Reactions of superelectrophilic BH_2^+, BCl_2^+ and $AlCl_2^+$ with carbonyl compounds and alkenes [1]

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Abstract

Density functional theory (DFT) method was employed to investigate the reactions of superelectrophilic BH_2^+, BCl_2^+ and $AlCl_2^+$ with carbonyl compounds (formaldehyde, acetaldehyde) and alkenes (ethene, propene). Addition to BH_2^+ with formaldehyde and acetaldehyde first give exothermically O-coordinated allylic type structures. Subsequent hydride shifts from BH_2 group to the carbonyl carbon were also calculated to be exothermic. However, the processes have considerable kinetic barrier. Similar reactions of BCl_2^+ and $AlCl_2^+$ were also studied. Reactions of BH_2^+, BCl_2^+ and $AlCl_2^+$ with alkenes (ethene, propene) were also computed and compared with the results obtained with those of formaldehyde and acetaldehyde.
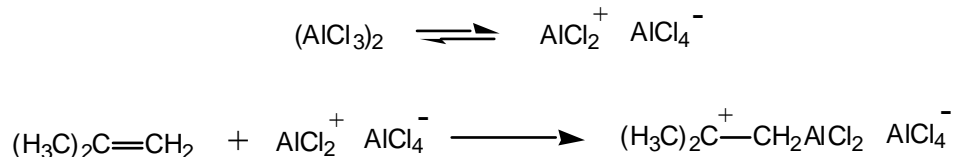
Keywords: Superelectrophiles, carbonyl compounds, alkenes, density function theory

Introduction

The parent dicoordinate boron cation, BH_2^+ is isoelectronic with the carbon analog CH_2^{2+} dication. The ion BH_2^+ is readily formed in the gas phase.[2,3] The structures of the BH_2^+ cation[2-4] and CH_2^{2+} dication[5] have been calculated by *ab initio* methods. The linear $D_{\infty h}$ symmetrical structures were found to be preferred for both BH_2^+ and CH_2^{2+}. Gas phase reactions of BH_2^+ with saturated hydrocarbons by experiment and theory have also been reported.[3] In contrast to the reactive methyl cation, the exothermicity of the reactions with BH_2^+ was found to be moderate and the energy profiles of the reactions were found to be well defined.[3]

Recently we reported[6] the calculated structures of the complexes of CO_2, COS and CS_2 with superelectrophilic[7] BH_4^+ species. BH_4^+ can be obtained in the gas phase by reacting BH_2^+ and

H_2.[2,3] Complexations of CO_2, COS and CS_2 with BH_4^+ were calculated to be exothermic in the range of 26-42 kcal/mol.[6] However, similar complexations of CO_2, COS and CS_2 with neutral BH_3 lead to very weak complexes with long B-O or B-S bonds. It is indicated that the BH_4^+ complexes are significantly activated compared with their parents and readily undergo ionic hydrogenation.[6] Similar to BH_4^+, superelectrophilic BH_2^+ also should be significantly more reactive than Lewis acidic BH_3. In continuation of our work we now report investigation of the reactions of BH_2^+ 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.[8] We also studied reactions of the analogous BCl_2^+ and $AlCl_2^+$. In the mechanism of initiation step of aluminum chloride catalyzed alkene polymerization under aprotic conditions Olah suggested[9] the involvement of superelectrophilic $AlCl_2^+$ (**Scheme 1**). The intermediate $AlCl_2^+$ an analog of BCl_2^+, can be formed by self ionization of aluminum trichloride dimer.

$$(AlCl_3)_2 \rightleftharpoons AlCl_2^+ \ AlCl_4^-$$

$$(H_3C)_2C{=}CH_2 \ + \ AlCl_2^+ \ AlCl_4^- \longrightarrow (H_3C)_2\overset{+}{C}{-}CH_2AlCl_2 \ AlCl_4^-$$

