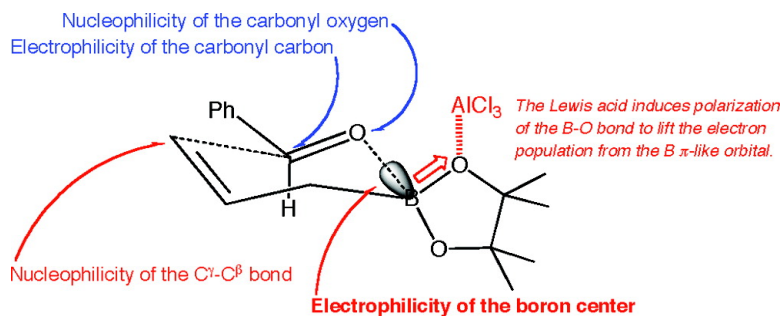


## Quantum Chemical Study of Lewis Acid Catalyzed Allylboration of Aldehydes

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## Quantum Chemical Study of Lewis Acid Catalyzed Allylboration of Aldehydes

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**Abstract:** The reaction rate enhancement in the reaction of allylboronate with benzaldehyde in the presence of  $\text{AlCl}_3$  has been studied theoretically. B3LYP calculations find a relatively high activation barrier for the reaction of pinacol allylboronate with benzaldehyde in the absence of the Lewis acid. The reaction paths that go through the transition states coordinated by an  $\text{AlCl}_3$  molecule at one of the two oxygen atoms in the boronate give significantly lower values of activation energy. An analysis of electron populations and orbitals taking part in bond formation indicates that the  $\text{AlCl}_3$  molecule attached to the boronate oxygen atom strengthens the electrophilicity of the boron center, while it weakens the nucleophilicity of the  $\text{C}^\gamma\text{--C}^\beta$  bond. The result supports the electrophilic boronate activation mechanism proposed by Rauniyar and Hall on the basis of experiments and kinetic studies. In contrast, the reaction path in which  $\text{AlCl}_3$  is coordinated to the carbonyl oxygen of benzaldehyde shows a higher activation barrier, though the initial reactant complex is more stable than those in other reaction paths. The  $\text{AlCl}_3$  molecule reduces the reactivity of aldehyde by depressing the nucleophilicity of the  $\sigma$ -type lone pair of electrons on the carbonyl oxygen, though the electrophilicity of the carbonyl  $\pi$  orbital is strengthened to some extent. The significance of charge polarization within allylboronate in enhancing the reactivity of boron by the Lewis acid is discussed.

### Introduction

The reaction of allylic organometallic reagents with carbonyl compounds is one of the most important reactions for organic synthesis.<sup>1–5</sup> In particular, the allylation reaction of allylboron reagents is extremely useful because excellent diastereoselectivity is achieved.<sup>6–8</sup> A search of allylboron reagents which provide high diastereoselectivity has been made since the 1980s, leading to a proposition that the diastereoselectivity in the reaction arises from the formation of a six-membered cyclic transition state.<sup>9–14</sup> Some theoretical investigations have also

supported the cyclic structures of the transition state.<sup>15–20</sup> Brown and co-workers investigated the effects of solvent, temperature,

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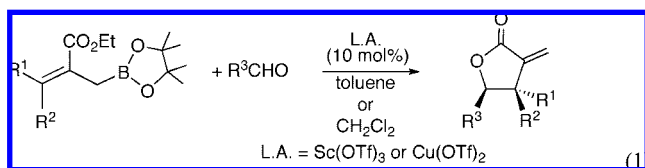
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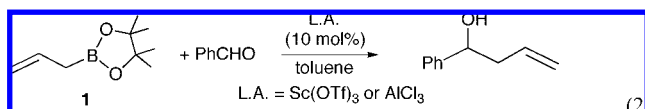
and the structure of allylborons on the rates of allylboration and suggested that the reactivity of allylborons would depend on the electrophilicity of the boron center.<sup>21</sup> Omoto and Fujimoto performed a theoretical analysis by using an *ab initio* MO method and found a good correlation between the theoretically estimated electrophilicity of the boron center and the activation energy evaluated by the *ab initio* calculations.<sup>18</sup>

Recently, the Lewis acid catalyzed activation of allylboronates was proposed.<sup>5,22–28</sup> Hall and co-workers showed a rate enhancement by a Lewis acid in the diastereospecific allylation reaction of 2-carboxyester-3,3-disubstituted allylboronates with aldehydes to afford  $\alpha$ -methylene butyrolactone.<sup>23–25</sup>

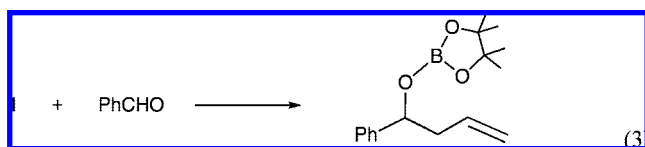


On the basis of experiments and kinetic studies, Rauniyar and Hall proposed the electrophilic boronate activation mechanism.<sup>26</sup> More recently, they have developed Brønsted acid catalysts for enantioselective allylboration.<sup>29</sup>

Miyaura and co-workers found that the reaction of pinacol allylboronate (**1**) with aldehydes is greatly accelerated by a Lewis acid such as  $\text{AlCl}_3$  and  $\text{Sc}(\text{OTf})_3$  at  $-78^\circ\text{C}$ , while the reaction does not proceed in the absence of a Lewis acid.<sup>27</sup> They showed the first example of catalytic allylboration with moderate enantioselectivity.



The reaction of **1** with benzaldehyde reported in the work by Miyaura and co-workers provides a good reaction model for our quantum chemical study of the role of Lewis acid catalysts in allylboration of aldehydes. We investigate first the path of the reaction in the absence of a Lewis acid (path (i)).



Then, three paths are suggested for the reaction in which a monomeric  $\text{AlCl}_3$  molecule is attached to one of the oxygens in **1**, denoted here by paths (ii) and (iii), and to the oxygen in the aldehyde, path (iv). We attempt to see the differences in

these reaction paths by inspecting the changes in electron populations and the orbitals that play dominant roles in electron delocalization.

