a low-lying bonding molecular orbital which can accommodate two electrons, thereby facilitating reduction of polyoxometalates of these types.

The spectrum of the cutoctahedron corresponding to the topology of the $XM_{12}O_{40}^{n-}$ derivatives has not only the single +4 eigenvalue but also the triply degenerate +2 eigenvalue corresponding to three additional bonding orbitals which can accommodate an additional six electrons. For this reason eight-electron reduction of the $XM_{12}O_{40}^{n-}$ d^0 early-transition-metal derivatives might be expected to be favorable since eight electrons are required to fill the bonding orbitals of the cuboctahedron, i.e., the four bonding orbitals corresponding to the positive eigenvalues +4 and +2. However, experimental evidence indicates that when six electrons are added to a sufficiently stable $XW_{12}O_{40}$ derivative, rearrangement occurs to a more localized $XW_9^{VI}W_3^{IV}O_{40}^{n-}$ structure in which the three W^{IV} atoms form a bonded triangle[29] with W–W = 2.50 Å similar to the W–W of 2.51 Å in the tungsten(IV) complex[30] $[W_3O_4F_9]^{5-}$. This bonded W_3 triangle corresponds to one of the triangular faces of the W_{12} macrocuboctahedron in $XW_{12}O_{40}^{n-}$. This rearrangement of the $XW_{12}O_{40}^{n-}$ derivatives to a more localized structure upon six-electron reduction is an indication of the weakness of the binodal orbital aromaticity in these polyoxometalates corresponding to a low value for β in eq 3. Thus a configuration with three W–W localized two-cen-

ter-two-electron σ bonds is more stable than a delocalized configuration with six electrons in the bonding molecular orbitals generated by binodal orbital overlap; i.e., $\beta_\sigma \gg \beta_d$ where $\beta_\sigma = (\Delta E_{bonding} - \Delta E_{antibonding})/2$ for a W–W σ bond and β_d is the energy unit in eq 3 from overlap of the d_{xy} orbitals on the 12 tungsten atoms.

The concept of binodal aromaticity in reduced early-transition-metal polyoxometalates may be related to their classification as mixed-valence compounds. Robin and Day[31] classify mixed-valence compounds into the following three classes: class I, fully localized corresponding to an insulator in an infinite system; class II, partially delocalized corresponding to a semiconductor in an infinite system; class III, completely delocalized corresponding to a metal in an infinite system. ESR studies on the one-electron reduced polyoxometalates $M_6O_{19}^{n-}$ and $XM_{12}O_{40}^{n-}$ suggest class II mixed-valence species.[15,32,33] Although such species are delocalized at accessible temperatures, they behave as localized systems at sufficiently low temperatures similar to semiconductors.[15,32,33] This is in accord with the much smaller overlap (i.e., lower β in eq 3) of the metal d_{xy} orbitals associated with binodal orbital aromaticity as compared with the boron sp hybrid anodal internal orbitals in the deltahedral boranes $B_nH_n^{2-}$ or the carbon uninodal p orbitals in benzene.

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Contribution from the Departament de Quimica, Universitat Autonoma de Barcelona, 08193 Bellaterra, Barcelona, Spain, and Laboratoire de Chimie Théorique (URA 506, ICMO), Bât. 490, Université de Paris-Sud, 91405 Orsay Cedex, France

Ab Initio Study of the Coordination Modes of Tetrahydroborato Ligands: The High-Spin Complex V(BH4)3(PH3)2

Agusti Lledos,*,† Miquel Duran,† Yves Jean,‡ and François Volatron*,‡

The structure of the high-spin complex d^2-V(BH4)3(PH3)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 complex V(BH4)3(PMe3)2 recently characterized by Girolami and co-workers, in which the three tetrahydroborato ligands are coordinated in an η^2 fashion. Thirteen structures which differ in the coordination mode of the BH4⁻ ligands (η^1, η^2, or η^3) are optimized by an analytical gradient method. In agreement with experimental data, the (η^2,η^2,η^2) structure, where all bridging hydrogens are lying in the plane of the boron atoms, is found to be the most stable. This result, together with the energy ordering of the other structures, is rationalized both through usual electron counting and through molecular orbital analysis. Average bond lengths are given for each coordination mode, and the mechanisms for exchange between bridging and terminal hydrogens in the BH4⁻ group are briefly discussed.

