Ab Initio Study of the Coordination Modes of Tetrahydroborato Ligands: Structure of the $Ti(BH_4)_3$ Complex

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The structure of the d^1-$Ti(BH_4)_3$ complex is studied by means of ab initio UHF calculations including correlation energy at the MP2 level. Twenty structures which differ by the coordination mode of the BH_4^- ligands are optimized through an analytical gradient method, using the double-ζ basis set I. In agreement with the experimental data, the C_{3h} (η^3, η^3, η^3) structure is found to be the most stable, a result which is confirmed by calculations with the extended basis set II. The geometry of the absolute minimum and the energy ordering of the other structures are rationalized through electron counting around the metal atom. Average bond lengths are given for each coordination mode, and a mechanism for exchange between bridging and terminal hydrogen atoms is proposed, with an activation energy of only 5.1 kcal/mol (basis set II).

The coordination mode of the tetrahydroborato ligand is a fascinating problem since it can bind a transition metal with one (η^1), two (η^2), or three (η^3) bridging hydrogens (H_b).[1] Depending on the way it is bound to the metal, it behaves as a 2-, 4-, or 6-electron donor, respectively.[2] Therefore, the coordination mode has been often related to the 18-electron rule. As an example the tetrahydroborato ligand is bound in an η^1 fashion in the $Cu(BH_4)(PMePh_2)_3$ complex,[3] in which the total number of electrons is 10 (Cu) + 3×2 (phosphines) + 2 (BH_4^-) = 18; the loss of a phosphine group $[Cu(BH_4)(PPh_3)_2]$[4] entails a change in the coordination mode of BH_4^- ($\eta^1 \rightarrow \eta^2$) in order to keep the 18-electron count. When more than one tetrahydroborato group is bound to the metal, symmetry restrictions must be taken into account to obtain the proper electron count.[2,5] On the other hand, the ideal electron number may be different from 18 in paramagnetic complexes: for instance, it is 16 in high-spin d^2 complexes and 17 in d^1 ones. These two points having been noted, the basic relationship between the coordination mode and the number of electron around the metal still applies in rather complicated systems such as those we studied previously by ab initio calculations [$M(BH_4)_3(PH_3)_2$; M = V,[6] Sc,[7] Ti[8]].

In this work, we have been interested in the d^1-$Ti(BH_4)_3$ titanium complex whose structure was characterized recently[9] by an electron diffraction study: each borohydride group binds the metal in an η^3 fashion, the overall complex symmetry being C_{3h}. This coordination mode is called (η^3, η^3, η^3) or (3,3,3) in a more compact way. Ab initio calculations of all possible coordination modes have been performed for this complex. The results are discussed with reference to electron counting around the metal center, and a mechanism for exchange between bridging (H_b) and nonbridging (H_t) hydrogen atoms is proposed.

Method of Calculation

Open-shell calculations were performed on the $Ti(BH_4)_3$ complex in its lowest doublet state with an all-electron ab initio method at the unrestricted Hartree–Fock (UHF–SCF) level using the GAUSSIAN 86 system of programs.[10] Two basis sets were used. The first one (basis set I) was a valence double-ζ basis set[11] applied to the titanium atom. Its valence shell was considered to include 3d, 4s, and 4p orbitals; i.e., the basis set for the metal is 33321/3321/21. For all the atoms of the BH_4^- groups, a 3-21G valence double-ζ basis set[12] was chosen. The geometry of each structure was optimized with the Schlegel method[13] using analytically computed gradients. Correlation effects on the optimal geometries were taken into account by using the perturbational MP2 algorithm.

For the lowest energy structures, similar calculations (geometry optimization at the UHF level followed by MP2 calculation on the optimized geometry) were performed using a larger basis set (basis set II). For the titanium atom, d functions with an exponent of 0.0729 were added[14] to obtain a triple-ζ description of the d orbitals. A 6-31G** basis set[15] was used for the B and H atoms.

