

Article

Theoretical Insight on the Formation Mechanism of a Trisubstituted Derivative of *Closo*-Decaborate Anion $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$

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Abstract: A theoretical modelling of the interaction process between a protonated complex of carboxonium derivative $[2,6-B_{10}H_8O_2CCH_3 \cdot H^{fac}]^0$ and acetonitrile molecule CH_3CN was carried out. As a result of the process, a trisubstituted $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ derivative was formed. This reaction has an electrophile-induced nucleophilic substitution (EINS) mechanism. The main intermediates and transition states of the substitution process were established. As in the case of all previously investigated EINS processes, the key intermediate was an anion with a dihydrogen H_2 fragment attached to one boron atom ($B(H_2)$ structure motif). The process of nucleophilic substitution can proceed on a different position of the cluster cage. The main potential pathways were assessed. It was established that substitution on the B_4 position of the cluster cage was the most energetically favourable, and the $[2,4,6-B_{10}H_7O_2CCH_3(NCCH_3)]^0$ isomer was formed.

Keywords: EINS; molecular mechanism; *closo*-borate anions; boron clusters; DFT



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1. Introduction

Closo-borate anions $[B_nH_n]^{2-}$ $n = 6-12$ are versatile building blocks for creating molecular platforms, with a plethora of useful applications in medicine, electrochemistry, magnetic materials, etc. [1–5]. The main approach for the formation of such platforms is the process of the substitution of a hydrogen atom to create different *exo*-polyhedral substituents [6–10]. Thus, investigation of the substitution process in *closo*-borate anions is one of the central cornerstones of modern chemistry in relation to boron clusters [11–14].

The process of substitution of *exo*-polyhedral hydrogen atoms can be achieved by different mechanisms, such as nucleophilic, electrophilic and radical substitution of *exo*-polyhedral hydrogen atoms [15–20]. To date, the most commonly investigated mechanism has been electrophile-induced nucleophilic substitution (EINS) [21–23]. Various classes of organic molecules, such as ethers, esters and nitriles, can act as nucleophiles in EINS processes [23–25]. Brønsted and Lewis acids can act as an electrophile inducer [26,27]. For *closo*-decaborate anions, the most common inducers are CF_3COOH and CF_3SO_3H . The mechanism of the EINS process has been described in detail in several articles [28–30]. This process involves several steps. The first step is the protonation of the boron cluster, with the formation of $[B_nH_n(H^{fac})]^-$. Depending on the nature of the cluster, the proton can be localised on one facet, or it can transfer through one of the equatorial belts. In the next step,

H^{fac} migrates with the formation of a key intermediate with the general form $[B_nH_{n-1}H_2]^-$. In the following step, a H_2 molecule is eliminated and a $[B_nH_{n-1}]^-$ intermediate is formed. In this intermediate, one of the boron atoms has a vacant orbital, which makes this intermediate highly reactive. In the final step, this intermediate interacts with a molecule of the nucleophile Nu, with the formation of the target product $[B_nH_{n-1}Nu]^-$.

Depending on the type of electrophile inducer and nucleophile molecule, it is possible to vary the degree of substitution introduced into the boron cluster cage. The introduction of several substituents to the cluster cage allows one to design multifunctional borylated platforms. Previously, several disubstituted derivatives of *closo*-borate anions have been investigated. Disubstituted oxonium and nitrilium derivative were obtained on the basis of interactions between *closo*-decaborate anions $[B_{10}H_{10}]^{2-}$ and ethers or nitriles, in the presence of trifluoromethanic acid CF_3SO_3H as an electrophile inducer [31,32].

Is it possible to obtain a trisubstituted product on the basis of the EINS process? To answer this question, it was decided to focus on carboxonium derivatives of *closo*-borate anions with the general form $[B_{10}H_8O_2CR]^-$. The given type of anions is disubstituted and have a total charge equal to -1 . Thus, it is possible to introduce an additional isomer to these systems on the basis of the EINS process. Currently, these derivatives are actively studied and can be obtained on the basis of the interaction between $[B_{10}H_{11}]^-$ and carboxylic acid [33]. The mechanism of formation of a disubstituted derivative was established on the basis of the formation of $[B_{10}H_8O_2CC_6H_5]^-$ [34]. This process involves the EINS mechanism and goes through the formation of $[B_{10}H_9H_2]^-$. After H_2 elimination, a monosubstituted derivative of the general form $[B_{10}H_9OC(OH)R]^-$ is formed. This derivative undergoes intermolecular cyclisation and finally $[B_{10}H_8O_2CC_6H_5]^-$ is formed. In addition, the process of protonation of $[B_{10}H_8O_2CCH_3]^-$ was investigated [35]. Trifluoromethansulphonic acid, CF_3SO_3H , was used as an electrophile inducer. In contrast to the unsubstituted $[B_{10}H_{11}]^-$ anion, in the case of $[2,6-B_{10}H_8O_2CCH_3 \cdot H^{fac}]^0$, the additional proton did not migrate along the equatorial belt and was localised on the boron cage facet opposite the B atoms associated with the *exo*-polyhedral substitution.

Thus, in the present study, the DFT modelling of the interaction between $[2,6-B_{10}H_8O_2CCH_3 \cdot H^{fac}]^0$ and a molecule of acetonitrile CH_3CN was performed. As a result of the given process, a trisubstituted $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ derivative was formed. Such a derivative was chosen due to its wide range of possibilities for further modification. The nitrilium group attached to the boron cluster moiety can react with various nucleophiles. The $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ derivative can be applied for the formation of a molecular platform with specific properties.

2. Results and Discussion

The *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ has two types of boron atom: apical and equatorial. When an additional substituent is introduced into the cluster cage, the equatorial atoms become nonequivalent. Substitution of the *exo*-polyhedral hydrogen atom can be carried out at different positions of the cluster cage. Thus, in the course of this work, different pathways of the substitution process were calculated. In addition, a comparison of the process of substitution of the hydrogen atom in $[B_{10}H_8O_2CCH_3(H^{fac})]^0$ and for the unsubstituted $[B_{10}H_{11}]^-$ species was carried out. Optimisation of geometries and calculation of Hessian matrices were carried out at the wB97X-D3/def2-TZVPP level. In addition, for a more accurate evaluation of energetic parameters for all equilibria geometries, single-point DLPNO-CCSDT/cc-pvdz calculations were performed. All calculations were performed in dichloromethane CH_2Cl_2 media, in order to approximate the conditions of theoretical modelling to the real experimental conditions. Dichloromethane was chosen as the solvent, since it does not react with the *closo*-borate anions and the results obtained in this work can be used for comparison with other types of nucleophiles.

