

# Reactions of superelectrophilic $\text{BH}_2^+$ , $\text{BCl}_2^+$ and $\text{AlCl}_2^+$ with carbonyl compounds and alkenes <sup>1</sup>

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Dedicated to commemorate the 100<sup>th</sup> birthday anniversary of late  
Professor C. D. Nenitzescu

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## Abstract

Density functional theory (DFT) method was employed to investigate the reactions of superelectrophilic  $\text{BH}_2^+$ ,  $\text{BCl}_2^+$  and  $\text{AlCl}_2^+$  with carbonyl compounds (formaldehyde, acetaldehyde) and alkenes (ethene, propene). Addition to  $\text{BH}_2^+$  with formaldehyde and acetaldehyde first give exothermically O-coordinated allylic type structures. Subsequent hydride shifts from  $\text{BH}_2$  group to the carbonyl carbon were also calculated to be exothermic. However, the processes have considerable kinetic barrier. Similar reactions of  $\text{BCl}_2^+$  and  $\text{AlCl}_2^+$  were also studied. Reactions of  $\text{BH}_2^+$ ,  $\text{BCl}_2^+$  and  $\text{AlCl}_2^+$  with alkenes (ethene, propene) were also computed and compared with the results obtained with those of formaldehyde and acetaldehyde.

**Keywords:** Superelectrophiles, carbonyl compounds, alkenes, density function theory

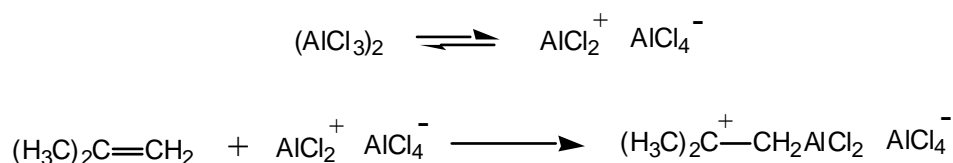
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## Introduction

The parent dicoordinate boron cation,  $\text{BH}_2^+$  is isoelectronic with the carbon analog  $\text{CH}_2^{2+}$  dication. The ion  $\text{BH}_2^+$  is readily formed in the gas phase.<sup>2,3</sup> The structures of the  $\text{BH}_2^+$  cation<sup>2-4</sup> and  $\text{CH}_2^{2+}$  dication<sup>5</sup> have been calculated by *ab initio* methods. The linear  $D_{\infty h}$  symmetrical structures were found to be preferred for both  $\text{BH}_2^+$  and  $\text{CH}_2^{2+}$ . Gas phase reactions of  $\text{BH}_2^+$  with saturated hydrocarbons by experiment and theory have also been reported.<sup>3</sup> In contrast to the reactive methyl cation, the exothermicity of the reactions with  $\text{BH}_2^+$  was found to be moderate and the energy profiles of the reactions were found to be well defined.<sup>3</sup>

Recently we reported<sup>6</sup> the calculated structures of the complexes of  $\text{CO}_2$ ,  $\text{COS}$  and  $\text{CS}_2$  with superelectrophilic<sup>7</sup>  $\text{BH}_4^+$  species.  $\text{BH}_4^+$  can be obtained in the gas phase by reacting  $\text{BH}_2^+$  and