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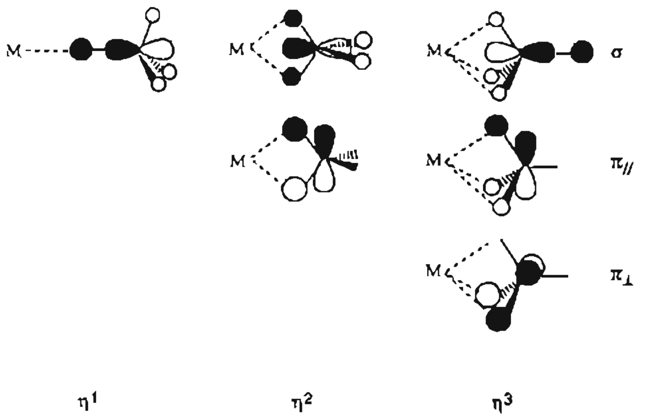


Figure 1. BH_4^- orbitals involved in η^1, η^2, and η^3 coordination modes.

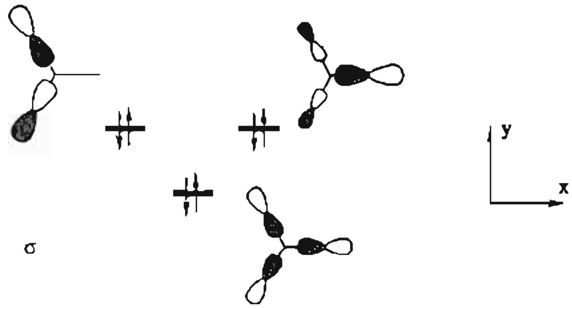
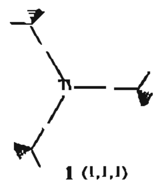


Figure 2. Symmetry-adapted combinations of the σ orbitals in the (1,1,1) structure (**1**). For the sake of clarity, the σ orbitals are pictured as simple p orbitals.

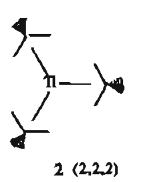
Molecular Orbital Analysis

The three degenerate t_2 occupied molecular orbitals (MOs) of BH_4^- may interact significantly with the metal atomic orbitals (AOs). Depending on the coordination mode, only one (η^1), two (η^2), or three (η^3) MOs are involved in these interactions. In the following, these orbitals will be called σ, $\pi_\parallel$, and $\pi_\perp$, respectively (Figure 1).

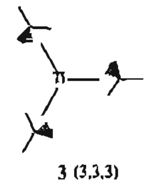
To illustrate the way the electron counting can be achieved, let us simply consider the most symmetrical structures in which the BH_4^- ligands are all bound in the same way to the metal (mono-, bi-, and tridentate, **1**–**4**), the Ti and B atoms being coplanar.



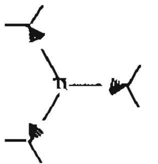
1 (1,1,1)



2 (2,2,2)



3 (3,3,3)



4 (2*,2*,2*)

In the (1,1,1) structure (**1**), only the σ orbitals on the ligands are involved. Their proper symmetry combinations can interact with three metal orbitals (for instance, s, p_x, and p_y; Figure 2) so that the three ligands act as a 6-electron donor in this coordination mode. Since one electron is remaining in the d block (d^1 complex), the total number of electrons is 7 in the (1,1,1) structure.

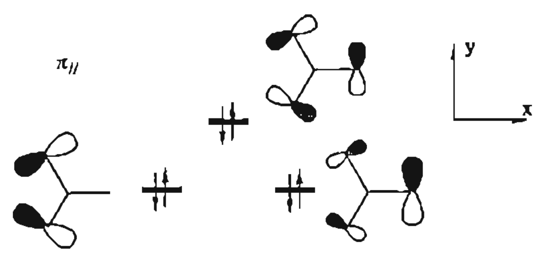


Figure 3. Symmetry-adapted combinations of the $\pi_\parallel$ orbitals in the (2,2,2) structure (**2**). For the sake of clarity, the $\pi_\parallel$ orbitals are pictured as simple p orbitals.

