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Transition metal tetrahydroborato complexes: an orbital interaction analysis of their structure and bonding

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Abstract

Detailed structural and electronic analyses based on orbital interaction models for a large number of tetrahydroborato transition-metal complexes were provided to account for the relationship between their structure and bonding. Three points were made as the result of discussion: (a) most of the tetrahydroborato transition-metal complexes conform to the 18 electron rule, especially for complexes with only one BH_4^- ligand; (b) usually, complexes with more than 18 valence electrons are considered as ionic complexes. Our detailed analyses reveal that both ionic and electronic effects play important roles in the stereochemistry in these tetrahydroborato complexes. The ionic effect tends to maximize the coordination number while the electronic effect influences the orientation of ligands; (c) complexes with more than

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18 valence electrons (which usually have two or more BH_4^- ligands) adopt structures allowing the extra electrons to be exclusively delocalized in the BH_4^- ligands. Although some complexes are formally 18-electron species, the number of electrons involved in the metal-ligand bonding is not necessarily 18.

Keywords: Structure and bonding; Tetrahydroborato complexes

1. Introduction

Transition metal tetrahydroborato complexes have received considerable attention in recent decades, not only because they are of practical use in syntheses and catalysis but also because they represent a very interesting topic in structure and bonding of transition-metal chemistry [1]. During the last several decades, many tetrahydroborato complexes have been synthesized and characterized structurally by means of electron diffraction, neutron diffraction, X-ray diffraction, IR, NMR, etc. [2].

Owing to the negative charge of the tetrahydroborato ligand, the metal–tetrahydroborato bonding could be either ionic or dative through one or more B—H bonding pairs. The nature of the bonding and coordination mode of the BH_4^- ligand in these complexes has been the subject of considerable interest [1,3]. Although the ionic (or electrostatic) interaction is quite apparent in some salt-like ionic tetrahydroborato complexes, in many other complexes, three coordination modes, η^1, η^2 and η^3, are commonly found (see Fig. 1(a)). Early in 1959, Parry and Edwards suggested that the concept of a coordinate covalent bond (i.e. a dative bond between the metal and the coordinate B—H bond) could be extended to include three-center bridge bonds. In 1977, a primarily qualitative bonding analysis for a large number of tetrahydroborato complexes, based on valence-bond, effective atomic number and molecular orbital models, was summarized by Marks and Kolb in their excellent review [1]. Since then, a number of theoretical analyses on some specific complexes have also been reported [2,4,5]. Recently, the nature of B—H—M bonding was deeply explored by Parry in his excellent and understandable work [3]. It was pointed out by Parry and Edwards that the B—H—M linkage in complexes containing metal and (B—H) interaction is clearly and unequivocally the basis for compound stability. The coordinate covalent bond nature of the B—H—M three-center–two-electron bridging bond seems quite widely accepted [6].

In many tetrahydroborato complexes, the BH_4^- ligand is usually coordinated to transition metal atoms in the η^1, η^2 or η^3 mode (see Fig. 1(a)). In these different coordination modes, each B—H—M linkage can be viewed as a three-center–two-electron bond. Molecular orbital (MO) analyses of mono-tetrahydroborato complexes have shown that each BH_4^- ligand acts as a two-, four-, or six-electron donor in the η^1, η^2 or η^3 coordination modes respectively [7–9]. In other words, each B—H unit donates its σ-bonding electron pair to the metal center to form a metal–ligand dative bond. Complexes with these characteristics of bonding are also called σ-complexes [10]. The different coordination modes of the BH_4^- ligand in some complexes, particularly for those mono-tetrahydroborato complexes, can be easily

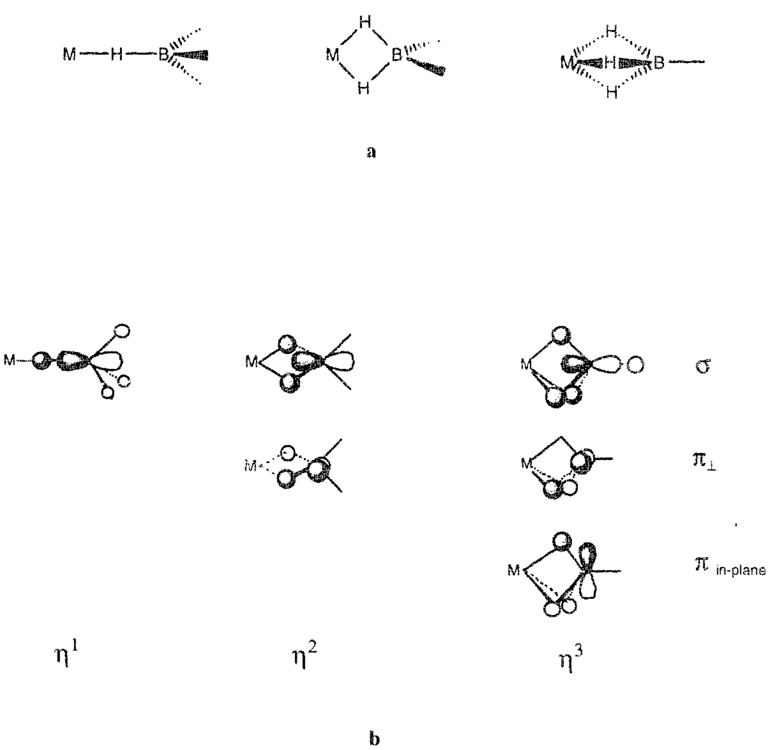


Fig. 1. (a) Three different coordination modes of a BH_4^-. (b) BH_4^- orbitals involved in the η^1, η^2 and η^3 coordination modes.

understood according to the 18-electron rule. For some other complexes, such as $M(\eta^3\text{-}BH_4)_4$ (M = Zr, Y, Hf) [11-13], this rule cannot be simply applied since formally they have 24 electrons. Recently, Lledos and his co-workers reported their ab initio study on complexes which do not conform to the 18-electron rule, such as $M(BH_4)_3(PH_3)_2$ (M = V, Sc and Ti) [2,4] and $Ti(BH_4)_3$ [5]. They have shown that the number of electrons around the metal atom depends on the symmetry of the molecule and on the number of unpaired electrons.

Despite these theoretical studies, a general-theoretical analysis for this class of transition-metal complex has not yet been reported. In this paper, a theoretical analysis based on orbital interaction argument is offered to account for the relationship between structure and bonding for a variety of transition-metal tetrahydroborato complexes. We develop specific examples and then summarize our results.

2. Coordination mode of BH_4^- anion

As mentioned above, a unidentate (η^1), bidentate (η^2) or tridentate (η^3) BH_4^- ligand acts as a two-, four- or six-electron donor in metal–ligand interactions. In terms of the MO model, for an M-(η^1-BH_4) unit, one B—H σ bonding orbital is used in the metal–ligand interaction. For η^2 and η^3 coordination modes, two (one σ and one π) and three (one σ and two π) B—H bonding orbitals are used. These B—H bonding orbitals are illustrated in Fig. 1(b). In the following discussion, η^2-BH_4^- will be distinguished by $\eta^2_{\parallel}$ for cases when the line connecting the two bridging hydrogen atoms is parallel to the upright direction on the page where a complex is shown and by $\eta^2_{\perp}$ for cases when the line is perpendicular to the upright direction. The subscripts, $\perp$ and $\parallel$, of η^2 serve only for illustration and have no physical meaning or implications.

It should be noted here that in some complexes the BH_4^- ligand may coordinate to the metal atom in an unusual mode, the so called 'side on' mode [4b,14]. In these complexes, it is difficult to define how many bridging hydrogen atoms are bound to the metal atom.