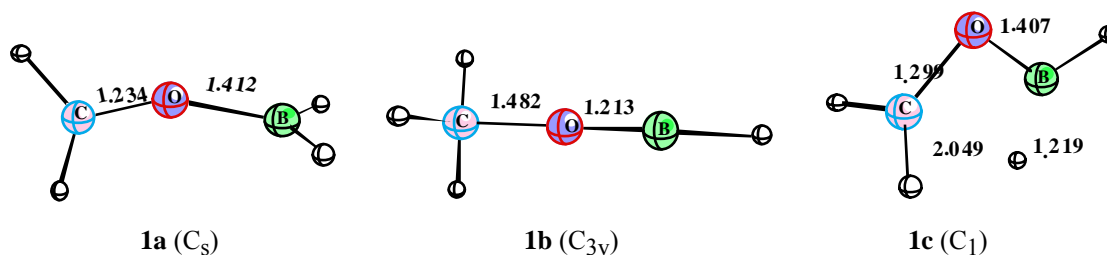
H<sub>2</sub>.<sup>2,3</sup> Complexations of CO<sub>2</sub>, COS and CS<sub>2</sub> with BH<sub>4</sub><sup>+</sup> were calculated to be exothermic in the range of 26-42 kcal/mol.<sup>6</sup> However, similar complexations of CO<sub>2</sub>, COS and CS<sub>2</sub> with neutral BH<sub>3</sub> lead to very weak complexes with long B-O or B-S bonds. It is indicated that the BH<sub>4</sub><sup>+</sup> complexes are significantly activated compared with their parents and readily undergo ionic hydrogenation.<sup>6</sup> Similar to BH<sub>4</sub><sup>+</sup>, superelectrophilic BH<sub>2</sub><sup>+</sup> also should be significantly more reactive than Lewis acidic BH<sub>3</sub>. In continuation of our work we now report investigation of the reactions of BH<sub>2</sub><sup>+</sup> with some carbonyl compounds (formaldehyde, acetaldehyde) and alkenes (ethene, propene) by the density functional theory (DFT) method. Related Brown's hydroboration of alkenes has been widely utilized in organic synthesis.<sup>8</sup> We also studied reactions of the analogous BCl<sub>2</sub><sup>+</sup> and AlCl<sub>2</sub><sup>+</sup>. In the mechanism of initiation step of aluminum chloride catalyzed alkene polymerization under aprotic conditions Olah suggested<sup>9</sup> the involvement of superelectrophilic AlCl<sub>2</sub><sup>+</sup> (**Scheme 1**). The intermediate AlCl<sub>2</sub><sup>+</sup> an analog of BCl<sub>2</sub><sup>+</sup>, can be formed by self ionization of aluminum trichloride dimer.

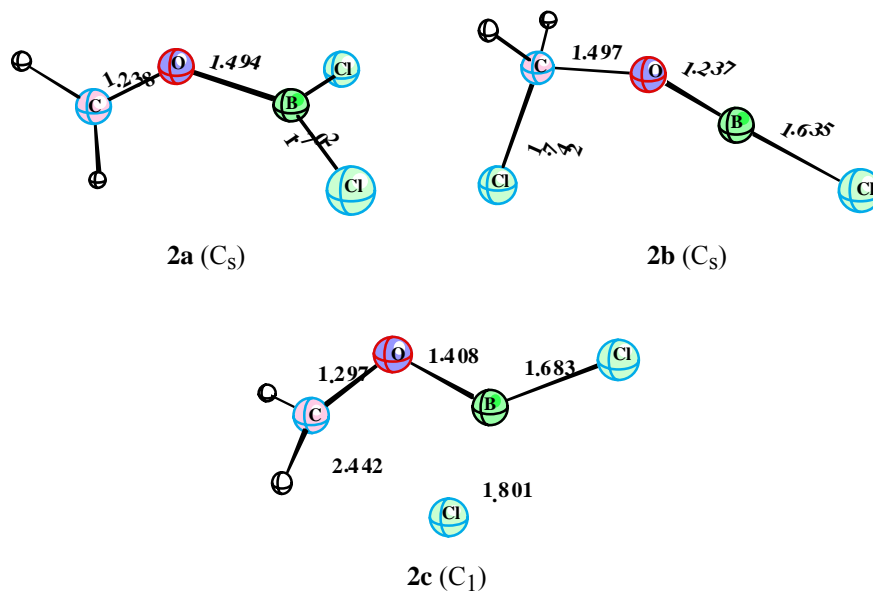


### Scheme 1

#### Calculations

Calculations were carried out with the Gaussian 98 program system.<sup>10</sup> The geometry optimizations were performed using the DFT<sup>11</sup> method at the B3LYP<sup>12</sup>/6-311+G\*\* level.<sup>13</sup> Vibrational frequencies at the B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) or transition state (NIMAG = 1) and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.96. Final energies were calculated at the B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\* + ZPE level. Calculated energies are given in Table 1. B3LYP/6-311+G\*\* geometrical parameters and final energies will be discussed throughout, unless stated otherwise.



