

Ab Initio Study of the Coordination Modes of Tetrahydroborato Ligands: Structure and Reactivity of the $\text{Al}(\text{BH}_4)_3$ Complex

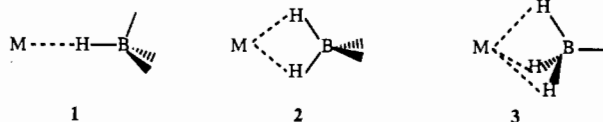
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Aluminum borohydride is studied by means of ab initio calculations taking into account correlation energy. For the (η^2, η^2, η^2) structure, the rotational barrier associated with the conrotation of the three BH_4^- groups around the Al–B axis is found to be very low ($0.2 \text{ kcal}\cdot\text{mol}^{-1}$). A rationalization based on an orbital analysis is given. Changing the coordination mode ($\eta^2 \rightarrow \eta^3$) of one borohydride group leads to the (η^2, η^2, η^3) structure which is the transition state of the hydrogen exchange mechanism. This is a low energy process ($2.2 \text{ kcal}\cdot\text{mol}^{-1}$) which explains that the coalescence could not be experimentally observed. Another change in the coordination mode ($\eta^2 \rightarrow \eta^1$) of one borohydride group leads to the (η^1, η^2, η^2) structure which is the transition state of the dissociation mechanism $\text{Al}(\text{BH}_4)_3 \rightarrow \text{AlH}(\text{BH}_4)_2 + \text{BH}_3$. This is a high-energy process ($24.8 \text{ kcal}\cdot\text{mol}^{-1}$) probably because the products are electronically deficient.

Borohydride complexes of transition metals have been widely studied both at experimental and theoretical levels. BH_4^- can bind to metal atoms in three ways, depending on the number of bridging hydrogens between boron and metal atoms (1, 2, 3).^{1–3}



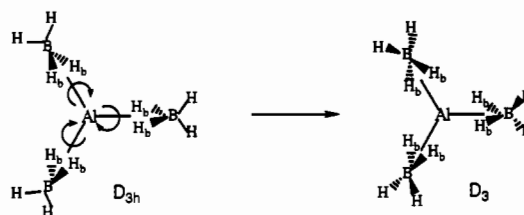
It has been shown that the coordination mode (η^1, η^2, η^3) of this ligand is related to the number of electrons it gives to the metal. A BH_4^- ligand acts as a 2-, 4-, or 6-electron donor when it is η^1 -, η^2 -, or η^3 -bonded to the metal, respectively.^{4–6} The coordination mode of the BH_4^- ligand can therefore be simply predicted by applying the 18-electron rule.

The tetrahydroborato ligand can also bind to non-transition metal atoms such as beryllium, aluminum, etc. For the $\text{Be}(\text{BH}_4)_2$ molecule, Hori et al.⁷ have shown that the electron count recalled above is still at work in these complexes, the 18-electron rule being replaced by the octet rule. For instance, in $\text{Be}(\text{BH}_4)_2$, each BH_4^- group acts as a 4-electron donor so that eight electrons are around the Be^{2+} cation.

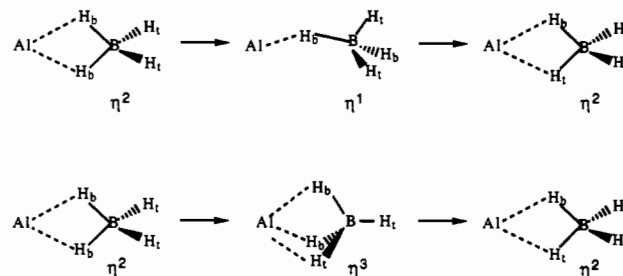
The $\text{Al}(\text{BH}_4)_3$ complex has been characterized by Haaland et al.⁸ by electron diffraction. The boron and aluminum atoms are coplanar, each BH_4^- group being η^2 -coordinated to the aluminum. However, the authors could not state conclusively the overall symmetry of this complex. It was hypothesized that this complex can be of D_{3h} symmetry (the planes defined by bridging hydrogen (H_b) and boron atoms being perpendicular to the AlB_3 plane) or of D_3 symmetry (deduced from the D_{3h} one by a conrotation of the three BH_2 planes). In this last case, the rotation angle has been found to be close to 17° (Scheme 1).