**Computational Details.** The quantum chemical calculations were carried out with the *Gaussian03*<sup>30</sup> and *GAMESS*<sup>31</sup> program packages. Geometry optimization and analytical vibrational frequency analysis were performed by the B3LYP Kohn–Sham DFT method<sup>32,33</sup> with the 6-311G\*\* basis sets<sup>34</sup> (B3LYP/6-311G\*\*). The intrinsic reaction coordinate (IRC) calculations<sup>35</sup> were carried out to confirm that the obtained transition states were connected both with the reactants and with the products.

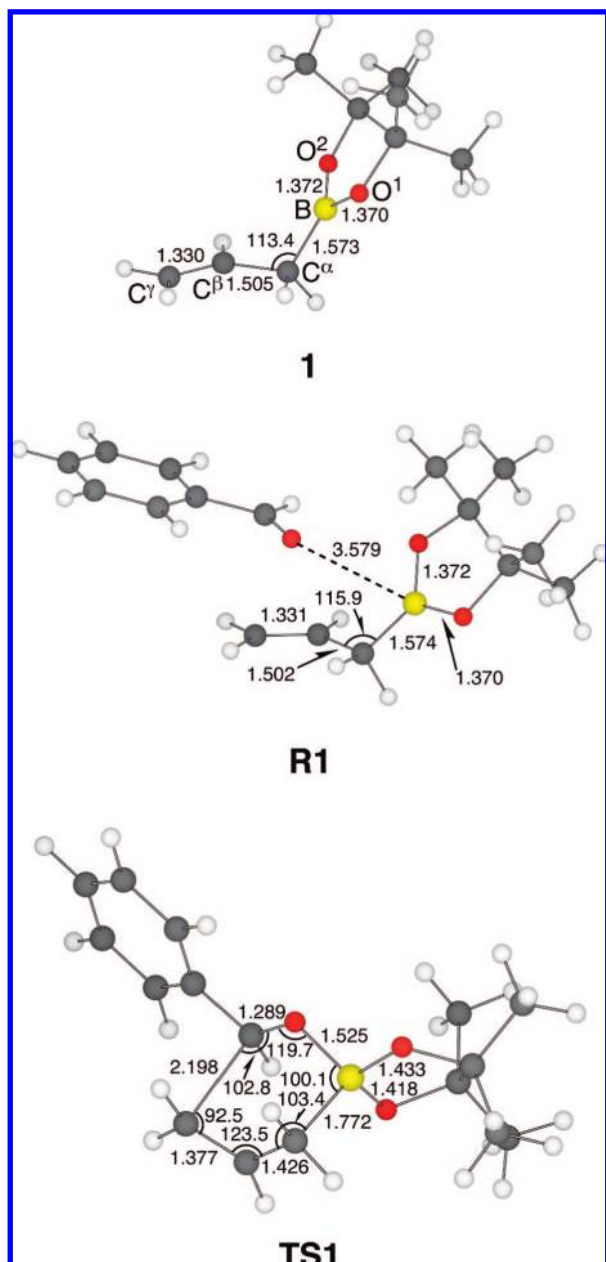
## Results and Discussion

**Structures and Energetics.** In the reaction path (i), which corresponds to the reaction between **1** and benzaldehyde in the absence of  $\text{AlCl}_3$  catalyst, a loose reactant complex **R1** has been shown to be formed, as illustrated in Figure 1. In **R1**, the distance between the boron atom in **1** and the oxygen atom in benzaldehyde is 3.579 Å. This is considerably long compared with that at the transition state, providing a very small complexation energy of 2.2 kcal/mol. The transition state, **TS1**, possesses a six-membered ring form. This result is in agreement with the previous theoretical studies.<sup>15–20</sup> The activation energy relative to the initial state (**1** + PhCHO) is +13.5 kcal/mol and the reaction is exothermic by 29.0 kcal/mol, as shown in Figure 2. The barrier height in the Gibbs free energy at 298.15 K has been calculated to be very high, being +30.1 kcal/mol. This theoretical result is in coincidence with the low reaction rates of uncatalyzed allylboration observed in experimental studies.<sup>23,27</sup>

When the reaction system includes an  $\text{AlCl}_3$  molecule as a Lewis acid catalyst, there are feasible coordination sites both in **1** and in the aldehyde. In the case of the complexation of  $\text{AlCl}_3$  with **1**, the complexes **Cx1** and **Cx2**, in which an  $\text{AlCl}_3$  molecule is attached to an oxygen atom in the boronate, have been obtained. Another complex, **Cx3**, has been located in which an  $\text{AlCl}_3$  molecule is attached to the carbonyl oxygen of benzaldehyde. Let us examine first the reaction path (ii) shown in Figure 3, in which the complex **Cx1** reacts with benzaldehyde. The coordination of  $\text{AlCl}_3$  to **1** to afford **Cx1** gives large stabilization ( $\Delta E = -24.2$  kcal/mol), as illustrated in Figure 4.

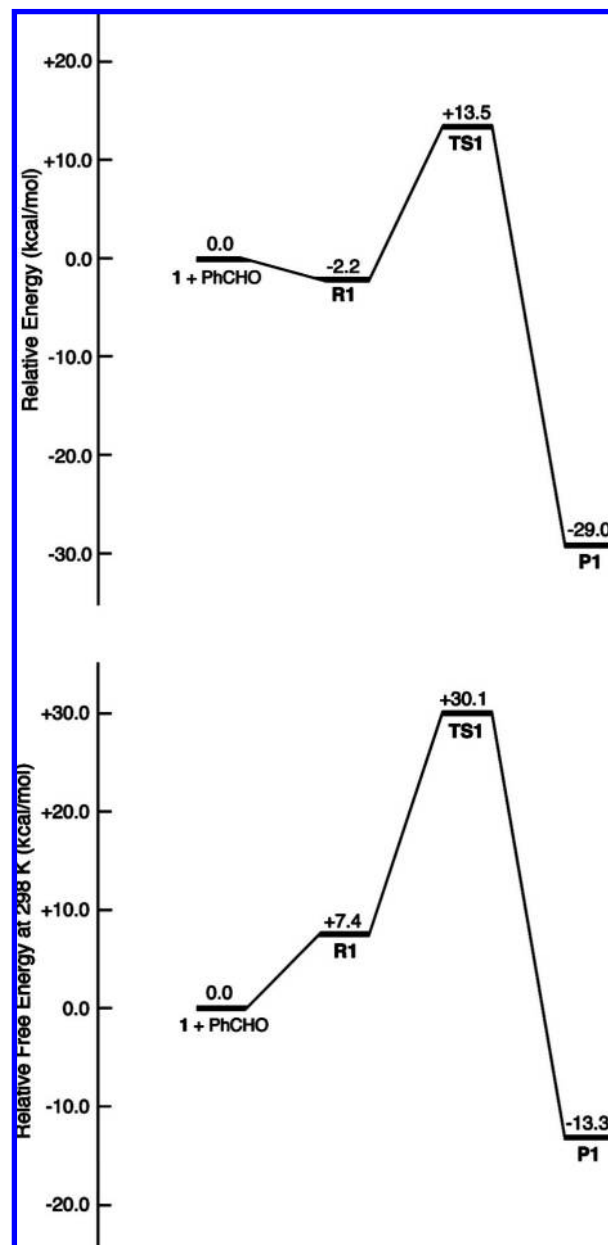
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**Figure 1.** Structures of allylboronate **1**, a reactant complex with benzaldehyde, and the transition state in path (i) optimized at the B3LYP/6-311G\*\* level of theory. Bond lengths and bond angles are given in angstroms and degrees, respectively.

