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Ab Initio Study of the Coordination Modes of Tetrahydroborato Ligands: What Is the Actual Structure of the $Ti(BH_4)_3(PMe_3)_2$ Complex?

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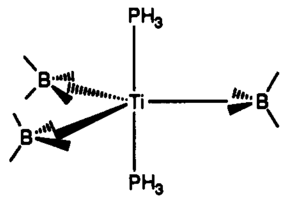
The structure of the d^1 complex $Ti(BH_4)_3(PH_3)_2$ is studied by means of ab initio UHF calculations including correlation energy at the MP2 level. This complex is used as a model for the $Ti(BH_4)_3(PMe_3)_2$ complex characterized by Girolami et al. Sixteen structures which differ by the borohydride coordination modes are optimized through an analytical gradient method. The energetical ordering of these structures is analyzed through an electron count. We find that the optimal structure corresponds to a η^2,η^2,η^3 coordination mode, a result in disagreement with the experimental data, which have been interpreted in terms of η^1,η^1,η^2 coordination. Possible interpretations of this discrepancy are discussed.

The coordination mode of tetrahydroborato ligands, BH_4^-, is a very intriguing problem since this ligand can bind the metal with one (η^1), two (η^2) or three (η^3) bridging hydrogen atoms. In recent years, numerous transition metal tetrahydroborato complexes have been characterized by X-ray or neutron diffraction or by IR and NMR spectroscopy.[1] All the coordination modes have been experimentally characterized with various metals. Among these complexes, we have been interested in three of them containing three BH_4^- groups: $Sc(BH_4)_3(THF)_2$,[2] $Ti(BH_4)_3(PMe_3)_2$,[3] $V(BH_4)_3(PMe_3)_2$.[4] In each case, the complex adopts a distorted trigonal-bipyramidal geometry with the BH_4^- groups at the equatorial positions. The coordination modes of the tetrahydroborato ligands differ in these complexes (X-ray diffraction). In the scandium complex (d^0), two groups are η^3 and one η^2. This structure (η^2,η^3,η^3) is noted henceforth (2,3,3). The structure of the titanium d^1 complex is described as close to (1,1,2) while that of the high-spin complex of vanadium (d^2) is (2,2,2). These results suggest a relationship between the electronic configuration of the metal in the complex and the coordination mode of the BH_4^- ligands.

The coordination mode of one tetrahydroborato ligand can be related to the number of electrons it gives to the metal:[5] an η^1, η^2, or η^3 coordination corresponds to a BH_4^- group acting as a 2-, 4-, or 6-electron donor respectively. The coordination mode can then be simply predicted by applying the 18-electron rule. The situation becomes more complicated when more than one BH_4^- group is bounded to the metal. In a previous work,[6] we have shown that this electron count still apply in the $V(BH_4)_3(PH_3)_2$ complex, provided symmetry restrictions are taken into account. In this case, the (2,2,2) structure is the most stable since it leads to a 16-electron complex which is the optimal situation for this high-spin d^2 structure. Preliminary calculations on the scandium complex[7] have also shown the validity of this description.

The most remarkable feature of the X-ray structure of the titanium complex $Ti(BH_4)_3(PMe_3)_2$ (**1**) is the unusual η^1 coordination mode of two of the tetrahydroborato ligands which have been described as "agostic". The third one is bidentate (η^2), the two bridging hydrogen atoms lying in the equatorial plane of the distorted trigonal-bipyramidal geometry.



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In this paper, the model complex $Ti(BH_4)_3(PH_3)_2$ (**1**) is studied by means of ab initio calculations. All the possible coordination modes of the three BH_4^- ligands have been studied. The results are compared to the experimental X-ray structure and discussed through the electron counting presented previously.

Method of Calculation

The $Ti(BH_4)_3(PMe_3)_2$ complex was modeled by replacing the phosphine methyl groups by hydrogens. Open-shell calculations were performed on this model complex in its lowest doublet state with an all-electron ab initio method at the unrestricted Hartree-Fock (UHF-SCF) level with

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Table I. Symmetries, Electron Counts and Relative Energies (in kcal/mol) of the 10 Idealized Structures at the UHF and MP2 Levels[a]

structure	overall sym	state sym	electron count	UHF	MP2
(1,1,1)	C_{3h}	E″	11	46.4	69.5
(1,1,2)	C_{2v}	B_1	13	25.1	41.4
(1,1,3)	C_s	A″	15	24.5	37.0
(1,2,2)	C_s	A″	15	11.2	20.6
(2,2,2)	D_{3h}	E″	15	4.0	7.0
(1,2,3)	C_s	A″	17	11.9	18.4
(2,2,3)	C_s	A″	17	0.0	0.0
(2,3,3)	C_{2v}	A_2	19	6.8	7.8
(1,3,3)	C_s	A″	19	19.5	25.5
(3,3,3)	C_s	A′	19	22.5	23.4