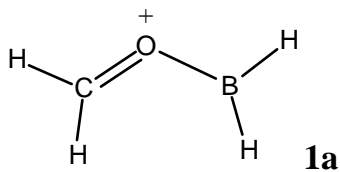


**Figure 1.** B3LYP/6-311+G\*\* structures of 1a-1c and 2a-2c.

## Results and Discussion

### Reactions of $BH_2^+$ and $BCl_2^+$ with formaldehyde

Reaction of  $BH_2^+$  with formaldehyde first leads to a O-coordinated non-planar allylic type species **1a** ( $C_s$  symmetrical) with C-O and B-O bond distances of 1.234 and 1.412 Å, respectively (**Figure 1**). Possible planar isomer as shown in **Scheme 1**, although a minimum on the potential energy surface, is 4.1 kcal/mol less stable than **1a**.



Initial adduct **1a** is more stable than the reactants  $BH_2^+$  and formaldehyde by 72.3 kcal/mol (**Table 1**). Subsequent hydride shift from the  $BH_2$  group to the carbonyl carbon leads to  $C_{3v}$  symmetrical cation **1b** (**Figure 1**). The process was calculated to be exothermic by 27.6 kcal/mol. The ion **1b** is characterized with a short B-O distance of 1.213 Å. We have located transition structure, **1c** (**Figure 1**) for the hydride transfer process which lies 24.2 kcal/mol higher in energy than **1a**. Thus **1a** has a significant kinetic barrier for hydride transfer. The nature of transition state **1c** was also checked by IRC (intrinsic reaction coordinate) calculations.<sup>10</sup>

Reaction of  $BCl_2^+$  with formaldehyde also first leads to a O-coordinated **2a** with C-O and B-O bond distances are 1.238 and 1.494 Å, respectively (**Figure 1**). Formation of **2a** from  $BCl_2^+$

and formaldehyde was computed to be exothermic by 41.3 kcal/mol. Subsequent chloride shift leads to **2b** (Figure 1). The process, however, is endothermic by 13.2 kcal/mol. Transition structure, **2c** (Figure 1) for the process lies 17.2 kcal/mol higher in energy than **2a**.

**Table 1.** Total energies (-au), ZPE<sup>a</sup> and relative energies (kcal/mol)<sup>b</sup>

no.	B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE	rel. energy (kcal/mol)
<b>1a</b>	140.30138	30.7	27.6
<b>1b</b>	140.34795	32.3	0.0
<b>1c</b>	140.26113	29.6	51.8
BH <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=O	140.17941	26.5	99.9
<b>2a</b>	1059.64810	22.3	0.0
<b>2b</b>	1059.62826	23.0	13.2
<b>2c</b>	1059.62000	21.9	17.2
BCl <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=O	1059.57810	19.7	41.3
<b>3a</b>	179.66087	47.3	13.6
<b>3b</b>	179.68550	49.2	0.0
<b>3c</b>	179.62357	46.7	36.4
BH <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=O	179.51980	43.7	98.3
<b>4a</b>	1099.00966	38.8	0.0
<b>4b</b>	1098.96802	39.4	26.7
<b>4c</b>	1098.96479	39.3	28.7
BCl <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=O	1098.91849	36.9	55.3
<b>5a</b>	104.34875	44.3	8.1
<b>5b</b>	104.36244	44.8	0.0
<b>5c</b>	104.34013	43.8	13.0
BH <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=CH <sub>2</sub>	104.25316	41.1	64.9
<b>6a</b>	1023.69373	35.9	0.0
<b>6b</b>	1023.69039	36.7	2.9
<b>6c</b>	1023.68460	35.8	5.6
BCl <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=CH <sub>2</sub>	1023.65185	34.3	24.7
<b>7a</b>	143.69565	60.5	0.0
<b>7b</b>	143.69058	61.8	4.5