In recent years, there has been a considerable interest in transition-metal tetrahydroborato complexes. Several complexes have been synthesized and characterized by X-ray[1–20] or neutron diffraction[21–23] or by IR and NMR spectroscopy.[24–33] Besides their importance in homogeneous catalysis, these complexes are of great interest because three modes of coordination of the BH4⁻ moiety have been proved, depending on the number of bridging hydrogens between the metal and boron atoms. These coordination modes are called η^1, η^2, and η^3 (1–3).
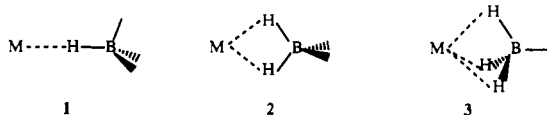
Until the 1980s, the coordination mode was mostly determined on the basis of IR data. However, this method may be imprecise, since the B–H stretching vibrations cannot be uniquely related

to one coordination mode.[7b,23] X-ray diffraction studies may also be imprecise because of the hazardous location of the H atoms

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Table I. Relative Energies (kcal/mol) of the Various Structures at the UHF and UMP2 Levels[a]

|	(1,1,1)	(1,1,2)	(1,1,3)	(1,2,2)	(1,2,3)	(1,3,3)	(2,2,2)	(2,2,3)	(2,3,3)	(3,3,3)
UHF	37.5	18.2	16.8	1.1	16.8	39.8	0.0	8.1	21.1	39.6
UMP$_2$	61.6	34.8	26.3	8.3	25.9	51.2	0.0	9.0	22.4	42.7

[a] The most stable structure (2,2,2) has been taken as origin of the energies ($E_{UHF} = -1696.18198$ au; $E_{UMP2} = -1696.58870$ au).

by this technique.[22,23] Nevertheless, an accurate determination of the metal–boron bond length is a good indication of the coordination mode, since this length decreases with the number of bridging hydrogens.[34] At present, neutron diffraction studies seem to give the most reliable determination of the structure of these complexes. Finally, the way BH_4^- bonds to transition metals may also be related to alkane activation. Since CH_4 and BH_4^- are isoelectronic, it is thought that the coordination mode of BH_4^- should be a good indication of the way in which CH_4 is activated by the metal.

For mono(tetrahydroborato) closed-shell complexes, the coordination mode of the BH_4^- group can be easily predicted from a simple electron count. Molecular orbital descriptions of these complexes have shown that the BH_4^- group acts as a 2-, 4-, or 6-electron donor in an η^1, η^2, or η^3 coordination mode, respectively.[29,37,40] The optimal coordination is obtained in order to

get a formally 18-electron complex. For instance, in Cu-$(BH_4)(PPh_3)_2$, BH_4^- is coordinated in an η^2 fashion[2] (4-electron donor), which leads to a 18-electron complex. If one phosphine ligand is added to the copper as in $Cu(BH_4)(PPh_2Me)_3$, then the BH_4^- group coordinates to the metal atom in an η^1 fashion[22] in order to keep the 18-electron count. Numerous examples of mono(tetrahydroborato) complexes illustrate this simple relationship between the BH_4^- coordination mode and the 18-electron rule. The situation becomes more complex when several BH_4^- ligands are bound to the metal. For instance, in $Zr(\eta^3\text{-}BH_4)_4$ or in $Hf(\eta^3\text{-}BH_4)_4$,[35–39] it has been shown that each of the four BH_4^- groups cannot act as a 6-electron donor (leading to a 24-electron complex!) because there are not enough acceptor orbitals on the metal. However, an 18-electron count is still obtained when symmetry restrictions are taken in account for orbital interactions.[29,36,37]

Recently, Girolami and co-workers[16–20] have synthesized and characterized by X-ray diffraction complexes of titanium and vanadium containing two or three BH_4^- groups. In one of them, $V(BH_4)_3(PMe_3)_2$, the overall coordination around the vanadium atom resembles a trigonal bipyramid (TBP) with respect to the boron atoms.[20] The two phosphine ligands occupy axial sites, while the three boron atoms are in the equatorial positions. Each BH_4^- group is η^2 bound to the metal atom and the six bridging hydrogens lie in the equatorial plane (4). This complex is high spin, the paramagnetism being due to two unpaired electrons on the vanadium(III) center.

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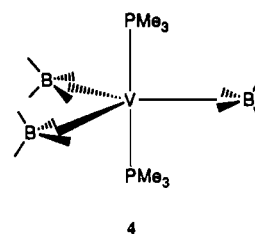
In this paper, the electronic structure of this vanadium complex is studied by means of ab initio calculations for all the possible coordination modes of the three BH_4^- groups. The results are discussed through a molecular orbital analysis and electron counting as described above.