Throughout this paper, a boron p component (instead of those shown in Fig. 1(b) will be used to represent a π-symmetry hydroborate orbital, which is used for metal–tetrahydroborato bonding, and only the subscripts, z^2, x^2–y^2, xy, xz and yz, will be used to describe the metal d orbitals, respectively, for theoretical simplicity. In the following discussion, each BH_4^- ligand is considered to contribute one to the coordination number for the use of definition only and bridging hydrogens are not counted except as explicitly specified.

3. Mono-nuclear complexes

3.1. Three-coordinate complexes: $M(BH_4)_nL_{3-n}$

With respect to the boron atom of BH_4^-, three-coordinate complexes are of trigonal-planar geometry. Complexes with a formula like $M(\eta^3\text{-}BH_4)_3$ may be considered as the most complicated and typical species of this kind. Starting with the orbital interaction analysis for such complexes will make it easier to understand the electronic structures of the others. The strategy for doing this analysis is as follows. First, we obtain the linear combinations for the BH_4^- ligands' σ orbitals, and then do the same for the $\pi_{\perp}$ and for the $\pi_{\text{in-plane}}$ orbitals (see Fig. 1(b) for the definition of $\pi_{\perp}$ and $\pi_{\text{in-plane}}$). Finally, we match these combinations with the central metal atom's atomic s, p, and d orbitals. Following these steps, one obtains the orbital interactions between the central metal atom and the ligands in an $M(\eta^3\text{-}BH_4)_3$ complex (see **1**), as illustrated in Figs. 2, 3 and 4. When the z axis is defined as perpendicular to the molecular plane, the p_x, p_y and s orbitals of the metal atom interact with the three σ orbitals of the three BH_4^- ligands to form three bonding MOs. The three $\pi_{\perp}$-orbital combinations of BH_4^- ligands are symmetry-adapted with

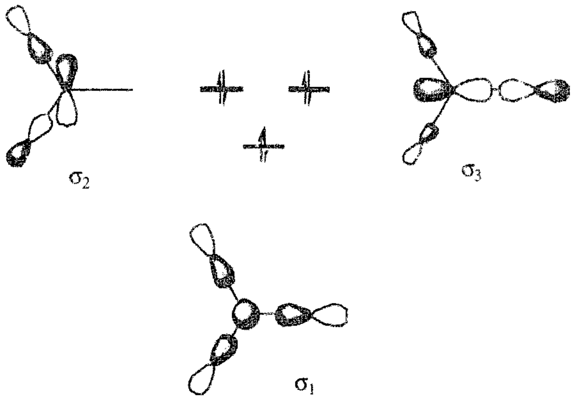


Fig. 2. σ-type orbital interaction between metal atom (p$_x$, $_y$, s) and ligands.

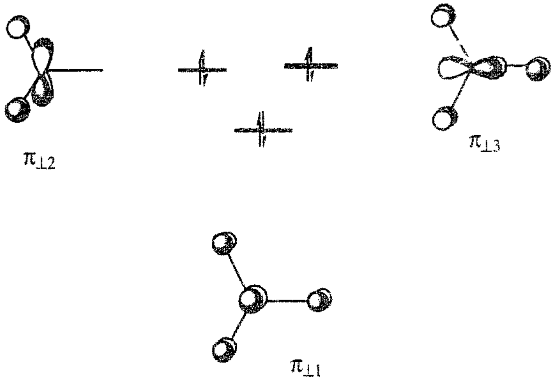


Fig. 3. $\pi_\perp$-type orbital interaction between metal atom (xz, yz, p$_z$) and ligands.

the p$_z$, xz and yz atomic orbitals (AOs), and the three $\pi_{\text{in-plane}}$ orbitals can only interact with two AOs, xy and x^2-y^2, to form two bonding MOs and one non-bonding MO which is exclusively delocalized on the BH_4^- ligands. The z^2 orbital of the central metal atom also remains non-bonding. Therefore, the maximum number of non-bonding d electrons in $M(\eta^3\text{-}BH_4)_3$ will be two. A d^2 $M(\eta^3\text{-}BH_4)_3$ complex can be viewed as isoelectronic with $Os(NR)_3$ [15], if NR is formally taken as an $[NR]^{2-}$ ligand. $Ti(\eta^3\text{-}BH_4)_3$ provides an example of a d^1 configuration with the z^2

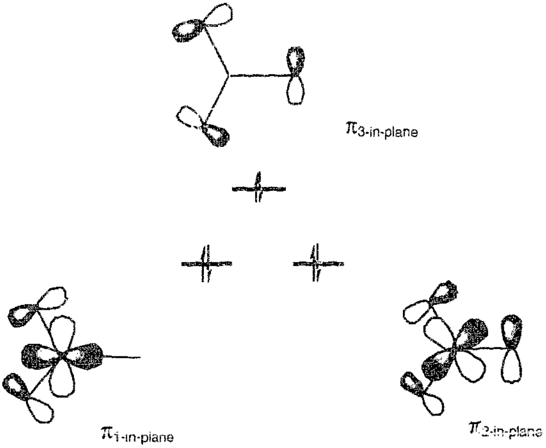
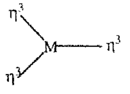


Fig. 4. $\pi_{\text{in-plane}}$-type orbital interaction between metal atom (x^2-y^2, xy) and ligands.

orbital being partially occupied and was recently reported by Dain et al. [5]. Electron diffraction, as well as MO analysis from EHMO calculations, was used to determine its molecular structure in the gas phase [5]. The total number of valence electrons in this titanium complex is 19 ($3(\sigma)^2+6(\pi)^2+(d)^1$). Of the 18 ligand electrons, effectively only 16 are involved in the metal–ligand bonding since one $\pi_{\text{in-plane}}$ linear combination cannot find a symmetry-adapted metal orbital (see Fig. 4 $\pi_{\text{in-plane}}$ MO). An ab initio study on the structure of this complex has been reported and supports this analysis [16]. Other analogous complexes, $Y(BH_4)_3$ [1,17,18] and $Sc(BH_4)_3$ [7,19] are predicted here to adopt the same structure as $Ti(BH_4)_3$. Although these complexes are formally 18-electron species, only 16 electrons are involved in the metal–ligand bonding.

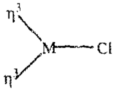


$Ti(\eta^3\text{-}BH_4)_3$ [5] *19e*

$Y(\eta^3\text{-}BH_4)_3$ [1,17,18] *

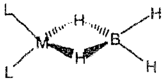
$Sc(\eta^3\text{-}BH_4)_3$ [7,19] **

1



$YCl(\eta^3\text{-}BH_4)_2$ [1,17,18] *

2



$(Ph_3P)_2Cu(\eta^2{}_{\perp}\text{-}BH4)$ [20a,b]

$(dmpe)(Cu(\eta^2{}_{\perp}\text{-}BH4))_2$ [20c]

$(dmph)Cu(\eta^2{}_{\perp}\text{-}BH4)$ [20d]

$(bdph)_2Cu(\eta^2{}_{\perp}\text{-}BH4)$ [20e]

3

* A theoretical prediction.

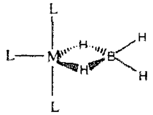
** Characterized by NMR

Three other yttrium complexes, $YCl(BH_4)_2$, $YCl_2(BH_4)$ and $(CH_3O)_2Y(BH_4)$, have also been reported [17,18] and have been reviewed by Marks and Kolb [1]. Although their structural details are still unknown, the BH_4^- ligands in these complexes can be expected to coordinate to the metal atom in η^3-modes (see structure **2**). These complexes can be taken as analogues to $M(\eta^3\text{-}BH_4)_3$ complexes if the π electrons of Cl^- or CH_3O^- are also considered.

