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A Three-Center Orbital Interaction in the Diels−Alder Reactions Catalyzed by Lewis Acids

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Ab initio calculations were performed on title reactions between butadiene and acrolein with BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $ZnCl_2$, $SnCl_2$, and $SnCl_4$. A dimethyl ether molecule is explicitly considered in various reaction systems to examine solvent effects. First, the reaction path of an $AlCl_3$-promoting reaction was examined thoroughly. This reaction has two channels. The first one involves a weak reactant-like complex (precursor) and a normal [4 + 2] addition. The second does three elementary processes, one-center addition, ring closing, and Claisen shift. The first channel is more favorable by 12.1 kcal/mol (B3LYP/6-311+G(2d,p) SCRF//B3LYP/6-31G* SCRF) than the second one. Then the first channels with other Lewis acids were traced with and without an ether molecule. The ether molecule has an appreciable effect not on geometries but on activation energies. BCl_3 is desolvated and has extraordinarily strong catalytic ability. Even with the strongest catalyst, not a [2 + 4] but a normal [4 + 2] cycloaddition takes place. Except for BCl_3, $SnCl_4$ is the strongest Lewis acid with the ether molecule. The frontier orbital, LUMO, of acrolein is distorted in the course of the reaction so that the formation of two C−C covalent bonds is possible. The precursor formation and the one-center addition were discussed also by the frontier orbital theory.

I. Introduction

Lewis-acid catalysts are known to enhance the reaction rates and endo selectivities of Diels−Alder reactions.[1] The dienophiles activated with a carbonyl group are subject to catalysis. Lewis-acid catalysts form complexes at carbonyl oxygen atoms, leading to the increased electron-withdrawing capacity of the carbonyl groups of the dienophiles. The enhanced reactivity has been simulated in many theoretical studies.[2] We reported previously the results of the ab initio calculations on Diels−Alder reactions composed of butadiene and $AlCl_3$ or BF_3 catalyzed acrolein.[3a] The BF_3-containing reaction was found to give a normal [4 + 2] product via a novel [2 + 4] (not a direct [4 + 2]) cycloaddition and subsequent Claisen rearrangement ([3,3] sigmatropic shift). In this "[*m* + *n*]" notation, the former "*m*" means the number of π electrons offered in cycloaddition by butadiene, and the latter "*n*" does that by acrolein. The addition TS has a very flat and ambiguous potential energy surface, and by MP2/6-31G* calculations of Garcia et al. a [4 + 2] TS character was obtained.[3b] Also, Garcia et al. demonstrated that the B3LYP/6-31G* calculation gave a not [2 + 4] but [4 + 2] reaction.[3c]

Despite accumulated theoretical results, there are various problems yet unresolved.

(1) The possibility of the combination of [2 + 4] addition and the [3,3] sigmatropic shift needs to be investigated by the use of other Lewis acids than BF_3.

(2) When the Lewis acid, BF_3 or $AlCl_3$, was used alone, the catalytic strength is overestimated. The solvent molecule (e.g., ether in $BF_3{\cdot}OEt_2$) must be considered for the proper estimate of the strength.

(3) In simple reacting systems, such as butadiene−ethylene[4] and butadiene−cyclopropene,[5] the stepwise reaction channels involving singlet biradical intermediates are coexistent with normal concerted ones. For Lewis-acid catalyzed systems, those two channels must

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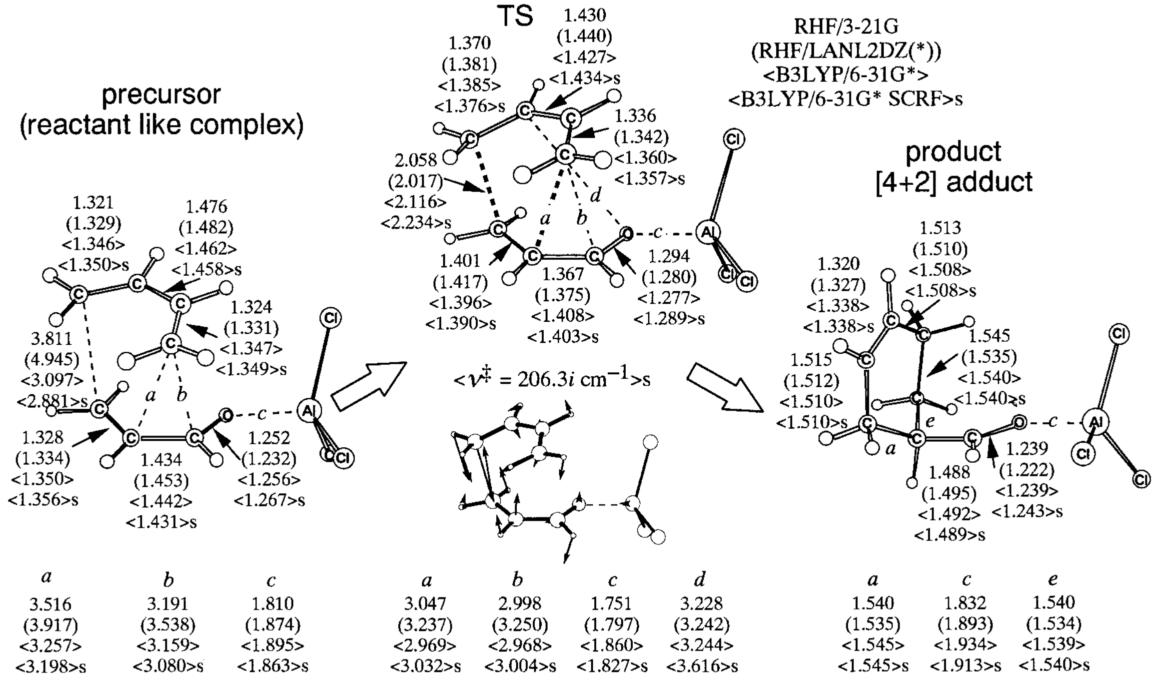

Figure 1. Geometries of the Diels−Alder reaction between butadiene and acrolein catalyzed by $AlCl_3$. They are optimized with RHF/3-21G, (RHF/LANL2DZ(*)), <B3LYP/6-31G*>, and <B3LYP/6-31G* SCRF>s methods. Distances are in angstroms. Small empty circles stand for hydrogen atoms. For TS, the <B3LYP/6-31G* SCRF>s reaction-coordinate vector corresponding to the sole imaginary frequency, $\nu^{\ddagger} = 206.3i$ cm^{-1}, is shown.

be sought. In particular, the ring-closing path from the biradical intermediate to the cyclohexene product has not been obtained, and the potential surface of the acid-promoted systems needs to be fully elucidated.

(4) In our previous work,[3a] the endo selectivity enhanced by Lewis acid was discussed in terms of the frontier-orbital theory.[6] However, the role of the back charge-transfer for the covalent-bond formation is still open to question. The orbital-mixing in the reaction progress must be examined. A decisive orbital concept on the Lewis-acid-catalyzed Diels−Alder reaction is desirable.

To solve those problems, we have carried out ab initio calculations on various Lewis-acid-catalyzed Diels−Alder reactions between butadiene and acrolein. Seven chloride Lewis acids, BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $ZnCl_2$, $SnCl_2$,and $SnCl_4$, are considered for systematic comparison of the catalytic strength. A dimethyl ether molecule is explicitly considered to refine the overestimated catalytic strength. It will be shown that the potential surface of the Lewis-acid-catalyzed reaction is different from what has been thought so far.

II. Method of Calculations

Ab initio calculations have been performed using GAUSSIAN94 program package[7] installed both on a CONVEX SPP 1200/XA computer in the Information Processing Center of Nara University of Education and on a CONVEX SPP 1600/XA computer in the Computer Center of Nara University.

Four types of geometry optimizations have been carried out for the BCl_3- and $AlCl_3$-catalyzed acrolein−butadiene systems. They are RHF/3-21G, RHF/LANL2DZ(*),[8] and B3LYP/6-31G*[9] without and with the Onsager solvent effect.[10] In the present calculations, the fourth-row atoms, indium in $InCl_3$ and tin in $SnCl_2$ and $SnCl_4$, are included. The inclusion prohibits the use of 6-31G basis sets, and the ECP (effective core potential)-containing basis set is needed to make systematic calculations of all Lewis acids. The LANL2DZ basis set was employed, which, however, does not include polarization functions. As an extra basis set, 6 d orbitals (* in 6-31G*) are added to LANL2DZ of reaction-center atoms, carbon and oxygen, with exponents 0.8.[11] Since the LANL2DZ(*) basis set is large, we carried out RHF/LANL2DZ(*) calculations. These results were found to be fortunately similar to those of B3LYP/6-31G* ones for $AlCl_3$- and BCl_3-containing systems. For $GaCl_3$-, $InCl_3$-, $ZnCl_2$-, $SnCl_2$-, and $SnCl_4$-catalyzed systems, RHF/3-21G and RHF/LANL2DZ(*) methods have been used for geometry optimizations.

For saddle points (opt = ts), vibrational analyses by RHF/3-21G, RHF/LANL2DZ(*), and B3LYP/6-31G* SCRF methods have been made so as to check whether sole imaginary frequencies have been correctly obtained.