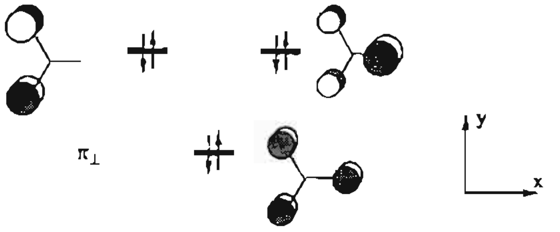


Figure 4. Symmetry-adapted combinations of the $\pi_\perp$ orbitals in the (3,3,3) structure (**3**). For the sake of clarity, the $\pi_\perp$ orbitals are pictured as simple p orbitals.

In the (2,2,2) complex (**2**), with all the bridging hydrogen atoms lying in the TiB_3 plane, the $\pi_\parallel$ orbitals must be considered in addition to the σ ones. The two lowest symmetry combinations can interact with the xy and $x^2 - y^2$ d metal orbitals (Figure 3). The highest one is of f symmetry (three nodal planes) and cannot find any symmetry-adapted orbital on the metal. Consequently, the three BH_4^- ligands act as a 4-electron donor through their $\pi_\parallel$ orbitals, and the (2,2,2) complex can be described as a 6 (σ) + 4 ($\pi_\parallel$) + 1 (Ti) = 11-electron complex.

In the (3,3,3) structure (**3**), the three $\pi_\perp$ orbitals are involved. They mix to give three symmetry-adapted orbitals which can interact with p_z, xz, and yz metal orbitals (Figure 4). The three BH_4^- groups act as a 6-electron donor through their $\pi_\perp$ orbitals, so that the (3,3,3) structure can be described as a 6 (σ) + 4 ($\pi_\parallel$) + 6 ($\pi_\perp$) + 1 (Ti) = 17-electron complex.

Finally, let us consider structure **4**, with three bidentate BH_4^- ligands in which the H_bBH_b planes are *orthogonal* to the TiB_3 plane (this type of structure is actually found for the $Al(BH_4)_3$ complex[16]). In this structure, noted (2*,2*,2*), σ and $\pi_\perp$ orbitals on the BH_4^- ligands are involved so that 6 (σ) + 6 ($\pi_\perp$) electrons are given to the metal. The (2*,2*,2*) complex is therefore a 12 + 1 = 13-electron one. This orbital analysis and the resulting electron counting can be extended to all less symmetrical coordination modes (Table II). Note that the experimental structure (3,3,3) is a 17-electron one, the expected ideal electron count for a d^1 complex.

Geometrical Model

For each structure, all the geometrical parameters are optimized at the UHF level by assuming first a local symmetry for each metal–BH_4 fragment (C_{3v} for η^1 and η^3 coordinations and C_{2v} for η^2 and η^{2*} coordinations) and a coplanar arrangement of the titanium and boron atoms (idealized structures). For the most important structures, these symmetry constraints are relaxed and the Hessian matrix is calculated to characterize the nature (minimum, saddle point, or hill-top) of the extremum.

Results

Idealized Structures. All 20 possible structures depending on the coordination mode of each BH_4^- group (η^1, η^2, η^3, or η^{2*}) have

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Table I. Bond Lengths (Å) Optimized with Basis Set I for the Various Coordination Modes

η^1 Coordination

	(1,1,1)	(1,1,2)	(1,1,2*)	(1,2,2)	(1,2*,2*)	(1,1,3)	(1,2,3)	(1,2*,3)	(1,3,3)	(1,2,2*)	av[a]
Ti–B	3.214	3.231	3.243	3.329	3.243	3.226	3.298	3.232	3.227	3.291	3.253
B–H_b	1.505	1.516	1.530	1.632	1.534	1.506	1.594	1.517	1.514	1.582	1.543
B–H_t	1.196	1.196	1.196	1.193	1.196	1.197	1.194	1.196	1.196	1.194	1.195