**Table 1.** Continued

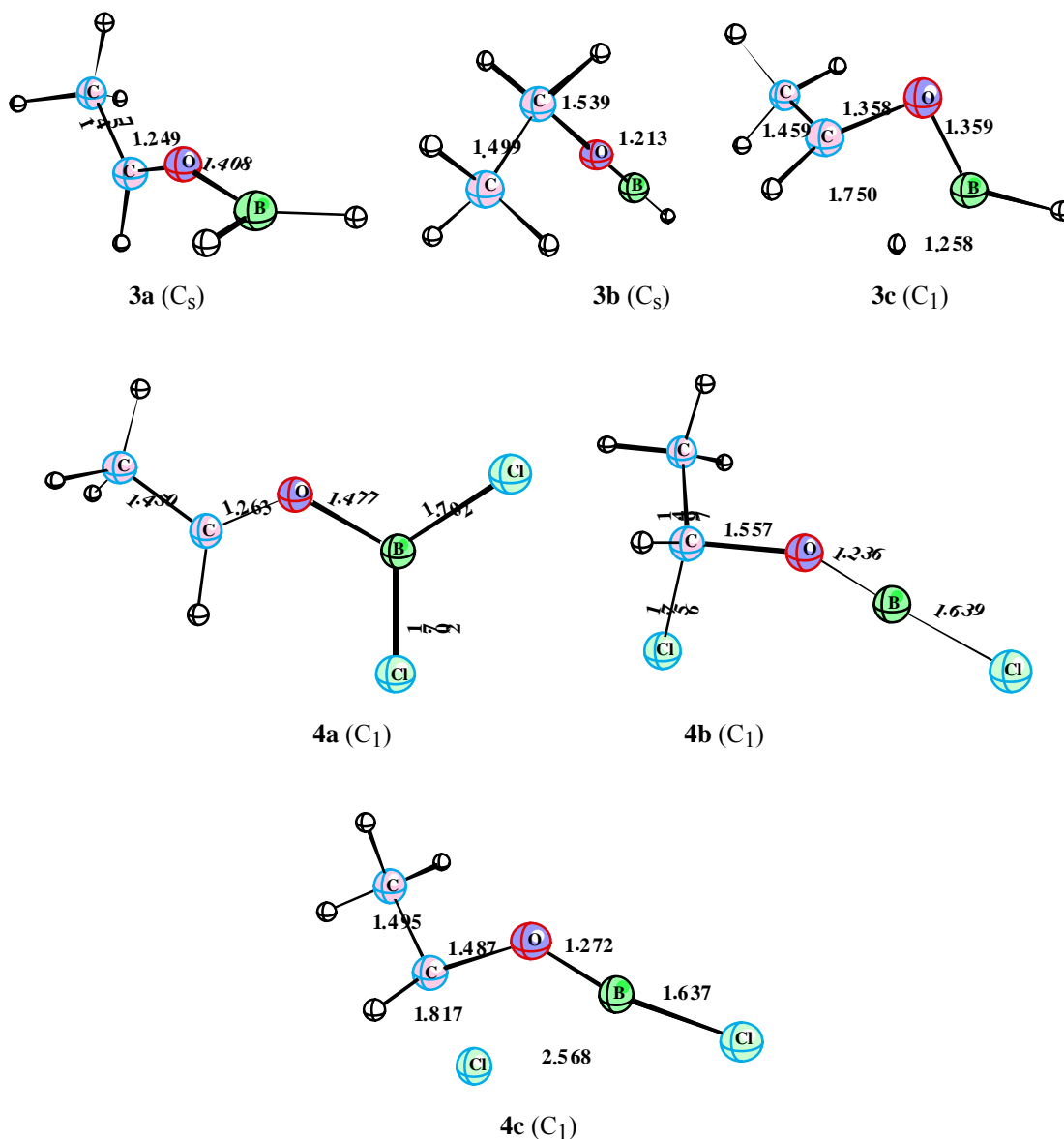
<b>7c</b>	143.68100	60.6	9.3
BH <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=CH <sub>2</sub>	143.58013	58.0	70.0
<b>8a</b>	1063.04632	52.4	0.0
BCl <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=CH <sub>2</sub>	1062.97882	51.2	41.2
<b>9a</b>	1277.33402	19.9	0.0
AlCl <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=O	1277.24917	18.0	51.4
<b>10a</b>	1316.69188	36.7	0.0
AlCl <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=O	1316.58956	35.2	62.7
<b>11a</b>	1241.38165	34.1	0.0
<b>11b</b>	1241.35461	34.7	17.6
<b>11c</b>	1241.35715	34.1	15.4
AlCl <sub>2</sub> <sup>+</sup> + H <sub>2</sub> C=CH <sub>2</sub>	1241.32292	32.6	35.4
<b>12a</b>	1280.72667	50.8	0.0
AlCl <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CH=CH <sub>2</sub>	1280.64989	49.5	46.9
H <sub>2</sub> C=O	114.54176	16.0	
CH <sub>3</sub> CH=O	153.88215	33.2	
H <sub>2</sub> C=CH <sub>2</sub>	78.61551	30.6	
CH <sub>3</sub> CH=CH <sub>2</sub>	117.94248	47.5	
BH <sub>2</sub> <sup>+</sup>	25.63765	10.5	
BCl <sub>2</sub> <sup>+</sup>	945.03634	3.7	
AlCl <sub>2</sub> <sup>+</sup>	1162.70741	2.0	

<sup>a</sup> Zero point vibrational energies (ZPE) at B3LYP/6-311+G\*\*// B3LYP/6-311+G\*\* scaled by a factor of 0.96; <sup>b</sup> rel. energies at the B3LYP/6-311+G\*\*//B3LYP/6-311+G\*\* + ZPE level.