Energy diagrams of the $AlCl_3$-catalyzed butadiene−

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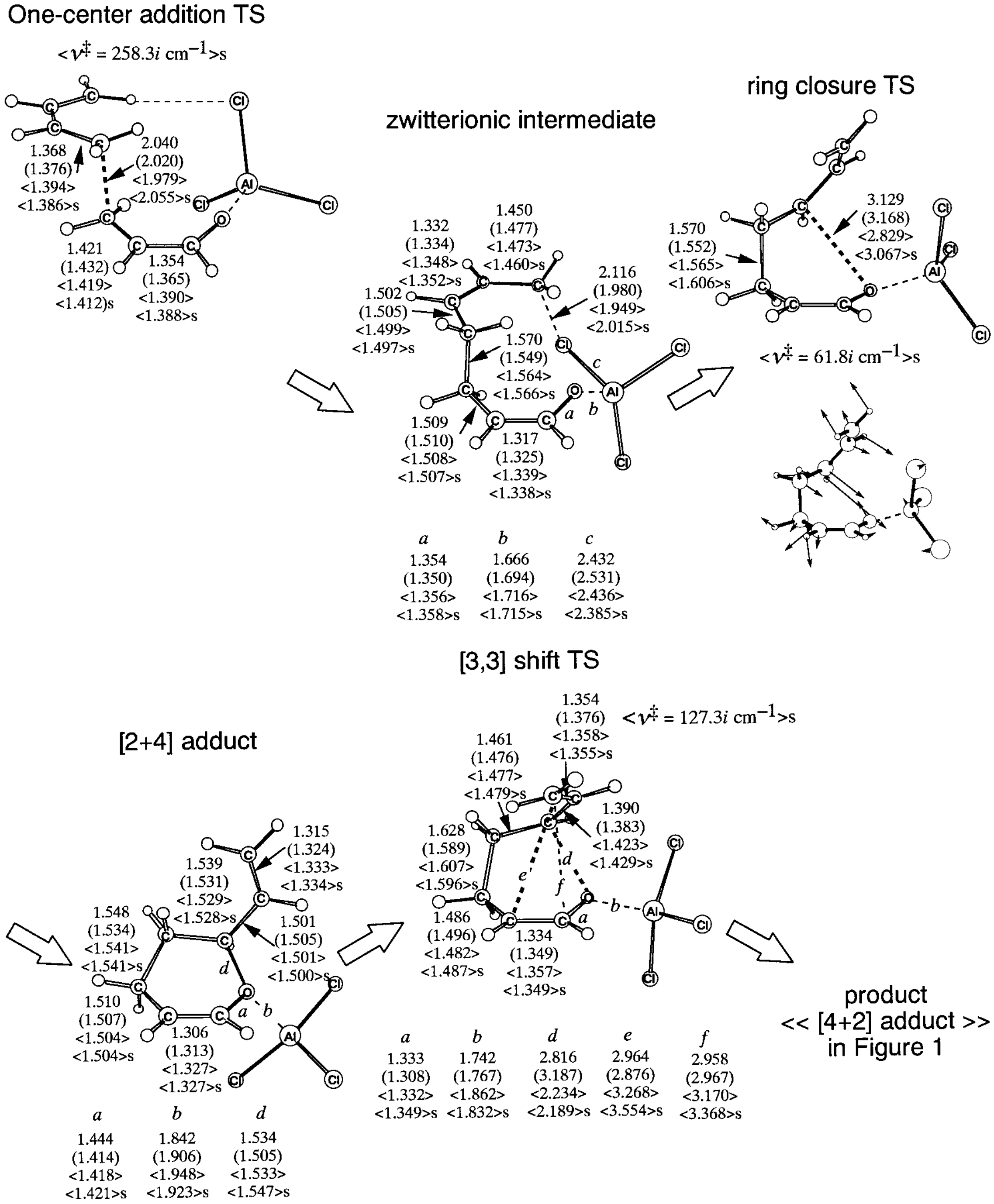

Figure 2. Geometries of the other reaction channel for the $AlCl_3$-containing Diels–Alder reaction.

acrolein system in Figure 3 have been drawn by the use of the energies obtained by the single-point calculations on the B3LYP/6-31G* SCRF geometry: B3LYP/6-311+G(2d,p) with SCRF//B3LYP/6-31G* with SCRF. This combination of the geometry optimization and subsequent single-point energy calculation (without SCRF) is recommended as a highly accurate and practical method.[12] For the butadiene–acrolein catalyzed by $AlCl_3$ and butadiene–ethylene systems, single-point CISD/6-31G*//(U)B3LYP/6-31G* calculations were made to evaluate whether the one-center adducts are biradical or zwitterionic intermediates. Activation energies (E_a's) in Table 1 and Figure 12 were calculated by B3LYP/LANL2DZ(*) with SCRF//RHF/LANL2DZ(*) method.

III. Mechanism of the $AlCl_3$-Containing Diels–Alder Reaction

It is known well that the Diels–Alder reaction has a stepwise process which is competitive with the [4 + 2] addition path. For the butadiene–ethylene reaction, for example, the stepwise path involves a biradical intermediate. Figure 1 shows a geometry change along the concerted reaction between butadiene and $AlCl_3$-catalyzed acrolein leading to the cyclohexene product. First, a weakly bound reactant-like complex (called hereafter

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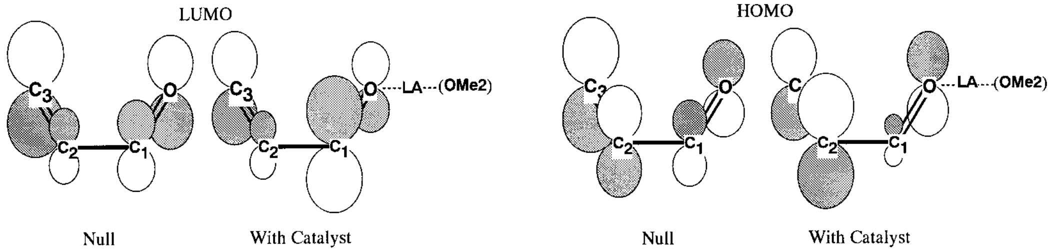
Table 1. Frontier-Orbital Energies and Coefficients of the Acrolein Coordinated by a Lewis Acid (LA)[a]



LA	E_{LUMO}	C_3	C_2	C_1	O	E_a	LA	E_{HOMO}	C_3	C_2	C_1	O	E_a
	LUMO Coefficients of Acrolein							HOMO Coefficients of Acrolein					
null	0.226	**0.636**	−0.429	−0.516	0.589	13.5	null	−0.325	**0.583**	0.557	−0.205	−0.410	13.5
BCl_3	0.072	0.595	−0.197	−**0.690**	0.524	−3.9	BCl_3	−0.420	0.466	**0.528**	−0.035	−0.394	−3.9
+ OMe_2	0.081	0.595	−0.207	−**0.685**	0.531	−6.6	+ OMe_2	−0.415	0.477	**0.538**	−0.037	−0.392	−6.6
$AlCl_3$	0.079	0.598	−0.215	−**0.679**	0.537	−2.0	$AlCl_3$	−0.428	0.508	**0.586**	0.023	−0.352	−2.0
+ OMe_2	0.137	0.601	−0.269	−**0.646**	0.561	2.7	+ OMe_2	−0.389	0.442	**0.495**	0.022	−0.278	2.7
$GaCl_3$	0.080	0.594	−0.211	−**0.680**	0.527	−1.3	$GaCl_3$	−0.432	0.458	**0.539**	0.059	−0.284	−1.3
+ OMe_2	0.138	0.598	−0.269	−**0.646**	0.554	3.3	+ OMe_2	−0.391	0.403	**0.455**	0.027	−0.233	3.3
$InCl_3$	0.098	0.597	−0.242	−**0.663**	0.548	−4.1	$InCl_3$	−0.414	0.529	**0.592**	−0.017	−0.371	−4.1
+ OMe_2	0.141	0.601	−0.281	−**0.638**	0.562	2.7	+ OMe_2	−0.382	0.527	**0.572**	−0.047	−0.363	2.7
$ZnCl_2$	0.147	0.519	−0.231	−**0.554**	**0.554**	1.5	$ZnCl_2$	−0.364	0.548	**0.608**	0.053	−0.355	1.5
+ OMe_2	0.142	0.557	−0.256	−**0.612**	0.522	6.0	+ OMe_2	−0.361	0.396	**0.406**	−0.071	−0.301	6.0
$SnCl_2$	0.121	0.590	−0.223	−**0.653**	0.542	1.4	$SnCl_2$	−0.386	0.519	**0.597**	−0.019	−0.378	1.4
+ OMe_2	0.169	0.602	−0.321	−**0.607**	0.564	9.5	+ OMe_2	−0.365	0.430	**0.450**	−0.057	−0.279	9.5
$SnCl_4$	0.098	0.594	−0.235	−**0.665**	0.548	1.0	$SnCl_4$	−0.411	0.496	**0.556**	−0.021	−0.361	1.0
+ OMe_2	0.111	0.598	−0.235	−**0.668**	0.542	−0.8	+ OMe_2	−0.393	0.491	**0.542**	−0.056	−0.390	−0.8

[a] Orbital energies (E_{LUMO}, E_{HOMO}) calculated by RHF/STO-3G//RHF/LANL2DZ(*) are in hartree units. E_a values stand for activation energies in kcal/mol calculated by the energy difference between TS and reactants by B3LYP/LANL2DZ(*) SCRF//RHF/LANL2DZ(*) method. E_a values are negative in some reactions where the stability of precursors is large. Of course, activation barrier energies relative to energies of those precursors are positive. "Null" means the acrolein without the Lewis acid. The table shows the values of LUMO and HOMO of acrolein. The shapes of the LUMO and HOMO are shown below the table title. Underlined numbers in $ZnCl_2$ and $SnCl_2$ rows indicate that the dimethyl ether molecules reverse their reactivities.