η^2 Coordination

	(1,1,2)	(1,2,2)	(1,2,3)	(2,2,2)	(2,2,2*)	(2,2*,2*)	(2,2,3)	(2,3,3)	(1,2,2*)	(2,2*,3)	av[a]
Ti–B	2.425	2.418	2.426	2.447	2.424	2.430	2.452	2.467	2.435	2.427	2.435
B–H_b	1.287	1.287	1.287	1.264	1.284	1.284	1.264	1.262	1.287	1.282	1.279
B–H_t	1.190	1.192	1.192	1.194	1.191	1.190	1.194	1.195	1.191	1.191	1.192

η^3 Coordination

	(1,1,3)	(1,2,3)	(1,2*,3)	(1,3,3)	(2,2,3)	(2*,2*,3)	(2,3,3)	(2*,3,3)	(3,3,3)	(2,2*,3)	av[a]
Ti–B	2.168	2.170	2.176	2.176	2.193	2.178	2.200	2.180	2.198	2.172	2.181
B–H_b	1.256	1.254	1.254	1.254	1.245	1.250	1.242	1.250	1.246	1.252	1.250
B–H_t	1.175	1.175	1.175	1.175	1.177	1.175	1.178	1.176	1.178	1.175	1.176

η^{2*} Coordination

	(1,1,2*)	(1,2*,2*)	(1,2*,3)	(2,2,2*)	(2,2*,2*)	(2*,2*,2*)	(2*,2*,3)	(2*,3,3)	(1,2,2*)	(2,2*,3)	av[a]
Ti–B	2.377	2.383	2.395	2.401	2.386	2.383	2.390	2.407	2.389	2.403	2.391
B–H_b	1.296	1.292	1.293	1.305	1.294	1.288	1.290	1.298	1.294	1.301	1.295
B–H_t	1.190	1.190	1.190	1.187	1.189	1.191	1.190	1.189	1.190	1.189	1.189

[a] Average values.

been optimized using basis set I. The TiB_3 arrangement is found to be nearly trigonal: in most cases, the B–Ti–B angles are in the range 115–125°. Exceptions are found when two sterically encumbered groups (η^2 or η^3) may distort toward a less encumbered one (η^1 or η^{2*}). The corresponding B–Ti–B angle increases in the range 129.8° [η^3–Ti–η^3 in (2*,3,3)] to 143.4° [η^2–Ti–η^2 in (1,2,2)].

In Table I are reported the Ti–B, B–H_b, and B–H_t bond lengths for each coordination mode in the 20 complexes. As noted in a previous study,[6] these geometrical parameters are fairly constant for a given coordinating mode. For η^1 coordination, the Ti–B distance varies from 3.21 to 3.30 Å[17] (except for (1,2,2)) and B–H_b from 1.50 to 1.63 Å, while B–H_t is almost constant at 1.20 Å. Similar conclusions apply to the η^2 (Ti–B = 2.41–2.47 Å; B–H_b = 1.26–1.29 Å; B–H_t = 1.19–1.20 Å), η^{2*} (Ti–B = 2.37–2.41 Å; B–H_b = 1.28–1.31 Å; B–$H_t \approx 1.19$ Å), and η^3 (Ti–B = 2.16–2.20 Å; B–H_b = 1.24–1.26 Å; B–$H_t \approx 1.18$ Å) coordination modes. As expected, the average Ti–B bond length decreases along with an increasing number of bridging hydrogen atoms: 3.25 Å (η^1) > 2.44 Å (η^2) ≈ 2.39 Å (η^{2*}) > 2.18 Å (η^3). In the same way, the B–H_b bond length decreases within this series: 1.54 Å (η^1) > 1.28 Å (η^2) ≈ 1.30 Å (η^{2*}) > 1.25 Å (η^3).

The relative energies of the idealized structures are reported in Table II, at both UHF and MP2 levels. The overall complex symmetry, the electronic ground-state symmetry, and the electron count for each structure are also given. Among the 20 structures, two are by far more stable at both UHF and MP2 levels: (3,3,3) and (2*,3,3). It is noteworthy that they are the only ones with the ideal 17-electron count and that the lowest energy one is (3,3,3), in agreement with the electron diffraction data.[9] Its electronic state is $^2A_1$, the unpaired electron being located in the d_{z^2} orbital. All the other structures have less than 17 electrons (between 7 and 15), and their relative energy increases with the electron deficiency (Figure 5). Such energy increases with the deviation from the ideal electron count have already been found in $M(BH_4)_3(PH_3)_2$ complexes (M = V[6], Ti[8]).