NMR studies⁹ show all the protons to be equivalent, i.e., the exchange between bridging and terminal hydrogens is fast. The

Scheme 1



Scheme 2



coalescence could not be observed in the temperature range studied ($-30/+50^\circ\text{C}$). Such phenomenon is frequently observed in borohydride complexes. Two mechanisms are generally proposed for hydrogen exchange within BH_4^- groups in η^2 -coordination mode.^{10,11} Both involve a change in the coordination mode ($\eta^2 \rightarrow \eta^3$ or $\eta^2 \rightarrow \eta^1$) of one borohydride group (Scheme 2).

Another feature of the NMR spectrum of $\text{Al}(\text{BH}_4)_3$ is its unusual behavior when temperature increases from -30 to $+50^\circ\text{C}$.⁹ It has been proposed that a dimerization can occur with departure of a diborane molecule:



When THF is used as solvent, the monomeric species can be stabilized by complexation and characterized. The above reaction can therefore be viewed as resulting from a B–H bond breaking in the monomer:



In this paper, the $\text{Al}(\text{BH}_4)_3$ complex is studied by means of ab initio calculations. Our aim is to characterize the geometrical

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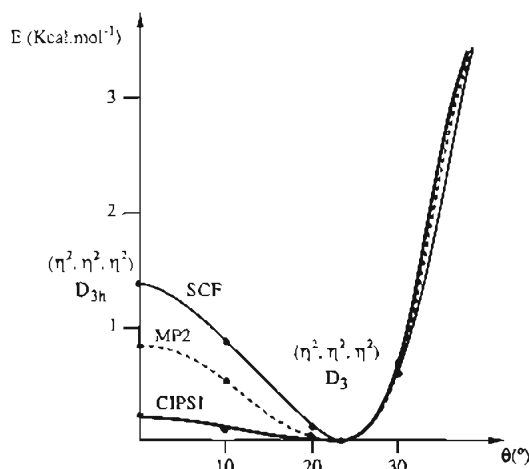


Figure 1. Rotational energy curve associated with the conrotation of the three BH_4^- groups at various levels of calculation: SCF, solid line; MP2, dashed line; CIPSI, bold line.

symmetry of the complex and to give some insights into the hydrogen exchange mechanism. In the following, we shall focus our attention on the three structures, (η^2, η^2, η^2) , (η^2, η^2, η^3) , and (η^1, η^2, η^2) . For sake of simplicity an (η^a, η^b, η^c) structure will be called (a, b, c) in a more compact way.

Method of Calculation

Ab initio calculations have been undertaken with the 6-31 G^* basis set¹² with the help of the MONSTERGAUSS set of programs.¹³ Independent calculations on $\text{Ti}(\text{BH}_4)_3$ ¹⁴ have shown that extension of the basis set (inclusion of 2p orbitals on hydrogens for instance) does not improve significantly the results. All internal coordinates have been optimized by an analytical gradient method at the SCF level. We have tested on the minimum D_3 structure the influence of correlation (MP2 level) on the optimization process. Since the MP2 and SCF results are close (see below), all the geometry optimizations have been performed at the SCF level. The nature of the extrema (minimum or transition state) on the potential energy surface has been determined by the diagonalization of the hessian matrix calculated without any symmetry constraint. Correlation effects have been taken into account through the CIPSI algorithm,¹⁵ which allows a mixed variational/perturbational calculation of the correlation energy. In these calculations, all the determinants whose coefficient in the wave function is larger than a threshold τ ($\tau = 0.015$) are diagonalized variationally (S -space). The contribution of all the determinants generated by single or double excitation from the S -space generators is estimated through a second-order perturbational treatment. In practice, starting from the SCF wave function (S containing only one determinant) gives a simple MP2 calculation. Then, the generated determinants having a contribution to the first-order perturbed wave function greater than τ are iteratively included to the S -space until convergence.