Many $CuL_2(\eta^2\text{-}BH_4)$ (**3**) have been synthesized and characterized by X-ray diffraction or spectroscopic methods [20]. They are the simplest and most common species of the three coordination complexes. These complexes can also be described as pseudo-tetrahedral structures (**3**) and conform to the 18-electron rule.

3.2. Four-coordinate complexes: $M(BH_4)_nL_{4-n}$

Complexes with formulae of $M(BH_4)_nL_{4-n}$ can adopt two different geometries, square-planar or tetrahedral, if bridging hydrogen atoms are not considered. It is understandable that d^8 (or low spin d^7) species prefer to adopt a square-planar geometry [21] and can be formulated as $M(\eta^2\text{-}BH_4)L_3$ (see structure **4**). The metal p_z orbital, which is empty for a d^8 complex, can interact with the $\pi_\perp$ orbital of BH_4^- to further stabilize the whole system. Three examples, $Co(terpyridine)(\eta^2\text{-}BH_4)$ [22], $Ni(H)(pcy_3)_2(\eta^2\text{-}BH_4)$ [23], and $d^7\text{–}Co(H)(pcy_3)_2(\eta^2\text{-}BH_4)$ [24], are found in the literature. These complexes can also be viewed as a pentagonal-bipyramidal if the bridging hydrogen atoms are taken into account ($\eta^2\text{-}BH_4^-$ is taken as a bidentate ligand). As an exception to the general structure (**4**), the d^8-$Co(tdphe)(\eta^2\text{-}BH_4)$ complex [25] adopts a tetrahedral structure (see **5**) due to the chelated 1,1,1-tris(diphenylphosphinomethyl)ethane ligand. These complexes are all 18-electron species.

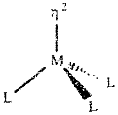


(terpyridine)$Co(\eta^2_\perp\text{-}BH_4)$ [22]

$(pcy_3)_2HNi(\eta^2_\perp\text{-}BH_4)$ [23]

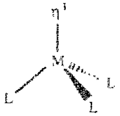
$(pcy_3)_2HCo(\eta^2_\perp\text{–}BH_4)$ [24] *17e*

4



(tdphe)$Co(\eta^2\text{-}BH_4)$ [25]

5



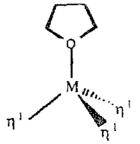
$(Ph_2MeP)_3Ag(\eta^1\text{-}BH_4)$ [26]

$(Ph_2MeP)_3Cu(\eta^1\text{-}BH_4)$ [27]

6

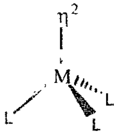
$M(BH_4)_nL_{4-n}$ complexes with d^{10} or high spin d^5 metal centers have only η^1-BH_4^- ligands and adopt a tetrahedral structure since the metal atom has only four vacant orbitals (four sp^3 hybrid orbitals) to accept ligand electron pairs according to the 18-electron rule. $(Ph_2MeP)_3Ag(\eta^1\text{-}BH_4)$ [26] and $(Ph_2MeP)_3Cu(\eta^1\text{-}BH_4)$ [27] (see **6**) are typical examples of this kind with 18-electron configurations. (thf)Mn(η^1-

$BH_4)_3$ [28] is a d^5 species. Despite lack of detailed experimental data, the manganese complex can be expected to feature a d^5 high-spin configuration with three η^1-BH_4^- ligands (structure **7**).



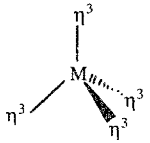
(thf)Mn(η^1-BH_4)$_3$ [28] *13e*

7



(tmen)ZnCl(η^2-BH_4) [29] *20e*
(phen)(Ph_3P)Cu(η^2-BH_4) [30] *20e*
(hdmpb)Cd(η^2-BH_4) [31] *20e*

8



[Y(η^3-BH_4)$_4$]$^-$ [11] *24e*
Hf(η^3-BH_4)$_4$ [12] *24e*
Zr(η^3-BH_4)$_4$ [13] *24e*

9

The X-ray diffraction results of ZnCl(tmen)(BH_4) [29], Cu(phen)(Ph_3P)(BH_4) [30] and (hdmpb)Cd(η^2-BH_4) [31] have shown that, in these complexes, the BH_4^- ligand coordinates with the central atom through an η^2-mode although the complexes are all d^{10} metal centers. These complexes are 20-electron species and do not obey the 18-electron rule. This is not too surprising in view of the fact that many complexes with Cu and Zn centers are ionic and do not necessarily conform to the 18-electron rule.

M(η^3-BH_4)$_4$ complexes (structure **9**) with d^0 centers are interesting species because of their unusual 24-electron configurations. Owing to the large excess of valence electrons around the central metal atom, these complexes were usually considered as ionic. A careful examination of the relevant orbital interaction shows that electronic interaction also plays an important role in the stabilization of these complexes. The linear combinations of the four BH_4^- ligands' σ and π orbitals transform as $a_1+e+2t_2+t_1$ and the central metal orbitals as a_1+e+2t_2. The relevant orbital interaction for an M(η^3-BH_4)$_4$ complex is shown in Fig. 5. There are three non-bonding orbitals (t_1) which are exclusively delocalized only on ligands. For a 24-electron M(η^3-BH_4)$_4$ complex, the six extra electrons can occupy these three non-bonding ligand orbitals without causing any destabilization in the metal–ligand bonding interactions because no other metal orbitals span the t_1 irreducible representation [19]. One may conclude that the ionic factor tends to maximize the coordination number while the electronic factor favors a geometry in which any excessive electron can be accommodated in non-bonding orbitals delocalized on ligands. These complexes, in fact, are isoelectronic and isostructural with MoO_4^{2-}, WO_4^{2-} and OsO_4. Three such complexes, [Y(η^3-BH_4)$_4$]$^-$ [11], Hf(η^3-BH_4)$_4$ [12], and Zr(η^3-BH_4)$_4$ [13], have been synthesized and characterized by X-ray diffraction.

Complex (bp)Ti(η^3-BH_4)$_2$ [32] is a d^0 species with two η^3-BH_4^- ligands (structure **10**).

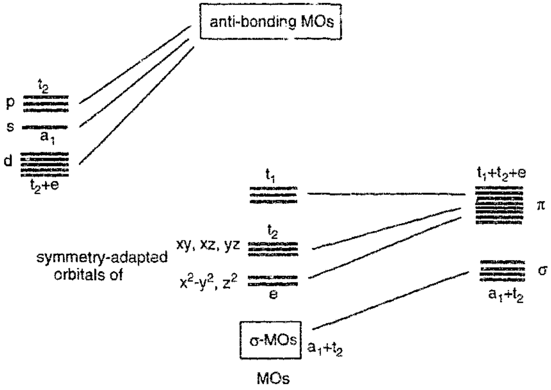
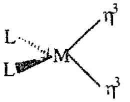
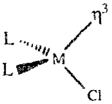


Fig. 5. Orbital interaction diagram for a tetrahedral $M(\eta^3\text{-}BH_4)_4$ complex.