Scheme 1

Calculations

Calculations were carried out with the Gaussian 98 program system.[10] The geometry optimizations were performed using the DFT[11] method at the B3LYP[12]/6-311+G** level.[13] 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.
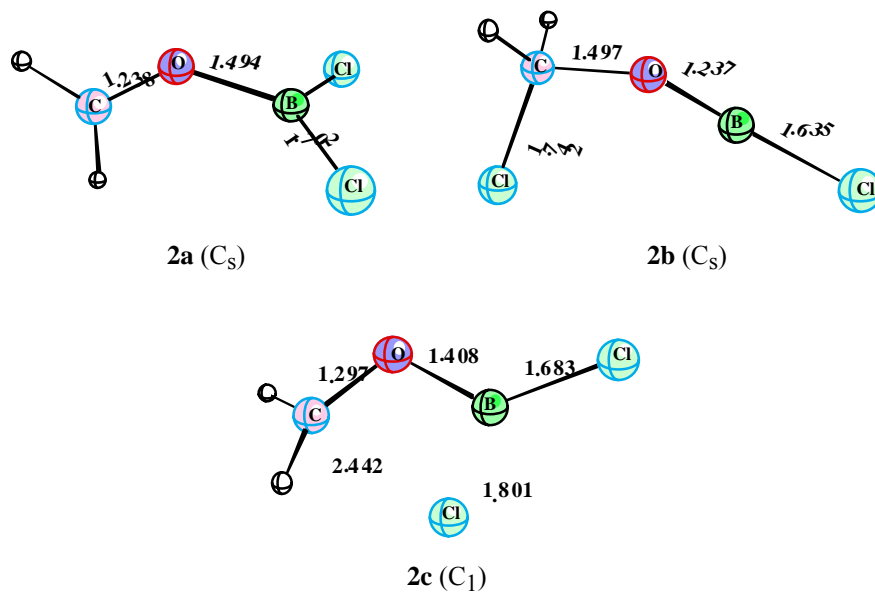

1a (C_s)   **1b** (C_{3v})   **1c** (C_1)

2a (C_S)   **2b** (C_S)

2c (C_1)
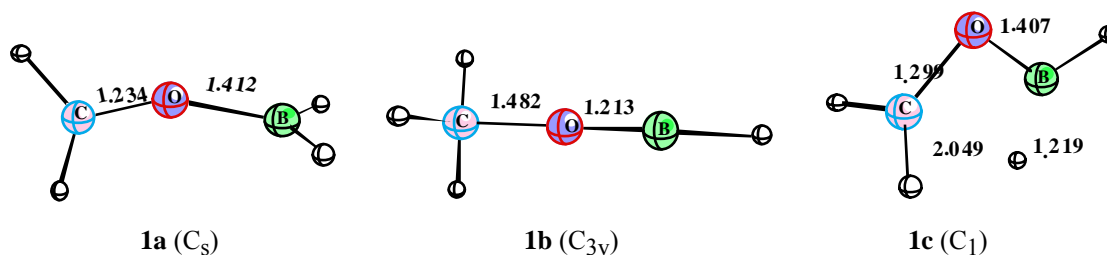
Figure 1. B3LYP/6-311+G** structures of 1a-1c and 2a-2c.

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**.
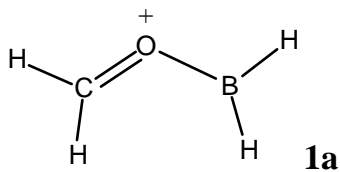
Initial adduct **1a** is more stable than the reactants BH_2^+ and formaldehyde by 72.3 kcal/mol (**Table 1**). Subsequent hydride shift from the BH_2 group to the carbonyl carbon leads to C_{3v} symmetrical cation **1b** (**Figure 1**). The process was calculated to be exothermic by 27.6 kcal/mol. The 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.[10]

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[a] and relative energies (kcal/mol)[b]

no.	B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE	rel. energy (kcal/mol)
1a	140.30138	30.7	27.6
1b	140.34795	32.3	0.0
1c	140.26113	29.6	51.8
$BH_2^+ + H_2C=O$	140.17941	26.5	99.9
2a	1059.64810	22.3	0.0
2b	1059.62826	23.0	13.2
2c	1059.62000	21.9	17.2
$BCl_2^+ + H_2C=O$	1059.57810	19.7	41.3
3a	179.66087	47.3	13.6
3b	179.68550	49.2	0.0
3c	179.62357	46.7	36.4
$BH_2^+ + CH_3CH=O$	179.51980	43.7	98.3
4a	1099.00966	38.8	0.0
4b	1098.96802	39.4	26.7
4c	1098.96479	39.3	28.7
$BCl_2^+ + CH_3CH=O$	1098.91849	36.9	55.3
5a	104.34875	44.3	8.1
5b	104.36244	44.8	0.0
5c	104.34013	43.8	13.0
$BH_2^+ + H_2C=CH_2$	104.25316	41.1	64.9
6a	1023.69373	35.9	0.0
6b	1023.69039	36.7	2.9
6c	1023.68460	35.8	5.6
$BCl_2^+ + H_2C=CH_2$	1023.65185	34.3	24.7
7a	143.69565	60.5	0.0
7b	143.69058	61.8	4.5