Results and Discussion

Structure of the minimum. As shown previously by independent calculations,¹⁶ the D_{3h} structure is a transition state which interconverts two minima of D_3 symmetry. The rotational curve is depicted in Figure 1, the θ angle being the rotational angle of the three BH_4^- planes ($\theta = 0^\circ$ corresponding to the D_{3h} structure). The D_3 minimum is found at $\theta = 23.2^\circ$, a value close to the experimental one (17°). This minimum has been reoptimized at the MP2 level. Both sets of results are given in Table 1 together

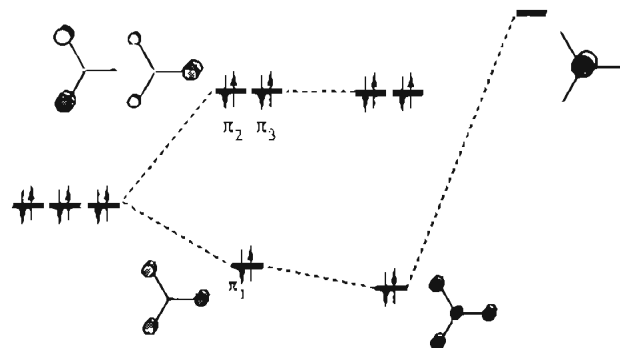


Figure 2. π orbitals interaction between the Al^{3+} cation and the $(\text{BH}_4^-)_3$ moiety.

Table 1. Main Geometrical Parameters (\AA , deg) of the D_3 Minimum Optimized at the SCF and MP2 Levels with Experimental Data Given for Comparison

geometrical params	SCF level	MP2 level	exptl
Al-B	2.177	2.149	2.143
B-H _p	1.285	1.270	1.283
B-H _t	1.189	1.194	1.196
H _p -B-H _p	106.3	109.2	114.0
H _t -B-H _t	121.6	121.2	116.2
θ	23.2	21.6	17.2

with the experimental data. The improvement of the geometrical parameters is slight. In the following, the geometry optimization will therefore be performed at the SCF level.

The energy barrier is small ($1.4 \text{ kcal}\cdot\text{mol}^{-1}$ at the SCF level) and is reduced when correlation energy is taken into account (0.9 and $0.2 \text{ kcal}\cdot\text{mol}^{-1}$ at the MP2 and CIPSI level respectively). It should be noted here that the synchronous rotation of the BH_4^- groups is a very soft motion: the associated frequency is only 245 cm^{-1} in the D_3 structure. This low value, together with the weak interconversion barrier, explains why the experimental determination of the molecular symmetry point group is almost impossible. As a matter of fact, our results show that the coupled rotation of the BH_4^- is almost free in the range $-30^\circ/+30^\circ$. We therefore cannot definitively come to a conclusion on the optimal symmetry of this complex although the D_3 geometry is preferred at each level of calculations.

Bock et al.¹⁶ have interpreted this symmetry lowering as resulting from the reduction of the Coulombic interactions between the hydridic bridging hydrogens. An alternative interpretation of this motion can be drawn from molecular orbital analysis. Each BH_4^- group interacts with the Al^{3+} central cation through two orbitals: one of σ symmetry (4a) and the second of π symmetry (4b).



The σ manifold is roughly insensitive to the rotational angle value. The three π orbitals combine to give the three symmetry adapted orbitals, π_1 , π_2 , and π_3 depicted in Figure 2 (left-hand side).