Method of Calculation

The $V(BH_4)_3(PMe_3)_2$ complex was modeled by replacing the methyl groups by hydrogens. Since the complex has been found experimentally to be high spin, open-shell calculations were performed on this model complex in its lowest triplet state. Calculations were performed with an all-electron ab initio method at the unrestricted Hartree–Fock (UHF-SCF) level with the help of the GAUSSIAN 86 system of programs.[41a] In each case, the spin contamination is weak ($S^2 < 2.03$). For the vanadium atom, a valence double-ζ basis set was used.[42a] The valence shell was

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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[42b] was also chosen. For the atoms of the phosphine ligands, a minimal basis set was used.[42c] The geometry of each structure was optimized with the Schlegel[41b] method using analytically computed gradients. Correlation effects on the optimal geometries were taken into account by the perturbational MP2 algorithm. In the study of Al_2H_4 systems, Lammertsma et al.[43] have shown that the energetic ordering of η^1, η^2, and η^3 coordination modes of the AlH_4^- moiety from the more sophisticated calculations (MP4) is well reproduced at this level. Similar conclusions have been reached by Tomasi et al.[44] in the study of the $M(BH_4)_2$ complexes (M = Be, Mg, Ca).

Geometrical Model

The internal structure of the phosphines was kept frozen. The P–V distance was fixed at the experimental value of 2.51 Å. All other geometrical parameters were optimized by assuming a local symmetry for each metal–BH_4 fragment (C_{3v} for η^1 and η^3 coordination and C_{2v} for η^2 coordination). Note, however, that η^1 coordination usually gives a nonlinear metal–hydrogen–boron arrangement[7,8,13,17,19a,22] but Bo and Dedieu[45] have shown that this relaxation leads to a weak stabilization (1.4 kcal/mol in the $Cu(BH_4)(PH_3)_3$ complex). Except when specified, we did not try to relax the linearity constraint for η^1 coordination. For η^2 coordination, we initially fixed the bridging hydrogens in the equatorial plane. Their rotation will be studied later in this paper. Within these geometrical restrictions, the ten possible structures depending on the coordination mode of each BH_4^- group were optimized. For sake of clarity, a structure corresponding to an η^a,η^b,η^c mode is called (a,b,c).

Results

Energies. The relatives energies of the various structures in their lowest triplet state are reported in Table I. The (2,2,2) complex is found to be the most stable, whatever the level of calculation, a result in agreement with the experimental stucture.

At the UHF level, there are only two other structures lying at less than 10 kcal/mol above the minimum. These are the (2,2,3) and the (1,2,2) structures, the energy of the latter being only 1.1 kcal/mol above the absolute minimum. At this level, the (2,2,2) and (1,2,2) structures appear to be competitive. Four structures are lying in the range 15–22 kcal/mol above the minimum. Finally, three structures (1,1,1), (1,3,3), and (3,3,3) are located very high in energy (about 40 kcal/mol) with respect to the minimum. We have relaxed the linearity constrain of the η^1 group in the (1,2,2) complex, since it is the closest in energy to the minimum. Further optimization leads back to the (1,2,2) complex and does not collapse to the (2,2,2). This structure is therefore a real minimum on the potential energy surface.

At the MP2 level, an analogous energetic order is found; there are still two structures less than 10 kcal/mol above the minimum. Their order is identical with that found at the UHF level. However, the relative energy of (1,2,2) increases to 8.3 kcal/mol and it becomes roughly isoenergetic with (2,2,3). Therefore, at the MP2 level, the (2,2,2) complex is definitely the most stable. In the range 22–35 kcal/mol above the minimum, one finds the same four structures as at the UHF level. Note that the energy gaps between these structures are larger than those at the UHF level. The three highest energy structures found at the UHF level remain the highest at the MP2 level. The energy differences between these three structures also dramatically increase upon going from the UHF to the MP2 level.

It is noteworthy that the correlation energy depends on the coordination mode. It is almost the same for the (2,2,2), (2,2,3), and (3,3,3) (compare the UHF and MP2 relative energies in Table I). Conversely, the correlation energy is weaker for structures with at least one BH_4^- group in an η^1 coordination, there being roughly 10 kcal/mol destabilization for each η^1 BH_4^- group at the MP2 level, with respect to the UHF results. Consequently, the (1,1,1) structure is strongly destabilized at the correlated level and becomes the highest in energy. Similar results have been obtained by Lammertsma et al.[46] in the study of the different

Table II. Bond Lengths (Å) for η^1 Coordination

	(1,1,1)	(1,1,2)	(1,1,3)	(1,2,2)	(1,2,3)	(1,3,3)
V–B	3.048	3.046	3.039	3.049	3.061	3.090
B–H_b	1.364	1.357	1.343	1.367	1.372	1.379
B–H_t	1.203	1.204	1.205	1.204	1.203	1.202