Table 1. Continued

7c	143.68100	60.6	9.3
$BH_2^+ + CH_3CH=CH_2$	143.58013	58.0	70.0
8a	1063.04632	52.4	0.0
$BCl_2^+ + CH_3CH=CH_2$	1062.97882	51.2	41.2
9a	1277.33402	19.9	0.0
$AlCl_2^+ + H_2C=O$	1277.24917	18.0	51.4
10a	1316.69188	36.7	0.0
$AlCl_2^+ + CH_3CH=O$	1316.58956	35.2	62.7
11a	1241.38165	34.1	0.0
11b	1241.35461	34.7	17.6
11c	1241.35715	34.1	15.4
$AlCl_2^+ + H_2C=CH_2$	1241.32292	32.6	35.4
12a	1280.72667	50.8	0.0
$AlCl_2^+ + CH_3CH=CH_2$	1280.64989	49.5	46.9
$H_2C=O$	114.54176	16.0	
$CH_3CH=O$	153.88215	33.2	
$H_2C=CH_2$	78.61551	30.6	
$CH_3CH=CH_2$	117.94248	47.5	
BH_2^+	25.63765	10.5	
BCl_2^+	945.03634	3.7	
$AlCl_2^+$	1162.70741	2.0	

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

Reactions of BH_2^+ and BCl_2^+ with acetaldehyde

For comparison, we have also calculated the reaction of BH_2^+ 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_2^+ 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_2^+ 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.
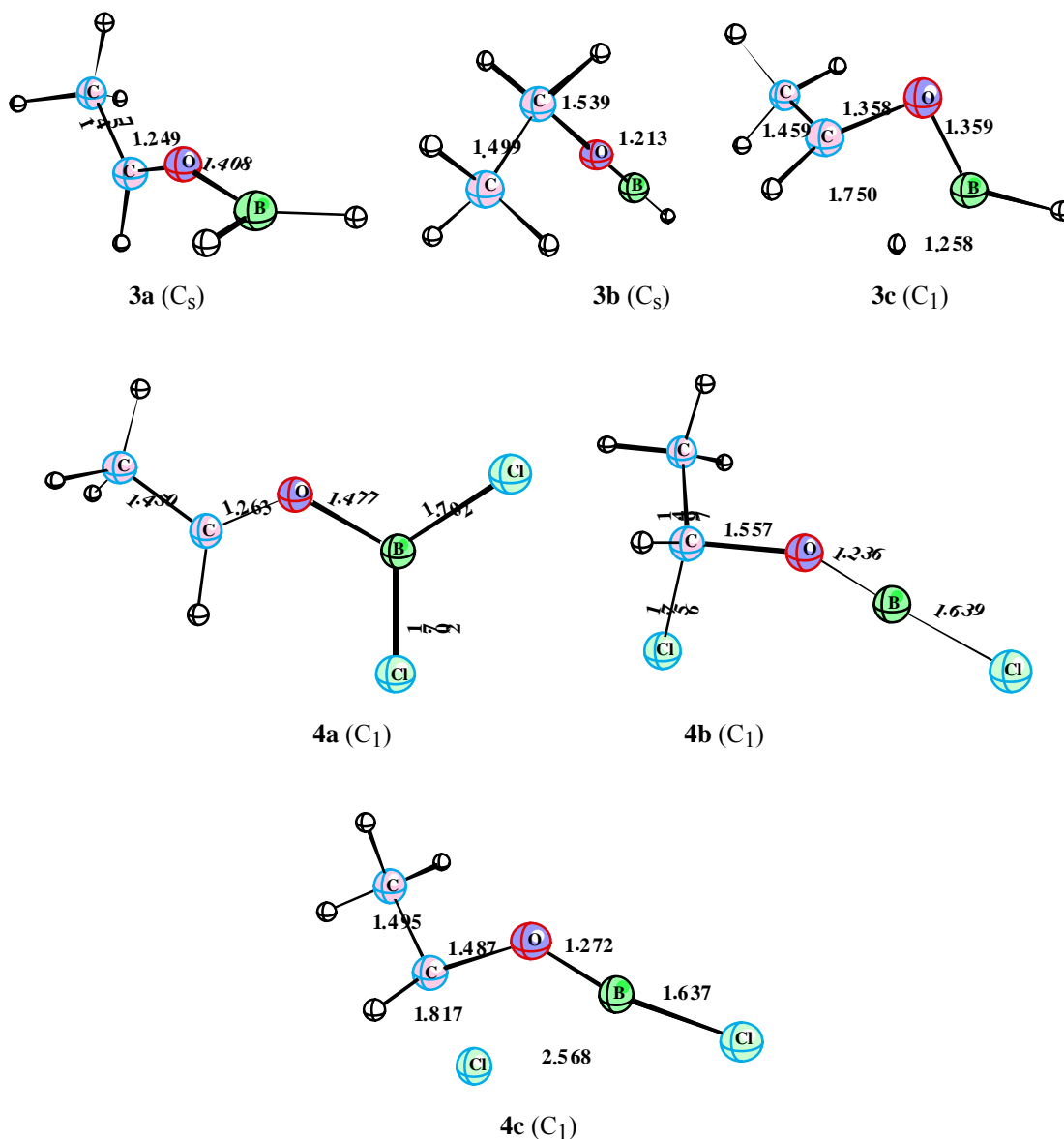