[a] The origin of the energies is that of the (2,2,3) structure (E_{UHF} = −1602.2082 au and E_{MP2} = −1602.6005 au).

the help of the GAUSSIAN 86 system of programs.[8] For each computed structure, the spin contamination is weak (S^2 between 0.75 and 0.77). For the titanium atom, a valence double-ζ basis set was used.[9] The 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[10] was also chosen. For the atoms of the phosphine ligands, a minimal basis set was used.[11] The geometry of each structure was optimized with the Schlegel[12] method using analytically computed gradients. Correlation effects on the optimal geometries were taken into account by the perturbational MP2 algorithm.

Geometrical Model

The internal structure of the phosphines has been kept frozen (P-H = 1.42 Å; H-P-H = 93.2°) and the Ti-P distances fixed at the experimental value (2.555 Å). All the other geometrical parameters are optimized 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 coordination). For η^2 coordination, the bridging hydrogen atoms are kept in the equatorial plane while in η^1 and η^3 coordinations the rotational angle around the Ti-B axis is optimized. Once the most important structures are found, these symmetry constraints are relaxed for further calculations. In some cases, a partial Hessian matrix (restricted to the nonfrozen parameters) has been calculated in order to characterize the nature (minimum or saddle point) of the extremum within a given symmetry point group. Finally, a few reaction paths between the structures of lowest energies are computed.

Results

Idealized Structures. The relative energies of 10 structures are reported in Table I, at both the UHF and MP2 levels. These values are obtained assuming the local symmetry defined above for each metal-BH_4 group. The overall complex symmetry and the electronic ground state symmetry are also given in Table I. The electron count for these structures has been presented in ref 6.

The general features of the results are similar at both levels of calculation. The lowest energy structure is (2,2,3) (**2**) at both UHF and MP2 levels of calculation. Above this structure, two others are rather low in energy: (2,2,2) (**3**) and (2,3,3) (**4**) which lie 4.0 and 6.8 kcal/mol, respectively, above the minimum at the UHF level (7.0 and 7.8 kcal/mol at that of MP2). All other structures are more than 11 (UHF) or 18 kcal/mol (MP2) above the minimum.

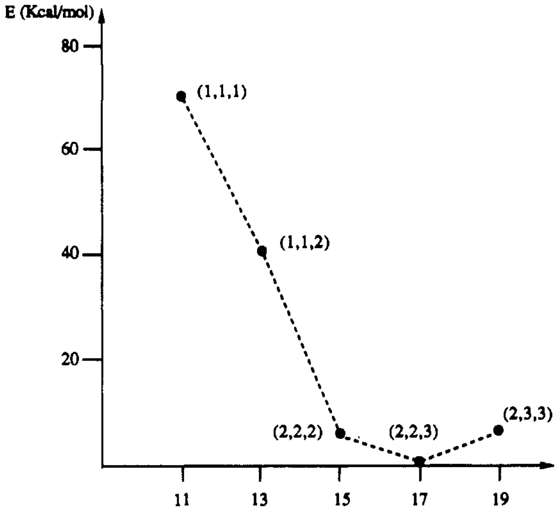
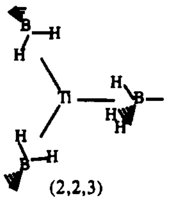


Figure 1. Correlation between the electron count and the energy (at the MP2 level) in the $Ti(BH_4)_3(PH_3)_2$ d^1 complex (for each electron count, only the lowest energy structure is reported).

Table II. Main Geometrical Parameters in the Structures (2,2,2), (2,2,3), and (2,3,3), Where Bond Lengths are in Å and Angles Are in deg

	(2,2,3)	(2,2,2)	(2,3,3)
Ti-B (η^2)	2.510	2.490	2.532
Ti-B (η^3)	2.266		2.322
(η^2)B-H_b	1.255	1.253	1.257
(η^3)B-H_b	1.234		1.235
P-Ti-P	158.3	180	155.3



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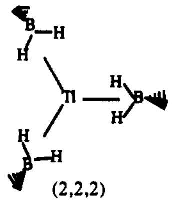

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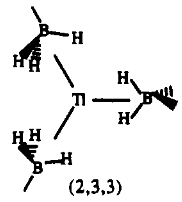

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These energy results are consistent with the electron counting around the metal: the ideal situation for this d^1 complex is reached when all metal orbitals (s, p, and d) except one are used for bonding interactions (σ or π) with the ligands, the remaining nonbonding orbital carrying the unpaired d electron. The ideal count is therefore as follows: (8 × 2) + 1 = 17. As expected, *the lowest energy structure, (2,2,3), belongs to the 17-electron species family* (Table I). The two following structures, (2,2,2) and (2,3,3) have a lack or an excess of two electrons, and structures with a larger deviation from the ideal count are higher in energy (Figure 1).