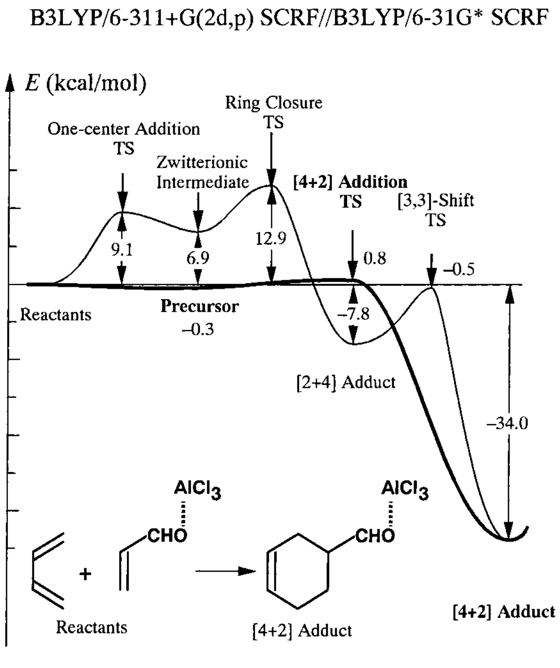


Figure 3. Energy diagrams of the $AlCl_3$-containing reaction between butadiene and acrolein calculated with B3LYP/6-311+G(2d,p) SCRF = dipole//B3LYP/6-31G* SCRF = dipole. The dielectric constant ϵ is 5.02 for dimethyl ether at 25 °C.

"precursor") is generated, where a three-center interaction stabilizes the complex. At the transition state (TS), the left-side C···C bond formation is dominated. This TS is for the [4 + 2] cycloaddition. The [2 + 4] TS found in RHF calculations of the BF_3-containing reaction[3a] has been searched for by tuning Hessian matrix elements. However, every attempt leads to the switch of [2 + 4] → [4 + 2]. The $AlCl_3$-containing reaction has been confirmed to have a unique [4 + 2] TS. The precursor was confirmed to be located at the [4 + 2] channel by IRC calculations.[13]

The stepwise process of the $AlCl_3$-containing reaction is shown in Figure 2. The first path is a one-center addition. This TS geometry is similar to that of the butadiene−ethylene reaction reported by Houk et al.[4b] The C−O−Al angle of the coordination bond is large, 176.8°, (170.6°), ⟨159.8°⟩, or ⟨163.7°⟩s, owing to a C−H···Cl hydrogen bond. An intermediate is generated, which is not biradical but zwitterionic. The character was examined in two ways. First, the intermediate geometry was optimized by UB3LYP/6-31G* with the broken symmetry initial guess orbitals (IOP(4/13 = 1)). Despite the reinforced singlet−biradical requirement, the spin S^2 expectation value is kept to be zero during the geometry optimization. Second, CISD/6-31G* single-point calculations on the butadiene−ethylene biradical intermediate and the present one were made. The CI coefficients of (HOMO → LUMO) doubly excited configurations are 0.128 for the butadiene−ethylene intermediate and 0.021 for the present system. The present system may be ionic in the two-configuration SCF sense, because the adiabatic configuration Ψ_0 is not so contaminated. The intermediate is stabilized by a through-space charge-transfer (CT) interaction from a lone pair orbital of a chloride to the cationic methylene carbon.

Here, the next path including the isomerization of the zwitterionic intermediate needs to be sought. A ring closure TS has been found, which gives surprisingly a [2 + 4] adduct. The direct (the intermediate → the [4 + 2]

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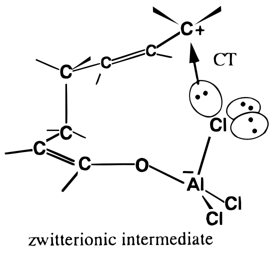
(13) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

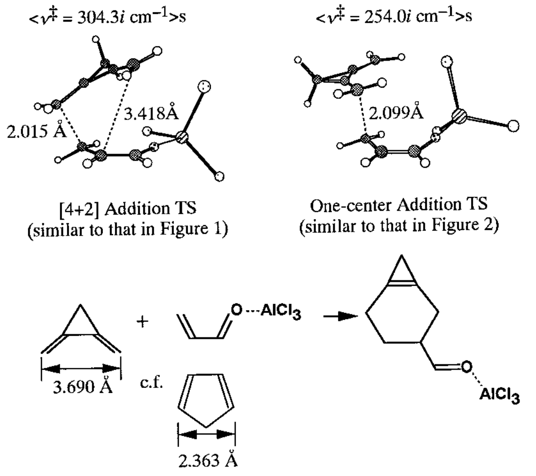


product) path could not be found. For BF_3, the [2 + 4] adduct was obtained directly by RHF calculations.[3a] But the direct [2 + 4] adduct formation is absent by calculations with electron correlations.[3b,c] For $AlCl_3$, the [2 + 4] adduct has been obtained via the zwitterionic intermediate. The [2 + 4] adduct can be isomerized via a Claisen shift to the product ([4 + 2] adduct). Figure 2 has demonstrated that the [4 + 2] adduct can be generated by a novel channel which is completely different from that in Figure 1. That channel has three TSs. They are for the one-center addition, ring-closing and [3,3] sigmatropic rearrangement.

Figure 3 shows energy diagrams of B3LYP/6-311+G(2d,p) SCRF//B3LYP/6-31G* SCRF of two channels. The stabilizing energy due to the precursor formation in the first channel is 0.3 kcal/mol. The energy is overcome by the entropy term, and the precursor is not detectable experimentally. Comparison of the [4 + 2] addition and the one-center addition TSs indicates that the former path is more favorable by 8.3 (9.1−0.8) kcal/mol. The $AlCl_3$-containing reaction, thus, proceeds in the normal [4 + 2] cycloaddition path (Figure 1). In the second channel (Figure 2), energy levels of three TSs are medium (9.1 kcal/mol), high (12.9 kcal/mol), and low (−0.5 kcal/mol).

Generally, the [4 + 2] addition is more favorable than the one-center addition.[14a] In fact, substituents such as dimethyl and amino groups (2,3-dimethylbutadiene and 2-aminobutadiene) do not affect the reactivity difference so much. That is, even in reactions between those substituted butadienes and acrolein catalyzed by $AlCl_3$, [4 + 2] TSs are favored over one-center TSs with the similar TS energy differences (2−4 kcal/mol).[14b] But, when the distance between two terminal carbons of butadiene is enlarged (e.g., 1,2-dimethylenecyclopropane in Scheme 1), the one-center addition TS becomes competitive with the [4 + 2] TS (only slightly less stable by 2.0 kcal/mol with B3LYP/6-31G* SCRF method). In the [4 + 2] TS, stability of the three-center interaction is lost by the too large distance between the terminal methylene carbons in the diene. The 1,2-dimethylenecyclopropane is one extreme reactant, and cyclopentadiene is the other (contrary) extreme one.

Scheme 1. Two TS Geometries (B3LYP/6-31G* SCRF) of a Reaction between 1,2-Dimethylenecyclopropane and Acrolein Catalyzed by $AlCl_3$



[4+2] Addition TS (similar to that in Figure 1)

One-center Addition TS (similar to that in Figure 2)

Thus, although two channels need to be compared formally, only the [4 + 2] addition channel is probable in most cases. Hereafter, the [4 + 2] addition channel will be investigated for other Lewis acids than $AlCl_3$.

So far, the s-cis acrolein catalyzed by $AlCl_3$ has been examined. Garcia et al. studied extensively the reactivity difference between s-cis and s-trans acroleins catalyzed by BF_3.[3c] The endo s-cis orientation was confirmed to be most likely. Here, the precursor and [4 + 2] TS involving the s-trans acrolein is scrutinized. As a reactant, the s-trans acrolein with $AlCl_3$ is 3.0 kcal/mol (B3LYP/6-311+G(2d,p) SCRF//B3LYP/6-31G* SCRF) more stable than the s-cis isomer. The precursor gets the small stabilization energy, 1.4 kcal/mol, which is similar to that, 0.3 kcal/mol, for the s-cis acrolein (Figure 3). The energy barrier (relative to the energies of reactants) of [4 + 2] TS is 5.6 kcal/mol. This value is substantially larger than that, 0.8 kcal/mol (Figure 3), for s-cis acrolein. The [2 + 4]-type secondary orbital interaction in the s-cis form brought about the latter small activation energy. The interaction will be discussed in the Section VI.

IV. Solvent Effect on the Lewis-Acid-Catalyzed Diels−Alder Reaction

In the previous section, the [4 + 2] cycloaddition path of the $AlCl_3$-containing Diels−Alder reaction has been investigated. In this section, a dimethyl ether molecule is explicitly involved in the reacting system with $AlCl_3$