3a (C$_S$)   **3b** (C$_S$)   **3c** (C$_1$)

4a (C$_1$)   **4b** (C$_1$)

4c (C$_1$)

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 be endothermic by 26.7 kcal/mol and the barrier through transition state **4c** was calculated to be 28.7 kcal/mol.
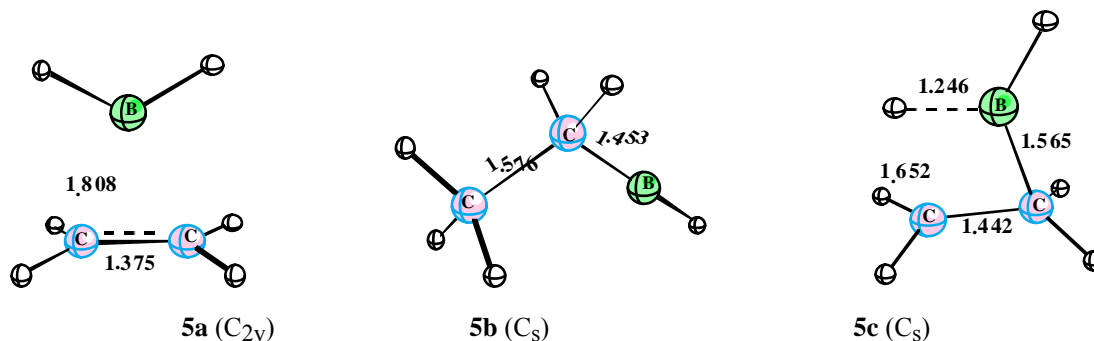
5a (C_{2v})   **5b** (C_S)   **5c** (C_S)

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

Reactions of BH_2^+ and BCl_2^+ with ethene

Reaction of BH_2^+ with the parent alkene, ethene resulting in a bridged 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 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 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 BH_3 and a number of alkenes, allenes and alkynes by *ab initio* methods.[14]
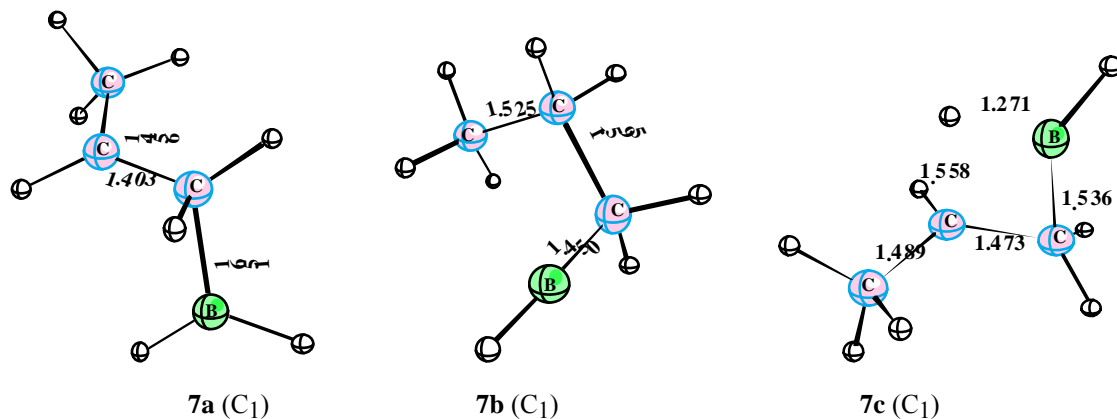