$(bp)Ti(\eta^3\text{-}BH_4)_2$ [32] *16e*
$(tmen)Ti(\eta^3\text{-}BH_4)_2$ [33]
$(tmen)Zr(\eta^3\text{-}BH_4)_2$ [33]

10



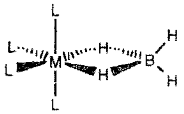
$(tmen)TiCl(\eta^3\text{-}BH_4)$ [33]

11

This molecule provides an example of d^0-$M(\eta^3\text{-}BH_4)_2L_2$ complexes. One can view $M(\eta^3\text{-}BH_4)_2L_2$ as isostructural with MCp_2L_2 complexes since an η^3-BH_4 unit can be viewed as isolobal with an η^5-Cp^- ligand. A d^0-MCp_2L_2 complex can be found in $ZrCp_2Cl_2$. There are also d^2-MCp_2L_2 species reported in the literature, such as $MoCp_2H_2$ and $TiCp_2(CO)_2$. As an isoelectronic species, $(tmen)Zr(\eta^3\text{-}BH_4)_2$ [33] and $(tmen)TiCl(\eta^3\text{-}BH_4)$ [33] (**11**) provide two examples of such a d^2-configuration complex. The latter complex is a 16-electron species and has the maximum number of bridging hydrogen bonds for the BH_4^- ligand. However, the X-ray diffraction result of $(tmen)Ti(BH_4)_2$ [33] indicates that both η^3- and η^2-BH_4^- are found in this complex although in the ^1H and ^{11}B NMR results no difference between these two BH_4^- ligands is apparent. More accurate experimental methods or high level theoretical calculation may help to determine the exact coordinate mode in this complex.

3.3. *Five-coordinate complexes: $M(BH_4)_nL_{5-n}$*

Usually, five coordinate complexes can adopt two different geometries, square-pyramidal and trigonal-bipyramidal. We will only discuss complexes with the latter structure, since we have not found any examples of the former so far.



$[(CO)_4M(\eta^2_\perp\text{-BH4})]^-$ (M=Cr,Mo) [34a,b]

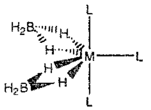
$(Ph_3P)_2(mphi)Ru(\eta^2_\perp\text{-BH4})$ [34c]

$(tripod)HFe(\eta^2_\perp\text{-BH4})$ [34d,e]

$(Ph_3P)_3HRu(\eta^2_\perp\text{-BH4})$ [34f]

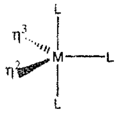
$(PMe_3)_2W(NO)(CO)(\eta^2_\perp\text{-BH}_4)$ [34g]

12



$(thf)_3Mn(\eta^2_\perp\text{-BH}_4)_2$ [35]

13



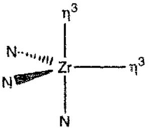
$(bp)Zr(thf)(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)$ [32] *16e*

14

Many d^6 five-coordinate complexes [34] have only one $\eta^2\text{-BH}_4^-$ ligand and adopt structure **12**. The structures of these complexes are easy to understand since they can also be described as pseudo-octahedral if the two bridging hydrogen atoms are considered. These d^6 pseudo-octahedral complexes conform to the 18-electron rule.

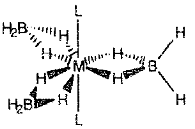
When two BH_4^- ligands are present, two structures are found. Complex $(thf)_3Mn(\eta^2\text{-BH}_4)_2$ [35] has a d^4 electronic configuration and adopts structure **13**. In this complex, besides the five σ-symmetry coordinate bonds (three M–L and two M–BH_4), the x^2–y^2 and xy orbitals can interact with the two π orbitals of the two BH_4^- ligands to form two more bonding MOs shown in Fig. 6. This complex can also be viewed as a pseudo pentagonal-bipyramidal geometry. With the four electrons occupying the xz and yz orbitals, the complex again has an 18-electron configuration.

$(bp)Zr(thf)(BH_4)_2$ [32], and $(N\text{-}N\text{-}N)Zr(\eta^3\text{-BH}_4)_2$ (where N-N-N = $(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2$ dianion) [36] are d^0 species. They offer two interesting examples of structures **14** and **15** respectively. The latter complex (**15**) conforms to the 18-electron rule. In the former complex, one of the two d orbitals (xz and yz, which are occupied in complex **13**) is to interact with the $\pi_\parallel$ component of the $\eta^3\text{-BH}_4^-$ ligand. The other d orbital is empty and may be used to interact with π orbitals from the bp or thf ligands. This usage might explain why the former adopts a structure which does not conform to the 18-electron rule.



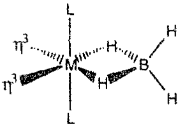
$(N\text{-}N\text{-}N)Zr(\eta^3\text{-BH}_4)_2$ [36]

15



$(Me_3P)_2V(\eta^2_\perp\text{-BH}_4)_3$ [37] *16e*

16



$(thf)_2Sc(\eta^3\text{-BH}_4)_2(\eta^3_\perp\text{-BH}_4)$ [38]

17

Recently, Lledos et al. reported their ab initio studies of the coordination mode of $V(BH_4)_3(PH_3)_2$ [2], as a model complex of high-spin d^2-$V(BH_4)_3(PMe_3)_2$ [37]. They found that, in agreement with the experimental data, $V(\eta^2\text{-}BH_4)_3(PR_3)_2$ (see **16**) is the most stable structure when compared with other structures having different coordination modes. In this complex, the two phosphine ligands occupy the two axial positions while the three BH_4^- ligands are in the equatorial plane of a pseudo trigonal-bipyramid. In the most stable structure all bridging hydrogens are in the equatorial plane. The ligand arrangement can be easily understood within an orbital interaction framework. The s, p_x, and p_y orbitals of the vanadium atom interact with the σ-orbitals of the three BH_4^- ligands (Fig. 2), the x^2–y^2 and xy orbitals overlap with two $\pi_\perp$-orbitals of BH_4^- in the equatorial plane (as in Fig. 4). The p_z and z^2 orbitals are used to form two σ bonds with the two phosphine ligands. The doubly degenerate d orbitals, xz and yz, accommodate the two d electrons in a high-spin fashion. Apparently, if the bridging hydrogens are not in the equatorial plane, the two singly occupied d orbitals will be destabilized through interaction with the bridging hydrogen atoms. Therefore, these complexes are 18-electron species with only 16 electrons occupying the metal and metal–ligand bonding MOs. The remaining two valence electrons are mainly delocalized in the three BH_4^- ligands (as the $\pi_{3\text{-in-plane}}$ orbital in Fig. 4). $(thf)_2Sc(BH_4)_3$ [38] has a similar geometry to $V(\eta^2\text{-}BH_4)_3(PMe_3)_2$ with a different arrangement of the bridging hydrogens. This complex was found to be formulated as $(thf)_2Sc(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2$ (**17**). Since the scandium complex is a d^0 species, the two d orbitals (xz and yz), which are singly occupied in the vanadium complex, are now empty. To maximize the metal–ligand interaction, the xz and yz orbitals can be utilized to interact with the two $\pi_\perp$ symmetry orbitals of the two BH_4^- ligands. Therefore, compared with the vanadium complex, the scandium complex has one η^2-BH_4^- and two η^3-BH_4^- ligands.

$Ti(BH_4)_3(PMe_3)_2$ [4b, 14] is another interesting example of five-coordinate complexes. It is a d^1 species. Based on the argument above, we would expect the complex to be formulated as $Ti(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)(PMe_3)_2$. However, our theoretical prediction is not so consistent with the X-ray crystal diffraction result [14], which showed two unusual 'side on' BH_4^- and one $\eta^2{}_\perp$-BH_4^- ligands (structure **18**).

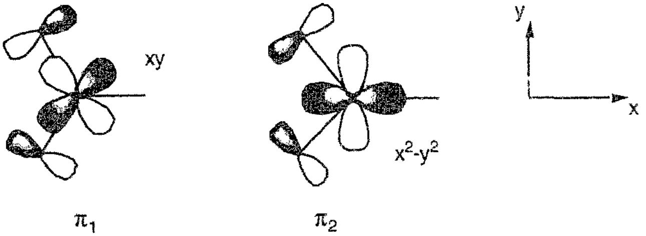
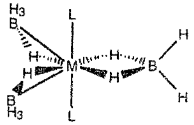
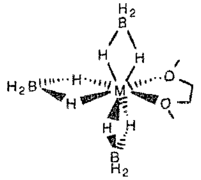


Fig. 6. The possible π orbital interaction between metal atom and ligands in complexes with structure **13**.