As stated in the authors' previous work [35], in the most stable isomer of $[B_{10}H_8O_2CCH_3(H^{fac})]^0$ an additional proton, H^{fac} , is localised on the facet opposite the substituted boron atom. H^{fac} attaches mainly to the apical boron atom and the B_3 equatorial boron atom

(Figure 1). Thus, this isomer of $[B_{10}H_8O_2CCH_3(H^{fac})]^0$ was considered in the present work and was chosen as the starting point for mechanism calculation. The sum of the energy of $[B_{10}H_8O_2CCH_3(H^{fac})]^0$ and CH_3CN was accepted as the reference point and the relative Gibbs energy was equal to 0 kJ/mol.

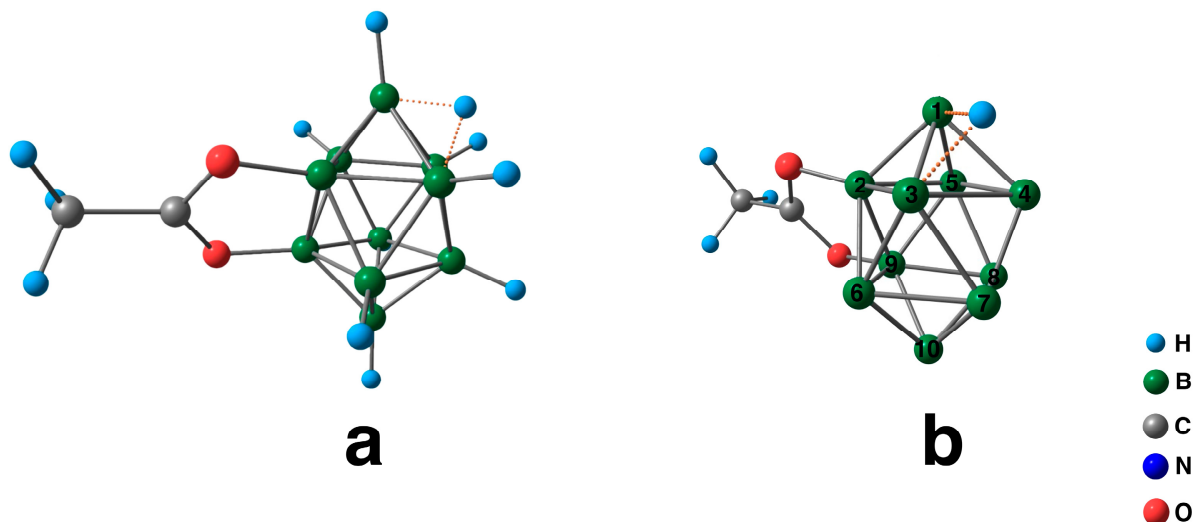


Figure 1. (a) Optimised structure of $[B_{10}H_8O_2CCH_3(H^{fac})]^0$. (b) Atomic number order in $[B_{10}H_8O_2CCH_3(H^{fac})]^0$. *Exo*-polyhedral atoms of hydrogen were omitted for clarity. Interactions between boron atoms and H^{fac} are marked with orange dotted lines.

The first step of nucleophilic substitution in $[B_{10}H_8O_2CCH_3(H^{fac})]^-$ is proton migration, with the formation of $[B_{10}H_7O_2CCH_3(H_2)]^-$. The process of proton migration occurred through the formation of a transition state, as in the case of anion $[B_{10}H_{11}]^-$ [28,34]. H^{fac} can migrate to three different boron atoms: two equatorial boron atoms and one apical boron atom. Thus, three possible pathways of proton migration are possible (TS_{migr-B_1} , TS_{migr-B_3} , TS_{migr-B_4}). The geometric parameters for all transition states are similar. The main structure feature is the coordination of two hydrogen atoms to one boron atom (Figure 2). The B-H bond distance was in the range of 1.22–1.23 Å for all isomers. The distance between the two hydrogen atoms was equal to 1.13 Å in the case of TS_{migr-B_3} equatorial isomers, 1.16 Å in case of TS_{migr-B_4} and 1.21 Å in case of TS_{migr-B_1} . However, the transition states had energy differences. The transition state in which the proton migrates to the B4 boron atom (TS_{elim-B_4}) had the lowest energy barrier (33.1 kJ/mol for wB97X-D3/def2-TZVPP and 43.6 kJ/mol for DLPNO-CCSDT/cc-pvdz). For the TS_{migr-B_3} transition state, the energy barrier was equal to 38.6 kJ/mol (wB97X-D3/def2-TZVPP) or 48.2 kJ/mol (DLPNO-CCSDT/cc-pvdz). The TS_{elim-B_1} transition state in which the proton migrates to the apical boron atom had the highest energy barrier (46.6 kJ/mol for wB97X-D3/def2-TZVPP and 53.7 kJ/mol for DLPNO-CCSDT/cc-pvdz). Thus, analysing the energy profiles of possible pathways, one can conclude that the migration of hydrogen to the B4 atom was the most probable. It is noteworthy that, in the case of the $[B_{10}H_{11}]^-$ anion, the transition state energy barriers were higher than with the carboxonium derivative $[B_{10}H_8O_2CCH_3(H^{fac})]^0$. If the proton migrated to the equatorial boron atom ($B_{10_TS_{migr_eq}}$), the energy barrier was equal to 59.1 kJ/mol for wB97X-D3/def2-TZVPP or 68.2 kJ/mol for DLPNO-CCSDT/cc-pvdz. In the case of migration to an apical position ($B_{10_TS_{migr_ap}}$), the energy barrier was equal to 49.1 kJ/mol for wB97X-D3/def2-TZVPP or 57.2 kJ/mol for DLPNO-CCSDT/cc-pvdz.