### Reactions of BH<sub>2</sub><sup>+</sup> and BCl<sub>2</sub><sup>+</sup> with acetaldehyde

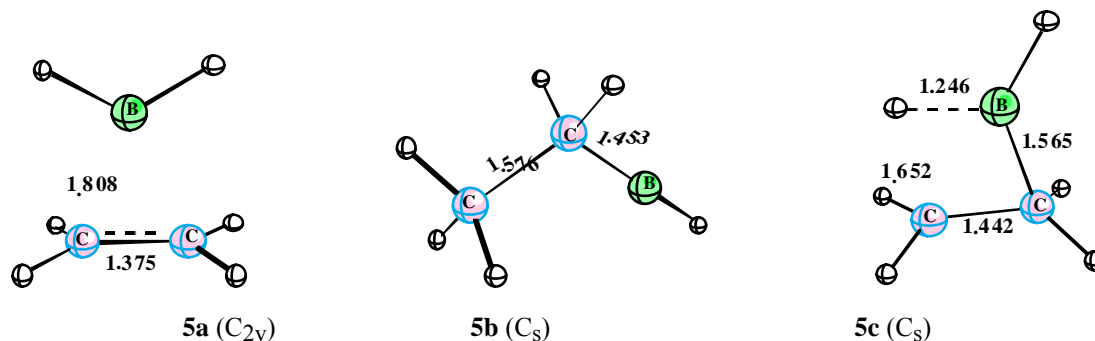
For comparison, we have also calculated the reaction of BH<sub>2</sub><sup>+</sup> with the next higher homologue acetaldehyde. Initial adduct was also found to be the allylic type structure **3a** (**Figure 2**). Formation of **3a** from BH<sub>2</sub><sup>+</sup> and acetaldehyde was computed to be exothermic by 84.7 kcal/mol. The reaction is 12.4 kcal/mol more exothermic than the reaction of BH<sub>2</sub><sup>+</sup> with acetaldehyde (**Table 1**). Hydride shift in **3a** to give **3b** was found to be exothermic by 8.1 kcal/mol. This is considerably less exothermic compared to that in **1a**. The barrier for hydride transfer in **3a**

through transition state **3c** was calculated to be 22.8 kcal/mol. Structures of **3b** and **3c** are depicted in Figure 2.



**Figure 2.** B3LYP/6-311+G\*\* structures of 3a-c and 4a-4c.

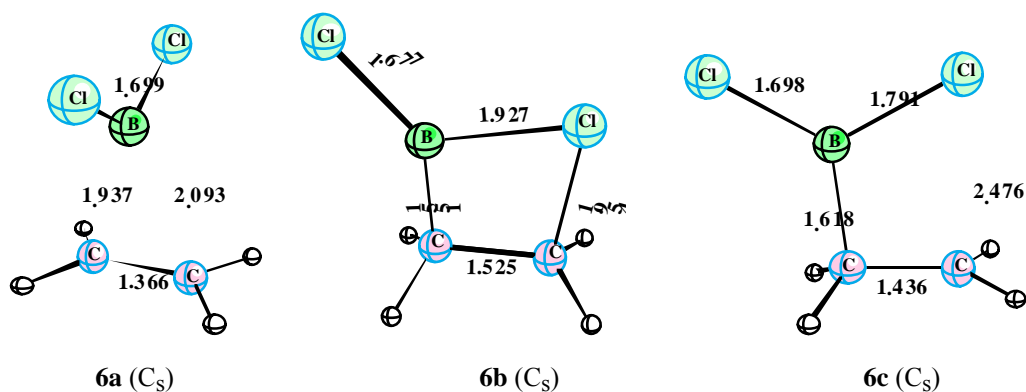
Reaction of  $BCl_2^+$  with acetaldehyde also gives the similar allylic structure **4a** (Figure 2). Chloride shift in **4a** to give **4b** was found to be endothermic by 26.7 kcal/mol and the barrier through transition state **4c** was calculated to be 28.7 kcal/mol.