(Me$_3$P)$_2$Ti($\eta^2_\perp$-BH$_4$) (η^2-BH$_4$)$_2$ [4b,14] *17e*

18



(dme)Ti((η^2-BH$_4$)$_3$ [39] *17e*

19

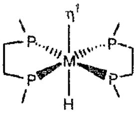
Detailed ab initio calculations on this titanium complex have been reported by Volatron et al. [4b] and the result is consistent with our prediction.

Ti(dme)(η^2-BH$_4$)$_3$ [39] is also a five-coordinate complex with three BH_4^- ligands. Owing to the bidentate ligand (dme), it has a quite different structure. In this complex, unlike in Ti(BH$_4$)$_3$(PMe$_3$)$_2$, two BH_4^- ligands are in the two axial positions while the other one is in the equatorial plane (structure **19**). This arrangement makes it possible for the three BH_4^- ligands to interact with the metal atom in η^2-modes without any restriction on symmetry. The d^1 electron occupies the non-bonding xy orbital. This complex features a 17-electron configuration.

3.4. *Six-coordinate complexes: M(BH$_4$)$_n$L$_{6-n}$*

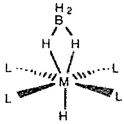
Pseudo-octahedral geometry is the structural feature of many six-coordinate complexes. In this geometry, three d orbitals, xy, xz and yz, of the central atom are available to interact with the π symmetry orbitals of BH_4^- ligands if they are not occupied with d electrons.

Several complexes with one BH_4^- ligand have been found in the literature, i.e. (dmpe)$_2$HFe(η^1-BH$_4$) [40] (see **20**), ((C$_5$H$_9$)$_3$P)$_2$(H)$_3$Os(η^2-BH$_4$) [41] and (dmpe)$_2$HCr(η^2-BH$_4$) [42] (see **21**). Their coordination and structural characteristics can be understood by the 18-electron rule, i.e. d^6 complexes adopt **20** and d^4 complexes adopt **21**.



(dmpe)$_2$HFe(η^1-BH$_4$) [40]

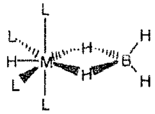
20



((C$_5$H$_9$)$_3$P)$_2$(H)$_3$Os(η^2-BH$_4$) [41]

(dmpe)$_2$HCr(η^2-BH$_4$) [42]

21

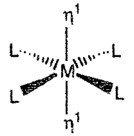


(Me$_3$P)$_4$HMo($\eta^2_\perp$-BH$_4$) [43]

22

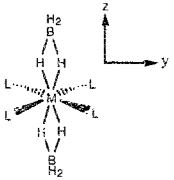
Another d^4 complex, $(Me_3P)_4HMo(\eta^2\text{-}BH_4)$ [43], has been reported (with X-ray diffraction) to adopt structure **22** rather than **21**, although its molecular formula is similar to that of $(dmpe)_2HCr(\eta^2\text{-}BH_4)$ [42]. This complex can also be viewed as a pseudo-pentagonal bipyramidal molecule and conforms to the 18-electron rule.

$(dmpe)_2V(BH_4)_2$ [37,44] and $(dmpe)_2Ti(BH_4)_2$ [44,45] are two examples of six-coordinate complexes with two BH_4^- ligands. In the d^3-$(dmpe)_2V(BH_4)_2$ [37,44] complex, three non-bonding d orbitals are singly occupied by the three metal d electrons. This complex features a high-spin d^3 15-electron configuration with two BH_4^- units in η^1-coordination modes (structure **23**).



$(dmpe)_2V(\eta^1\text{-}BH_4)_2$ [37,44] *15e*

23

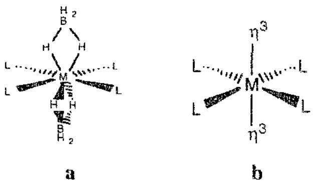


$(dmpe)_2Ti(\eta^2\text{-}BH_4)_2$ [44,45]

24

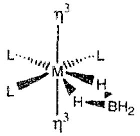
The ESR spectrum result showed that the complex has $S=3/2$, and therefore supports this analysis [44]. $(dmpe)_2Ti(BH_4)_2$ [44,45] is a d^2 species and adopts a structure **24**. In such a ligand arrangement, one expects that this complex is a high-spin species because there are two d orbitals (x^2-y^2 and xz, see Cartesian coordinates in **24**) which are pure non-bonding and not available for metal–(BH_4^-) π-bonding. One also expects that each of the two Ti–$(\eta^2\text{-}BH_4)$ bonds must be weaker than a normal Ti–$(\eta^2\text{-}BH_4^-)$ bond because one orbital (yz) is shared by the two $\pi_\perp$ symmetry orbitals of the two BH_4^- units. The weaker Ti—$(\eta^2\text{-}BH_4)$ bonds lead to stronger B–H_b (H_b: bridging hydrogen bonds). Indeed, the IR experiment [44] found that the $\nu(BH_b)$ in this complex is greater than that in other titanium complexes with a normal η^2-BH_4 ligand, such as $Cp_2Ti(\eta^2\text{-}BH_4)$ and $Ti(\eta^2\text{-}BH_4)_3(PMe_3)_2$. The explanation for the stronger B—H_b bonds above is quite different from the one presented by Jensen and Girolami. They concluded that the Ti—BH_4 bonds in this complex are weak and ionic [37].

$[(thf)_4Y(BH_4)_2]^+$ [11] and $(thf)_3Y(BH_4)_3$ [46] are two examples with a d^0 configuration and have two and three BH_4^- ligands respectively. The X-ray crystallographic result of $[(thf)_4Y(BH_4)_2]^+$ [11] showed that the two BH_4^- ligands occupy the two axial positions. The information on the coordination modes of the two BH_4^- anions is not available from X-ray diffraction. As the metal atom has only two symmetry-adapted orbitals, xz and yz, which can be used to interact with the π-symmetry orbitals of the ligands on the axial, one possibility for the structure is that the two BH_4^- ligands are in normal η^2-modes with four H_b atoms not being in a plane (structure **25a**).



[(thf)$_4$Y(BH$_4$)$_2$]$^+$ [11] *16e*

25



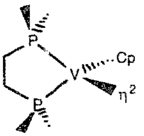
(thf)$_3$Y(BH$_4$)$_3$ [46]

26

The other possibility is that both BH_4^- ligands are coordinated to the metal through η^3-modes. In the latter case, $[(thf)_4Y(\eta^3\text{-}BH_4)_2]^+$ (**25b**) is isoelectronic to many *trans*-di-oxo metal complexes. The latter possibility is quite likely because most tetrahydroborato complexes adopt a structure with the maximum metal–BH_4^- coordination number (3) as long as no electronic destabilization occurs. In complex (thf)$_3$Y(BH$_4$)$_3$ (**26**), the two axial BH_4^- ligands are found (by X-ray diffraction) to be in η^3-coordination modes and the remaining one is in a normal η^2-mode with two hydrogen atoms being in the equatorial plane. The interaction between the xy orbital of the central atom and the $\pi_\perp$ symmetry orbital of the equatorial BH_4^- ligand is responsible for the two bridging hydrogen atoms being in the equatorial plane. The xz and yz orbitals interact with π symmetry orbitals of the two BH_4^- ligands in the axial positions (see **26**).