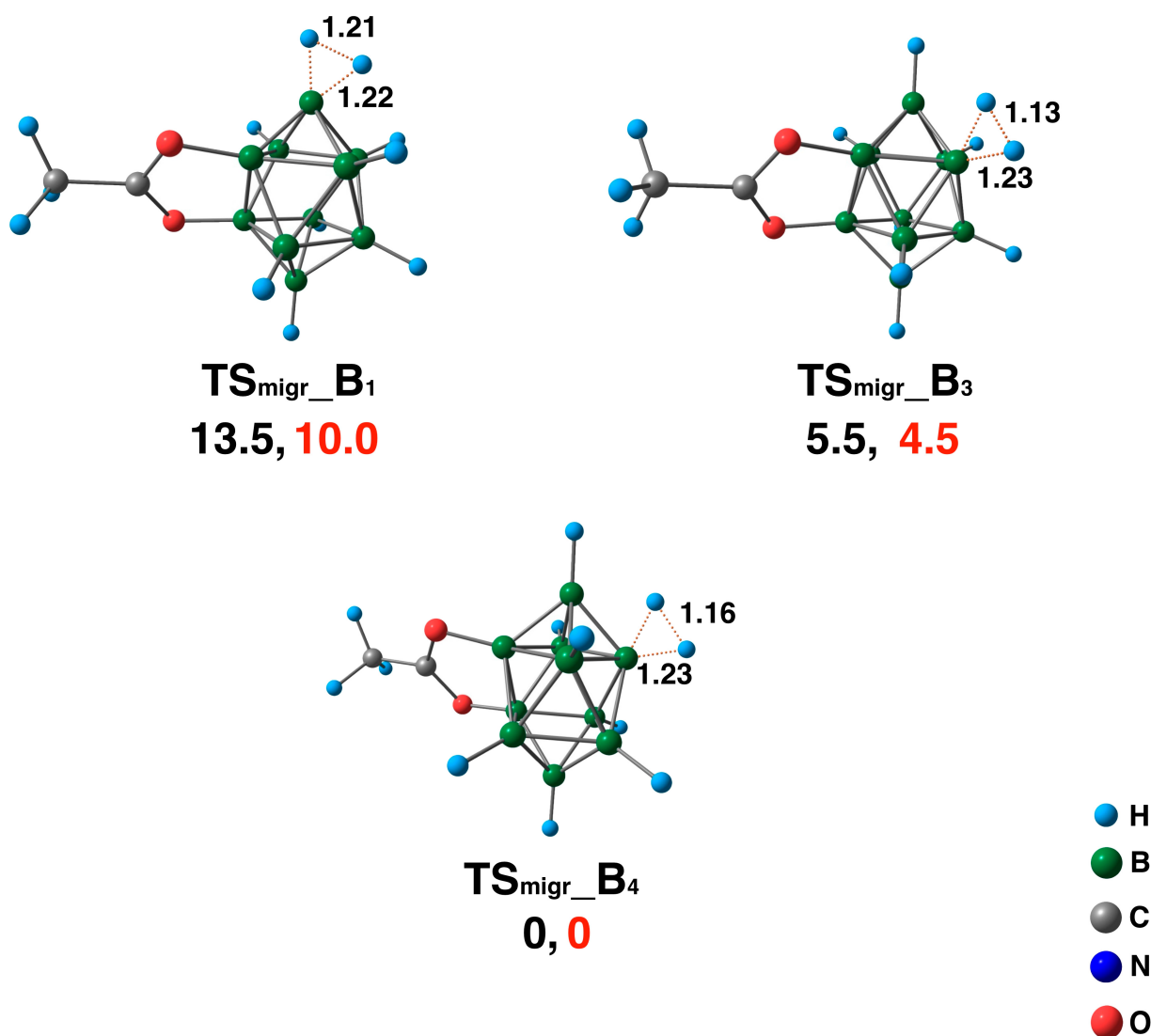


Figure 2. Optimised structures of hydrogen migration transition states TS_{migr}_B₁, TS_{migr}_B₃ and TS_{migr}_B₄. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red. Bond lengths are given in Angstroms, Å. Interactions between boron atoms and H^{fac} are marked with orange dotted lines.

Proton migration led to the formation of an intermediate in which the dihydrogen H₂ fragment coordinated to one boron atom of the cluster cage. The nature of the interaction between the boron atom and the H₂ fragment has been discussed in detail in several articles [28,29]. As in the case of transition state structures, the anion [B₁₀H₇O₂CCH₃(H₂)][−] has three possible isomers: H₂_B₁, H₂_B₃ and H₂_B₄ (Figure 3). For all isomers, the geometric parameters were quite similar. The distance between the hydrogen atoms was equal to 0.86–0.87 Å. The distance between a boron atom and a hydrogen atom was equal to 1.28–1.31 Å. The main geometric difference between transition state structures and [B₁₀H₇O₂CCH₃(H₂)][−] intermediates was the shortening of the H–H contacts and the broadening of the B–H contacts in an intermediate structure, compared with a transition state structure. It is noteworthy that the main geometric parameters were similar to analogous parameters in [B₁₀H₉(H₂)][−]; therefore, the nature of the introduced oxonium substituent had a slight effect on the bond parameters in the BH₂ fragment. The isomer in which the H₂ molecule was coordinated to the B₄ atom (H₂_B₄) had a lower energy than the other isomers. The differences from the H₂_B₃ were 7.7 kJ/mol according to the wB97X-D3/def2-TZVPP calculation and 7.2 kJ/mol according to the DLPNO-CCSDT/cc-

pvdz calculation. The isomer in which the dihydrogen fragment was coordinated with the apical boron atom H₂_B₁ had the highest relative energy. The differences between H₂_B₁ and H₂_B₄ were equal to 23.2 kJ/mol according to the wB97X-D3/def2-TZVPP calculation and 19.9 kJ/mol according to the DLPNO-CCSDT calculation. In the case of the [B₁₀H₉(H₂)][−] anion, the differences between the equatorial (B₁₀_H₂_eq) and apical isomers (B₁₀_H₂_ap) were equal to 11.6 kJ/mol using wB97X-D3/def2-TZVPP and 9.8 kJ/mol using DLPNO-CCSDT/cc-pvdz.