Table III. Bond Lengths (Å) for η^2 Coordination

	(1,1,2)	(1,2,2)	(1,2,3)	(2,2,2)	(2,2,3)	(2,3,3)
V–B	2.391	2.396	2.384	2.445	2.430	2.400
B–H_b	1.276	1.273	1.272	1.252	1.258	1.267
B–H_t	1.193	1.194	1.193	1.198	1.196	1.193

Table IV. Bond Lengths (Å) for η^3 Coordination

	(1,1,3)	(1,2,3)	(1,3,3)	(2,2,3)	(2,3,3)	(3,3,3)
V–B	2.171	2.374	2.368	2.367	2.374	2.371
B–H_b	1.251	1.230	1.231	1.229	1.227	1.225
B–H_t	1.179	1.189	1.188	1.190	1.190	1.190

Table V. Average Values for the V–B[48] and B–H Bond Lengths (Å), Depending on the Coordination Mode

	η^1	η^2	η^3
V–B	3.06	2.41	2.34
B–H_b	1.36	1.27	1.23
B–H_t	1.20	1.19	1.19

coordination modes of the GaH_4^- group in the digallane species Ga_2H_4.

A final comment concerns the exchange mechanism between bridging and terminal hydrogens in one BH_4^- group. Although exchange could not be observed by NMR spectroscopy in the vanadium complex because of the presence of unpaired electrons on the metal center, it is a common process which occurs at low energy in almost all tetrahydroborato–transition-metal complexes.[1] The usual mechanism proposed to rationalize this exchange involves a change in the coordination mode ($\eta^2 \rightarrow \eta^3$) or ($\eta^2 \rightarrow \eta^1$) of the BH_4^- group.[47] Our results suggest that both of these mechanisms are available to the vanadium complex since (1,2,2) and (2,2,3) are the lowest energy structures above the minimum. An energy barrier of ≈ 9 kcal/mol is within the range of the observed exchange barrier on related complexes. Since the two interconversion paths ($\eta^2 \rightarrow \eta^3$) and ($\eta^2 \rightarrow \eta^1$) lead to almost isoenergetic structures (1,2,2) and (2,2,3), we cannot conclude which is the preferred exchange process. However, it is clear from our results that the exchange within one BH_4^- group is preferred over simultaneous exchange within two or three BH_4^- groups, which would lead to high energy structures such as (2,3,3) or (1,1,2). No cooperative effects are expected for these processes.

Geometries. For each coordination mode the significant bond lengths are reported in Tables II–IV, where H_b and H_t mean bridging and terminal hydrogens, respectively. In all the cases, boron and vanadium atoms are roughly in a trigonal geometry.

It can be seen from these results that the various V–B and B–H bond lengths associated with a given coordination mode depend only slightly on the overall coordination scheme around the vanadium atom. For instance, the B–V distance in an η^1-BH_4^- (Table II) varies from 3.04 Å in (1,1,3) to 3.09 Å in (1,3,3). In the same way, the B–H_b distances lie in the range 1.25 Å (2,2,2) to 1.28 Å (1,1,2) for a η^2-BH_4^- group (Table III). It is therefore possible to give average bond lengths values associated with each coordination mode (Table V).

These average values show that the V–B distance increases in the order η^3 (2.34 Å) < η^2 (2.41 Å) < η^1 (3.06 Å). The same trend is found for the B–H_b bond length: 1.23, 1.27, and 1.36

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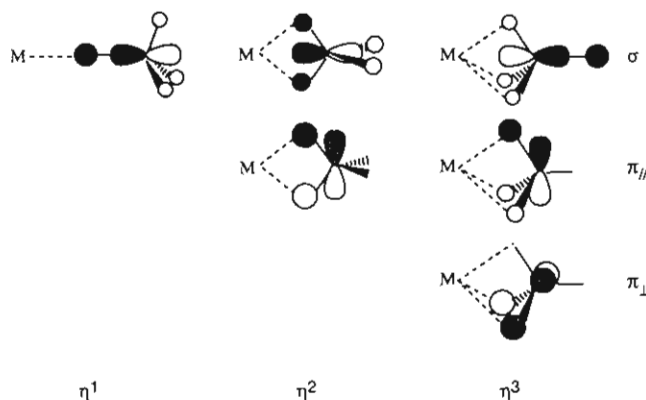
Figure 1. BH_4^- orbitals involved in η^1, η^2, and η^3 coordination modes.