In the D_{3h} structure, only the lowest symmetry orbital, π_1 , can interact with the 3p Al^{3+} vacant orbital. This two-electron stabilization represents the conjugation between the aluminum cation and the borohydride moiety. The rotation of the BH_4^- groups reduces this conjugation, which is unfavorable. On the other hand, the through-space interaction of these three orbitals (which leads to the splitting depicted in Figure 2, left-hand side) is destabilizing since six electrons occupy three orbitals. This pair repulsion is basically analogous to the well-known 4-electron 2-orbital repulsion and depends essentially on the overlap S

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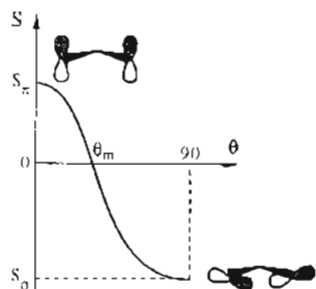
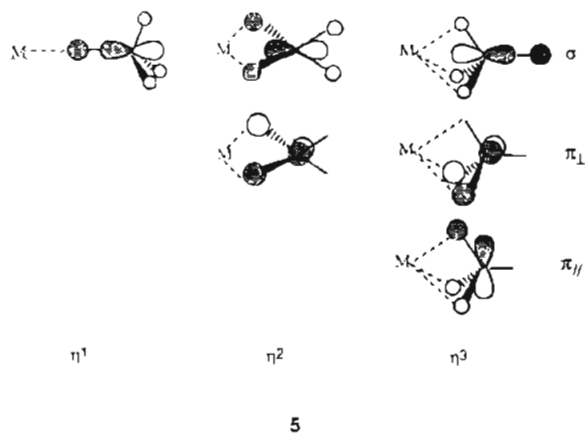


Figure 3. Qualitative evolution of the overlap (S) between two π orbitals with the rotational angle θ .

between the interacting orbitals. When the BH_4^- groups rotate, the overlap decreases from a positive value S_π (D_{3h} structure) to a negative one S_σ when a 90° rotation is completed. The overlap becomes zero for an intermediate value θ_m at which the pairs repulsion cancels (Figure 3). As a result, the rotation of the BH_4^- groups leads to two opposite effects: a weakening of the stabilizing conjugation and a weakening of the pairs repulsion. The position of the minimum results from the balance of these two effects, and an optimal θ value of 23.2° is found. Such competition has been shown to be also at work in BD_3 systems where D is a π -donor substituent ($\text{D} = \text{NH}_2, \text{OH}$) and has been tested on model systems.¹⁷

Electron Counting in $\text{Al}(\text{BH}_4)_3$. As recalled in the introduction, the BH_4^- group can act as a 2-, 4-, or 6-electron donor depending on its coordination mode. When it is η^1 -coordinated, only one orbital (the σ orbital) can interact with the aluminum atom. Two orbitals (σ and π_\perp) are available in the η^2 -coordination and three (σ , π_\perp , and π_\parallel) in the η^3 one (5).



5

In the most symmetrical structures, (1,1,1), (2,2,2), and (3,3,3), the interacting BH_4^- orbitals generate symmetry orbitals which can interact with the aluminum cation vacant AOs. In the σ manifold, the $(\text{BH}_4^-)_3$ orbitals interact with s , p_x , and p_y (Figure 4); in the π_\perp one they interact with p_x , d_{xz} and d_{yz} (Figure 5). Only two interactions are symmetry allowed in the π_\parallel manifold, with d_{xy} and $d_{x^2-y^2}$ since the highest $(\text{BH}_4^-)_3$ orbital is of f symmetry (Figure 6).

As a result, six electrons can be transferred from the σ orbitals, six from the π_\perp ones and only four from the π_\parallel ones, if d aluminum AOs are considered as valence orbitals. If the aluminum is normal-valent, i.e. only 3s and 3p orbitals are taken into account, there are six electrons in (1,1,1) and eight in (2,2,2), and (3,3,3). Two electron counts are therefore possible whether aluminum d orbitals are taken into account or not. The results are summarized in Table 2 for all the possible structures.

We find the d orbital population to be small (less than 0.15 electron) indicating that the d orbitals are used as polarization functions and cannot be considered as valence orbitals. Moreover,

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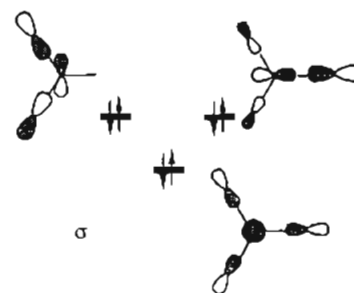


Figure 4. Orbital interactions between the Al^{3+} cation and the $(\text{BH}_4^-)_3$ moiety in the σ manifold. For the sake of simplicity, only the boron 2p component of the borohydride orbitals is represented.