We shall now focus on the actual geometry of the two lowest energy structures, (3,3,3) and (2*,3,3). In the following, only MP2 results are given, the variations at the UHF level being very similar.

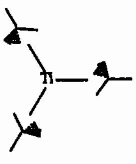
Table II. Symmetries, Electron Counts, and Relative Energies (kcal/mol) of the 20 Idealized Structures at the UHF and MP2 Levels (Basis Set I)[a]

struct	overall symm	state symm	electron count	energy	
				UHF	MP2
(1,1,1)	C_{3h}	$^2E''$	7	82.5	113.2
(1,1,2)	C_{2v}	$^2B_1$	9	63.8	88.3
(1,1,2*)	C_{2v}	$^2A_1$	9	59.2	82.4
(1,1,3)	C_s	$^2A'$	11	50.7	71.1
(1,2,2)	C_s	$^2A''$	11	45.6	62.1
(1,2,2*)	C_s	$^2A'$	11	42.7	59.5
(1,2*,2*)	C_s	$^2A'$	11	37.8	53.6
(2,2,2)	D_{3h}	$^2A_1'$	11	47.9	53.5
(1,2,3)	C_s	$^2A'$	13	33.5	46.2
(1,2*,3)	C_s	$^2A'$	13	29.0	42.7
(2,2,3)	C_s	$^2A'$	13	31.6	35.9
(2,2,2*)	C_{2v}	$^2A_1$	13	26.8	34.7
(2,2*,2*)	C_{2v}	$^2A_1$	13	21.9	30.5
(2*,2*,2*)	D_{3h}	$^2A_1'$	13	18.9	26.6
(1,3,3)	C_s	$^2A'$	15	20.5	30.2
(2,3,3)	C_{2v}	$^2A_1$	15	18.8	20.3
(2,2*,3)	C_s	$^2A'$	15	12.8	18.3
(2*,2*,3)	C_s	$^2A'$	15	11.5	14.9
(2*,3,3)	C_{2v}	$^2A_1$	17	0.8	3.2
(3,3,3)	C_{3h}	$^2A'$	17	0.0	0.0

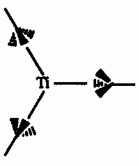
[a] The origin of the energies is that of the idealized C_{3h} (3,3,3) structure (E_{UHF} = −924.7833 au, and E_{MP2} = −925.0719 au).

Further Geometry Optimizations of the (3,3,3) and (2*,3,3) Structures. Since the (3,3,3) and (2*,3,3) structures are found very close in energy, a more detailed study is required. In particular, we shall analyze the role of the rotational orientation of the η^3 groups in each structure and the influence of the basis set extension (basis set I → basis set II) on their geometry and relative energy.

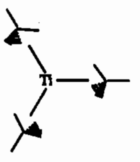
(i) Basis Set I. The (3,3,3) structure whose energy is given in Table II is that depicted in **5**. The orientation of the three



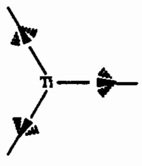
5 (C_{3h})



6 (C_s)



7 (C_s)



8 (C_{3v})

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(17) Note that this value should taken with care since the η^1 coordination generally leads to a nonlinear M–H_b–B arrangement whereas the linearity of these atoms is imposed in our calculations on idealized structures.