The main geometrical parameters associated with the three lowest energy structures are given in Table II. Some general trends already found in our previous study[6] are noteworthy here: as the number of bridged hydrogen atoms (H_b) increases, the metal–boron and B–H_b distances decrease. The theoretical Ti-B bond lengths are slightly overestimated with respect to the experimental data: the Ti(III)–(η^2-BH_4) bond length is found to be 2.411 Å in $Ti(BH_4)_3(dme)$[13] and 2.37 Å in $Cp_2Ti(\eta^2\text{-}BH_4)$.[14]

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Table III. Symmetries, Electron Count, and Relative Energies (in kcal/mol) of Structures Involving the η^{2*}-Coordination Mode at the UHF and MP2 Levels[a]

structure	overall sym	state sym	electron count	UHF	MP2
(2*,2*,2*)	C_{2v}	B_2	15	48.4	49.7
(2*,2*,3)	C_s	A''	17	42.0	43.8
(2,2*,2*)	C_{2v}	B_1	17	23.4	26.0
(2,2,2*)	C_{2v}	A_2	17	–0.7	1.3
(2,2*,3)	C_s	A''	19	16.3	17.0
(2*,3,3)	C_{2v}	A_2	19	30.2	31.6

[a] The origin of the energies is that of the (2,2,3) structure (Table I).

In Ti(η^3-BH$_4$)$_3$ the Ti–B bond length is 2.218 Å.[15] Note however that our theoretical values for the B–H$_b$ bond length in the η^3-coordination (1.234–1.235 Å) are in very good agreement with the electron diffraction data for Ti(η^3-BH$_4$)$_3$ (1.230 Å).[15] In all structures except (2,2,2), in which the D_{3h} symmetry is imposed, P–Ti–P is significantly different from 180° (in the range 155–160°), the Ti–P bonds being always bent away from the η^3 group(s). This bending reduces the four-electron repulsion between the axial Ti–P bonds and the BH$_4^-$ ligand(s) which have bridging hydrogen atoms out of the equatorial plane of the complex.

The most striking feature of these results is the high energy level of the (1,1,2) structure, which was proposed from the X-ray crystallographic determination:[3] it lies 25.8 kcal/mol above the minimum at the UHF level (41.4 kcal/mol at that of MP2). These energy differences are large and significant at our level of calculation. Note they are consistent with the electron count around the metal since the (1,1,2) structure is very electron deficient (13- instead of 17-electron for (2,2,3)). However, recall that, in these calculations, a local C_{3v} symmetry is preserved at each Ti-η^1 group, i.e. a colinearity between B–H (bridged) and B–Ti bonds. In all the experimental structures possessing an η^1-BH$_4^-$ group, the metal–H$_b$–B arrangement is bent. Moreover, in the structure of the titanium complex, the Ti–B–H$_b$ bond angle is 45(4)°. Relaxing the linearity constraint in (1,1,2) leads to collapse to the (2,2,2) structure, in which the (B–H, B–Ti) angle is approximately 53° and no intermediate minimum is found. We therefore conclude a disagreement between the X-ray structure and the results of our calculations: the (1,1,2) structure is found to be high in energy and is not a true minimum on the potential energy surface.

Let us now return to the three lowest energy structures (2,2,3), (2,2,2), and (2,3,3). As mentioned before, the bridging hydrogen atoms of the η^2 groups were kept in the equatorial plane of the complex (see structures **2**, **3**, and **4**). Structures in which these groups are rotated by 90° around the Ti–B axis are now studied, leading to a coordination mode denoted as η^{2*} or 2* (**5**).

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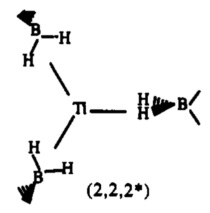
The results given in Table III show that one of these new structures, (2,2,2*) (**6**), is almost isoenergetic with the lowest energy structure found previously, (2,2,3) (**2**). It is even slightly more stable at the UHF level (–0.7 kcal/mol) but is a little higher in energy at that of MP2 (+1.3 kcal/mol). At this level of calculation, these energy differences are too small to be significant. Note finally that the (2,2,2*) structure belongs to the 17-electron species family as did (2,2,3).