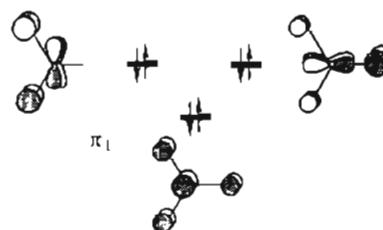


Figure 5. Orbital interactions between the Al^{3+} cation and the $(\text{BH}_4^-)_3$ moiety in the π_\perp manifold. For the sake of simplicity, only the boron 2p component of the borohydride orbitals is represented.

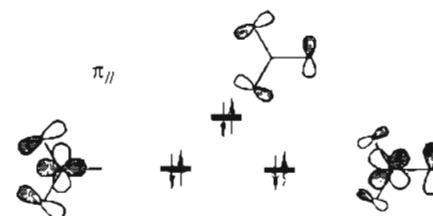
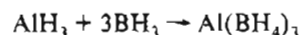


Figure 6. Orbital interactions between the Al^{3+} cation and the $(\text{BH}_4^-)_3$ moiety in the π_\parallel manifold. For the sake of simplicity, only the boron 2p component of the borohydride orbitals is represented.

we have calculated the enthalpy variation associated with the reaction



with and without d orbitals on aluminum. In both cases, it is negative ($55 \text{ kcal}\cdot\text{mol}^{-1}$ at the 6-31G* level and $37 \text{ kcal}\cdot\text{mol}^{-1}$ when d aluminum orbitals are omitted) which shows that d orbitals are not needed to ensure the stability of this complex. A similar argument has been invoked by Reed and Schleyer¹⁸ to show that the stability of the SiH_5^- anion does not qualitatively depend on the presence of d orbitals on the silicon. On the basis of these results, it can be stated that the aluminum is normal-valent in this complex. Consequently, the electron count without d orbitals on aluminum must be used for this complex: only the (1,1,1) structure is electron deficient, all the other combinations of the three coordination mode leading to eight electrons around the aluminum. This result is in contrast with those obtained on transition metal complexes where the most stable coordination mode can be easily predicted by applying the 18-electron rule.

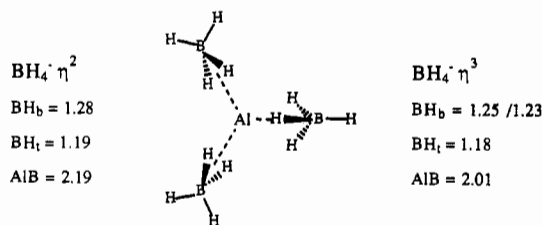
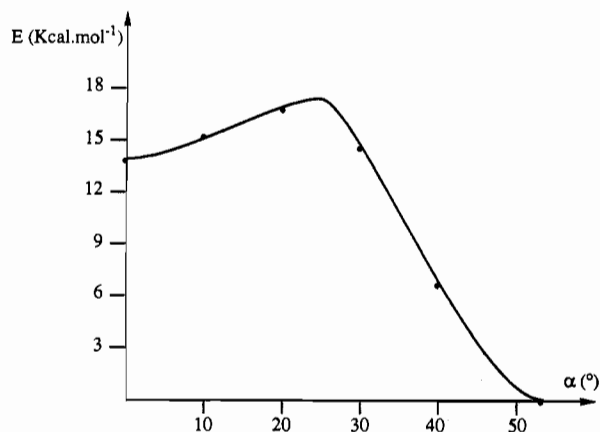
Optimization of the (2,2,3) Structure. The (2,2,3) structure has been optimized within the C_s symmetry point group. The main geometrical parameters are depicted in Figure 7.