Table VI. Experimental and Theoretical Geometrical Parameters (Bond Distances, Å; Angles, deg)

	V–B	B–H_b	B–H_t	H_t–B–H_t	H_b–B–H_b
exp	2.36–2.37	1.08–1.19	0.97–1.07	114–116	95–100
theor	2.445	1.252	1.198	117.8	103.9

Å for η^3, η^2, and η^1 coordination, respectively. The more bridged hydrogens there are, the shorter the B–H_b bond appears to be. These results agree well with chemical intuition but are inconsistent with the neutron diffraction data of Takusagawa et al.,[22] who have found that the most elongated B–H bond in the $Cu(BH_4)$-$(PPh_2Me)_3$ complex was not a B–H_b but a B–H_t bond. This surprising result was attributed to disorder in the BH_4^- group. Note finally that the average value of the B–H_t bond lengths is almost constant (1.19–1.20 Å), whatever the coordination mode.

Comparison with the Experimental Structure. The optimized geometry of the (2,2,2) complex belongs to the D_{3h} symmetry point group. Any distortion from this symmetry raises the energy, and further optimization leads to a D_{3h} geometry. The main optimized parameters are given in Table VI, where they are compared to the experimental ones.

The V–B bond length (2.445 Å) is overestimated compared to experiment (2.36–2.37 Å). Similar deviations (in the range 0.04–0.08 Å) have been found at the 3-21G level for copper compounds.[41] This discrepancy may therefore be attributed to the limited size of the 3-21G basis set. An analogous lengthening of the Cu–B distance has already been observed in the calculation of the $Cu(BH_4)(PH_3)_2$ complex.[49] Larger disagreement is found for the boron–hydrogen bond lengths: the theoretical values are larger than the experimental ones by about 0.2 Å. This probably comes from the inaccurate location of hydrogen atoms by X-ray diffraction. Our B–H bond lengths (both for H_b and H_t atoms) agree well with the results of neutron diffraction of η^2-BH_4^- groups.[21,23] Finally, the calculated angles in the BH_4^- group are no longer tetrahedral; the H_t–B–H_t angle opens to 117.8° whereas the H_b–B–H_b angle decreases to 103.9°. This distortion is in agreement with the experimental structure.

Molecular Orbital Analysis and Electron Counting

The way in which a BH_4^- ligand interacts with a transition metal depends on its coordination mode (η^1, η^2, or η^3). Basically, this ligand is isoelectronic with methane and is characterized by four occupied MOs (a_1 and t_2). The low-lying fully symmetric a_1 orbital can be neglected in the bonding scheme,[29,35,40] as shown by Hori et al.[50] in their ab initio study of $Be(BH_4)_2$. Due to the low electronegativity of the boron atom, t_2 orbitals are mainly developed on the hydrogen atoms. A significant d–t_2 overlap is therefore found only if the hydrogen atom involved in a particular t_2 orbital points toward the metal. As a consequence, the interaction scheme depends strongly on the coordination mode. A single t_2 orbital interacts with the metal in the η^1 coordination mode, while two and three orbitals are involved in the η^2 and η^3
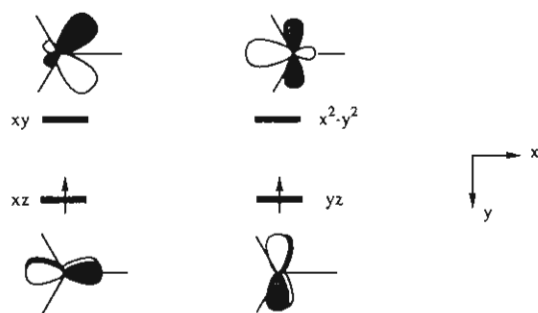
(49) Hori, K.; Tachibana, A. *Theor. Chim. Acta* **1986**, *70*, 153.
(50) Hori, K.; Saito, G.; Teramae, H. *J. Phys. Chem.* **1988**, *92*, 3796.

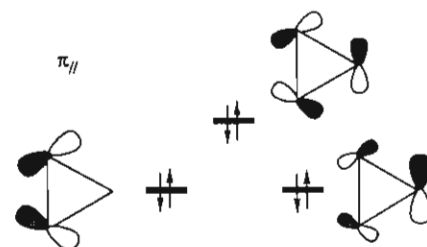**Figure 2.** Low-lying d orbitals in the (1,1,1) complex.

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

modes, respectively. In the following, the three t_2 orbitals will be called σ, $\pi_\parallel$, and $\pi_\perp$ (Figure 1). Now it can be seen that the ligand orbital involved in an η^1 coordination mode is σ, those in η^2 and η^3 being (σ, $\pi_\parallel$) and (σ, $\pi_\parallel$, $\pi_\perp$), respectively. *As long as low-lying orbitals of proper symmetry are present on the metal fragment*, η^1-BH_4^- acts as a 2-electron donor and η^2-BH_4^- and η^3-BH_4^- act as 4- and 6-electron donors, respectively.