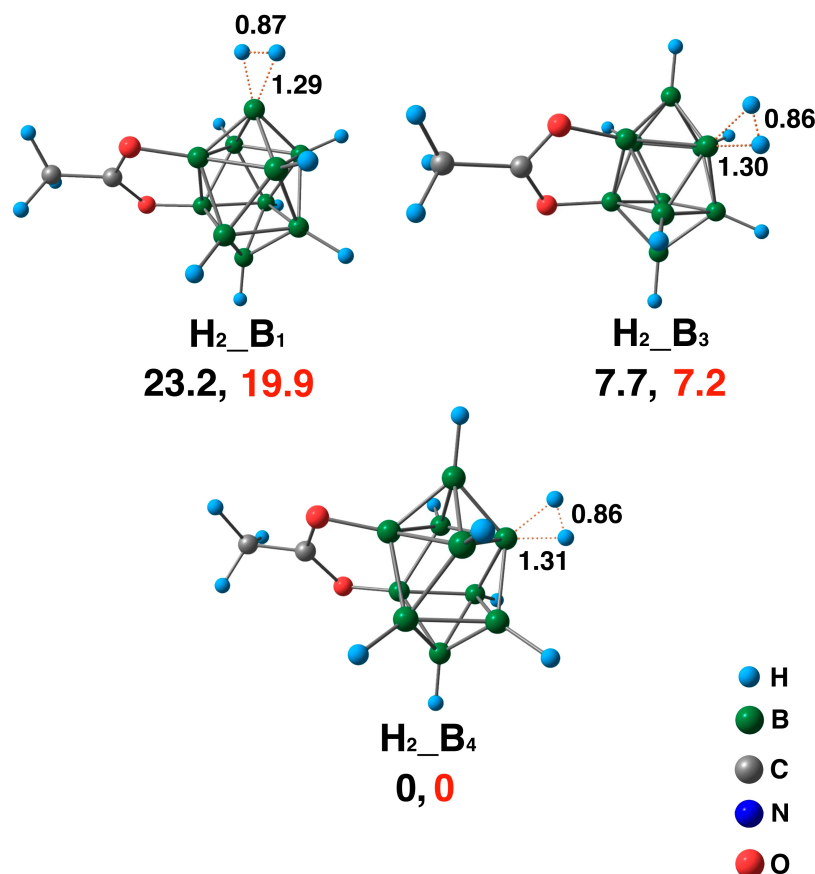


Figure 3. Optimised structures of H₂_B₁, H₂_B₃ and H₂_B₄. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red. Bond lengths are given in Angstroms, Å. Interactions between boron atoms and H^{fac} are marked with orange dotted lines. Interactions between boron atoms and H^{fac} are marked with orange dotted lines.

As in case of our previous study devoted to mechanism of formation of [B₁₀H₈O₂CPh][−], the nature of B-H₂ contact was investigated with the help of QTAIM formalism. Similar to the previously studied systems [B₁₀H₉H₂] and [B₁₀H₈(OCOPh)H₂], the analysis of the molecular graph of the of H₂_B₁, H₂_B₃ and H₂_B₄ revealed that the bond path from the boron atom was directed to the H-H bond centre (Figure 4). The B₁_H₂ isomer had the highest value of electron density at bond critical point (bcp) (Table S2). In addition, this isomer was characterized by the highest value of energy at bcp and the delocalization index. Thus, one can conclude that B₁_H₂ had the strongest covalent interaction between the boron atom and dihydrogen fragment. The B₄_H₂ isomer had the highest value of electron density at bcp devoted to the H-H interaction. This isomer was characterized by the highest value of energy at bcp and the delocalization index. B₄_H₂ isomer had the strongest covalent interaction between two hydrogen atoms in the H₂ fragment.

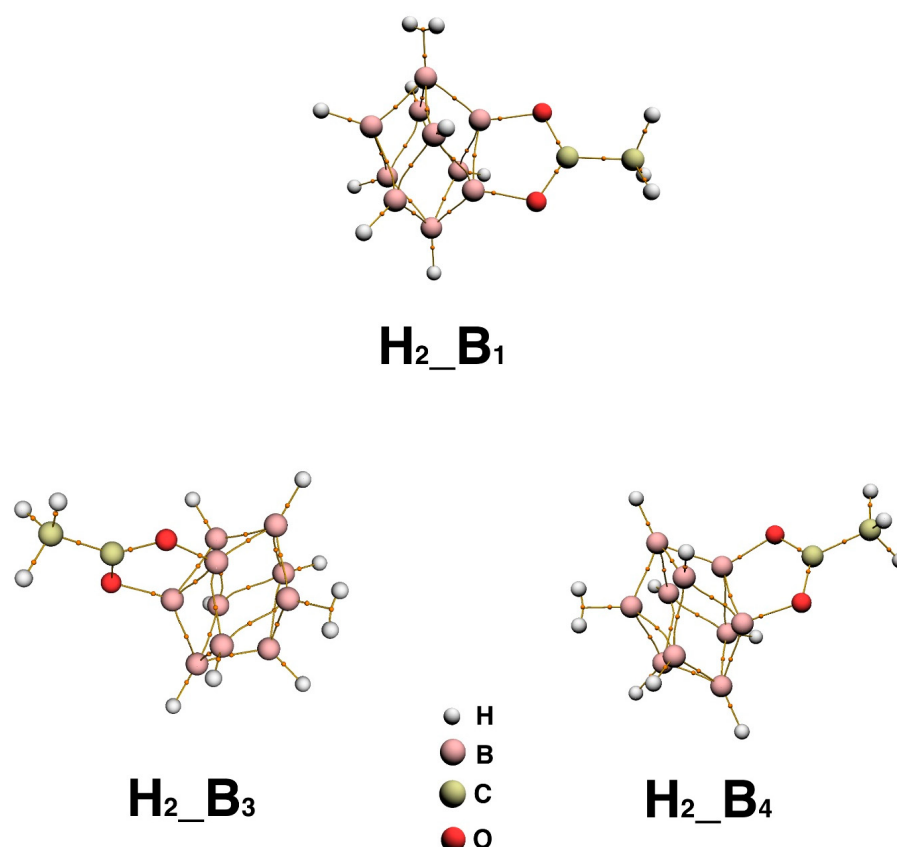


Figure 4. Molecular graph showing the results of the topological analysis of the electron density distribution in the model structure of H₂_B₁, H₂_B₃ and H₂_B₄.