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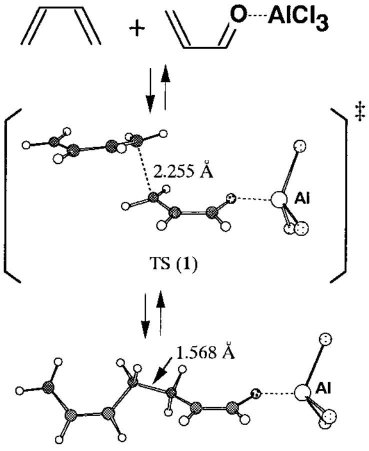
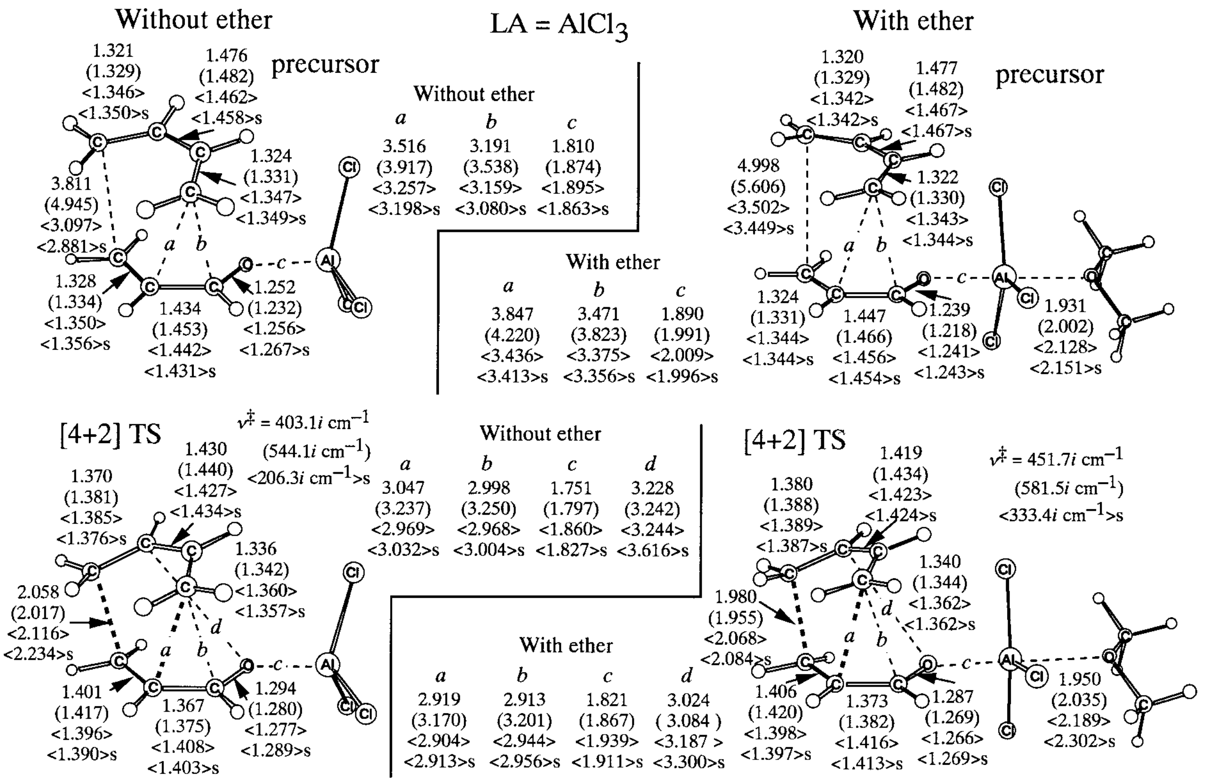
(14) (a) There is a complete *trans* addition path with TS (**1**) leading to an alternative zwitterionic intermediate (**2**). The activation energy of **1** is even smaller (1.0 kcal/mol by B3LYP/6-311+G(2d,p) SCRF//B3LYP/6-31G* SCRF) than that of [4 + 2] TS. But, the resultant intermediate, **2**, does not have a channel to any ring closures, and **2** is merely under an equilibrium of association and dissociation.



zwitterionic intermediate (**2**)

(b) For a reaction between 2,3-dimethylbutadiene and acrolein with $AlCl_3$ (AC−LA), total energies of TSs calculated by RHF/3-21G//RHF/3-21G method are −2034.173987 au ([4 + 2] addition) and −2034.170203 au (one-center addition). For a reaction between 2-aminobutadiene and AC−LA, they are −2011.276254 au ([4 + 2] addition) and −2011.269103 au (one-center addition).



Without ether (precursor)

a	b	c
3.516	3.191	1.810
(3.917)	(3.538)	(1.874)
<3.257>	<3.159>	<1.895>
<3.198>s	<3.080>s	<1.863>s

With ether (precursor)

a	b	c
3.847	3.471	1.890
(4.220)	(3.823)	(1.991)
<3.436>	<3.375>	<2.009>
<3.413>s	<3.356>s	<1.996>s

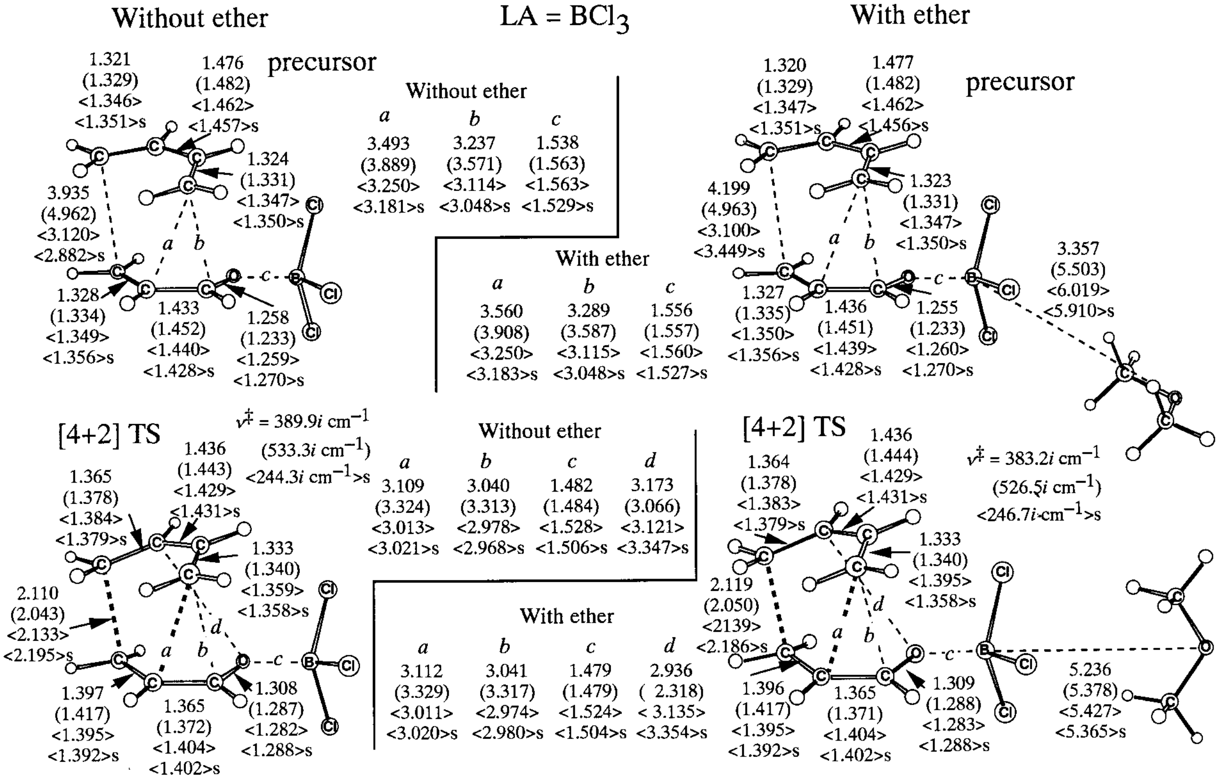
Without ether ([4+2] TS)

a	b	c	d
3.047	2.998	1.751	3.228
(3.237)	(3.250)	(1.797)	(3.242)
<2.969>	<2.968>	<1.860>	<3.244>
<3.032>s	<3.004>s	<1.827>s	<3.616>s

With ether ([4+2] TS)

a	b	c	d
2.919	2.913	1.821	3.024
(3.170)	(3.201)	(1.867)	(3.084)
<2.904>	<2.944>	<1.939>	<3.187 >
<2.913>s	<2.956>s	<1.911>s	<3.300>s

Figure 4. Geometries of precursors (weakly bound complexes prior to cycloaddition) and transition states (TSs) of $AlCl_3$-containing reactions without (left) and with (right) a dimethyl ether molecule. LA denotes a Lewis acid. The geometries without the ether are the same as those in Figure 1.



Without ether (precursor)

a	b	c
3.493	3.237	1.538
(3.889)	(3.571)	(1.563)
<3.250>	<3.114>	<1.563>
<3.181>s	<3.048>s	<1.529>s

With ether (precursor)

a	b	c
3.560	3.289	1.556
(3.908)	(3.587)	(1.557)
<3.250>	<3.115>	<1.560>
<3.183>s	<3.048>s	<1.527>s

Without ether ([4+2] TS)

a	b	c	d
3.109	3.040	1.482	3.173
(3.324)	(3.313)	(1.484)	(3.066)
<3.013>	<2.978>	<1.528>	<3.121>
<3.021>s	<2.968>s	<1.506>s	<3.347>s

With ether ([4+2] TS)

a	b	c	d
3.112	3.041	1.479	2.936
(3.329)	(3.317)	(1.479)	(2.318)
<3.011>	<2.974>	<1.524>	< 3.135>
<3.020>s	<2.980>s	<1.504>s	<3.354>s

Figure 5. Geometries of precursors and TSs of BCl_3-containing reactions.

or BCl_3 as the Lewis acid (LA). This is because the ether, e.g., in BF_3·OEt_2, is a standard solvent in the Diels–Alder reaction. Figure 4 shows geometries of precursors (reactant-like complexes) and TSs with the $AlCl_3$ catalyst. The dimethyl ether molecule is coordinated to the backside of $AlCl_3$ and weakens its catalytic strength. In the precursor, the butadiene molecule is more distant from the $AlCl_3$-catalyzed acrolein with the ether molecule than that without it. However, in TS, the shape of the reaction center is almost insensitive to the presence or the absence