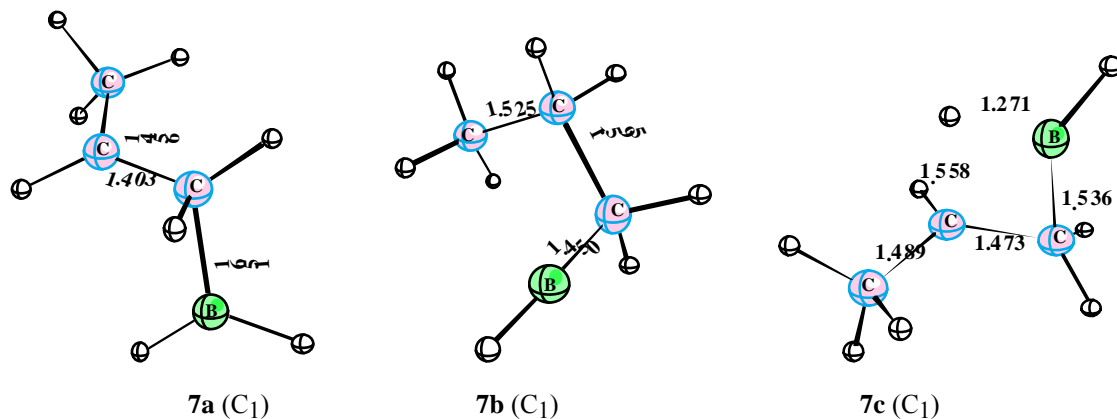


**Figure 3.** B3LYP/6-311+G\*\* structures of 5a-5c.

### Reactions of $\text{BH}_2^+$ and $\text{BCl}_2^+$ with ethene

Reaction of  $\text{BH}_2^+$  with the parent alkene, ethene resulting in a bridged  $\text{C}_{2v}$  symmetrical structure **5a** (Figure 3). Structure **5a** is characterized with a long B-C bond distance of 1.808 Å. The ion **5a** can be considered as a complex between  $\text{BH}_2^+$  and a ethene molecule attached by a three-center two-electron (3c-2e) bond involving boron atom and two carbon atoms. The reaction of  $\text{BH}_2^+$  and ethene was computed to be exothermic by 56.8 kcal/mol (Table 1). The hydride transfer reaction in the cation **5a** to give **5b** was calculated to be exothermic by only 8.1 kcal/mol. Thus thermodynamically, hydride transfer in the cation **5a** should be less favorable compared to that in the cation **1a**. Transition state **5c** for hydride transfer in **5a** was located and lies only 4.9 kcal/mol above **5a**. The 4.9 kcal/mol value is significantly less than compared to 24.2 kcal/mol calculated for **1a**. Hydride transfer in **5a**, therefore, should be facile compared to that in **1a**. In a related study Houk and co-workers have calculated the transition structures for the reactions of neutral  $\text{BH}_3$  and a number of alkenes, allenes and alkynes by *ab initio* methods.<sup>14</sup>





**Figure 4.** B3LYP/6-311+G\*\* structures of 6a-6c and 7a-7c.

Similar reaction of ethene with  $\text{BCl}_2^+$  resulting in a unsymmetrically bridged structure **6a** (Figure 4) can be considered as a complex between  $\text{BCl}_2^+$  and an ethene molecule. The reaction of  $\text{BCl}_2^+$  and ethene was computed to be exothermic only by 24.7 kcal/mol (Table 1). Attempts to find a chloride transferred minimum structure, similar to **5b**, failed because of rearrangement to form the more stable cyclic chloronium ion structure **6b**. The ion **6b** is only 2.9 kcal/mol less stable than **6a**. Transition state **6c**, connecting **6a** and **6b** was located and lies only 5.6 kcal/mol above **6a**.

#### Reactions of $\text{BH}_2^+$ and $\text{BCl}_2^+$ with propene

Unlike the reaction of  $\text{BH}_2^+$  and ethene, reaction of  $\text{BH}_2^+$  with propene gives a non-bridged unsymmetrical structure **7a** (Figure 4). In **7a** there is no bonding interaction between boron atom and carbocationic carbon. The reaction of  $\text{BH}_2^+$  with propene was computed to be exothermic by 70.0 kcal/mol (Table 1). The hydride shift in **7a** to give **7b** was found to be endothermic by 4.5 kcal/mol. Thus, based on thermodynamics hydride shift in **7a** is less favorable compared to that in the cation **5a**. Transition state **7c** for hydride transfer in **7a** was also located and lies 9.3 kcal/mol above **7a**. This value is substantially more than that calculated for **5a** (4.9 kcal/mol).