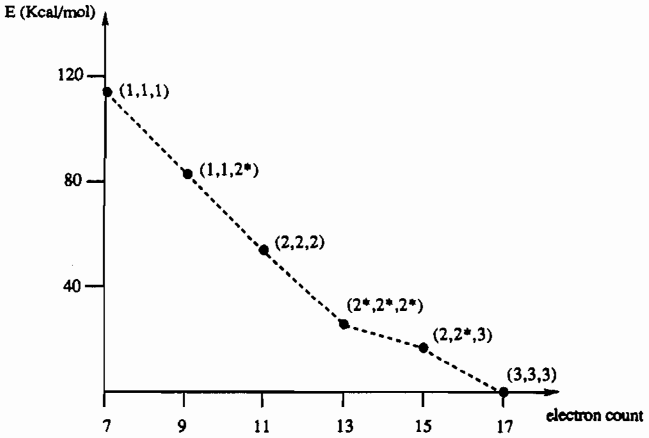


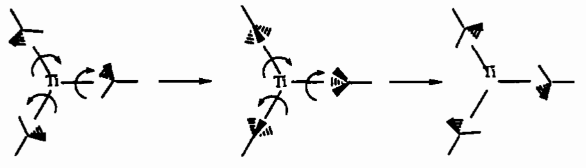
Figure 5. Correlation between the electron count and the energy (basis set I) in the d^1-$Ti(BH_4)_3$ complex. For each electron count, the lowest energy structure is given.

Table III. Relative Energies (kcal/mol) of the Various (3,3,3) and (2*,3,3) Structures at the MP2 Level (Basis Set I)

	5 (C_{3h})	**6** (C_s)	**7** (C_s)	**8** (C_{3v})	**9** (C_{2v})	**10** (C_s)	**11** (C_2)
idealized	0.0	1.6	3.7	6.7	3.2	3.6	3.7
optimized[a]	−1.6	0.6	1.6	5.0	2.8	3.4	3.6
fully optimized[b]	−1.6	−0.3					2.5

[a] The constraint of local C_{2v} and C_{3v} symmetries for the η^{2*} and η^3 groups, respectively, is relaxed, but the overall symmetry (given in the first line of the table) is preserved. [b] All the symmetry constraints are relaxed.

Scheme I



5 (min.) 6 (TS) 5 (min.)

η^3-BH_4^- ligands is actually that found in the experimental structure. We have also studied structures **6**–**8**, which differ from **5** by the rotational angle value of the η^3 groups around the Ti–B axis.

When a local C_{3v} symmetry for each η^3-BH_4^- ligand is assumed (idealized geometries), structure **5** is found to be the most stable (Table III, first line). With the symmetry group for each structure being preserved, the constraint of local C_{3v} symmetry was relaxed. Each structure is stabilized by about 1–2 kcal/mol, but the energy ordering is preserved (**5** < **6** < **7** < **8**; Table III, second line). Finally, full geometry optimization without any symmetry restriction (C_1 group) was performed starting from these four structures. Only one minimum and one transition state (characterized by the diagonalization of the analytically calculated Hessian matrix) were found (Table III, third line). Structure **5** is a true minimum in which the C_{2h} symmetry is preserved. A structure close to **6** is found to be a transition state. Full optimization of structures **7** and **8** leads to the transition state **6** or to the absolute minimum **5**. It is noteworthy that the transition state **6** connects two equivalent structures of the minimum **5** by a concerted rotation of the three η^3 groups (Scheme I). The actual computed activation energy for this process is only 1.3 kcal/mol at the MP2 level.

The geometrical parameters associated with the absolute minimum (Figure 6) are given in Table IV. In agreement with the experimental data, the C_{3h} symmetry is preserved in the full geometry optimization, and the optimized bond lengths agree well with the experimental ones. The main difference from the diffraction structure is a slight pivoting of each BH_4^- ligand (Ti–B–H_t = 172.7°), so that the out-of-plane hydrogen atoms are closer to the metal than the in-plane ones (note however that a local C_{3v} symmetry for each Ti–BH_4 moiety was assumed in the experimental work, as it was in our calculations on idealized structures).

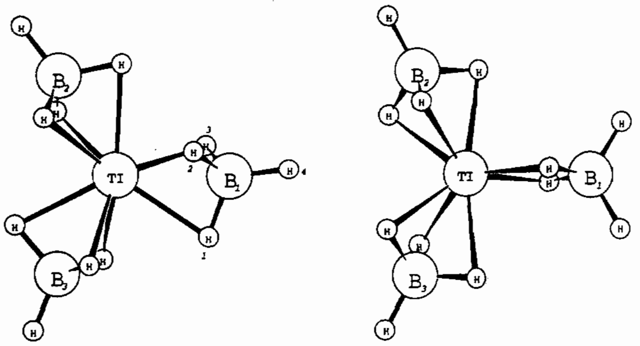


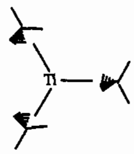
Figure 6. Optimized structures (UHF level) of the (3,3,3) and (2*,3,3) minima.

