond Sn5–C15 is found to be 2.132 Å, and the Sn9–C10 distance is 4.531 Å. So IN6b is the molecular complex of two 2-trichlorostannylbuta-1,3-diene (PR2) molecules. The value of the imaginary frequency associated with TS6 is found to be 429.0i cm^{-1}.
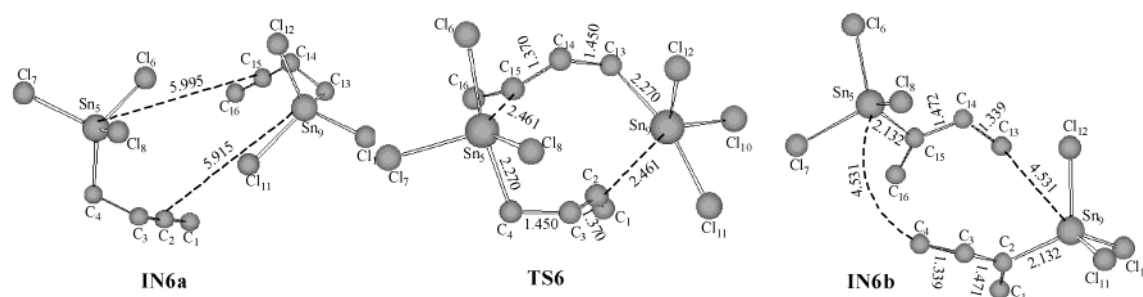
FIGURE 6. Optimized geometries (B3LYP/6-31G**) of the stationary points along reaction 6. All distances are in Å, and all angles are in deg. Hydrogen atoms have been removed for clarity.

This transition state is dominated by the Sn9−C2 and Sn2−C15 bond formation.

Discussion

Our calculations predicted that each of the six reactions has only one transition state and the transmetalation proceeds via the migration of the diene double bond. Analysis of the geometries of the transition states corresponding to these reactions indicated that the reactions take place along with the concerted reaction processes. The transition states for these reactions belong to the early-type of transition state, which can be seen from the relatively small geometric differences between the molecular complex (IN1a−IN6a) and the transition state (TS1−TS6). Since these reactions are exothermic reactions, this early TS is consistent with Hammond's suggestion.[31]

Although the concerted reaction processes are involved in the reactions, they have different energy barrier heights. The barrier height of reaction 1 was found to be the lowest among the six reactions. Since the effect of the chloro groups around the tin atom is pronounced, the electron-withdrawing effect of the halogens leads to an electron-deficient tin atom. The same effect of the $SnCl_3$ moiety decreases the electron density of the diene moieties of 1-trichlorostannylbuta-2,3-diene and 2-trichlorostannylbuta-1,3-diene. The other five reactions between the tin atom of $SnCl_4$ and the carbon atom of the diene moiety are thus less active than reaction 1 and are rate-controlling steps. However, the calculated results are obtained in a vacuum. The experimental reactions are generally carried out in a solvent. The polarity of the solvent may affect the energy barrier of the TS1 significantly. Further calculations on the reaction in the solvent are highly desirable.

It is clear that reactions 2, 3, 4, 5, and 6 are the isomerization of 1-trichlorostannylbuta-2,3-diene. The tin atom migrates from C_4 to C_2. Comparison with 1-trichlorostannylbuta-2,3-diene indicated that 2-trichlorostannylbuta-1,3-diene has a conjugated geometry and better p-orbital overlap. Therefore, the later is more stable (the total electronic energy is 24.4 kJ·mol^{-1} lower). The largest difference between reaction 2 and the other four reactions is whether $SnCl_4$ is involved in the reaction. When $SnCl_4$ is involved in reaction 2, the barrier height, 108.2 kJ·mol^{-1}, is the lowest. Since $SnCl_4$ is not only a reactant but also a product for reaction 2, it

actually acted as the catalyst for the transmetalation process. When $SnCl_4$ is not involved, the barrier is relatively high, such as 178.6 kJ·mol^{-1} for reaction 3 and 188.1 kJ·mol^{-1} for reaction 6.

Actually, the reactions 4−6 are the intermolecular interactions between the two initially formed molecules (reactions 4 and 6) or between the initially formed and the finally formed molecules (reaction 5). Reactions 4 and 5 have similar six-member cycles in their transition states (C2−C3−C4−Sn5−C13−Sn9 for reaction 4 and C2−C3−C4−Sn5−C14−Sn9 for reaction 5). The bond lengths between C and the $SnCl_3$ moiety range from 2.2 to 2.5 Å, and the C−C bond lengths in the six-member ring are between the single and double C−C bond lengths. But the barrier for reaction 4 is 52.0 kJ·mol^{-1} higher than that for reaction 5, because C13 with hybridization of sp^3 in reaction 4 is less active than C14 with hybridization of sp^2 in reaction 5. Reaction 6 has a different transition state geometry from reactions 4 and 5. It is an eight-member cyclic transition state. Usually the eight-member transition state is less stable than the six-member one. In contrast, in the present case the eight-member transition state TS6 is more stable than the six-member transition state TS4. This is because of the special characteristics of the reactant 1-trichlorostannylbuta-2,3-diene (PR1a). Because the two double bonds are close to each other, atom C2 with sp hybridization is active. When 1-trichlorostannylbuta-2,3-diene isomerizes to 2-trichlorostannylbuta-1,3-diene via the eight-member transition state, two atoms C2 and C15 change their hybridization from sp to sp^2, resulting in a lower energy barrier of 77.4 kJ·mol^{-1}.

The equilibrium constant for reactions 2−5 calculated from the change of the Gibbs free energy at 298 K and 1 atm (−21.4 kJ·mol^{-1}) is found to be 5.57×10^3, in agreement with the experimental results[19] in which 1-trichlorostannylbuta-2,3-diene is completely isomerized to 2-trichlorostannylbuta-1,3-diene within 6 h. In that experiment, Hatakeyama and co-workers[19] observed that one of the two products (1-trichlorostannylbuta-2,3-diene and 2-trichlorostannylbuta-1,3-diene), 1-trichlorostannylbuta-2,3-diene, mainly reacts with aldehydes to produce dienols. Although 2-tributylstannylbuta-1,3-diene used in the experiment is slightly larger than 2-trimethylstannylbuta-1,3-diene in our calculations, a similar transmetalation process is expected. Since the product is a mixture of allyltin halide isomers, the isomers could play an important roles in further reactions with the

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electrophiles (e.g. aldehydes[19]). Research attempting to address these issues is currently underway in our group.

Conclusion

The transmetalation of 2-trimethylstannylbuta-1,3-diene with $SnCl_4$ has been studied at the B3LYP/6-31G** level. In this work, six reactions have been investigated. The calculations showed that the reactant reacts with $SnCl_4$ via transmetalation to generate 1-trichlorostannylbuta-2,3-diene, which then isomerizes to form 2-trichlorostannylbuta-1,3-diene. These reactions carry out the transmetalation via migration of the diene double bond. Reactions 1, 2, 4, and 5 have only one six-member cyclic chairlike transition state, while reaction 6 has one eight-member cyclic transition state. Although all the reactions are consistent with the concerted reaction processes, they have different energy barrier heights. The barrier height of reaction 1 is found to be the lowest among the six reactions, so the isomerization step is the rate-controlling step. The isomerization process via transmetalation involving $SnCl_4$ (reaction 2) was found to be energetically more favorable than the other possible isomerization processes.

Supporting Information Available: B3LYP/6-31G** optimized geometries, energies of the stationary points, and imaginary frequencies of transition states corresponding to the six reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026515L