In free energy, **Cx1** is more stable than the initial state (**1** +  $\text{AlCl}_3$ ) by 11.2 kcal/mol, the entropy effect being overwhelmed by the energetic stabilization. The attack of benzaldehyde to **Cx1** gives the reactant complex **R2**. In **R2**, the distance between the carbonyl oxygen and the boron atom is much shorter than that in **R1** without  $\text{AlCl}_3$ , being 1.625 Å. This suggests that electrophilicity of the boron atom is enhanced by the coordination of  $\text{AlCl}_3$ . The distance of the B–C $\alpha$  bond is 1.612 Å, which is somewhat longer than that in **Cx1** (1.562 Å). At the six-membered cyclic transition state **TS2**, the B–O(carbonyl) distance is 1.481 Å and the C $\gamma$ –C(carbonyl) distance is 2.085 Å. These bonds being newly formed in the reaction are shorter than the corresponding bonds in **TS1**. The energy of **TS2** relative to the initial state (**1** +  $\text{AlCl}_3$  + PhCHO),  $\Delta E$ , is –24.6 kcal/mol. The change in free energy,  $\Delta G$ , has been calculated to be

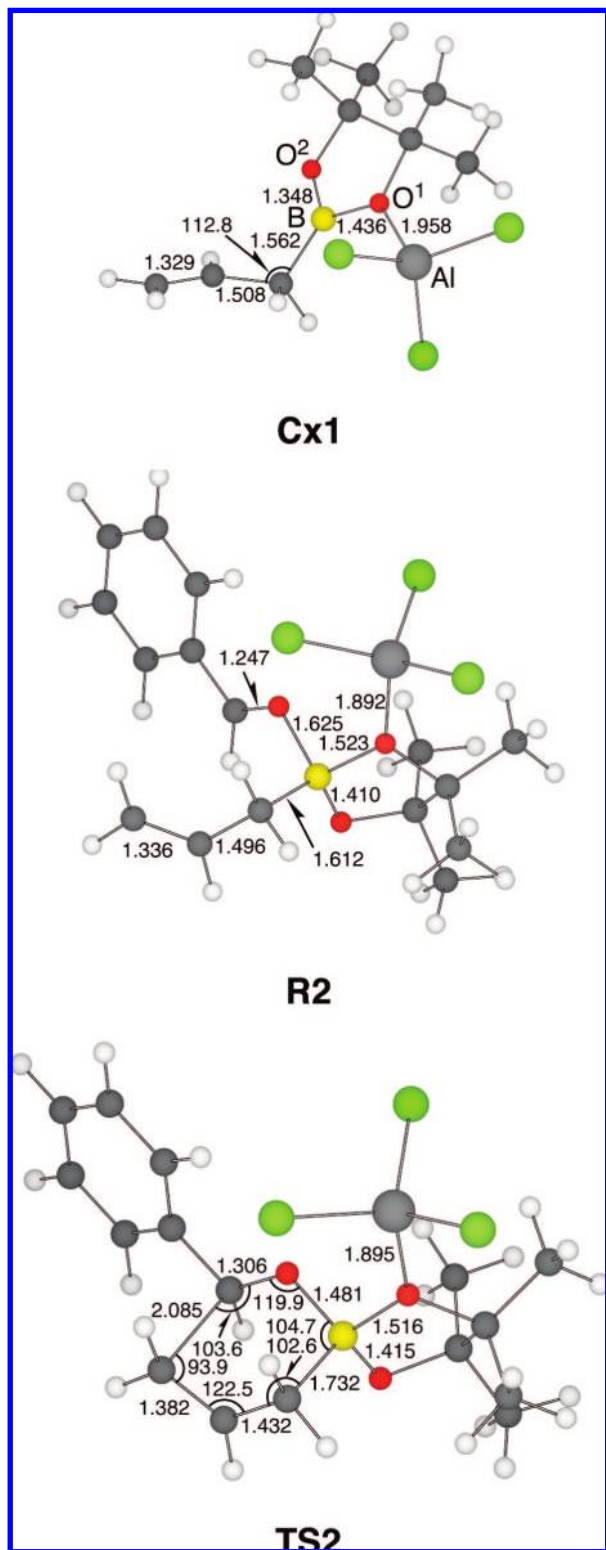


**Figure 2.** Relative energy and free energy diagrams for the reaction path (i) at the B3LYP/6-311G\*\* level of theory.

considerably small, +6.3 kcal/mol, compared with that in path (i). This result strongly suggests that the reaction along path (ii) is made facile in the presence of  $\text{AlCl}_3$ , consistent with the experimental observations by Hall and by Miyaura.<sup>23,27</sup> The relative energy and free energy for the species that appear in paths (i)–(iv) are summarized in Table 1.