It is now possible to analyze the orbital interactions in $V(B-H_4)_3(PH_3)_2$ complexes. For the sake of clarity, we shall focus first on the most symmetrical complexes (1,1,1), (2,2,2), and (3,3,3) depicted in **5**–**7** (in which the phosphine ligands have been omitted).
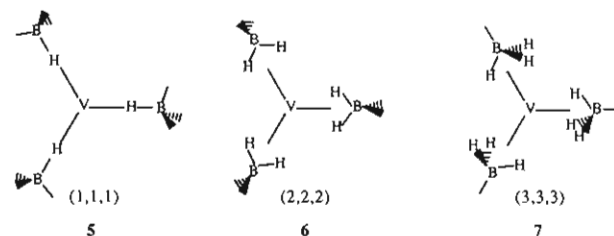
In the (1,1,1) complex (**5**), the three σ orbitals of each ligand combine to give symmetry-adapted orbitals which interact with the proper combination of the s, p, and d orbitals on the PH_3–V–PH_3 moiety. The overall orbital scheme is that of a D_{3h} TBP complex with two sets of degenerate MOs (Figure 2): two non-bonding (xz and yz) and two slightly antibonding (xy and $x^2 - y^2$). In this coordination scheme, the d^2-$V(BH_4)_3(PH_3)_2$ complex turns out to be a highly deficient complex with only 12 electrons around the metal (10 for the five σ bonds and 2 in the d block).

In the (2,2,2) complex (**6**), the three σ (η^2) orbitals play basically the same role as the σ (η^1) orbitals in the preceding complex. What is new is the participation of the $\pi_\parallel$ orbitals in the bonding scheme. They combine to give delocalized orbitals characteristic of a three-membered Möebius ring (Figure 3). The two lowest have the right symmetry to interact with the xy and $x^2 - y^2$ orbitals of the TBP structure (Figure 2). The highest one is of f symmetry and cannot find any symmetry-adapted orbital on the metal. Therefore the set of three BH_4^- ligands acts as a 4-electron donor through their $\pi_\parallel$ orbitals. Consequently, the (2,2,2) d^2-V-$(BH_4)_3(PH_3)_2$ complex can be described as a 16-electron complex (10 σ + 4 $\pi_\parallel$ + 2 d).
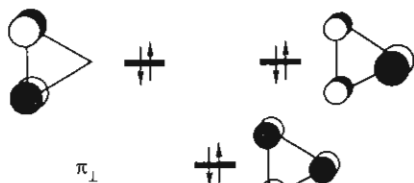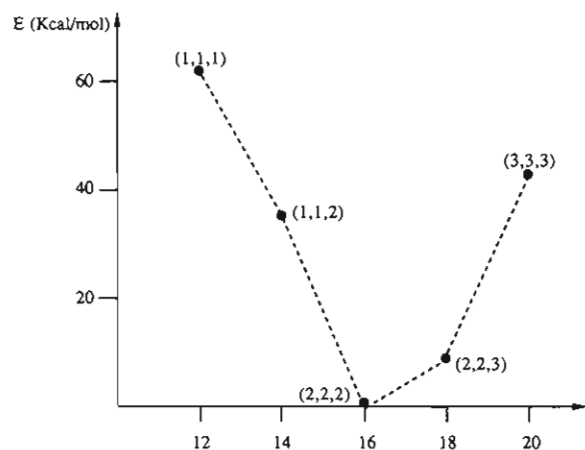
In the (3,3,3) complex (**7**), σ and $\pi_\parallel$ orbitals are still at work in a way identical with that described above. The $\pi_\perp$ orbitals are

Table VII. Electron Counting in the d^2-$V(BH_4)_3(PH_3)_2$ Complex, Depending on the Coordination Mode of the BH_4^- Ligands [Relative Energies (MP2 Level) in kcal/mol]

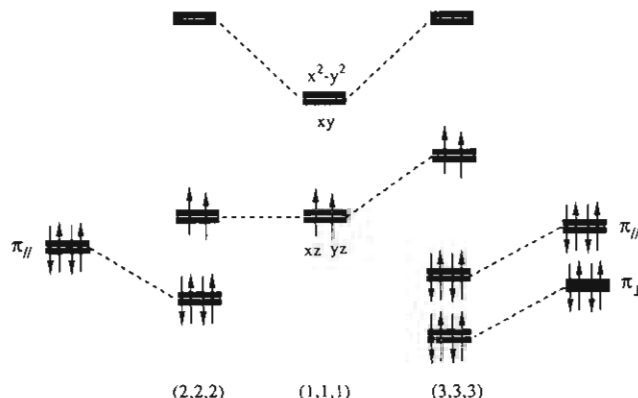|	(1,1,1)	(1,1,2)	(1,1,3)	(1,2,2)	(2,2,2)	(2,2,3)	(1,2,3)	(2,3,3)	(1,3,3)	(3,3,3)
d	2	2	2	2	2	2	2	2	2	2
σ	10	10	10	10	10	10	10	10	10	10
$\pi_\parallel$	0	2	2	4	4	4	4	4	4	4
$\pi_\perp$	0	0	2	0	0	2	2	4	4	4
tot.	12	14	16	16	16	18	18	20	20	20
E	61.6	34.8	26.3	8.3	0.0	9.0	25.9	22.4	51.2	42.7