3.5. Complexes with Cp rings (higher coordination numbers)

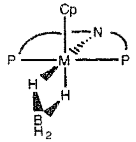
Complexes with η^5-cyclopentadienyl or its derivatives (Cp) are also commonly found [19,47]. The majority of these complexes contain a Cp$_2$M fragment and can be described with a general formula as Cp$_2$M(BH$_4$)$_n$(n=1,2) except Cp(Me$_2$PCH$_2$CH$_2$PMe$_2$)V(BH$_4$) [48] (structure **27**) and CpZr(η^2-BH$_4$)[N(SiMe$_2$CH$_2{}^i$Pr$_2$)$_2$] [49] (structure **28**).



Cp(Me$_2$P(CH$_2$)$_2$PMe$_2$)V(η^2-BH$_4$) [48]

17e

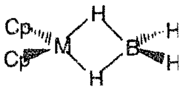
27



CpZr(η^2-BH$_4$)(P-N-P) [49]

(P-N-P=(N(SiMe$_2$CH$_2$PPr$^i{}_2$)$_2$)

28



Cp$_2$Nb(BH4) [47a]
Cp$_2$Sc(BH4)* [19]
Cp$_2$Ti(BH4) [47b,c] *17e*
(Bu$^t{}_2$Cp)$_2$Ti(BH4) [47d] *17e*
(Bu$^t{}_2$Cp)$_2$Sc(BH4) [19] *16e*
((SiMe$_3$)$_2$Cp)$_2$Sc(BH4)* [19] *16e*

29

* A theoretical prediction

These two complexes are both 17-electron species containing one η^2-BH_4^- and one η^5-Cp ligand. The structure of the d^3 17-electron complex, $Cp(Me_2PCH_2CH_2PMe_2)V(BH_4)$, can be understood by referring to the d^4 18-electron complexes, $((C_5H_9)_3P)_2(H)_3Os(\eta^2\text{-}BH_4)$ [41] and $(dmpe)_2HCr(\eta^2\text{-}BH_4)$ [42] (see **21**), since a Cp ring can be considered as a tridentate ligand. The d^1 17-electron complex, $CpZr(\eta^2\text{-}BH_4)[N(SiMe_2CH_2P^iPr_2)_2]$, can be viewed as a pseudo-octahedral structure (with respect to the centroid of the Cp ring) (see **28**). Its electronic structure can be easily understood if one considers that the Cp ligand uses $\sigma + 2\pi$ bonds to interact with the metal center and that one metal d orbital (xy) is singly occupied.

The orbital interaction analysis for a Cp_2M fragment is well-known and easily found in the literature [15,50]. As shown in Fig. 7, each Cp_2M fragment has three frontier orbitals, whose maximum amplitudes are in the plane m perpendicular to the Ct–M–Ct plane (Ct is the centroid of the Cp ring), available for bonding. It is understandable that any orbital interaction between the Cp_2M fragment and BH_4^- should be restricted in this plane m. Otherwise, the metal–Cp interactions will be destabilized.

In complexes with one BH_4^- ligand, η^2 is the optimal coordination mode since the third hydrogen atom cannot lie in the same plane m. Therefore, d^2 species of a $Cp_2M(\eta^2\text{-}BH_4)$ complex will obey the 18-electron rule, such as $Cp_2Nb(\eta^2\text{-}BH_4)$ [47d] (**29**). Complexes with d^1 configuration, such as $Cp_2Ti(\eta^2\text{-}BH_4)$ [47c,d] and $(^tBu_2Cp)_2Ti(\eta^2\text{-}BH_4)$ [47c], feature a 17-electron configuration and also adopt structure **29**. $(^tBu_2Cp)_2Sc(BH_4)$ [47f] provides an example of d^0 species in which the BH_4^- ligand is also in an η^2-mode. $(SiMe_3)_2Cp)_2Sc(BH_4)$ [47f] and $Cp_2Sc(BH_4)$ [47b] are two analogues of $(^tBu_2Cp)_2Sc(\eta^2\text{-}BH_4)$. Based on the above analysis, the BH_4^- ligand in either $Cp_2Sc(BH_4)$ or $(^tBu_2Cp)_2Sc(BH_4)$ should be in η^2-modes too. However, Mancini and co-workers suggested a η^3-BH_4^- ligand for the $Cp_2Sc(BH_4)$ complex in their early experimental work [47b]. This disagreement implies that for early transition-metal tetrahydroborato complexes the metal–BH_4 electrostatic interaction could be very significant.

Complexes with two BH_4^- and two Cp ligands are rarely found. $(MeCp)_2Hf(BH_4)_2$ [51] is the only example found in the literature. The X-ray diffraction of this d^0 species reveals that both BH_4^- ligands coordinate to the center in η^2-modes (see **30**).

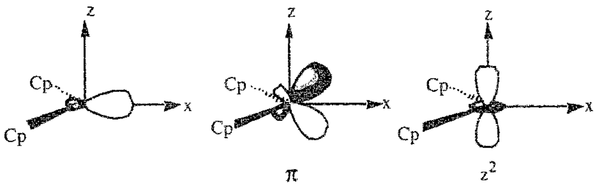
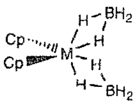
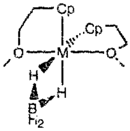


Fig. 7. The frontier orbitals of a Cp_2-M fragment.



$(MeCp)_2Hf(\eta^2\text{-}BH_4)_2$ [51]

30



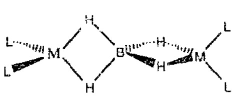
$Y(\sigma^1,\eta^5\text{-}MeOCH_2CH_2Cp)_2(\eta^2\text{-}BH_4)$ [52]

31

According to the analysis above, the four bridging hydrogens are expected to be in the plane *m*. However, it was found that these four hydrogens were slightly twisted out of the plane. This could be due to the steric congestion of the two adjacent bridging hydrogens. The complex has 20 electrons with the two extra valence electrons being mainly delocalized on the BH_4^- ligands. $Y(\sigma^1,\eta^5\text{-}MeOCH_2CH_2Cp)_2(\eta^2\text{-}BH_4)$ [52] is also a d^0 species but with one $\eta^2\text{-}BH_4^-$ and two $MeOCH_2CH_2Cp$ ligands. The crystallographic structure of this complex indicates that the two bridging hydrogen atoms of the BH_4^- ligand in this yttrium complex are not in the plane *m* (see structure **31**). This ligand arrangement seems inconsistent with the claim above. Although we do not have an explanation for this structure, the complex can be viewed as isoelectronic with many d^0-*cis*-dioxo metal complexes [15], such as $[MoO_2F_4]^{2-}$, if Cp^- is viewed as isolobal with O^{2-}.

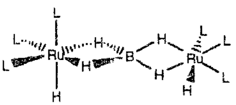
4. Species with multiple metal centers

In the discussion above, we have dealt with complexes containing only one metal center. Complexes discussed here are those containing two or more metal centers. Many examples (**32** to **44**) are found in the literature. One can understand their structures by first considering each metal center as an independent unit and then examining the possibility of metal–metal interaction.



$[((Ph_3P)_2Cu)_2(\mu_2\text{-}\eta^4\text{-}BH_4)]^+$ [53]

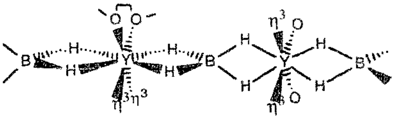
32



$[(tripod)HRu)_2(\mu_2\text{-}\eta^4\text{-}BH_4)]^+$ [54]

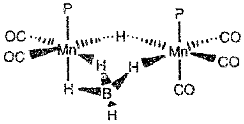
33

First, we consider complexes in which one BH_4^- ligand serves as a bridge. These complexes do not have metal–metal interactions. $[((Ph_3P)_2Cu)_2(\mu_2\text{-}\eta^2\text{-}BH_4)]^+$ [53] (**32**) and $[(tripod)HRu)_2(\mu_2\text{-}\eta^2\text{-}BH_4)]^+$ [54] (**33**) are two normal 18-electron complexes. The structure of $((dme)Y(\eta^2\text{-}BH_4)_2(\eta^3\text{-}BH_4)_2)_n$ [55] (**34**) was determined by X-ray diffraction.