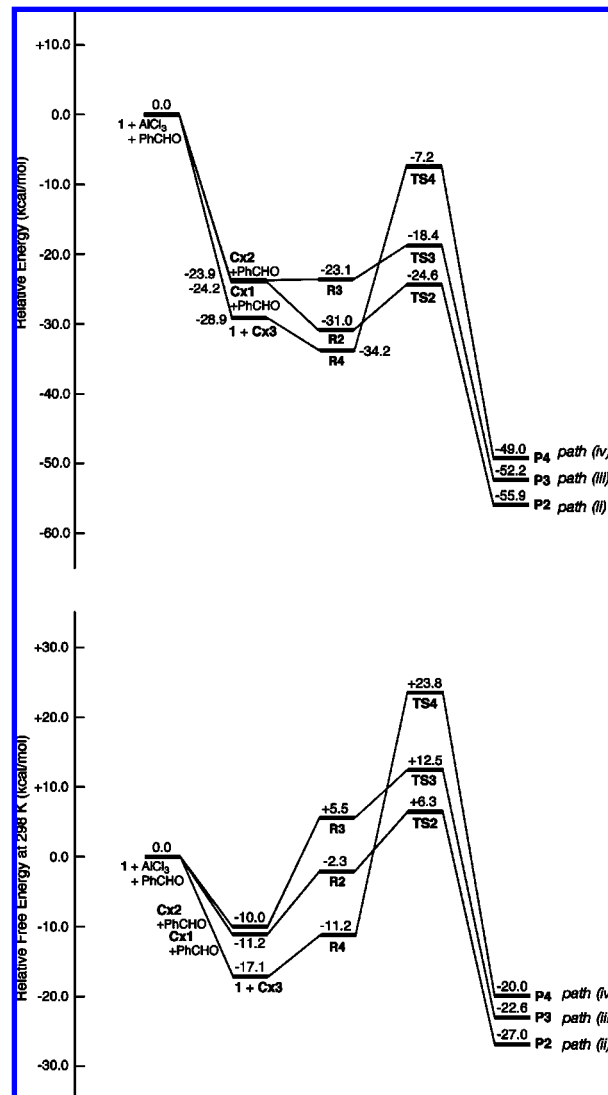
An attachment of  $\text{AlCl}_3$  to **1** affords another form of the complex, **Cx2**. Figure 4 shows that the stability of **Cx2** ( $\Delta E = -23.9$  kcal/mol) is almost the same as that of **Cx1** ( $\Delta E = -24.2$  kcal/mol). In the reaction of **Cx2** with benzaldehyde, denoted here by the reaction path (iii), the reactant complex **R3** is formed, as presented in Figure 5. This complex has been shown to be higher in energy than **R2** in path (ii) by 7.9 kcal/mol. The complexation energy in **R2** and in **R3** consists of two energy terms, the destabilization caused by the deformation of the two fragments (*DEF*), i.e., the (**1** +  $\text{AlCl}_3$ ) system and benzaldehyde, and the stabilization by the interaction between the two





**Figure 3.** Structures of **1** with an attached  $\text{AlCl}_3$  molecule, a reactant complex with benzaldehyde, and the transition state in path (ii) optimized at the B3LYP/6-311G\*\* level of theory. Bond lengths and bond angles are given in angstroms and degrees, respectively.

fragments (*INT*). As shown in Table 2, the *DEF* term in **R3** (+31.3 kcal/mol) is considerably higher than that in **R2** (+23.9 kcal/mol), while the *INT* term in **R3** (−30.5 kcal/mol) is almost the same as that in **R2** (−30.7 kcal/mol). One sees in Table 2 that the larger destabilization coming dominantly from the deformation of the (**1** +  $\text{AlCl}_3$ ) system makes **R3** less stable.



**Figure 4.** Relative energy and free energy diagrams for the  $\text{AlCl}_3$  catalyzed reaction paths (ii), (iii), and (iv) at the B3LYP/6-311G\*\* level of theory.

The calculation shows that the boron, two oxygens, and  $\text{C}^\alpha$  are placed nearly in a plane and that the  $\text{O}-\text{B}-\text{C}^\alpha-\text{C}^\beta$  dihedral angle is  $158.0^\circ$  for the oxygen with  $\text{AlCl}_3$  and  $-22.2^\circ$  for the oxygen without  $\text{AlCl}_3$  in **Cx1**. In this complex,  $\text{AlCl}_3$  is attached to the oxygen  $\text{O}^1$  which is farther away from the allyl moiety, and accordingly, the distortion in the dioxaborolane ring is not significant. This is seen in the  $\text{Al}-\text{O}^1-\text{B}-\text{O}^2$  dihedral angle of  $-179.5^\circ$ . In contrast,  $\text{AlCl}_3$  is added to the oxygen  $\text{O}^2$  which is placed closer to the allyl group in **Cx2**. Then, to avoid the repulsive interactions, the allyl group is rotated around the  $\text{B}-\text{C}^\alpha$  bond in the direction as to make the two become more separated from each other. At the same time, the dioxaborolane ring is distorted considerably from a nearly planar structure to place  $\text{AlCl}_3$  farther apart from the allyl group. The  $\text{Al}-\text{O}^2-\text{B}-\text{O}^1$  dihedral angle is now  $158.4^\circ$ . Though these two complexes are not so different in stability from each other, the attachment of benzaldehyde onto the boron center leads to a further distortion in the (**1** +  $\text{AlCl}_3$ ) system, which raises **R3** higher in energy than **R2**. The destabilization in **R3** caused by the distortion is brought into the transition state of the reaction, making **TS3** located 6.2 kcal/mol above **TS2** both in  $\Delta E$  and

**Table 1.** Relative Energy  $\Delta E$  and Relative Gibbs Free Energy  $\Delta G$  (298 K) at the B3LYP/6-311G\*\* Level of Theory (kcal/mol)

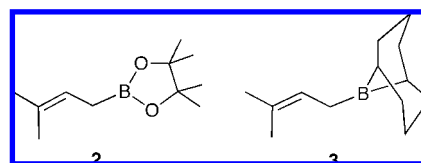
	$\Delta E$	$\Delta G$
path (i)		
<b>1</b> + PhCHO	0.0	0.0
<b>R1</b>	-2.2	+7.4
<b>TS1</b>	+13.5	+30.1
<b>P1</b>	-29.0	-13.3
path (ii)		
<b>1</b> + AlCl <sub>3</sub> + PhCHO	0.0	0.0
<b>Cx1</b> + PhCHO	-24.2	-11.2
<b>R2</b>	-31.0	-2.3
<b>TS2</b>	-24.6	+6.3
<b>P2</b>	-55.9	-27.0
path (iii)		
<b>1</b> + AlCl <sub>3</sub> + PhCHO	0.0	0.0
<b>Cx2</b> + PhCHO	-23.9	-10.0
<b>R3</b>	-23.1	+5.5
<b>TS3</b>	-18.4	+12.5
<b>P3</b>	-52.2	-22.6
path (iv)		
<b>1</b> + AlCl <sub>3</sub> + PhCHO	0.0	0.0
<b>1</b> + <b>Cx3</b>	-28.9	-17.1
<b>R4</b>	-34.2	-11.2
<b>TS4</b>	-7.2	+23.8
<b>P4</b>	-49.0	-20.0

in  $\Delta G$ . The reaction path (iii) is concluded here to be less likely in comparison with the path (ii).