The AlB_3 arrangement is planar and almost trigonal, the $(\eta^2\text{-B-Al-}\eta^3\text{-B})$ angle slightly increasing to 123° . As expected, the Al-B distance decreases when going from η^2 - to η^3 -coordination. This structure is located $5.4 \text{ kcal}\cdot\text{mol}^{-1}$ above the minimum (SCF level). The energy difference decreases to 2.7 (MP2) and $2.2 \text{ kcal}\cdot\text{mol}^{-1}$ (CIPSI) when correlation energy is taken into account. Vibrational frequency calculations (SCF level) show that this

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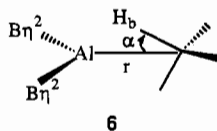
Table 2. Electronic Counts in the 10 Structures of the $\text{Al}(\text{BH}_4)_3$ Complex (Numbers in Parentheses Correspond to Electronic Count when Aluminum d Orbitals Are Taken into Account)

	(111)	(112)	(113)	(122)	(222)	(123)	(223)	(133)	(233)	(333)
σ	6	6	6	6	6	6	6	6	6	6
π_{\perp}	0	2	2	2(4)	2(6)	2(4)	2(6)	2(4)	2(6)	2(6)
π_{\parallel}	0	0	(2)	0	0	0(2)	0(2)	0(4)	0(4)	0(4)
N_{tot} without d	6	8	8	8	8	8	8	8	8	8
N_{tot} with d	6	8	10	10	12	12	14	14	16	16

**Figure 7.** Optimized bond lengths (Å) in the (2,2,3) structure.**Figure 8.** Energetic curves (SCF level) upon α diminution. The optimum (2,2,2) structure is located at $\alpha = 53^\circ$.

structure is a transition state on the potential energy surface (one imaginary frequency). The associated mode essentially develops on the coordinates of the η^3 group. Following the transition vector associated with the imaginary mode leads to a change ($\eta^3 \rightarrow \eta^2$) of the η^3 -coordinated borohydride group. This structure is therefore the transition state of the hydrogen exchange mechanism. This is a low-energy process since the associated activation energy is 2.2 kcal·mol⁻¹ at our best level of calculation. It explains why the coalescence can not be experimentally observed in the temperature range studied. This energy barrier is in the range of calculated energy barriers for similar hydrogen exchange processes: 2.1 kcal·mol⁻¹ in $\text{Ti}(\text{BH}_4)_3$;¹⁴ 1.9–7.4 kcal·mol⁻¹ in $\text{Be}(\text{BH}_4)_2$;^{7,19} 7.7 kcal·mol⁻¹ in $\text{AlH}_2(\text{BH}_4)$.²⁰ Note that in the last two examples, an identical mechanism ($\eta^2 \rightarrow \eta^3$) has been found to account for hydrogen exchange.

Optimization of the (1,2,2) Structure. In order to reach the (1,2,2) structure, we have computed an energetic curve taking the Al-B-H_b angle (α , 6) as reaction coordinate. It varies from 53° in the (2,2,2) complex to 0°.



All the other internal coordinates are optimized within the C_s symmetry. The curve is depicted in Figure 8 at the SCF level. Starting from the minimum, the energy raises when α decreases,

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goes through a maximum 16.8 kcal·mol⁻¹ above the minimum and is then slightly lowered to 14.1 kcal·mol⁻¹ at $\alpha = 0^\circ$.

The optimized bond lengths are given in Table 3 (first line) for the stationary point found near $\alpha = 0^\circ$ ($\alpha = 1.2^\circ$). The Al-B bond distance of the pivoting group is dramatically lengthened up to 4.19 Å; the bridging hydrogen is only bound to the aluminum atom (Al-H = 1.56 Å; B-H = 2.63 Å), and the BH₃ moiety is planar, its molecular plane being perpendicular to the Al-B axis. This structure can clearly be described as an association complex between $\text{AlH}(\text{BH}_4)_2$ and BH₃.