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

Figure 5. Correlation between the electron count and the energy in the d^2-$V(BH_4)_3(PH_3)_2$ complex.

Figure 6. π–d orbital interactions in (1,1,1), (2,2,2), and (3,3,3) complexes.

(1,2,2) complex, which is actually the second lowest in energy. For different electron counts, either the vacant MOs xy and $x^2 - y^2$ are not used to stabilize the $\pi_\parallel$ orbitals (as in the (1,1,1) complex), which is unfavorable, or the singly occupied orbitals xz and yz are destabilized by interaction with the $\pi_\perp$ orbitals (as in the (3,3,3) complex), which is also unfavorable. The link between Figure 6 and the formal electron count is clear. Two electrons occupy the xz and yz orbitals, and there are 0, 4, and 8 electrons in the π orbitals for the (1,1,1), (2,2,2), and (3,3,3) complexes, respectively. Adding the 10 electrons associated with the five σ bonds (not represented in Figure 6) it leads to 12-, 16-, and 20-electron complexes, respectively.

Beyond Electron Counting

In Figure 5 it was shown that the electron count is a powerful tool to analyze the problem of coordination mode in the high-spin d^2-$V(BH_4)_3(PH_3)_2$ complex. However, it remains unclear as to why complexes with the same electron number can have very different energies (Table I). A more detailed analysis is required to answer this question. First, a formal 2-electron transfer from the ligand to the metal is associated with an interaction between a ligand orbital and a low-lying orbital on the metal. This interaction can be stronger or weaker, depending on the overlap and the energy gap between interacting orbitals. For instance, both (1,2,2) and (2,2,2) complexes are predicted to be favored by the presence of two nonbonding d orbitals (xz and yz) with a single electron each and by the bonding interaction between xy and $x^2 - y^2$ and two $\pi_\parallel$ orbitals. However, (2,2,2) is more stable than (1,2,2) by 8.3 kcal/mol at the MP2 level. The main reason lies within the strength of the xy–$\pi_\parallel$ interaction which is greater in (2,2,2) because of the larger overlap (**8** vs **9**) between xy and $\pi_\parallel$.


A second point arises from the orbital interaction scheme which can differ for the same electron count. Let us compare for instance (2,2,2) and (1,1,3), which are both 16-electron complexes. In the former, two $\pi_\parallel$ orbitals are stabilized by the vacant xy and $x^2 - y^2$ orbitals, while xz and yz are unaffected (Figure 6, left-hand

now involved, and they mix to give a set of three symmetry-adapted MOs typical of a three-membered Hückel ring (Figure 4). The symmetry of the two highest degenerate MOs exactly fits that of the xz and yz orbitals (Figure 2). In principle, the lowest orbital could interact with the p_z orbital on the metal. However, this orbital is already used to build a bonding MO with the axial phosphine ligands, and its antibonding counterpart is too high in energy to play the role of an acceptor orbital. It follows that the BH_4^- ligands act as 4-electron donors through their $\pi_\perp$ orbitals. Accordingly, the (3,3,3) d^2-$V(BH_4)_3(PH_3)_2$ complex is a 20-electron complex ($10 \sigma + 4 \pi_\parallel + 4 \pi_\perp + 2$ d).

Using the same type of analysis, we can give an electron count for each of the ten optimized complexes (Table VII).