An AlCl<sub>3</sub> molecule may be coordinated to the carbonyl oxygen in benzaldehyde in this reaction to afford another complex, **Cx3**, given in Figure 6. An attack of **Cx3** to **1** gives a reactant complex **R4** in the reaction path (iv). The complex **R4** has been calculated to be more stable than the complexes **R2** and **R3**. In **R4**, the distance between the carbonyl oxygen atom and the boron atom is 4.054 Å, which is longer than that in **R1** (3.579 Å), while the distance between the carbonyl carbon atom and the C<sup>γ</sup> atom is 3.318 Å, which is shorter than that in **R1** (3.598 Å). The electrophilicity of the carbonyl carbon is enhanced in this complex by the coordination of AlCl<sub>3</sub>, and therefore, the carbonyl carbon interacts more strongly with the C<sup>γ</sup>-C<sup>β</sup> bond of **1**. As a result, the distance between the carbonyl carbon and the C<sup>γ</sup> atom in **1** is much shorter in **TS4**, 1.639 Å, than that in other transition states, **TS1**, **TS2**, and **TS3**. In contrast, the distance between the carbonyl oxygen and the boron atom is much longer in **TS4**, 2.202 Å, compared with the B-O bond in other transition states. These structural differences indicate that the C<sup>γ</sup>-C(carbonyl) interaction is strengthened, whereas the B-O(carbonyl) interaction is weakened seriously by the coordination of AlCl<sub>3</sub> to the aldehyde. In fact,  $\Delta E$  and  $\Delta G$  of **TS4** are -7.2 and +23.8 kcal/mol, respectively, both being much higher than those in paths (ii) and (iii), indicating that the deactivation of the carbonyl oxygen surpasses the activation of the carbonyl carbon by AlCl<sub>3</sub>. Path (iv) is unlikely.

The obtained results demonstrate that AlCl<sub>3</sub> catalyzes the allylboration by attaching to one of the oxygen atoms in allylboronate. These results are consistent with the experimental observations by Hall and co-workers. They have shown that Sc(OTf)<sub>3</sub> accelerates allylboration of aldehydes by 3,3-dimethyl allylboronate (**2**), but no acceleration of the reaction has been observed in the case of borabicyclononane analogue (**3**).<sup>22,26</sup> Further single-point calculations at the RHF/6-311G\*\*//B3LYP/6-311G\*\* level of theory and the MP2/6-311G\*\*//B3LYP/6-311G\*\* level of theory gave the same conclusion, though

calculations at the latter level resulted in considerably lower barrier heights.<sup>36</sup>



We examined above the changes in energy and in free energy,  $\Delta E$  and  $\Delta G$ , from the initial state (**1** + PhCHO + AlCl<sub>3</sub>) for paths (ii)–(iv). It is known that AlCl<sub>3</sub> forms a dimer Al<sub>2</sub>Cl<sub>6</sub>. At the present level of theory, the dimer Al<sub>2</sub>Cl<sub>6</sub> (*D*<sub>2h</sub> form) is more stable than 2AlCl<sub>3</sub> by 20.7 kcal/mol in energy and by 8.4 kcal/mol in free energy. When we adopt (**1** + PhCHO + Al<sub>2</sub>Cl<sub>6</sub>) as the initial state of path (ii),  $\Delta E$  and  $\Delta G$  for (**TS2** + AlCl<sub>3</sub>) are calculated to be -3.9 and +14.7 kcal/mol, respectively.

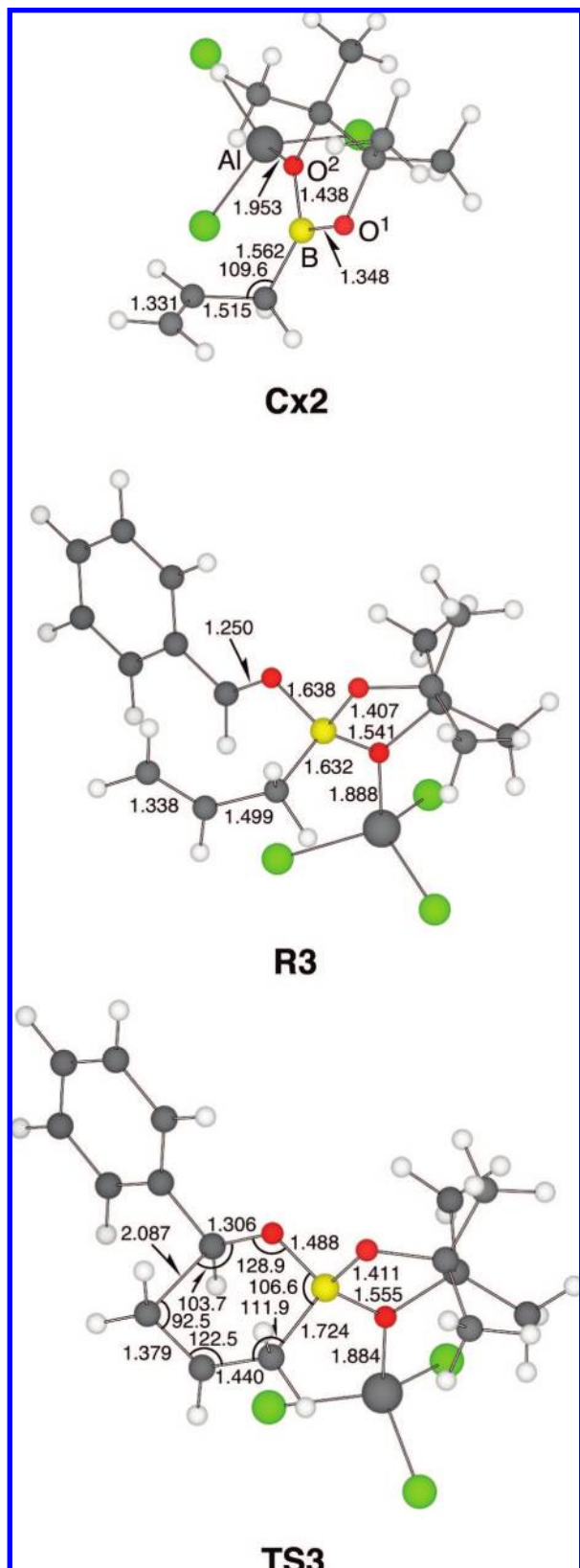
**Electron Distribution and the Role of AlCl<sub>3</sub>.** An analysis using the interaction frontier orbitals (IFOs)<sup>37,38</sup> shows that electron delocalization from benzaldehyde to the allylboronate at **TS1** is represented practically by a pair of orbitals ( $\phi'_1$ ;  $\psi'_1$ ), illustrated in Figure 7a. The orbital  $\phi'_1$  consists of the unoccupied canonical MOs of the allylboronate part, showing a large amplitude on the boron atom. The orbital  $\psi'_1$  spans the occupied subspace of the aldehyde MOs, yielding the  $\sigma$ -type orbital for the lone pair of electrons on the carbonyl oxygen. The orbitals  $\phi'_1$  and  $\psi'_1$  are located at +0.037 and -0.351 au in energy at the B3LYP/6-311G\*\* level, respectively. Electron delocalization from allylboronate to aldehyde is governed by a pair of orbitals ( $\phi'_2$ ;  $\psi'_2$ ), illustrated in Figure 7b. The orbital  $\phi'_2$  is the  $\pi$ -type bonding orbital composed of the occupied canonical MOs of allylboronate. The orbital  $\psi'_2$  is the  $\pi$  antibonding orbital localized on the C=O bond, given by a combination of the unoccupied MOs of aldehyde. The orbitals  $\phi'_2$  and  $\psi'_2$  are located at -0.221 and -0.063 au, respectively.