Table IV. Geometrical Parameters of the (3,3,3) C_{3h} Minimum Fully Optimized with Basis Sets I and II (Distances, Å; Angles, deg)

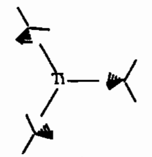
	basis set I	basis set II	exp[a]
Ti–B	2.201	2.179	2.218(15)
Ti–H_1	1.976	1.961	2.067(17)
Ti–$H_{2,3}$	2.155	2.113	2.067(17)
B–H_1	1.228	1.227	1.230(8)
B–$H_{2,3}$	1.258	1.257	1.230(8)
B–H_4	1.178	1.179	1.107(21)
H_1–B–Ti	71.6	70.5	
$H_{2,3}$–B–Ti	62.9	63.1	
H_4–B–Ti	172.7	173.3	180[b]

[a] Experimental values from ref 9. [b] Assumed.

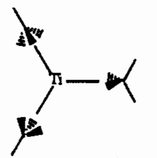
Let us now study in more detail the (2*,3,3) structure. The energy reported in Table II is that of the idealized structure depicted in **9**. At the MP2 level, it lies 3.2 kcal/mol above the idealized C_{3h} (3,3,3) structure (Table III). Two other structures have been studied for this (2*,3,3) complex, **10** (C_s) and **11** (C_2), which differ from **9** by the rotational angle value of the η^3 groups around the Ti–B axis. Assuming first idealized geometries for each structure, **9** is found more stable than **10** and **11** by 0.4 and 0.5 kcal/mol, respectively (Table III). Relaxing the local symmetry for the Ti–BH_4 moiety within the same overall symmetry stabilizes each structure by less than 0.5 kcal/mol, and **9** remains the lowest energy one. Finally, full geometry optimization (C_1 group) starting from these structures was carried out. Only one minimum was found and characterized by diagonalization of the Hessian matrix. Its geometry is close to that of **11**, and its energy is 4.1 kcal/mol above the absolute (3,3,3) minimum (Table III). Therefore this (2*,3,3) structure appears to be a secondary minimum on the whole potential energy surface.



9 (C_{2v})



10 (C_s)



11 (C_2)

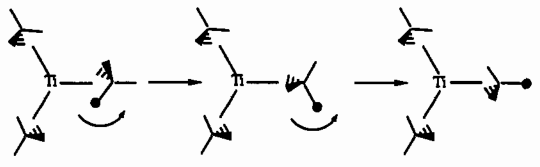
(ii) Basis Set II. The idealized geometries of structures **5**–**11** were reoptimized with basis set II. Relative energies are given in Table V. On the whole, the energetic results are almost unchanged in going from basis set I to basis set II (compare Tables III and V, first line). For the (3,3,3) complex, the C_{3h} structure **5** is still the most stable, while for complex (2*,3,3), the energies of structures **9**–**11** are about 5 kcal/mol above. The geometries of the absolute (3,3,3) and secondary (2*,3,3) minima,

Table V. Relative Energies (kcal/mol) of the Various (3,3,3) and (2*,3,3) Structures at the MP2 Level (Basis Set II)

	5 (C_{3h})	**6** (C_s)	**7** (C_s)	**8** (C_{3v})	**9** (C_{2v})	**10** (C_s)	**11** (C_2)
idealized	0.0[a]	1.5	4.0	7.0	4.8	5.2	5.0
fully optimized[b]	−1.2						3.9

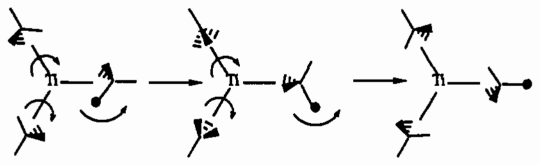
[a] E_{MP2} = 925.7358 au. [b] All symmetry constraints are relaxed (C_1 group).