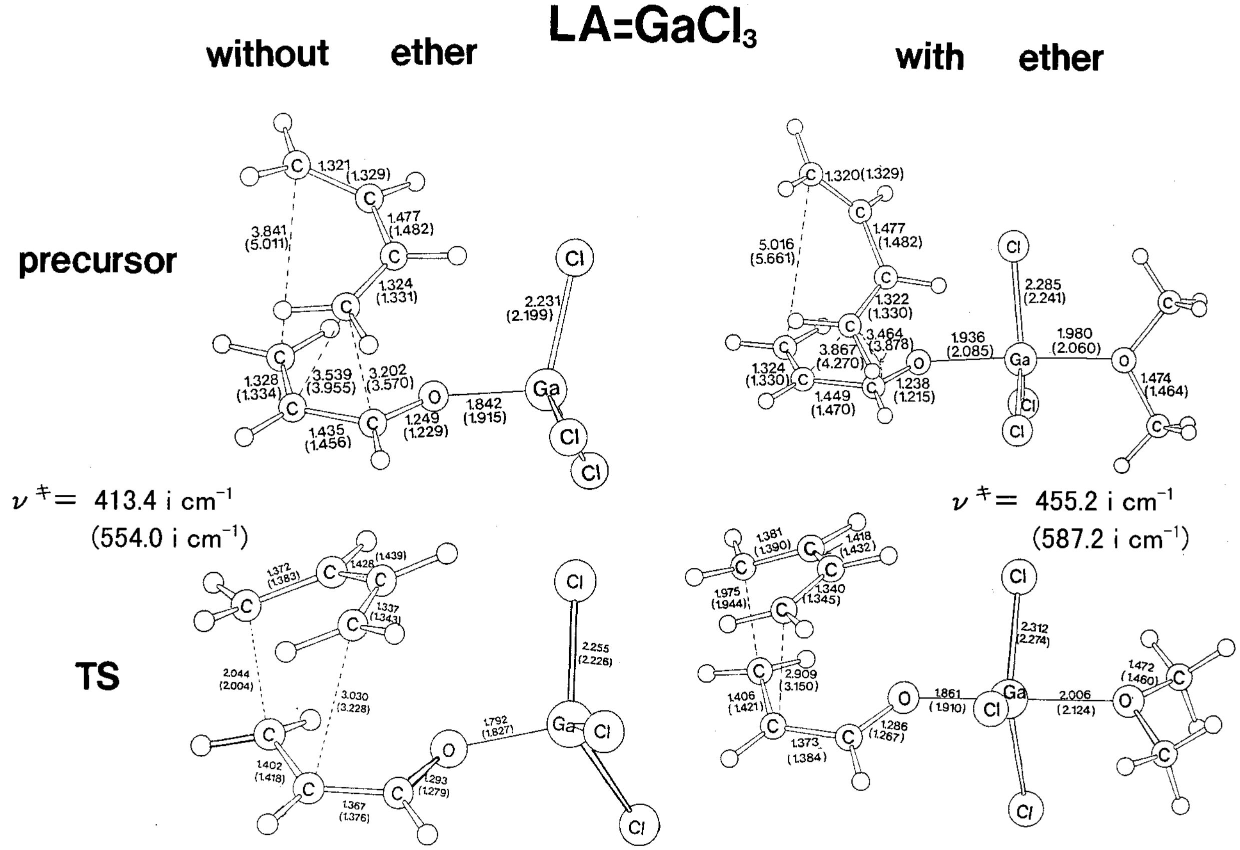


Figure 6. Geometries of precursors and TSs of GaCl$_3$-containing reactions.

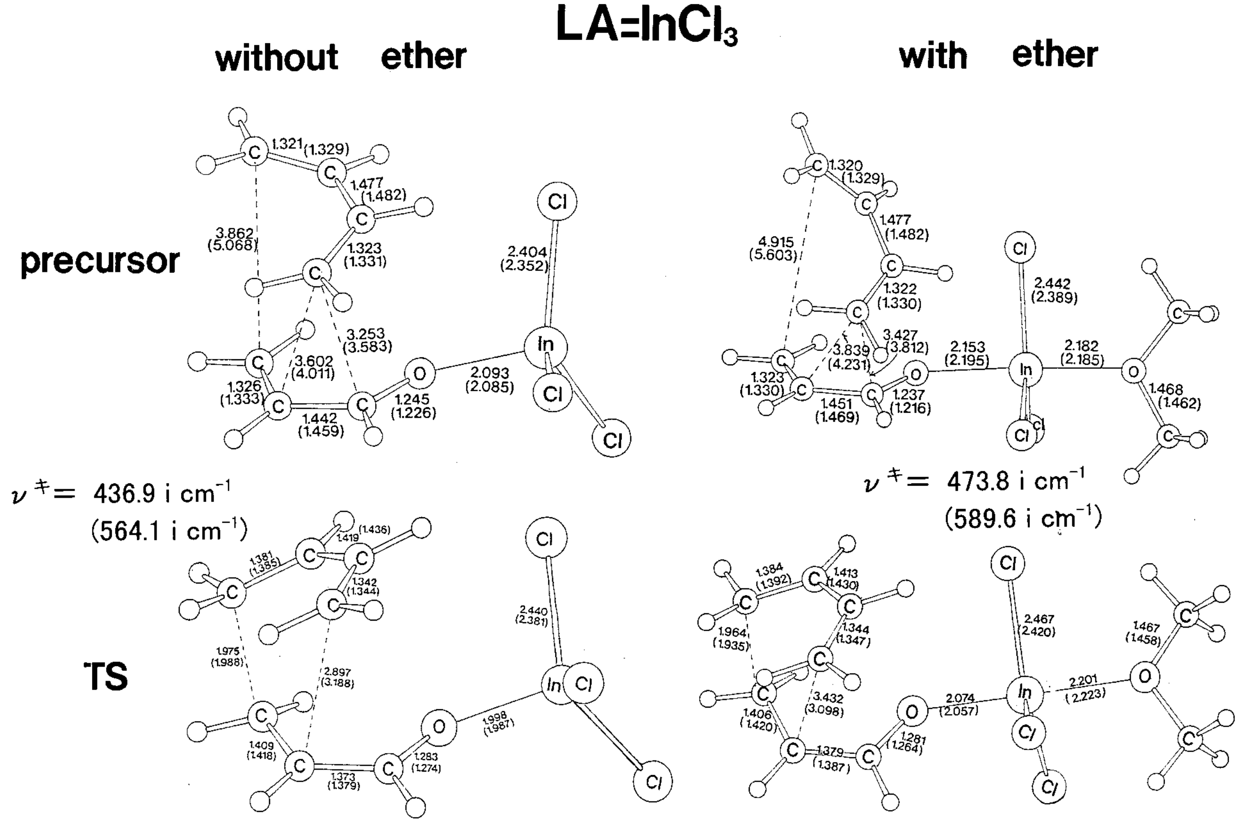


Figure 7. Geometries of precursors and TSs of InCl$_3$-containing reactions.

of the ether molecule. The similar distances, ~2 Å, between Al and OMe$_2$, in the precursor and TS indicate that the extent of the ether solvation is kept constant.

In the right edge of Table 1, B3LYP/LANL2DZ(*) SCRF//RHF/LANL2DZ(*) activation energies (E_a's) are displayed. Despite the structural similarity of TS, the ether

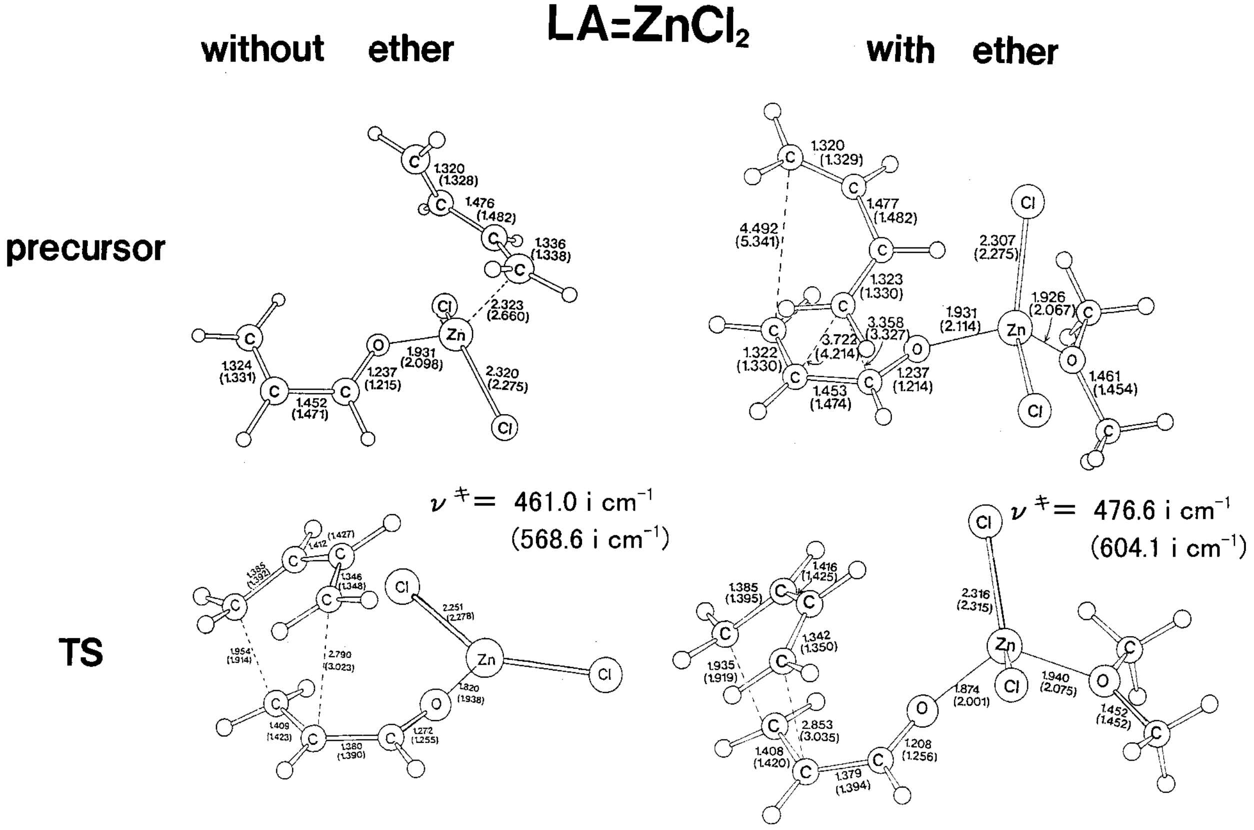


Figure 8. Geometries of precursors and TSs of $ZnCl_2$-containing reactions.

molecule enlarges E_a value (e.g., −2.0 → 2.7 kcal/mol for LA = $AlCl_3$), substantially.