In **TS2**, two pairs of interacting orbitals that look very much the same as those in **TS1** have been obtained (see Supporting Information). This signifies that the reaction mechanism has scarcely been modified by the presence of the Lewis acid. The electron-accepting orbital  $\phi'_1$  is placed, however, 0.067 au lower in **TS2** than in **TS1**. The electron-accepting ability of boron has been strengthened significantly by the attachment of AlCl<sub>3</sub>. Meanwhile, the electron-donating orbital  $\psi'_1$  of aldehyde is elevated by 0.014 au in **TS2** relative to that in **TS1**. In response to the increase in acidic character of the boron, the p-character on the carbonyl oxygen has been strengthened in  $\psi'_1$ . The energy gap between the electron-donating and -accepting levels is reduced significantly in **TS2**, to facilitate electron delocalization. On the other hand, the electron-donating orbital  $\phi'_2$  of allylboronate is lowered by 0.031 au in **TS2** relative to that in **TS1**. This indicates that the electron-donating strength of the C<sup>γ</sup>-C<sup>β</sup> bond in **1** is

(36) The activation energy was calculated to be +1.7, -48.9, -39.9, and -27.6 kcal/mol for the paths (i), (ii), (iii), and (iv), respectively, at the MP2/6-311G\*\*//B3LYP/6-311G\*\* level of theory. The estimated correlation energy appears to be large in this case, referring to the experimental observation that the reaction does not occur at -78°C in the absence of the catalyst (see ref 27). The calculations at the B3PW91/6-311G\*\* level gave +10.1, -28.6, -22.4, and -11.2 kcal/mol for the paths (i), (ii), (iii), and (iv), respectively, about 4 kcal/mol lower than the value of the B3LYP/6-311G\*\* level in each case.

(37) (a) Fukui, K.; Koga, N.; Fujimoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 196–197. (b) Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* **1984**, *88*, 3539–3544.

(38) Fujimoto, H. *Acc. Chem. Res.* **1987**, *20*, 448–453.



**Figure 5.** Structures of **1** with an attached  $\text{AlCl}_3$  molecule, a reactant complex with benzaldehyde, and the transition state in path (iii) optimized at the B3LYP/6-311G\*\* level of theory. Bond lengths and bond angles are given in angstroms and degrees, respectively.

weakened by the attachment of  $\text{AlCl}_3$ , though to a smaller extent as compared with the enhancement of the electron-accepting strength of the boron center.<sup>39</sup>

**Table 2.** Complexation Energies of **R2** and **R3** at the B3LYP/6-311G\*\* Level of Theory (kcal/mol)

	<b>R2</b>	<b>R3</b>
$DEF (\text{Cxn}^a)$	+21.8	+29.0
$DEF (\text{PhCHO})$	+2.1	+2.3
$DEF (\text{Cxn}^a + \text{PhCHO})$	+23.9	+31.3
$INT^b$	-30.7	-30.5
complexation energy ( $DEF + INT$ )	-6.8	+0.8

<sup>a</sup> The  $(\mathbf{1} + \text{AlCl}_3)$  system.  $n = 1$  for **R2** and  $n = 2$  for **R3**. <sup>b</sup> BSSEs estimated by the counterpoise method are 4.2 kcal/mol in **R2** and 4.0 kcal/mol in **R3**.

The natural population analysis<sup>40</sup> indicates that the attached  $\text{AlCl}_3$  withdraws the electron population from the allylboronate **1**, but its total net charge amounts only to  $-0.133$  in the  $(\mathbf{1} + \text{AlCl}_3)$  fragment that has been frozen to the same geometry as that in **TS2**. The electron population comes not only from the boron atom but also from other atoms in the dioxaborolane ring and from the allyl group mainly through the  $\sigma$  bonds in **1**. This should be a reason why the attached Lewis acid enhances the reactivity of boron and weakens the reactivity of the  $\text{C}^\gamma\text{--C}^\beta$  bond toward the aldehyde. It is interesting to see, however, that the  $\text{O}^1$  atom to which  $\text{AlCl}_3$  is added does not lose its electron population but increases its net charge in negative value from  $-0.787$  in **1** with the geometry that is kept the same as that in **TS1** to  $-0.933$  in the  $(\mathbf{1} + \text{AlCl}_3)$  fragment with the geometry in **TS2**. This suggests that the Lewis acid has another, probably more important, role. The calculation shows that the negative charge shifted to  $\text{AlCl}_3$  from the allylboronate is stored on the three chlorine atoms, still leaving a large positive charge on the Al center. The orbital analysis, as well as a configuration analysis of the wave function,<sup>41</sup> on **Cx1** demonstrates that the  $\text{O}^1$  atom placed under the strong influence of the positive charge on Al draws the electrons in the  $p\pi$ -type orbitals back to its own atomic orbitals from the boron and also from the other oxygen,  $\text{O}^2$ .<sup>42</sup>