We will now focus on the four lowest energy structures (**2**, **3**, **4**, and **6**) to ascertain whether energy ordering depends on further optimization of geometry. In the following, only MP2 results are given, the changes in those of UHF being very similar.



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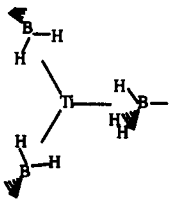
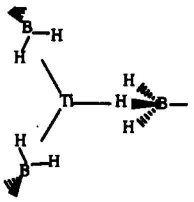
Further Geometry Optimizations. The (2,2,3) structure has been optimized keeping the equatorial plane as a symmetry plane (C_s), but relaxing the C_{3v} (C_{2v}) local symmetry constraint for η^3 (η^2) group(s). The stabilization energy with respect to the idealized C_s geometry is only 1.0 kcal/mol (Table IV), and despite a slight pivoting of the BH$_4^-$ ligands, the optimized structure can still be described as (2,2,3). Numerical calculation of the partial Hessian matrix leads to eigenvalues which are all positive: this structure (**7a**) is a true minimum on the C_s potential energy surface (at the UHF level), and it is the lowest energy one we have found at both UHF and MP2 levels. Finally, the rotational barrier of the η^3 group in this structure is very low since the computed energy difference between conformations **7a** (described above) and **7b** (fully optimized) is only 0.2 kcal/mol.



7a



7b

The effect of geometry optimization of (2,2,2*), without any symmetry constraint, is almost negligible from an energetic point of view (ΔE = –0.1 kcal/mol, Table IV), and the C_{2v} geometry is preserved. Therefore, the energy gap between (2,2,3) and (2,2,2*) increases to 2.2 kcal/mol, a value still too small to allow a definite conclusion. (We will return later to the path connecting these two structures.) At the UHF level, the computation of the partial Hessian matrix shows that this structure is a true minimum on the C_s potential energy surface.

Let us now consider the two structures in the range 7–8 kcal/mol above the minimum. As already stated by Girolami et al.,[3] the D_{3h} (2,2,2) structure is Jahn–Teller unstable, since there are two degenerate MOs with a single electron to accommodate. Keeping only a symmetry plane bisecting one η^2 group (C_s), we have optimized separately the geometries of the A' and A'' electronic states. The energy decreases are less than 0.1 kcal/mol. The geometries reached are actually of C_{2v} symmetry, very close to the D_{3h} structure and the two electronic states of A_1 and B_2 symmetry (Table IV). The main change is a slight concerted pivoting of the two η^2 groups symmetrical with respect to the C_s plane, either inward (A_2) or outward (B_1). In both cases these motions have small energetic consequences. This can be easily understood since the unpaired electron (responsible for the Jahn–Teller unstability) occupies one of the two degenerate orbitals which are essentially non bonding.

Finally, the (2,3,3) structure has been optimized in the C_s group, the plane of symmetry bissecting the η^2 group. Again both energetic (ΔE = –0.2 kcal/mol, Table IV) and geometric consequences of this optimization are small. The optimized structure is a minimum on the C_s potential energy surface (UHF level).

Computed Path between (2,2,3) and (2,2,2*) Structures. Since the energies of optimized (2,2,3) and (2,2,2*) structures are very

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Table IV. Relative Energies at the MP2 Level (in kcal/mol) of the Four Lowest Structures after Optimization[a]

	(2,2,3)	(2,2,2*)	(2,2,2)		(2,3,3)
overall symmetry	C_s	C_{2v}	C_{2v}	C_{2v}	C_s
symmetry of state	A″	A_2	A_2	B_1	A″
E	−1.0	1.2	7.0	7.0	7.6

[a] The origin of energies is that of the idealized (2,2,3) structure (Table I).