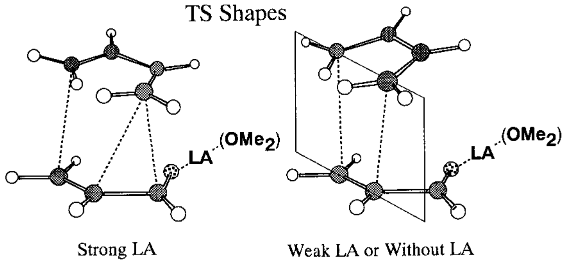
Figure 5 exhibits geometries for the BCl_3 catalyst. Noteworthy is the result that the ether molecule is far from BCl_3. The desolvation feature is involved already in the large B···OMe_2 distance, 3.321 Å (RHF/3-21G) or 5.420 Å (RHF/LANL2DZ(*)) of the acrolein···BCl_3···OMe_2 reactant (not shown but included in the Supporting Information). The charge transfer, acrolein → BCl_3, bring the electronic charge up to the boron atom. The charge accumulation on the boron atom expels the ether molecule. The *hard* B atom behaves extremely in comparison with the *soft* Al atom. In the precursor, the RHF/3-21G distance 3.357 Å is significantly smaller than the RHF/LANL2DZ(*) one 5.503 Å, and B3LYP/6-31G* SCRF one, 5.910 Å. The former distance corresponds to the B···OMe_2 geometry rather than B···Me_2O shown in Figure 5 and is a result of the overestimated polarity of the 3-21G basis set.

V. Catalytic Strength of Lewis Acids of the Third and Fourth Row Atoms

In the previous section, the strength of $AlCl_3$ and BCl_3 has been investigated. It is tempting to examine the strength of other valence isoelectronic Lewis acids, $GaCl_3$ and $InCl_3$, where the central electron-deficient atoms, B, Al, Ga, and In, belong to the 13th group. Also, the $ZnCl_2$, $SnCl_2$, and $SnCl_4$, which are standard chloride Lewis acids for organic syntheses, are considered here. RHF/3-21G and RHF/LANL2DZ(*) geometry optimizations were carried out, which are safely similar to those of B3LYP/6-31G* SCRF in Figures 1, 2, 4, and 5 (except the O···B distance by RHF/3-21G in the precursor with ether in Figure 5).

Figures 6 and 7 show the $GaCl_3$- and $InCl_3$-promoting Diels−Alder reactions, respectively. Geometries of the precursors and TSs are similar to those with $AlCl_3$ (Figure 4). It is confirmed that the precursors have weak interactions (3.2−3.4 Å by RHF/3-21G, distance *b* in Figures 1, 4, and 5) between carbonyl carbon atoms of acrolein and terminal methylene groups of butadiene. At each TS, the left-side C···C formation (ca. 2 Å) is dominated. Thus, primary interaction sites (in precursors) are different generally from those of the dominant C···C formation (in TSs).

Figure 8 exhibits a reaction with zinc chloride. Without the ether molecule, the butadiene molecule is linked with the zinc atom at the backside of Zn−acrolein coordination. When the ether molecule is included, the artificial model (with Zn···butadiene) is corrected to the normal precursor form. The catalytic strength of $ZnCl_2$ is weaker than MCl_3 (M = B, Al, Ga, In). The $ZnCl_2$ catalyst without an ether molecule lowers the energy level of the acrolein LUMO to a smaller extent than other Lewis acids as Table 1 shows. In fact, TS with an ether molecule has a shape of the reaction center similar to that without the Lewis acid.[3a] Four carbon atoms for formation of two C−C bonds are almost in a plane.



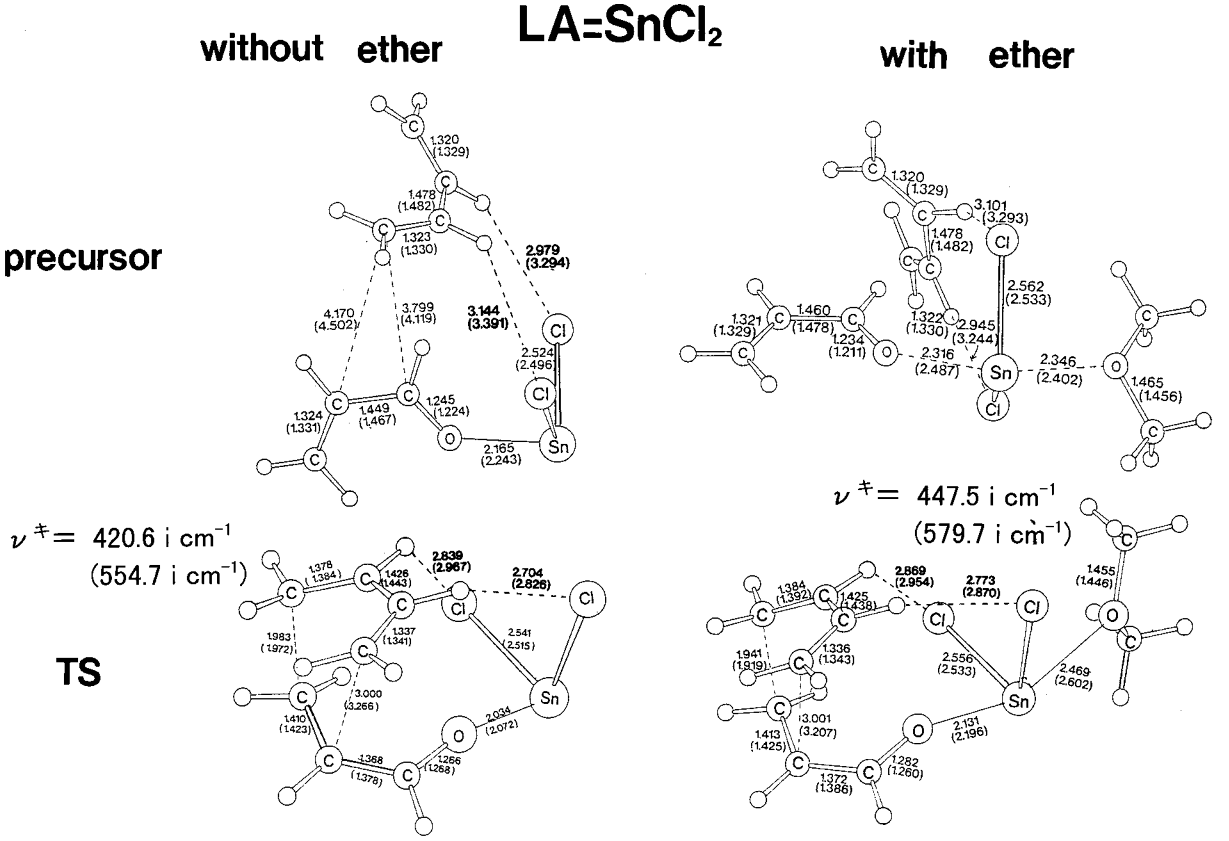


Figure 9. Geometries of precursors and TSs of $SnCl_2$-containing reactions.

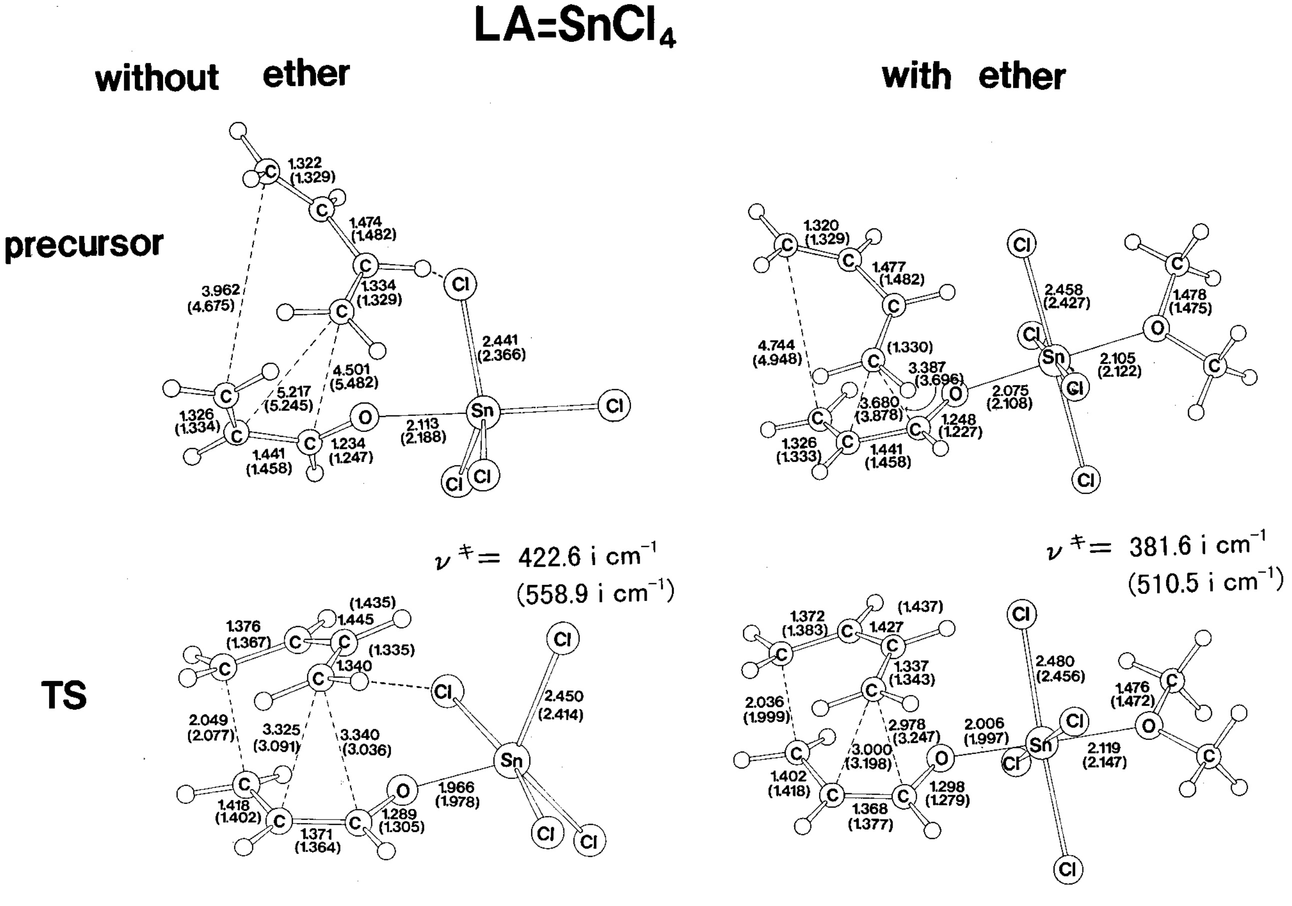


Figure 10. Geometries of precursors and TSs of $SnCl_4$-containing reactions.