Scheme II



5 10 7

Scheme III



5 11 5

characterized with basis set I, were reoptimized with the extended basis set without any symmetry constraints (C_1 group). The geometrical changes with respect to basis set I are very small (see Table IV for the (3,3,3) minimum), and the energy gap between the two minima only slightly increases from 4.1 to 5.1 kcal/mol. Thus, we infer that the higher quality calculations on key structures **5**–**11** do not modify the conclusions drawn from calculations with basis set I.

Mechanism for the Hydrogen Exchange. A low-energy structure of the (2*,3,3) type allows an easy exchange mechanism between bridging (H_b) and nonbridging (H_t) hydrogen atoms. Let us consider two exchange paths starting from the absolute (3,3,3) minimum: In the first one, an η^3 group is pivoting while the two others are kept frozen (Scheme II). In the second one, the pivoting of the η^3 group is accompanied by the rotation of the two others around the Ti–B axis (Scheme III).

In the first mechanism, structures **10** [(2*,3,3), C_s] and **7** [(3,3,3), C_s] are successively reached, neither being a stationary point (minimum or saddle point). On the contrary, in the second mechanism, the exchange between bridging and terminal hydrogen atoms relies on two absolute equivalent (3,3,3) minima, **5**, through the secondary (2*,3,3) minimum **11**. This mechanism was studied with both basis sets I and II.

Since **11** is a secondary minimum at the UHF level, a transition-state structure must lie between **5** and **11**. A stationary point was actually located with basis set I and characterized as a transition state by diagonalization of the Hessian matrix. Its geometry is close to that of **11**, and its energy, only 0.1 kcal/mol higher. Reoptimization of this transition state with the extended basis set II leads to very similar results for both geometry and energy: at the UHF level, it lies 0.2 kcal/mol above **11**, and the activation energy for the whole exchange process is 2.1 kcal/mol (Figure 7, dotted line). After recalculation at the MP2 level of the three stationary points, the shallow secondary minimum **11** disappears and becomes the highest energy point of the exchange mechanism (Figure 7, full line), the activation energy being 5.1 kcal/mol (basis set II; the value found with basis set I was 4.1 kcal/mol).

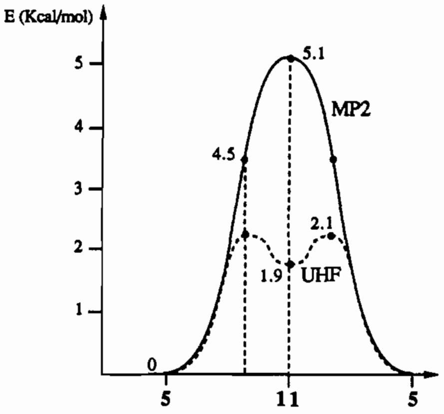


Figure 7. Schematic energy profile for the hydrogen-exchange mechanism depicted in Scheme III. The energies are given for calculations with basis set II.

Conclusion

Ab initio calculations have been performed on the d^1-$Ti(BH_4)_3$ complex, with rather limited (I) and extended (II) basis sets. At both levels of calculations, UHF and MP2 results show that the C_{3h} (η^3, η^3, η^3) structure is the most stable for this complex, the optimized bond lengths and bond angles being close to experimental values. On the other hand, simple molecular orbital analysis shows this structure belongs to the 17-electron family, which is the expected ideal count for this d^1 complex. A second 17-electron structure, (η^{2*}, η^3, η^3), is found 5.1 kcal/mol above the (η^3, η^3, η^3) absolute minimum (MP2 level). A mechanism for the exchange between bridging and nonbridging hydrogen atoms is proposed which interconverts two equivalent C_{3h} (η^3, η^3, η^3) structures through the (η^{2*}, η^3, η^3) one. The extension of the basis set (I → II) leads to almost identical results for the geometry and the energy of the lowest energy structure. Therefore, a double-ζ basis set such as basis set I gives accurate results for the most stable structures of this d^1 titanium complex.

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