$((dme)Y(\mu_2\text{-}\eta^4\text{-}BH_4)_2(\eta^3\text{-}BH_4)_2)_n$ [55]

34



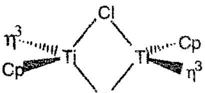
$(\mu\text{-}dppm)Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO)_5$ [56]

35

In this polymeric complex, each coordination unit can be viewed as octahedral with two cis η^3-BH_4 ligands in the square plane and two η^2-BH_4 ligand in the axial positions. Both η^2-BH_4^- ligands on the axial positions coordinate to the nearby centers to form a one-dimensional chain (see **34**). Each Y^{3+} ion is coordinated with 24 valence electrons. Therefore, the complex is usually considered as an ionic complex. It is interesting that the four H_b atoms of the two η^2-BH_4 ligands in a same coordination unit are in a single plane. This seems to indicate that the π symmetry orbitals of the η^2-BH_4 ligands interact with the xy orbital of the yttrium atom at the same time. This orientation implies the importance of electronic effects in this complex.

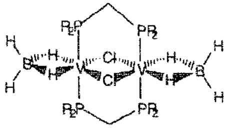
$(\mu\text{-}dppm)Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO)_5$ [56] provides an example in which the BH_4^- ligand is coordinated to two centers in two different modes (see **35**). Each manganese center in this complex conforms to the 18-electron rule.

Complexes with other bridges have also been found in the literature. In complex $((\eta^3\text{-}BH_4)TiCp)_2Cl_2$ [57] (**36**), each Ti center has 17 electrons with a d^1 configuration. The metal–metal distance, 3.447 Å, indicates no direct metal–metal bonding between the two d^1 centers. Weak spin–spin coupling through the two bridging chlorides may exist.



$((\eta^3\text{-}BH_4)TiCp)_2Cl_2$ [57] 17e

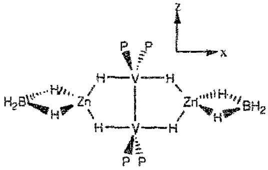
36



$(CH_2PMe_2)_2V_2Cl_2(\eta^2_\perp\text{-}BH_4)_2$ [58] 15e

$(\mu\text{-}dppm)_2V_2Cl_2(\eta^2_\perp\text{-}BH_4)_2$ [59]

37



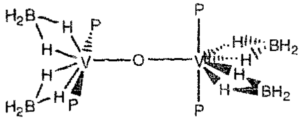
$V_2Zn_2(\mu\text{-}H)_4(PMePh_2)_4(\eta^2\text{-}BH_4)_2$ [60]

38

In $(CH_2PMe_2)_2V_2Cl_2(\eta^2\text{-}BH_4)_2$ [58] and $(dppm)_2V_2Cl_2(\eta^2\text{-}BH_4)_2$ [59] (see **37**), each vanadium center can be viewed as a d^3 high-spin 15-electron species. In view of the V—V distance (3.124 Å and 3.114 Å), direct V—V bonding is again unlikely. Weak anti-ferromagnetic interaction through the bridging chlorides will predominate between these two d^3 high-spin centers in both complexes.

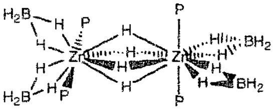
$V_2Zn_2(\mu\text{-}H)_4(PMePh_2)_4(\eta^2\text{-}BH_4)_2$ [60] (**38**) is another di-vanadium complex but with a much shorter V–V distance (2.40 Å). The structure was described as a diamond-shaped V_2Zn_2 aggregate (a squashed butterfly) with four edge-bridging hydrogen atoms [60]. The bridging hydrogen atoms of each $\eta^2\text{-}BH_4^-$ and the hydrogen atoms bridging V and Zn furnish tetrahedral ligation about zinc. The d^{10} Zn center conforms to the 18-electron rule. A significant interaction between the two d^4 V centers may be responsible for the short V—V bond.

$((Me_3P)_2V(\eta^2\text{-}BH_4)_2)O$ [37b] (see **39**) is a dimer bridged by an oxygen atom with a linear V–O–V unit.



$((Me_3P)_2V(\eta^2\text{-}BH_4)_2)O$ [37b]

39



$((PMe_3)_2Zr(\eta^2\text{-}BH_4)_2)_2(\mu_2\text{-}H)_4$ [62]

40

Around each vanadium center, two BH_4^- ligands coordinate to the central atom in η^2-modes with the four bridging hydrogen atoms being in a plane perpendicular to the P–V–P axis. In other words, the metal–ligand framework of each vanadium center is a pseudo-pentagonal-bipyramidal (PB) structure if the bridging hydrogen atoms are considered. The two PB substructures are geometrically related by a 90° rotation around the V–O–V axis. In a seven-coordinate PB complex, only two d

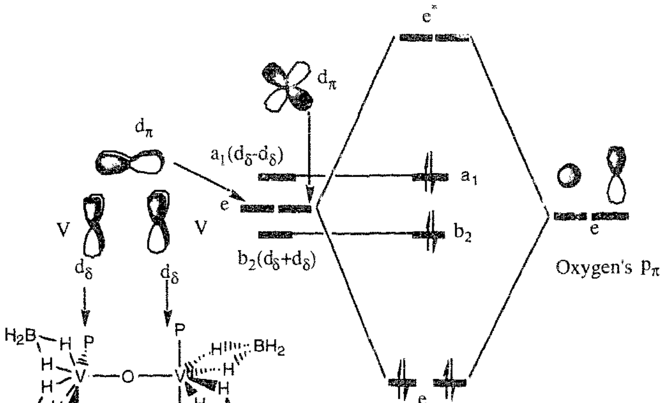
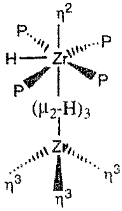


Fig. 8. The orbital interaction between the bridging oxygen and $(PMe_3)_2Zr(\eta^2\text{-}BH_4)$ fragment in $((PMe_3)_2V(\eta^2\text{-}BH_4)_2)_2O$. (Orbital symmetries are assigned based on a pseudo-D_{2d} point group.)

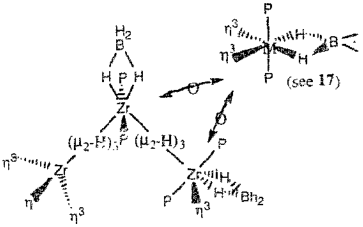
orbitals are available for d electrons. With respect to the V–O–V axis, one of the two d orbitals in each center is of d_δ character and cannot be used to interact with the bridging oxygen's p_π orbitals. The other one of the two d orbitals in each center will be used to interact with one of the two oxygen's p_π. The relevant interaction is shown in Fig. 8. If the bridging oxygen's p_π electrons are included, both V centers conform to the 18-electron rule. Detailed orbital interaction analysis for linear M–X–M systems can be found in the literature [62].

Recently, Mayo et al. [61] reported X-ray crystallographic results of $((PMe_3)_2Zr(\eta^2\text{-}BH_4)_2)_2(\mu_2\text{-}H)_4$ (see **40**). It has a structure similar to **39**. The orbital interaction between the four bridging hydrogen atoms and the two $(PMe_3)_2Zr(\eta^2\text{-}BH_4)_2$ fragments is illustrated with the diagram in Fig. 9. The linear combinations of four s orbitals of the bridging hydrogen atoms span one σ, two π and one δ symmetry representations to interact with the frontier orbitals from both $(PMe_3)_2Zr(\eta^2\text{-}BH_4)_2$ fragments. The σ and π interactions in this complex are quite similar to that in **39**. One of the two δ symmetry combinations $(d_\delta + d_\delta)$ can interact with the δ combination derived from the four s orbitals of the four bridging hydrogens.