6a (C_S)   **6b** (C_S)   **6c** (C_S)

7a (C$_1$)   **7b** (C$_1$)   **7c** (C$_1$)
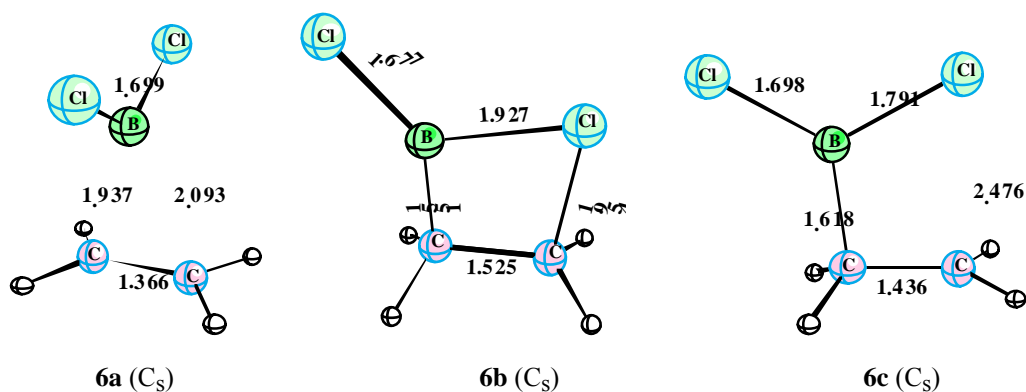
Figure 4. B3LYP/6-311+G** structures of 6a-6c and 7a-7c.

Similar reaction of ethene with BCl$_2^+$ resulting in a unsymmetrically bridged structure **6a** (**Figure 4**) can be considered as a complex between BCl$_2^+$ and an ethene molecule. The reaction of 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 BH$_2^+$ and BCl$_2^+$ with propene