In the next stage, the molecule of dihydrogen, H₂, was eliminated through the formation of the transition state (TS_{elim-B₁}, TS_{elim-B₃}, TS_{elim-B₄}). These transition states had a significantly longer distance between the boron atom and the dihydrogen fragment (Figure 5). In the case of the elimination of the hydrogen molecule from a B₃ boron atom (TS_{elim-B₃}), the distance between the boron atom and the hydrogen atoms of H₂ lay in the range of 1.96–1.98 Å. In the case of TS_{elim-B₄}, the distance between the boron atom and the hydrogen atoms of H₂ lay in the range of 2.19–2.21 Å. If the H₂ molecule was eliminated from the boron atom in the apical position (TS_{elim-B₁}), the contact was the shortest, lying in the range of 1.73–1.74 Å. Additionally, the transition state was stabilised by an acetonitrile molecule. The elimination process had a significant energy barrier. TS_{elim-B₄} had the lowest energy barrier: 145.2 kJ/mol (wB97X-D3/def2-TZVPP) and 109.5 kJ/mol (DLPNO-CCSDT/cc-pvdz). TS_{elim-B₃} had a similar value, but it was higher: 151 kJ/mol (wB97X-D3/def2-TZVPP) and 115.1 kJ/mol (DLPNO-CCSDT/cc-pvdz). TS_{elim-B₁} had the highest energy barrier values: 195.7 kJ/mol (wB97X-D3/def2-TZVPP) and 157.8 kJ/mol (DLPNO-CCSDT/cc-pvdz). Thus, the process of H₂ molecule elimination most probably occurred from the B₄ boron atom through the TS_{elim-B₄} transition state. In the case of elimination from the equatorial boron atom of the [B₁₀H₉(H₂)][−] anion (B₁₀_TS_{migr-eq}), the energy of the transition state was lower than that of the substituted carboxonium derivative. The relative Gibbs energies were equal to 139.9 kJ/mol (wB97X-D3/def2-TZVPP) and 104.2 kJ/mol (DLPNO-CCSDT/cc-pvdz). For elimination from the apical boron atom (B₁₀_TS_{migr-ap}), the energy barrier was almost the same as in the case of the carboxonium derivative. The relative Gibbs energies were equal to 195.7 kJ/mol (wB97X-D3/def2-TZVPP) and 159.1 kJ/mol (DLPNO-CCSDT/cc-pvdz). Previously, an analogous calculation was carried out, and the energy barrier of hydrogen elimination was lower than in our case [36]. This discrepancy may be due to inaccuracies in the calculation scheme. In par-

ticular, all solvents have been explicitly accounted for. Our results are in good agreement with those obtained for hydrogen atom substitution for chlorine [28,29].

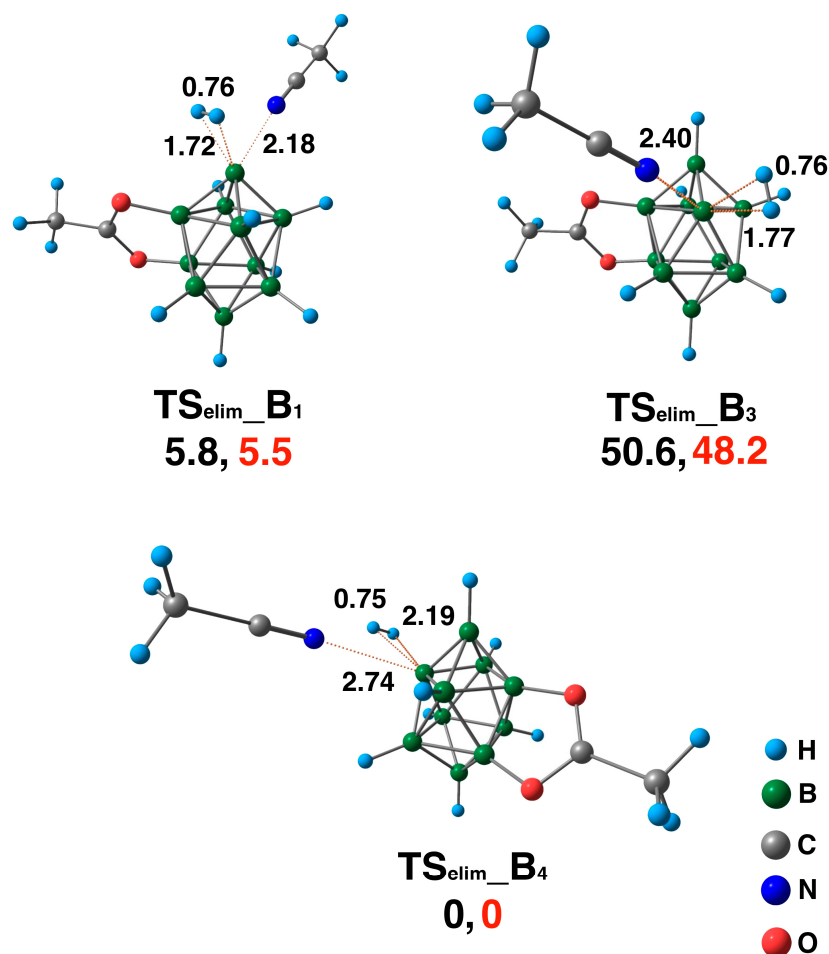


Figure 5. Optimised structures of hydrogen elimination transition states TS_{elim}_B₁, TS_{elim}_B₃ and TS_{elim}_B₄. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red. Bond lengths are given in Angstroms, Å. Interactions between boron atoms and H^{fac} are marked with orange dotted lines.

Finally, the target trisubstituted derivative was formed [B₁₀H₇O₂CCH₃(NCCH₃)]⁰. For equatorial isomers [B₁₀H₇O₂CCH₃(NCCH₃)]⁰ (Tris_B₃ and Tris_B₄), the B-N bond length was equal to 1.50 Å. For the apical isomer (Tris_B₁), the B-N bond distance was equal to 1.47 Å. The CN bond distance was equal to 1.14 Å in all cases (Figure 6). These geometric parameters were very similar, or analogous, to the mono-substituted nitrilium derivative [B₁₀H₉NCCH₃][−]. The process of formation of a trisubstituted product was very exergonic. Tris_B₄ had the most negative value of relative Gibbs energy. The overall Gibbs energy of the formation of the given isomer from [B₁₀H₈O₂CCH₃(H^{fac})]⁰ and CH₃CN was equal to −88.6 kJ/mol (wB97X-D3/def2-TZVPP) or −106.6 kJ/mol (DLPNO-CCSDT/cc-pvdz). The difference between Tris_B₄ and Tris_B₃ isomers was 5.1 kJ/mol according to the wB97X-D3/def2-TZVPP calculation or 5.64 kJ/mol according to the DLPNO-CCSDT/cc-pvdz calculation. Tris_B₁ had the highest value of relative Gibbs energy. The difference between Tris_B₁ and Tris_B₄ was equal to 7.5 kJ/mol according to the wB97X-D3/def2-TZVPP calculation or 8.9 kJ/mol according to the DLPNO-CCSDT/cc-pvdz calculation. For monosubstituted nitrilium derivatives, the energy difference of apical [1-B₁₀H₉NCCH₃][−] and equatorial [2-B₁₀H₉NCCH₃][−] isomers was equal to 1 kJ/mol (wB97X-D3/def2-TZVPP) or 1.4 kJ/mol (to DLPNO-CCSDT/cc-pvdz).