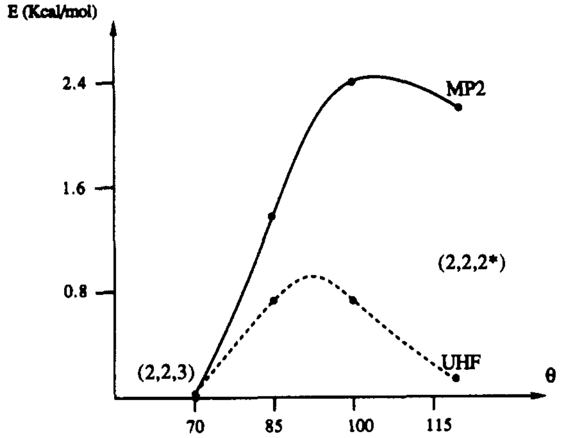
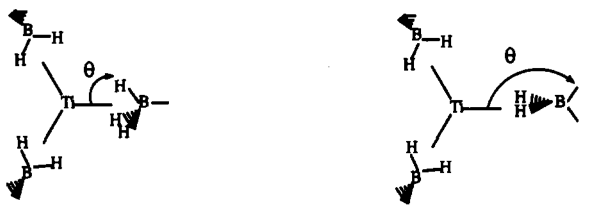


Figure 2. Computed path between the (2,2,3) and the (2,2,2*) structures at the UHF (dashed line) and MP2 (solid line) levels.

close to each other ($\Delta E = 2.2$ kcal/mol in favor of (2,2,3) at the MP2 level), we have computed the energetic profile associated with the path connecting these two structures to verify that there is no structure of lower energy between them. It has been done by varying the θ angle (**8**) from its value in (2,2,3) (70°) to the value reached in (2,2,2*) (120.7°), other geometrical parameters being optimized within the C_s constraint.



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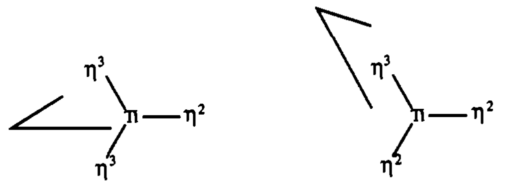
At the UHF level, the two structures are separated by a small energy barrier (less than 1 kcal/mol), both being a minimum on the C_s surface (Figure 2, dashed line). This result is consistent with our geometry optimizations which showed (previous section) that these two structures are true minima on this surface. This result is essentially preserved at the MP2 level, the barrier between (2,2,2*) and (2,2,3) being about 0.2 kcal/mol (Figure 2, solid line). The major point is that there is no structure of lower energy located between the two structures previously optimized, at both the UHF and MP2 levels of calculation.

Discussion

Our theoretical results clearly disagree with the structure proposed from X-ray determination of Girolami et al.[3] The idealized (1,1,2) structure is found to be very high in energy (which is consistent with its electron deficiency) and is not a minimum on the potential energy surface. The description of the experimental structure as a distorted (1,1,2) complex is therefore questionable.

From a geometrical point of view, the assignment of the experimental structure to the (2,3,3) one would allow a better understanding of the following points: (i) The two equal Ti–B distances are shorter than the third one. This is consistent with the (2,3,3) complex since a η^3 group is more strongly bound to the metal than a η^2 one, but not with the (1,1,2) coordination. (ii) Experimentally, the phosphines bend toward the η^2 group which is the less coordinated in the (2,3,3) complex. In the (1,1,2) structure, this bend should occur in the opposite sense (away from the η^2 group) since the η^1 groups are less encumbered. Indeed the optimization of the idealized (1,1,2) structure leads to a slight bending (P–Ti–P = 175.4°) toward the η^1 groups.

From an energetic point of view, the absolute minimum we have found on the potential energy surface is the (2,2,3) structure located 8.6 kcal/mol below the (2,3,3) one. This energy difference seems to be significant at our level of calculation. However, the structure of this minimum is actually inconsistent with the results of Girolami et al.: there are one long and two short Ti–B bonds, and the phosphines are bent toward the η^2 ligands.[16] This discrepancy may be explained in two ways. If the (2,2,3) structure is actually the lowest energy one, the complex experimentally synthetized might correspond to a local secondary minimum whose evolution to the absolute one is prevented by kinetic barriers. As shown above, it should be more adequatly described as a (2,3,3) complex rather than a (1,1,2) one. An other possibility could be an inadequate crystallographic characterization of the titanium complex. The (2,2,3) complex may also possess a crystallographic mirror plane (**9**) passing through the η^3 group. An inversion between the η^3 and η^2 groups belonging to this mirror plane may lead to an erroneous characterization of the structure ((2,2,3) → (2,3,3)). This would also account for the abnormal shape of the thermal ellipsoids whose larger axis are perpendicular to the symmetry plane.



(2,3,3) (2,2,3)

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(16) Note however that a model involving superposition of disordered η^2 and η^3 coordinations has been discussed by Girolami et al. (see Experimental Section of ref 3). This model was however rejected because it seemed less consistent with the crystallographic data.