Unlike the reaction of BH$_2^+$ and ethene, reaction of 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 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 BCl$_2^+$ results only in a minimum unbridged structure **8a**. Structure **8a** can be considered as an analog of a 1,3-carbodication. Structure of **8a** is depicted in Figure 5.
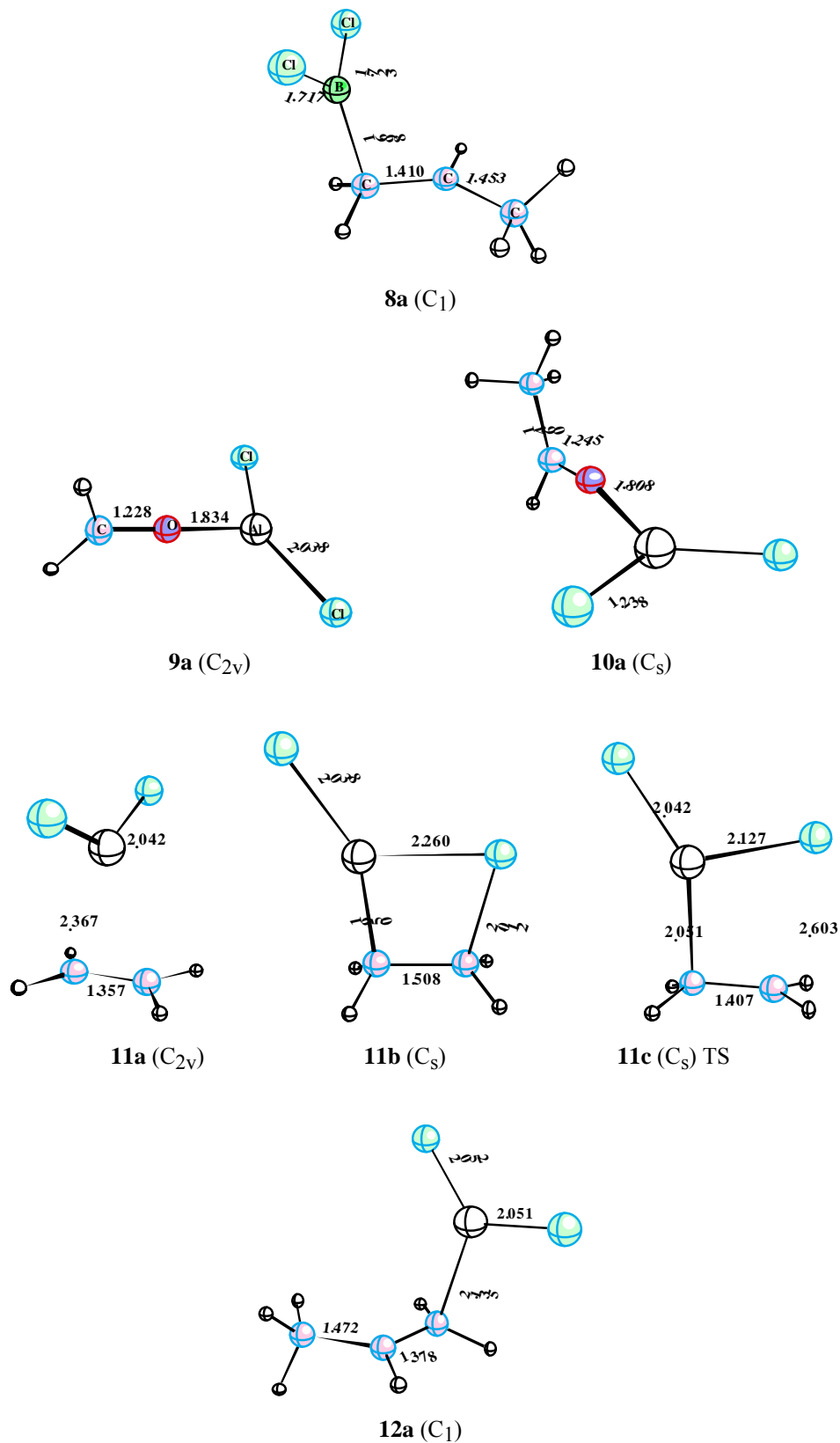
Figure 5. B3LYP/6-311+G** structures of **8a** − **12a**.

Reactions of AlCl$_2^+$ with formaldehyde, acetaldehyde, ethene and propene

Reactions of 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 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 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 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 AlCl$_2^+$ results only in a minimum unbridged structure **12a**. The structure of **12a** is depicted in Figure 5.

Superelectrophilic BCl$_2^+$ was suggested[15] to be involved in the reactions of boron trichloride with benzene (and other arenes) in the presence of AlCl$_3$ to give phenyldichloroborane.[16] 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 AlCl$_3$ is added chloroboranation takes place. Complexation with the nonbonded chlorine electron pairs activates boron trichloride resulting in the formation of highly reactive BCl$_2^+$ (or its equivalent complexes) (**Scheme 2**).
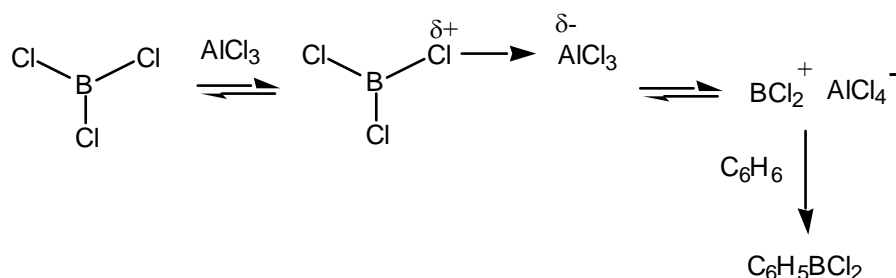
Scheme 2

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

Conclusions

The reactions of BH$_2^+$, BCl$_2^+$ and AlCl$_2^+$ with carbonyl compounds (formaldehyde, acetaldehyde) and alkenes (ethene, propene) were investigated by the DFT method. Reaction of 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_2 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_2^+ and $AlCl_2^+$ with formaldehyde and acetaldehyde were also studied. Addition and subsequent hydride or chloride shift reactions of BH_2^+, BCl_2^+ and $AlCl_2^+$ with ethene and propene were also calculated and compared with those of formaldehyde and acetaldehyde.

Acknowledgments

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