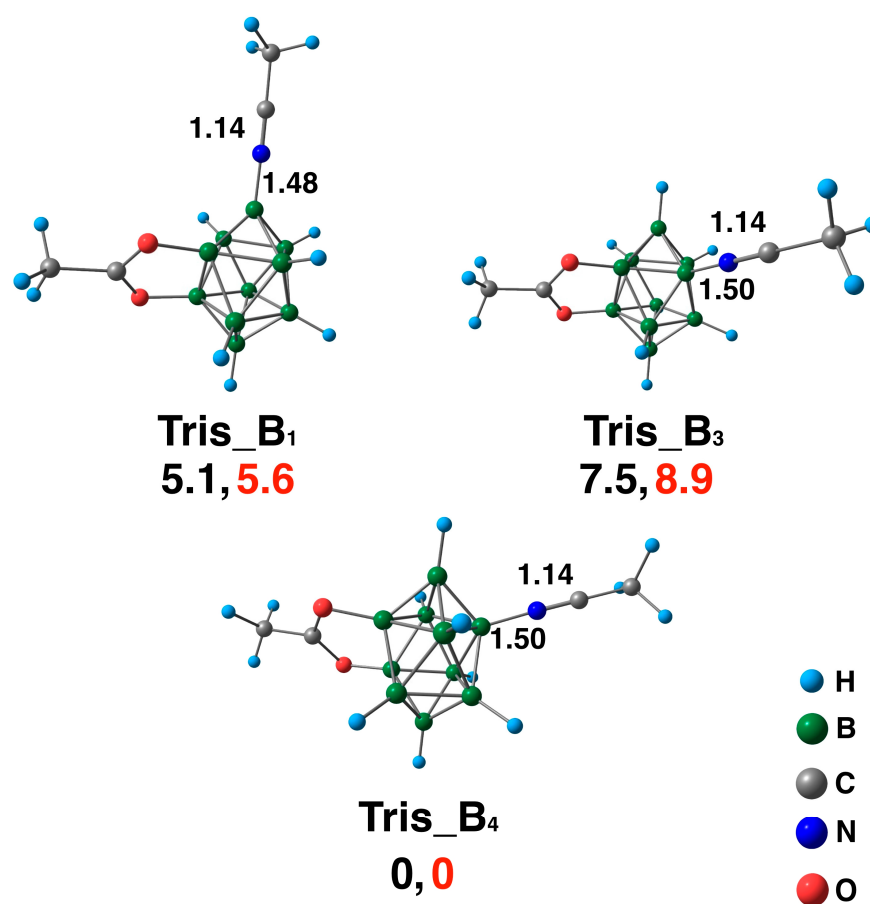


Figure 6. Optimised structures of target trisubstituted derivatives Tris_B₁, Tris_B₃ and Tris_B₄. Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red. Bond lengths are given in Angstroms, Å.

In addition to geometric parameters, the bond orders of $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ isomers were calculated with the help of natural bond orbital (NBO) formalism. The Wiberg bond orders in Natural Atomic Orbital (NAO) basis for B–O interactions were equal to 0.70 (wB97X-D3/def2-TZVPP) and 0.57–0.58 (DLPNO-CCSDT/cc-pvdz). These values were similar for the initial carboxonium derivative $[\text{B}_{10}\text{H}_8\text{O}_2\text{CCH}_3(\text{H}^{\text{fac}})]^0$. In the case of initial $[\text{B}_{10}\text{H}_8\text{O}_2\text{CCH}_3(\text{H}^{\text{fac}})]^0$, the B–O bond orders were equal to 0.72 (wB97X-D3/def2-TZVPP) and 0.59 (DLPNO-CCSDT/cc-pvdz). The C–O bond orders for $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ isomers lay in the range of 1.30–1.31 (wB97X-D3/def2-TZVPP) and 1.20–1.22 (DLPNO-CCSDT/cc-pvdz). In the case of $[\text{B}_{10}\text{H}_8\text{O}_2\text{CCH}_3(\text{H}^{\text{fac}})]^0$, the C–O bond orders were equal to 1.30 (wB97X-D3/def2-TZVPP) and 1.21 (DLPNO-CCSDT/cc-pvdz). The B–N bond orders lay in the range of 0.81–0.83 (wB97X-D3/def2-TZVPP) and 0.57–0.58 (DLPNO-CCSDT/cc-pvdz). These values were similar to monosubstituted nitrilium derivatives with the general form $[\text{B}_{10}\text{H}_9\text{NCCH}_3]^-$. For monosubstituted nitrilium derivatives, the bond orders lay in the range 0.81–0.82 (wB97X-D3/def2-TZVPP) and 0.70–0.73 (DLPNO-CCSDT/cc-pvdz). The $\text{C}\equiv\text{N}$ bond orders lay in the range of 2.58–2.60 (wB97X-D3/def2-TZVPP) and 2.54–2.55 (DLPNO-CCSDT/cc-pvdz). In the case of the analogous monosubstituted nitrilium derivative, the values of bond orders lay in the range of 2.59–2.60 (wB97X-D3/def2-TZVPP) and 2.56–2.57 (DLPNO-CCSDT/cc-pvdz). Thus, the main values of bond orders for trisubstituted derivatives were similar to the carboxonium derivative $[\text{B}_{10}\text{H}_8\text{O}_2\text{CCH}_3(\text{H}^{\text{fac}})]^0$ and nitrilium derivative $[\text{B}_{10}\text{H}_9\text{NCCH}_3]^-$.

The approach for preparation of the trisubstituted $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ derivative with *exo*-polyhedral nitrilium and carboxonium substituents was theoretically pro-

posed. This approach was based on the EINS process. The protonated carboxonium derivative $[B_{10}H_8O_2CCH_3(H^{fac})]^-$ can be used as the initial starting reagent. Such molecular species can interact with an acetonitrile molecule CH_3CN with the formation of $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ derivatives. Three different pathways of hydrogen substitution to the nitrile molecule in $[B_{10}H_8O_2CCH_3(H^{fac})]^-$ were considered (Figures 7 and S1–S3). The most energetically favourable pathway was the substitution of the hydrogen atom at the boron atom at the B_4 position. This route had the lowest energy of the $[B_{10}H_7O_2CCH_3(H_2)]^-$ species and transition states of the elimination stage. The Tris_ B_4 isomer had the most energetically favourable pathway among the other isomers of $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ (Table 1). Comparing the energetic parameters for the formation of the trisubstituted derivative $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ and monosubstituted derivative $[B_{10}H_9NCCH_3]^-$, one can conclude that these characteristics were very similar. In view of this circumstance, it is reasonable to expect that the process of formation of the trisubstituted derivative $[2,4,6-B_{10}H_7O_2CCH_3(NCCH_3)]^0$ will proceed as smoothly as the process of obtaining monosubstituted derivatives $[2-B_{10}H_9NCCH_3]^-$ [25].