It is interesting to try to correlate this electron count with the energy of the complexes. Although different values are found for complexes with the same electron count (we shall return to this point later), a clear trend is apparent in the series (1,1,1), (1,1,2), (2,2,2), (2,2,3), and (3,3,3), which includes the complexes described above. The high-spin 16-electron complex is the most stable, and the larger the deviation from this "ideal" number, the higher the energy (Figure 5). There is a simple explanation of this result. Since we are interested in a triplet d^2 complex, the best situation is that in which the degenerate xz and yz orbitals accommodate the two unpaired electrons and the xy and $x^2 - y^2$ orbitals are used to stabilize π ligand orbitals. These *two conditions* are fulfilled in the 16-electron (2,2,2) complex (Figure 6). As we have shown before, the singly occupied nonbonding xz and yz orbitals are unaffected by the coordination of BH_4^- ligands, while the vacant xy and $x^2 - y^2$ orbitals develop bonding interactions with the symmetry-adapted combinations of the $\pi_\parallel$ orbitals. Note that the same analysis applies to the 16-electron

Table VIII. Electron Counting in the d^2-$V(BH_4)_3(PH_3)_2$ Complex in the (2,2,2) Coordination Mode [Relative Energies (MP2 Level) in kcal/mol]

	(2,2,2)	(2,2,2)*	(2,2,2)**	(2,2,2)***
d	2	2	2	2
$\pi_\parallel$	4	4	2	0
$\pi_\perp$	0	2	4	4
tot.	16	18	18	16
E	0.0	10.2	22.0	71.0

side). In the latter, the interaction with the $\pi_\perp$ involves the singly occupied xz orbital, which is unfavorable (**10**).


(1,1,3)

10
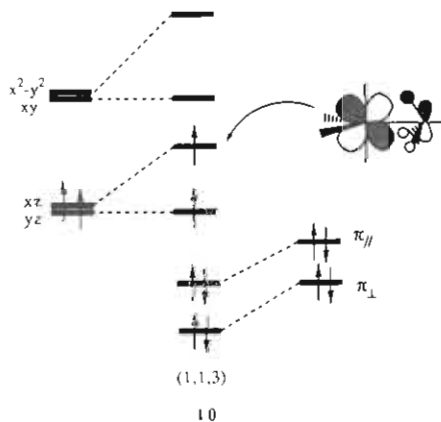
Finally, electron counting does not take into account 4-electron interactions between ligand orbitals and low-lying occupied orbitals on the metal fragment ($V(PH_3)_2$). A strong interaction of this type takes place between the bonding metal (p_z)–phosphine MO and the $\pi_\perp$ orbitals when one or more BH_4^- ligands adopt the η^3 coordination (**11**). The larger the number of η^3 groups, the higher the destabilization. All other things been equal, the η^3 coordination mode is disfavored in this complex.

11

These ideas can be illustrated by the study of η^2 coordination in which the BH_2 moiety bound to the metal is *orthogonal* to the equatorial plane (i.e. rotated by 90°). The three (2,2,2) complexes

in which one, two, or three η^2-BH_4^- ligands adopt this coordination have been optimized. They are called (2,2,2)*, (2,2,2)**, and (2,2,2)*** (**12–14**), respectively. The electron counts and the energies are given in Table VIII.
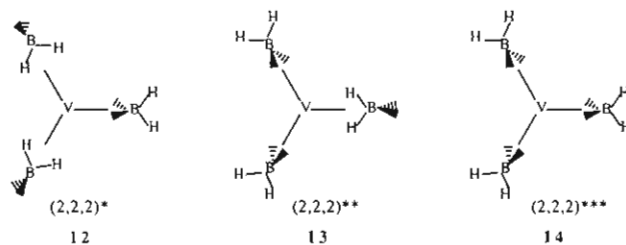
Although the (2,2,2)*** complex is a 16-electron one, it is extremely disfavored both because the orbitals used to stabilize $\pi_\perp$ are singly occupied (xz and yz) and because there is a strong repulsive interaction between the symmetrical $\pi_\perp$ orbital and the low-lying occupied metal (p_z)–phosphine orbital. This repulsive interaction is partially removed in (2,2,2)* and (2,2,2)** complexes by the bending of the phosphines away from the BH_4^- ligand(s) orthogonal to the equatorial plane (the calculated values of the PVP angle are 167.8 and 161.6°, respectively). Such a distortion cannot occur in the last complex, where the three ligands are orthogonal; thus, its energy is very high in spite of its favorable electron count.

Conclusion

The UHF + MP2 calculations accurately reproduce the geometry of the high-spin $V(BH_4)_3(PH_3)_2$ complex; the (2,2,2) structure with all the bridging hydrogen atoms lying in the plane of the boron atoms is found to be more stable than the other structures by at least 8 kcal/mol. There is a clear relationship between the energy of the structure and the usual electron count around the metal, which depends on the coordination mode of the BH_4^- ligands. In this d^2 high-spin complex, the ideal electron count is 16; a too low (i.e. 12 or 14) or a too high (i.e. 18 or 20) number of electron leads to higher energy structures. It is therefore proposed that this electron counting might be a simple way to eliminate such structures in a study of this type of complexes. However, a more detailed analysis of orbital interactions is required for a precise understanding of the results, in particular for comparison between structures with the same formal number of electrons.