Reaction of propene and  $\text{BCl}_2^+$  results only in a minimum unbridged structure **8a**. Structure **8a** can be considered as an analog of a 1,3-carbocation. Structure of **8a** is depicted in Figure 5.



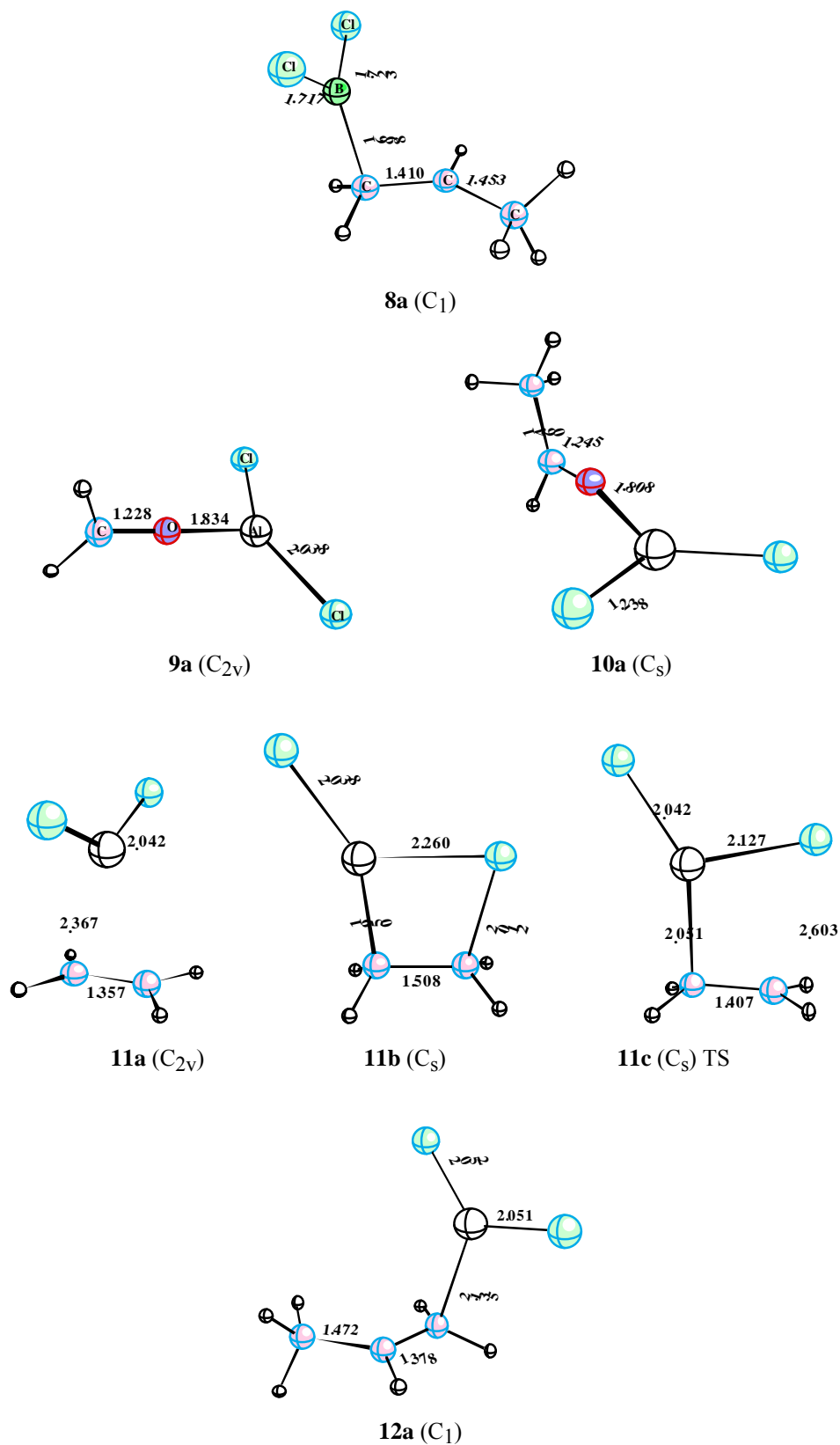


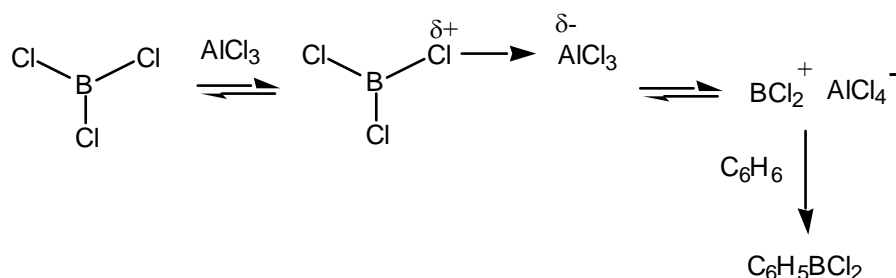
Figure 5. B3LYP/6-311+G\*\* structures of 8a – 12a.

### Reactions of $\text{AlCl}_2^+$ with formaldehyde, acetaldehyde, ethene and propene

Reactions of  $\text{AlCl}_2^+$  with formaldehyde and acetaldehyde lead to O-coordinated **9a** and **10a** (Figure 5), respectively, and they were found to be more exothermic than the corresponding reactions of  $\text{BCl}_2^+$  by 10.1 and 7.4 kcal/mol. Attempts to find chloride transferred minima failed because of rearrangement to form the more stable structures **9a** and **10a**.

Reaction of ethene with  $\text{AlCl}_2^+$  results in a symmetrically bridged structure **11a** (Figure 5). The reaction was computed to be also more exothermic than the corresponding reaction of  $\text{BCl}_2^+$  by 10.7 kcal/mol (Table 1). Attempts to find a chloride transferred minimum failed because of rearrangement to form the more stable cyclic chloronium ion structure **11b**. However, **11a** is 17.6 kcal/mol more stable than **11b**. Transition state **11c**, connecting **11a** and **11b** was located and lies 15.4 kcal/mol above **11a**. Reaction of propene and  $\text{AlCl}_2^+$  results only in a minimum unbridged structure **12a**. The structure of **12a** is depicted in Figure 5.