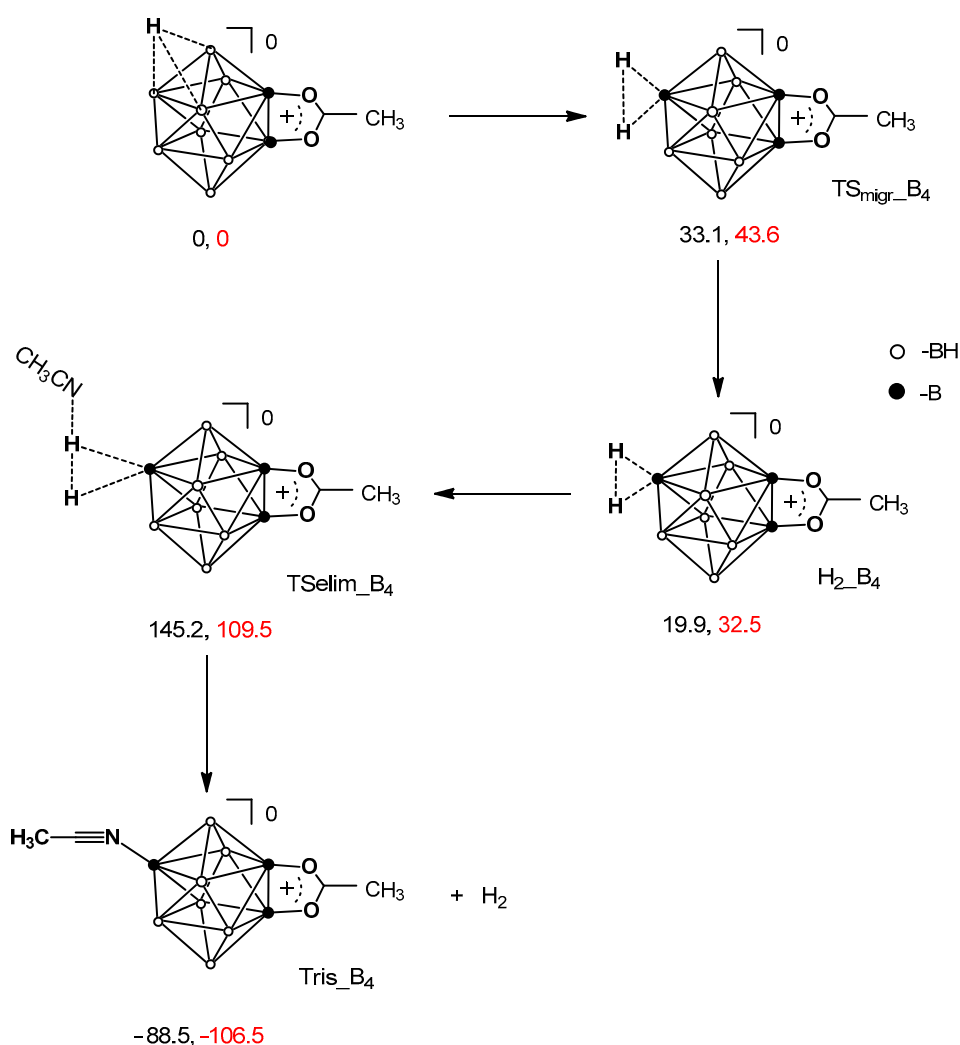


Figure 7. General scheme for the formation of trisubstituted derivative Tris_ B_4 . Relative Gibbs energy (wB97X-D3 level; kJ/mol) is marked in black and relative electronic energy (DLPNO-CCSDT level + ZPE corrections; kJ/mol) is marked in red.

Table 1. DFT (wB97X-D3/def2-TZVPP level of theory) relative Gibbs free energies of main molecular species and relative electronic energies with ZPE (DLPNO-CCSDT/cc-pvdz + ZPE level of theory) in kJ/mol.

Model Species	DFT	DLPNO-CCSDT
$[B_{10}H_8O_2CCH_3(H^{fac})] + CH_3CN$	0.0	0.0
Formation of Tris_B₁		
$TS_{migr_B_1} + CH_3CN$	46.6	53.7
$H_2_B_1 + CH_3CN$	43.1	52.3
$TS_{elim_B_1}$	195.9	157.8
$Tris_B_1 + H_2$	−81.1	−97.6
Formation of Tris_B₃		
$TS_{migr_B_3} + CH_3CN$	38.6	48.2
$H_2_B_3 + CH_3CN$	27.6	39.7
$TS_{elim_B_3}$	151.0	115.1
$Tris_B_3 + H_2$	−83.4	−100.9
Formation of Tris_B₄		
$TS_{migr_B_4} + CH_3CN$	33.1	43.6
$H_2_B_4 + CH_3CN$	19.9	32.5
$TS_{elim_B_4}$	145.2	109.5
$Tris_B_4 + H_2$	−88.5	−106.5
$[B_{10}H_{11}]^- + CH_3CN$	0.0	0.0
Formation of $[1-B_{10}H_9NCCH_3]^-$		
$B_{10_}TS_{migr_ap} + CH_3CN$	49.1	57.2
$B_{10_}H_2_ap + CH_3CN$	41.5	52.0
$B_{10_}TS_{elim_ap}$	195.7	159.1
$[1-B_{10}H_9NCCH_3]^- + H_2$	−57.9	−74.5
Formation of $[2-B_{10}H_9NCCH_3]^-$		
$B_{10_}TS_{migr_eq} + CH_3CN$	59.1	68.2
$B_{10_}H_2_eq + CH_3CN$	29.8	42.2
$B_{10_}TS_{elim_eq}$	139.9	104.2
$[2-B_{10}H_9NCCH_3]^- + H_2$	−58.9	−75.9

Thus, based on theoretical calculations, it is easy to suggest a proposed experimental approach to obtain the target trisubstituted derivative $[B_{10}H_7O_2CCH_3(NCCH_3)]^0$ (Figure 8). The protonated form of the carboxonium derivative $[2,6-B_{10}H_8O_2CCH_3^*H^{fac}]^0$ can easily be obtained in situ through the interaction of $[2,6-B_{10}H_8O_2CCH_3]^-$ with excess of trifluoromethanesulfonic acid CF_3SO_3H [35]. Then, as follows from the presented theoretical calculations, interactions between $[2,6-B_{10}H_8O_2CCH_3^*H^{fac}]^0$ and an acetonitrile molecule CH_3CN (in dichloromethane solution or in pure CH_3CN) will lead to the formation of the trisubstituted derivative $[2,4,6-B_{10}H_7O_2CCH_3(NCCH_3)]^0$. Heating the resulting solution to its boiling point will significantly reduce the total synthesis time.