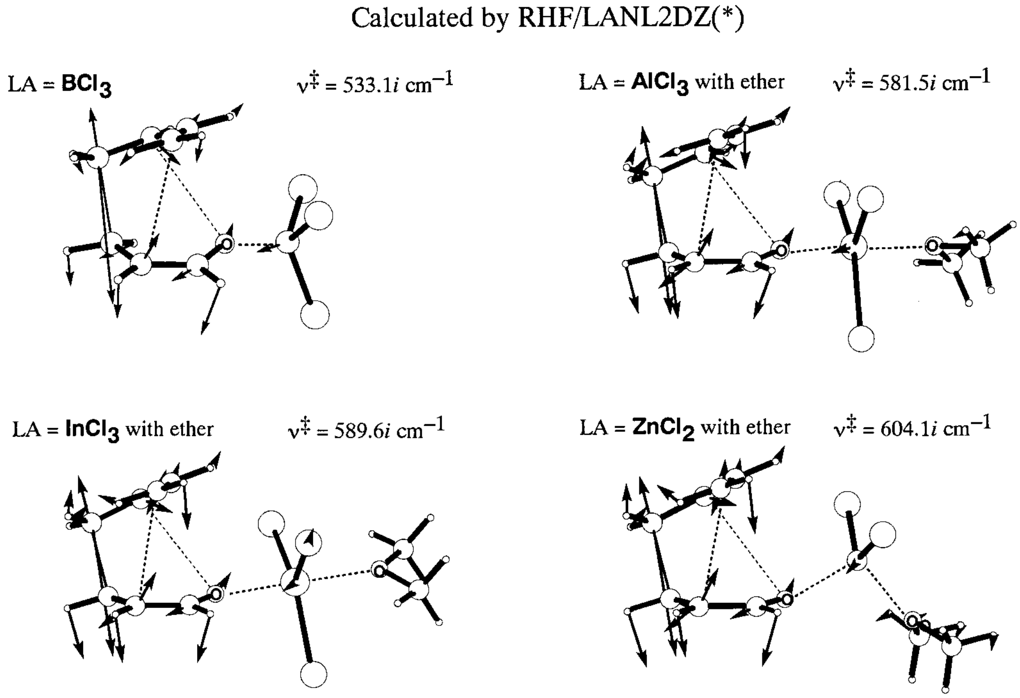
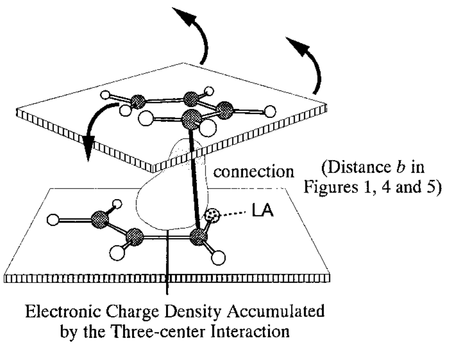


Figure 11. Reaction-coordinate vectors corresponding to respective sole imaginary frequencies, $\nu^{\ddagger}$'s. For LA = $AlCl_3$, $InCl_3$, and $ZnCl_2$, dimethyl ether-containing reactions are displayed. For LA = BCl_3, the ether-excluding reaction is used, because the BCl_3-catalyzed system has been found to be desolvated at TS (see Figure 5).

Figure 9 shows a reaction including tin dichloride. The tin dichloride has a large in-plane lone-pair orbital, and two chlorine atoms are directed upward to be linked with two methine hydrogen atoms of butadiene. The linkage is involved in every geometry of Figure 9. In precursors without and with the ether molecule, there are no direct butadiene−acrolein interactions. The weak catalytic operation of $SnCl_2$ is similar to that of $ZnCl_2$ (Figure 8).

Figure 10 exhibits geometries of a reaction catalyzed by tin tetrachloride. Without ether, there are slight hydrogen bonds between butadiene hydrogens and chloride ions in $SnCl_4$. But, with ether, those bonds disappear and typical octahedral coordinations around the tin center are formed in both precursor and TS. The (butadiene + acrolein) "ligand" may be stabilized effectively by the coordination. In fact, the "ligand" shape is similar to that (with ether, LA = $AlCl_3$) in Figure 4. The solvent effect of the ether molecule on geometries of the reaction system with LA = $SnCl_4$ is very large.

Results of Diels−Alder reactions with seven Lewis acids, BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $ZnCl_2$, $SnCl_2$, and $SnCl_4$ are summarized. The BCl_3 coordination is so strong that the ether molecule is practically unbound to the boron atom of BCl_3. Except for BCl_3, $SnCl_4$ is the strongest Lewis acid as E_a values in Table 1 show. At TSs, the three-center interactions are maintained and the left-side C···C covalent-bond formation proceeds by the use of this three-center interaction as the following picture shows. The three-center interaction connects the carbonyl carbon atom of acrolein and the terminal carbon atom of butadiene predominantly. The butadiene plane is propped up by this carbon−carbon connection and moves on the connection toward the left-side C−C bond formation.



The TS geometries are characterized by reaction coordinate vectors (Figure 11). The BCl_3-containing addition TS has a very flat and ambiguous potential surface similar to the BF_3-containing one.[3] The left side C···C bond formation is dominated, but the other covalent-bond formation is unclear. But, RHF/LANL2DZ(*) as well as B3LYP/6-31G* SCRF indicated that the BCl_3-containing reaction is a [4 + 2] cycloaddition. Except the reaction, other three reactions (LA = $AlCl_3$, $InCl_3$, and $ZnCl_2$) are evidently normal [4 + 2] additions in Figure 11. Thus, the [2 + 4] cycloaddition of LA = BF_3[3a] is not general but specific by low-level calculations, as pointed out by Garcia et al.[3b,c] In TSs of normal three reactions, the right methylene groups rotate substantially to cause the second covalent-bond formation. A driving force of this movement will be analyzed in terms of the frontier orbital theory in the next section.

VI. Frontier-Orbital Theory on the Diels−Alder Reaction Promoted by Lewis Acids

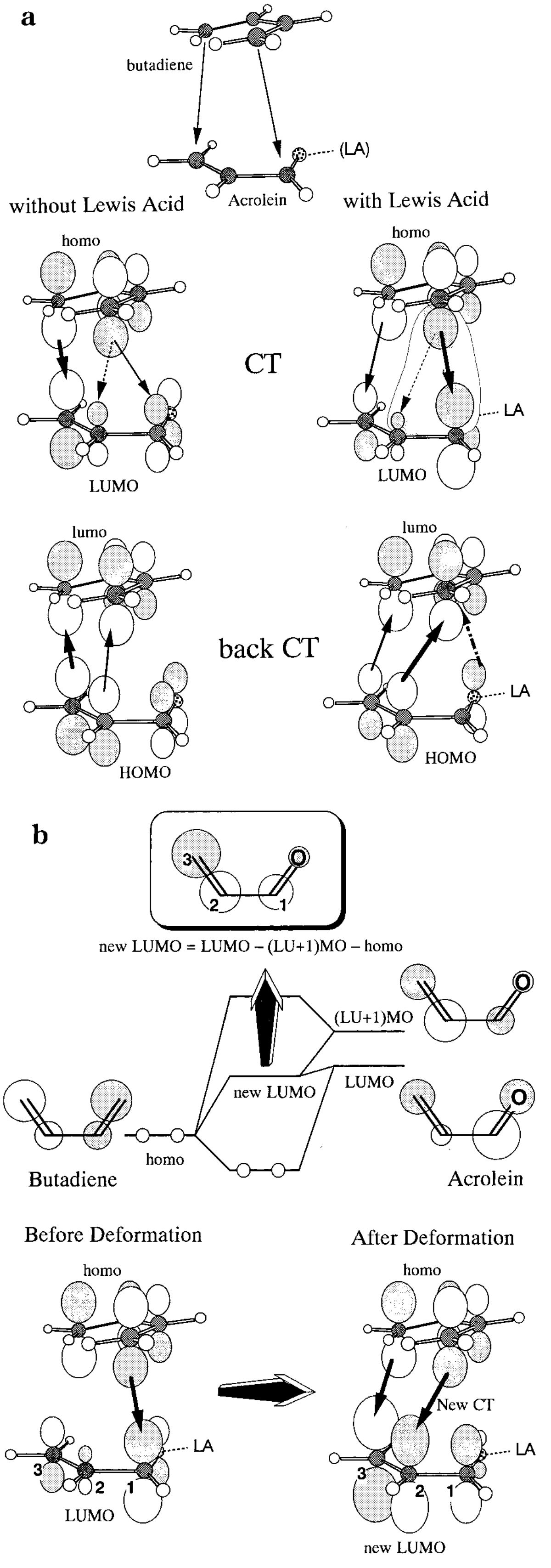
Table 1 shows orbital energies and orbital coefficients of LUMO of the acrolein without (Null) and with Lewis acids. As is known well, LUMO energies are lowered by Lewis acids, which means that the acrolein becomes more electrophilic. By addition of the ether molecule to the acid, LUMO energy levels are raised slightly (e.g., 0.079 → 0.137 au for $AlCl_3$). The catalytic strength overestimated by the acid alone is somewhat decreased. However, an ether molecule does not affect a catalytic ability of BCl_3 markedly. BCl_3 is bound to the oxygen atom of acrolein tightly because of its large coordination strength, and desolvates an ether molecule.