The same holds also for the species in the geometries at the transition states. The negative charge on  $\text{O}^1$  is enlarged by an attachment of  $\text{AlCl}_3$  in the **TS2** structure. The net charge on the boron center has been calculated to be  $+1.211$  in **1** with the geometry kept the same as that in **TS1**, but it becomes considerably larger,  $+1.300$ , in the  $(\mathbf{1} + \text{AlCl}_3)$  fragment with the geometry in **TS2**. The electron population is removed mainly from the atomic orbitals of boron that are responsible for the interaction with the aldehyde, and accordingly, the interacting orbital  $\phi'_1$  of **TS2** is lowered significantly in energy. The electron population shifted to the boron from the aldehyde carbonyl is also moved in part onto  $\text{O}^1$  to keep the boron electron-deficient

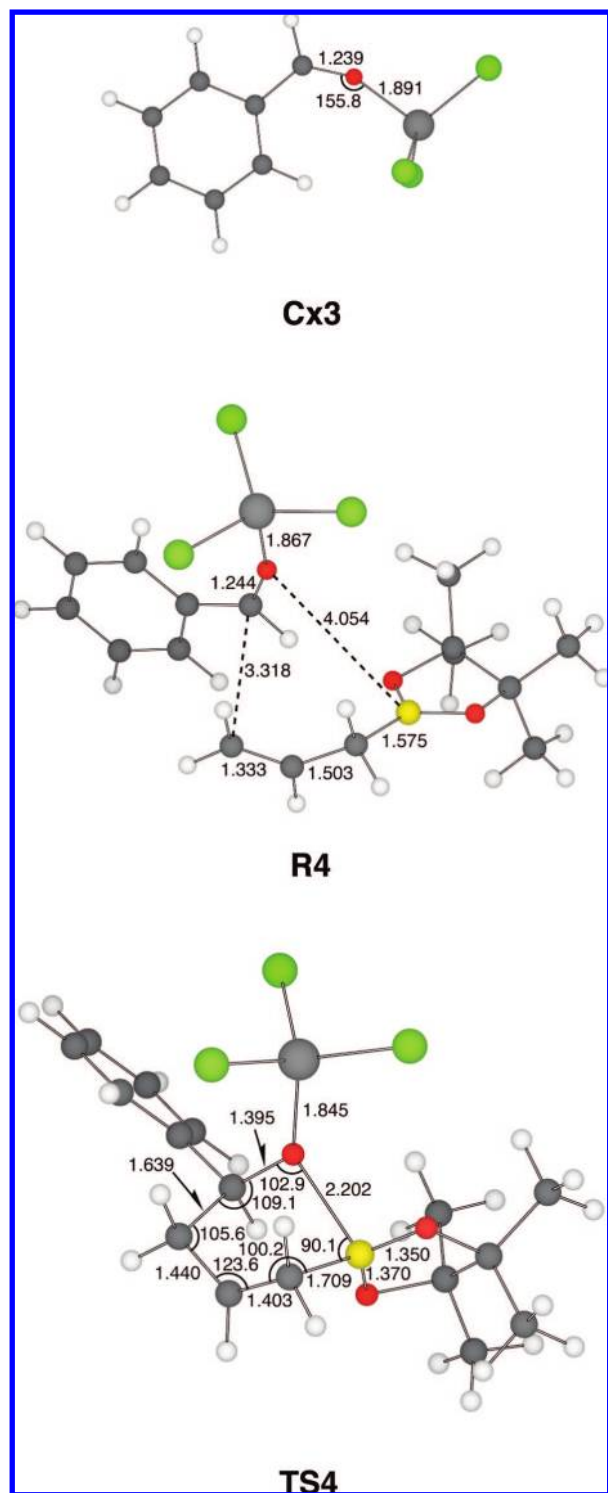
(39) The analysis at the RHF/6-311G\*\*/B3LYP/6-311G\*\* level of theory has led to the entirely same conclusion, though the energy levels of electron-donating orbitals are considerably lower and those of electron-accepting orbitals are higher than those calculated by using the B3LYP/6-311G\*\* Kohn–Sham orbitals.

(40) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(41) Fujimoto, H.; Kato, S.; Yamabe, S.; Fukui, K. *J. Chem. Phys.* **1974**, *60*, 572–578.

(42) A similar trend has also been found for  $\text{C}=\text{O}$  bonds. Houk *et al.* showed previously that the frontier orbitals of acrolein were distorted under an attack of a Lewis acid. They indicated that the frontier orbitals of protonated acrolein resembled those of an allyl cation mixed with the  $\pi$ -type lone-pair orbital on oxygen, while those of acrolein were basically slightly perturbed butadiene  $\pi$  MOs. Polarization of  $\pi$  electrons induced by the cationic field of the proton should be the important source of the observed results. See: Houk, K. N.; Strozler, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094–4096.



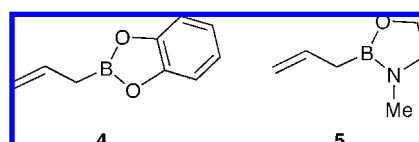


**Figure 6.** Structures of benzaldehyde with an attached  $\text{AlCl}_3$  molecule, a loose reactant complex with **1**, and the transition state in path (iv) optimized at the B3LYP/6-311G\*\* level of theory. Bond lengths and bond angles are given in angstroms and degrees, respectively.

in the reaction. It seems to be of great importance for Lewis acids to have strongly polarizable  $\text{M}-\text{X}$  bonds so that the X atoms accommodate a large part of the electronic charge shifted from the reactant to leave a positive charge on the M center when they are coordinated to the reactant. Then, the positive charge on M will induce polarization of charges within the reactant molecule to increase the acidic character of the reaction site.