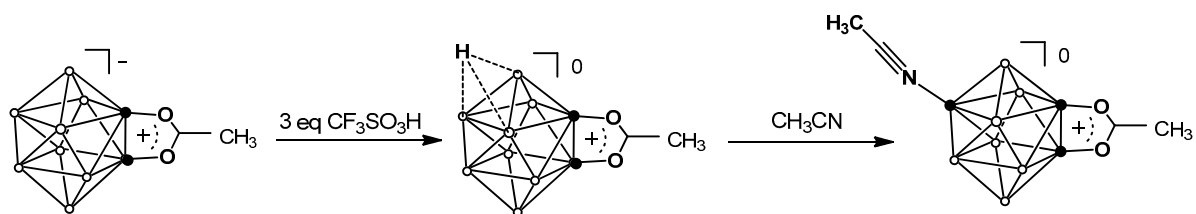


Figure 8. Proposed scheme of experimental formation of $[2,4,6\text{-B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$.

3. Materials and Methods

The DFT calculations were performed using the ORCA 4.2.1 program package [37]. The geometries of all model structures were fully optimised using the $\omega\text{B97X-D3}$ functional in combination with the def2-TZVPP basis sets [38–41]. This method is applicable for a wide range of quantum chemical issues: atomic charges and chemical reactivity of organic and inorganic systems [42–47]. Previously, we have successfully applied the $\omega\text{B97X-D3}$ functional for various calculations of *closo*-borate peculiarities: B-X (X = C, O, N, F) chemical bonding, non-covalent interactions, and molecular reactivity [35,48]. All calculations were performed using the RIJCOSX approximation with the def2/J auxiliary basis set [49]. Tight criteria of SCF convergence (“Tight SCF”) were employed for the calculations. The keywords “Grid5”, “FinalGrid6” and “GridX5” were used as parameters for the spatial integration grid. For more accurate estimation of thermodynamic characteristics, single point calculations at the DLPNO-CCSDT/cc-pvdz level were performed [50]. DLPNO-CCSDT calculations were carried out using the RIJK approximation with the cc-pvdz/c cc-pvtz/jk auxiliary basis sets. Very tight criteria of SCF convergence (“Verytight SCF”) were employed for the calculations. Zero-point corrections taken from the $\omega\text{B97X-D3/def2-TZVPP}$ computations were then added to the final energies. All considered *closo*-decaborate species had closed electron shells and the spin-restricted approximation was applied. During the geometry optimisation procedure, symmetry operations were not applied for the considered structures. Hessian matrices were calculated numerically for all model structures, to prove the location of correct minima on potential energy surfaces (no imaginary frequencies were found in any of the cases). The connectivity of each reaction step was also confirmed using the intrinsic reaction coordinate (IRC) calculations from the transition states [51–53]. Solvent molecules were not explicitly taken into account. Thus, solvent effects were considered using the Solvation Model based on Density (SMD) [54]. All calculations (geometry optimization, frequency calculation, DLPNO-CCSDT single point calculation, QTAIM analysis) were performed in a dichloromethane (CH_2Cl_2) phase. Topological analysis of the electron density distribution, based on the Quantum Theory of Atoms in Molecules (QTAIM) formalism developed by Bader [55–57], was employed with the Multiwfn program (version 3.7) [58]. The natural bond orbital (NBO) method was employed, using the NBO7 program package [59,60]. The Cartesian atomic coordinates for all optimised equilibrium model structures are presented in the Supplementary Materials. The visualisation of optimised structures was carried out with the help of the ChemCraft program (version 1.7) [61].

4. Conclusions

A comprehensive theoretical study of the mechanism for the formation of the trisubstituted derivative $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ was carried out. As in case of the mononitrilium derivative of *closo*-decaborate anion $[\text{B}_{10}\text{H}_9\text{NCCH}_3]^-$, the process of $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ preparation had an EINS mechanism. A trisubstituted compound was obtained on the basis of interaction of the protonated carboxonium derivative $[\text{B}_{10}\text{H}_8\text{O}_2\text{CCH}_3(\text{H}^{\text{fac}})]^0$ with an acetonitrile molecule CH_3CN . The target trisubstituted derivative $[\text{B}_{10}\text{H}_7\text{O}_2\text{CCH}_3(\text{NCCH}_3)]^0$ had several possible isomers. The main pathways for the formation of such isomers were considered. The most energetically favourable pathway was the substitution of the hydrogen atom at the boron atom in the B_4 position. This route had the lowest energies

of the $[B_{10}H_7O_2CCH_3(H_2)]^-$ intermediate and transition state at the elimination stage. Thus, the current theoretical study showed the possibility of obtaining a trisubstituted derivative based on a carboxonium derivative of *closo*-borate anions. This can be applied for developing a synthesis strategy for the preparation of such derivatives.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11050201/s1>, Table S1: Relative electronic energies (DLPNO-CCSDT/cc-pvdz level of theory) of main molecular species in kJ/mol; Table S2: Main topological parameters of electron density for interactions in B-H₂ fragments. $\rho(r)$ —electron density at the bcp, $\nabla^2\rho(r)$ —Laplacian of electron density at the bcp, G_{H_b} —total energy at the bcp, δ —delocalization index; Figure S1: Expanded general scheme for the formation of trisubstituted derivative Tris_B₄; Figure S2: General scheme for the formation of trisubstituted derivative Tris_B₁; Figure S3: General scheme for the formation of trisubstituted derivative Tris_B₃; Figure S4: General scheme of formation of $[2-B_{10}H_9NCCH_3]^-$; Figure S5: General scheme of formation of $[1-B_{10}H_9NCCH_3]^-$; Table S3: Cartesian atomic coordinates of the calculated optimised equilibrium model structures. Gibbs energy (wB97X-D3 level; kJ/mol), electronic energy (DLPNO-CCSDT level; kJ/mol), electronic energy + ZPE corrections (DLPNO-CCSDT level; kJ/mol). All coordinates are given in Angstrom units, Å.

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