Superelectrophilic  $\text{BCl}_2^+$  was suggested<sup>15</sup> to be involved in the reactions of boron trichloride with benzene (and other arenes) in the presence of  $\text{AlCl}_3$  to give phenyldichloroborane.<sup>16</sup> Boron trichloride itself is only a relatively weak electrophile because of extensive n-p back-donation. When boron trichloride is dissolved in benzene no reaction takes place, however, when  $\text{AlCl}_3$  is added chloroborination takes place. Complexation with the nonbonded chlorine electron pairs activates boron trichloride resulting in the formation of highly reactive  $\text{BCl}_2^+$  (or its equivalent complexes) (Scheme 2).



### Scheme 2

The present study shows that not only  $\pi$ - but also n-donor systems interact readily with  $\text{BCl}_2^+$  (or  $\text{BH}_2^+$ ).

### Conclusions

The reactions of  $\text{BH}_2^+$ ,  $\text{BCl}_2^+$  and  $\text{AlCl}_2^+$  with carbonyl compounds (formaldehyde, acetaldehyde) and alkenes (ethene, propene) were investigated by the DFT method. Reaction of  $\text{BH}_2^+$  with formaldehyde and acetaldehyde lead to O-coordinated allylic type structures **1a** and **3a**, respectively. Both reactions were computed to be facile and strongly exothermic. Subsequent

hydride shifts from BH<sub>2</sub> group to the carbonyl carbon to give **1b** and **3b**, respectively, were also calculated to be exothermic although there is a kinetic barrier to be overcome. Similar reactions of BCl<sub>2</sub><sup>+</sup> and AlCl<sub>2</sub><sup>+</sup> with formaldehyde and acetaldehyde were also studied. Addition and subsequent hydride or chloride shift reactions of BH<sub>2</sub><sup>+</sup>, BCl<sub>2</sub><sup>+</sup> and AlCl<sub>2</sub><sup>+</sup> with ethene and propene were also calculated and compared with those of formaldehyde and acetaldehyde.

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