Finally, we examine how **1** is activated by  $\text{AlCl}_3$ . We compare first the reactivity of boron in **1** toward benzaldehyde with that in the smallest boron compound,  $\text{BH}_3$ , as the reference. The lowest unoccupied (LU) MO (Kohn–Sham orbital) has been shown to play almost an exclusive role in electron delocalization from the aldehyde to  $\text{BH}_3$  at an early stage of interaction. The LUMO is located at  $-0.079$  au at the B3LYP/6-311G\*\* level. The projection of the renormalized boron components in the LUMO,  $\delta_r$ , onto the unoccupied MO space of  $\text{BH}_3$  yields practically the LUMO. We projected then this reference orbital onto the unoccupied orbital space of **1**.<sup>18,43</sup> The orbital has the energy expectation value,  $\lambda_{\text{unoc}}(\delta_r)$ , of 0.083 au, indicating that the boron center in **1** has an electron-accepting ability considerably weaker than that in  $\text{BH}_3$ .

For the purpose of comparison, we performed the same analysis on B-allyl-1,3,2-dioxabenzoborole, **4**, and B-allyl-3-methyl-1,3,2-oxazaborolidine, **5**, both having a five-membered ring containing the B atom, among the allylboration compounds studied experimentally by Brown and co-workers.<sup>21</sup> The  $\lambda_{\text{unoc}}(\delta_r)$  value was calculated to be 0.054 au for **4** and 0.093 au for **5**. The acidity of boron is suggested here to increase in the order **4** > **1** > **5**. The calculations of activation energy at the B3LYP/6-311G\*\* level of theory give a barrier height of 13.5 kcal/mol for **1**, 8.4 kcal/mol for **4**, and 17.7 kcal/mol for **5**, being qualitatively in agreement with the theoretically estimated acidic strength of the boron center. Compared with the compounds **1**, **4**, and **5**, the electron-accepting orbital of **Cx1** is located significantly lower, being 0.030 au. The acidic character of the boron atom in **1** has been enhanced by the withdrawal of electron population upon coordination of  $\text{AlCl}_3$  and also through the polarization induced by the positive charge on Al, though it is not yet as strong as that in  $\text{BH}_3$ .<sup>44</sup> It is seen that the difference in acidic character of the boron atom in an isolated state of these boron compounds is brought into transition states to determine the barrier height. This is partly because the  $\text{C}^\gamma-\text{C}$ (carbonyl) bonding interaction weakened in the presence of  $\text{AlCl}_3$  is balanced with the weakened overlap repulsion in that bond region, coming also from the reduced electron population on the allyl moiety.



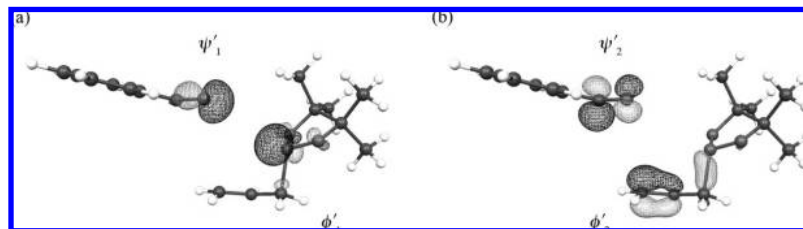
## Conclusion

We have examined in this work the Lewis acid catalyzed allylboration of benzaldehyde by using quantum chemical calculations. Reaction paths in which an  $\text{AlCl}_3$  molecule is coordinated to one of the oxygens in pinacol allylboration give considerably lower barrier heights than the path in the uncatalyzed reaction. This result is in good agreement with experimental observations by Miyaura and co-workers. The coordination of  $\text{AlCl}_3$  to the allylboration affords two forms of complexes. In one of them,  $\text{AlCl}_3$  is coordinated to the oxygen in the dioxaborolane ring located closer to the allyl group, and

(43) The reference function was taken to be equiangular from the three bonds connecting the boron atom and the adjacent atoms.

(44) The same conclusion has been derived by the use of MOs at the RHF/6-311G\*\*//B3LYP/6-311G\*\* level. The  $\lambda_{\text{unoc}}(\delta_r)$  values for **1**, **4**, **5**, **Cx1**, and  $\text{BH}_3$  have been calculated to be 0.252, 0.220, 0.256, 0.201, and 0.070 au, respectively.





**Figure 7.** Pairs of interacting orbitals of TS1, (a) ( $\phi'_1$ ;  $\psi'_1$ ) and (b) ( $\phi'_2$ ;  $\psi'_2$ ), calculated at the B3LYP/6-311G\*\* level of theory. The positive and negative regions of orbitals are discriminated by depth in black. The two fragments possess the same structures as those at the transition state, but their relative positions are held separated ensuring the two orbitals are not mixed.

in the other, the acid is attached to the oxygen placed more apart from the allyl group. They are close in stability, indicating that the basic strengths of two oxygens are similar in pinacol allylboronate. The path in which  $\text{AlCl}_3$  is coordinated to the oxygen in the dioxaborolane ring closer to the allyl group is accompanied by a stronger deformation of the allylboronate framework along the reaction course and, therefore, gives a higher energy of activation than the other path. An orbital analysis shows that the interaction between allylboronate and benzaldehyde is not modified in its nature, but electrophilicity of the boron center is strengthened in the presence of the Lewis acid. This supports the electrophilic boronate activation mechanism proposed by Rauniyar and Hall on the basis of experiments and kinetic studies. The Lewis acid attracts an electron pair of the Lewis base, an allylboronate molecule in this case. However, the principal role of  $\text{AlCl}_3$  as the catalyst manifested in this study is to polarize the B–O bond by providing a strong field of a positive charge on the Al atom onto the nearby oxygen to draw the delocalized  $\pi$ -like electrons back to the oxygen orbitals. The vacancy in the atomic orbital functions of boron

that play the dominant role in the formation of the new B–O bond with aldehyde leads naturally to a lowering of the unoccupied reactive orbital localized on that atom. In contrast, the path in which  $\text{AlCl}_3$  is coordinated to the aldehyde is not likely. Though the acid strengthens the electrophilicity of the carbonyl  $\pi$  orbital, the nucleophilicity of the lone pair of electrons of the carbonyl oxygen is reduced seriously in this path.

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**Supporting Information Available:** Tables listing energies and geometries, figures of interacting orbitals, scheme of charge polarization, and complete ref 30. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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