The separate species have been independently optimized and the results are given in Table 3 (second line). As a matter of fact, these geometrical parameters are very close to those of the association complex. The highest point of the energy curve has been fully optimized within the C_s symmetry. A stationary point has been found 14.3 kcal·mol⁻¹ above the minimum for $\alpha = 25.6^\circ$, the corresponding geometrical parameters being given in Table 3 (third line). Vibrational frequency calculations show this point is a true transition state. The normal coordinate associated with the imaginary frequency is essentially developed on the Al-H and B-H stretches. This structure is therefore the transition state of the dissociation reaction:



It can be viewed as a (1,2,2) complex: the two η^2 groups exhibit a geometry close to that found for the (2,2,2) one (compare Table 2, third line and the results given in Figure 7). The bridging hydrogen of the η^1 group is very near the $\text{Al}(\eta^2\text{B})_2$ plane which ensures a planar trigonal coordination around the aluminum atom, the Al-H distance being of 1.57 Å. The η^1 -BH₄ group is strongly distorted, the B-H_b bond length increasing up to 1.98 Å and being intermediate between those in the (2,2,2) structure (1.28 Å) and in the associated complex (2.63 Å). Note finally that the η^1 -coordination does not lead to a linear Al-H_b-B arrangement (Al-H_b-B = 121.5°). Such deviation from linearity has been experimentally found for η^1 -coordinated borohydrides.²¹

All the stationary points (transition state, associated complex and separated species) have been recalculated at the CIPSI level (Table 4). Whatever the calculation level, the associated complex is found to be slightly more stable (less than 1 kcal·mol⁻¹) than the transition state.

The reaction is found to be strongly endothermic (14.1 and 24.2 kcal·mol⁻¹ at the SCF and CIPSI levels, respectively). This large endothermicity probably originates from the electronic deficiency of the products. As a matter of fact, the above reaction is not experimentally observed: when obtained, the products are stabilized by complexation with THF or by dimerization. In both cases, the thermicity of the reaction is expected to be reduced by these interactions. Our calculated value is thus a prediction for the gas-phase reaction and can be considered as an upper limit of the enthalpy variation. As a consequence, the activation energy (which is close to the enthalpy variation) is probably

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Table 3. Optimized Geometrical Parameters (Å, deg) of the Associated Complex, Dissociated Species (AlH(BH₄)₂ and BH₃), and Transition State (1,2,2)

	$\eta^2\text{-BH}_4^-$			$\eta^1\text{-BH}_4^-$				
	BH _b	BH _t	Al-B	BH _b	BH _t	Al-B	Al-H	Al-H _b -B
associated complex	1.284	1.190	2.186	2.627	1.188	4.187	1.562	176.9
products	1.289	1.190	2.189	2.630	1.190		1.561	
TS $\eta^1\eta^2\eta^2$	1.285	1.190	2.181	1.979	1.190	3.103	1.571	121.5

Table 4. Relative Energies (in kcal·mol⁻¹) of the Characterized Stationary Points (Minimum, Transition State, Associated Complex, and Dissociated Species) at SCF and CIPSI Levels

	minimum (η^2, η^2, η^2)	TS (η^1, η^2, η^2)	associated complex	dissociated species
SCF	0	14.3	14.1	14.6
CIPSI	0	24.8	24.2	22.6

overestimated. However, the key step of this reaction (partial decoordination ($\eta^2 \rightarrow \eta^1$) of one BH₄⁻ group) should occur in the experimentally observed reactions.

Conclusion

Our study of aluminum borohydride leads to the following conclusions: (i) The most stable structure is of *D*_{3h} symmetry.

The origin of the distortion from the *D*_{3h} symmetry is interpreted as resulting from a diminution of π pair repulsion in the borohydride groups. (ii) The mechanism of hydrogen exchange goes through a $\eta^2 \rightarrow \eta^3$ change in the coordination mode of one borohydride ligand. (iii) Partial decoordination ($\eta^2 \rightarrow \eta^1$) of one borohydride ligand leads to the breaking of the B-H_b bond.

As already noted in transition metal complexes, the borohydride coordination mode is directly related to the stability and the reactivity of the complex. In the aluminum case, the BH bond breaking goes through a η^1 -coordination which is in accordance with chemical intuition but which has not been evidenced before.

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