As for LUMO coefficients, the largest one in the free acrolein is 0.636 at the C_3 atom (null in Table 1). On the other hand, that at the C_1 atom (carbonyl carbon) is the largest in the acrolein with a Lewis acid. The C_1 atom is not a reaction center, and precursors (reactant like complexes) have been brought about by the electrophilicity of C_1. The difference of the charge-transfer (CT, homo → LUMO) between without and with the acid is shown in the middle of Scheme 2a. In the Diels–Alder reaction with LA, the primary frontier-orbital interaction does not correspond to covalent-bond formation.

In Table 1, HOMO energies and coefficients of acrolein are exhibited. The most back charge-donating site is the C_3 atom without LA (null, 0.583). But, the site is the C_2 atom with LA (e.g., 0.586 for LA = $AlCl_3$ without ether). Thus, the back CT is contributive to the formation of the second C···C bond, as is shown in the bottom of Scheme 2a. The HOMO coefficient of C_2 of LA = BCl_3 without an ether molecule is the smallest and that of O is the largest among acroleins with LA. This combination of the coefficients is the origin of the peculiar [2 + 4] addition in the BF_3-promoted reaction by the use of the interrupted-line interaction.[3a] Also, the combination makes the endo cis [4 + 2] TS more favorable than the trans. That is, the [2 + 4] product formation is unrealistic, but the secondary interaction determines the orientation of [4 + 2] cycloadditions. In Scheme 2a, the role of the back CT on formation of C–C bonds is clear, but that of CT is unclear. Does CT really contribute to formation of the first (the left side) C···C bond for the LA-containing system?

Here, we need to take into account reorganization of the frontier orbitals in the precursor. The reorganization is caused by mixing of butadiene MOs with acrolein ones.[15] Since we focus our attention on LUMO of acrolein, the mixing of LUMO and the next LUMO, (LU+1)MO, of acrolein with homo of butadiene is most critical. Scheme 2b shows the reorganization. The three-body combination of LUMO, (LU+1)MO and homo leads to a (new) LUMO. At the initial stage of the reaction (i.e., formarion of the precursor), the active sites are the right-side methylene carbon of butadiene and the carbonyl carbon of acrolein (not the terminal methylene carbon). In the equation of the (new) LUMO, new LUMO = LUMO − (LU+1)MO − homo, the positive sign of LUMO means the antibonding nature between the active sites and the negative sign of (LU+1)MO does the bonding one between them. The nodal properties of LUMO and (LU+1)MO in Scheme 2b are reflected in the (new) LUMO according to the equation. The (new) LUMO has a large antibonding component at the vinyl bond of acrolein. The reorganization has made a (new) LUMO which is fit to the [4 + 2] cycloaddition of the "normal electron demand" via (new) CT. The movement of the right methylene group in Figure 11 has been brought about by the reorganization. The one-center addition TS in Figure 2 has used only left-sided overlaps of white lobes in the homo → LUMO CT. Scheme 2b has shown that the reaction progress gives rise to a correct orbital-interaction pattern for the covalent-bond formation.

Scheme 2. (a) Difference of Approaching Paths Originated from Frontier Orbital Shapes. (b) Deformation of the LUMO of Acrolein Oriented to the Diels–Alder Reaction by Orbital Mixing



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(15) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

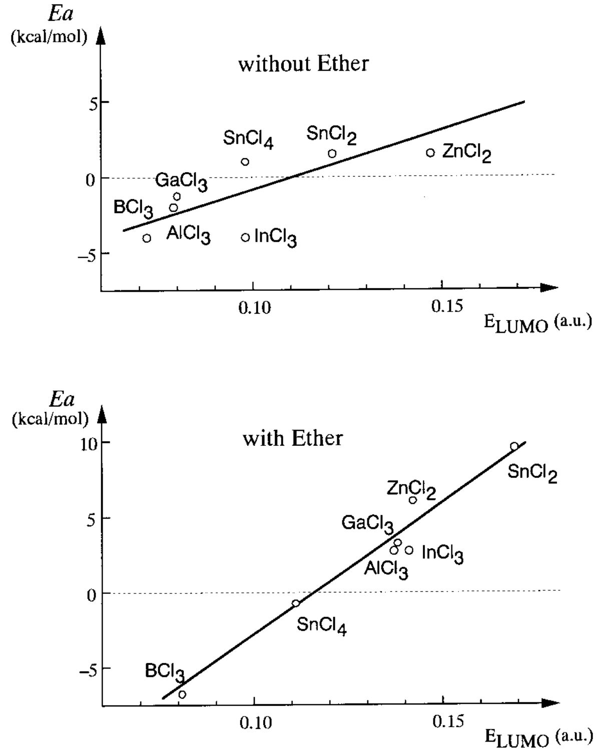

Figure 12. A Correlation between LUMO Orbital Enegies (RHF/STO-3G//RHF/3-21G, in au) of the Lewis-Acid-Catalyzed Acrolein and the Activation Energies (E_a's in kcal/mol). The E_a values are differences of B3LYP/LANL2DZ(*) SCRF//RHF/LANL2DZ(*) total energies between TSs and reactants (butadiene and acrolein coordinated by a Lewis acid without or with a dimethyl ether molecule). Those LUMO and E_a energies are taken from Table 1.

Figure 12 shows a correlation between calculated activation energies (E_a's) and LUMO energies (E_{LUMO}'s)-which are taken from Table 1. A rough linear correlation has been obtained. The correlation with ether is much clearer than without ether. BCl_3 is realized to be an extraordinarily strong Lewis acid with very low LUMO and activation energies (with ether). Except for BCl_3, $SnCl_4$ is the strongest and $SnCl_2$ is the weakest Lewis acid. The catalytic strength, as understood in organic chemistry, can be described by inclusion of the ether molecule. By the introduction of the ether molecule, E_a and E_{LUMO} values of $AlCl_3$, $GaCl_3$, $InCl_3$, and $ZnCl_2$ become similar.

$ZnCl_2$ and $SnCl_2$ are weak Lewis acids among the seven treated here. But $SnCl_2$ undergoes drastic solvation by the dimethyl ether. On the other hand, $ZnCl_2$ does not undergo much solvation. Without the ether, E_{LUMO} and E_a values of acrolein–$ZnCl_2$ are larger (0.147 au and 1.5 kcal/mol, respectively) than those of acrolein–$SnCl_2$ (0.121 au and 1.4 kcal/mol) in Table 1. With the ether, on the contrary, the values of acrolein–$ZnCl_2$–ether (0.142 au and 6.0 kcal/mol) are smaller than those of acrolein–$SnCl_2$–ether (0.169 au and 9.5 kcal/mol).

For LA = $SnCl_4$, inclusion of the ether molecule lowers the activation energy (1.0 kcal/mol → −0.8 kcal/mol). This is apparently inconsistent with the general change and the rise of LUMO energy. The octahedral form around the tin center in the butadiene–acrolein–$SnCl_4$-ether system may enhance effectively the charge donation from the carbonyl oxygen to the center in the TS. As the result, the TS is highly polarized, and the solvent molecules stabilize the TS.

VII. Concluding Remarks

This work has dealt theoretically with Diels–Alder reactions between butadiene and acrolein promoted by seven Lewis acids. The reaction has basically two channels. One is the normal [4 + 2] cycloaddition involving a transient reactant-like complex (precursor). The other has three elementary processes: a one-center addition leading to a zwitterionic intermediate, a ring-closing path to a [2 + 4] adduct, and finally a Claisen shift to the [4 + 2] product. The former channel is more favorable than the latter in most cases. The dimethyl ether molecule has been explicitly taken into account. The ether molecule does not change the geometries so much, but does enlarge the activation energies. BCl_3 is a remarkably strong Lewis acid and is desolvated from the ether molecule. An endo cis orientation of the [4 + 2] cycloaddition comes from the large lobe of the HOMO at the carbonyl oxygen for the HOMO → lumo back CT ("[2 + 4] type" secondary orbital interaction). Except for BCl_3, $SnCl_4$ is the strongest acid with the ether. $AlCl_3$, $GaCl_3$, and $InCl_3$ have similar catalytic abilities. $ZnCl_2$ and $SnCl_2$ are weak acids. In the normal [4 + 2] addition, the primary frontier orbital interaction does not correspond to the C···C bond formation, but through the orbital mixing at the precursor, the acrolein (new) LUMO becomes an active orbital for formation of two C···C covalent bonds. The back charge-transfer (HOMO → lumo) contributes to the second C···C bond formation.

Acknowledgment. We thank Mr. Tatsuo Dai and Ms. Yoko Kawaguchi for their assistance on the present calculations.

Supporting Information Available: Cartesian coordinates of optimized geometries shown in Figures 1, 2, and 4–10. This material is available free of charge via the Internet at http://pubs.acs.org.

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