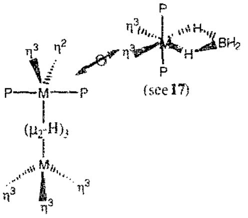
$(\eta^3\text{-}BH_4)_3Zr(\mu_2\text{-}H)_3Zr(H)(dmpe)_2(\eta^2\text{-}BH_4)$ [63]

41



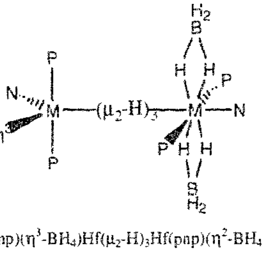
$(\eta^3\text{-}BH_4)_3Zr(\mu_2\text{-}H)_3Zr(PMe_3)_2(\eta^2\text{-}BH_4)(\mu_2\text{-}H)_3Zr\text{-}$
$(PMe_3)_2(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)$[63]

42



$(\eta^3\text{-}BH_4)_3Zr(\mu_2\text{-}H)_3Zr(PMe_3)_2(\eta^3\text{-}BH_4)_2$ [64]
$(\eta^3\text{-}BH_4)_3Hf(\mu_2\text{-}H)_3Hf(PMe_3)_2(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)$ [64]

43



$(pnp)(\eta^3\text{-}BH_4)Hf(\mu_2\text{-}H)_3Hf(pnp)(\eta^2\text{-}BH_4)_2$ [65]

44

There are several other examples of multi-bridging complexes found in the literature. $(\eta^3\text{-BH}_4)_3\text{Zr}(\mu_2\text{-H})_3\text{Zr(H)(dmpe)}_2(\eta^2\text{-BH}_4)$ [63] (**41**), $(\eta^3\text{-BH}_4)_3\text{Zr}(\mu_2\text{-H})_3\text{-Zr}(\eta^2\text{-BH}_4)(\mu_2\text{-H})_3(\text{PMe}_3)_2\text{Zr}(\text{PMe}_3)_2(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)$ [63] (**42**), and $(\eta^3\text{-BH}_4)_3\text{Zr}(\mu_2\text{-H})_3\text{Zr}(\eta^3\text{-BH}_4)(\text{PMe}_3)_2(\eta^2\text{-BH}_4)$ [64] (**43**) are three interesting d^0 complexes with two or three Zr centers bridging by $(\mu_2\text{-H})_3$ units. For each part of these complexes, the $(\mu_2\text{-H})_3$ unit can be considered as an isostructural ligand of an η^3-BH_4. For this reason, the structural and electronic features of these complexes are not too difficult to understand. Each complex contains an $(\eta^3\text{-BH}_4)_3\text{Zr}(\mu_2\text{-H})_3$ fragment which is isoelectronic and isostructural with $\text{M}(\eta^3\text{-BH}_4)_4$ (M = Zr, Hf, Y) (see **9**). According to the X-ray diffraction result, the $(\mu_2\text{-H})_3\text{Zr(H)(dmpe)}_2(\eta^2\text{-BH}_4)$ fragment in **41** will give a 20 electron count for the Zr center with a pentagonal-bipyramidal geometry. In this geometry, the hydride ligand coordinates to the Zr atom in the same plane (say the xy plane) as the two dmpe ligands. This is easily understood since the Zr center has five atomic orbitals in the xy plane, s, p_x, p_y, xy and x^2-y^2, which can be used to accept the five ligand electron pairs. By comparing this fragment with $(\text{thf})_3\text{Y}(\text{BH}_4)_3$ (see **26**), one can expect that the η^2-BH_4 ligand in the axial position may also coordinate to the center in an η^3 mode since both xz

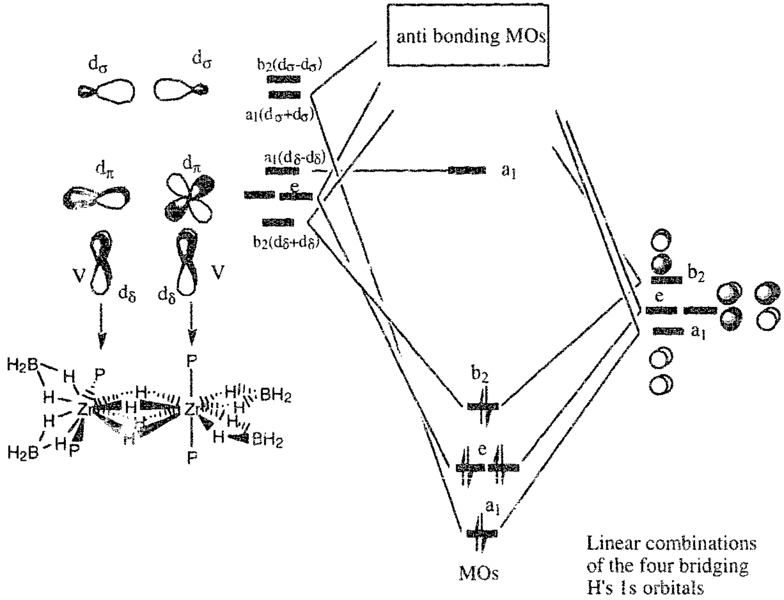


Fig. 9. The orbital interaction between four bridging hydrogen atoms and the $(\text{PMe}_3)_2\text{Zr}(\eta^2\text{-BH}_4)$ fragment in $((\text{PMe}_3)_2\text{Zr}(\eta^2\text{-BH}_4)_2)_2(\mu^2\text{-H})_4$. (Orbital symmetries are assigned based on a pseudo-D_{2d} point group.)

and *yz* orbitals are available to the BH_4 ligand's π orbitals, but this may weaken the interaction between the central atom and the $(\mu_2\text{-}H)_3$ unit at the same time. The other coordination centers in **42** and **43** can find their structural analogue in complex $(thf)_2Sc(\eta^3\text{-}BH_4)_2(\eta^2\text{-}BH_4)$ (**17**) discussed above. $(\eta^3\text{-}BH_4)_3Hf(\mu_2\text{-}H)_3Hf(PMe_3)_2(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)$ [64] (see **43**) is an analogue of $(\eta^3\text{-}BH_4)_3Zr(\mu_2\text{-}H)_3Zr(PMe_3)_2(\eta^3\text{-}BH_4)(\eta^2\text{-}BH_4)$. $(pnp)(\eta^3\text{-}BH_4)Hf(\mu_2\text{-}H)_3Hf(pnp)(\eta^2\text{-}BH_4)_2$ [65] (see **44**) is another Hf dimer with a bridging $(\mu_2\text{-}H)_3$ unit. In this complex, the $(pnp)(\eta^3\text{-}BH_4)Hf(\mu_2\text{-}H)_3$ fragment conforms to the 18-electron rule while the $(\mu_2\text{-}H)_3Hf(pnp)(\eta^2\text{-}BH_4)_2$ fragment has 20 valence electrons with the four bridging hydrogens from the two $\eta^2\text{-}BH_4^-$ ligands lying in a plane. This arrangement of the four bridging hydrogens indicates that the two π symmetry orbitals from the two $\eta^2\text{-}BH_4^-$ ligands interact with the central atom by sharing the same d orbital (with π symmetry) and that the two extra ligand electrons are mainly delocalized in the two $\eta^2\text{-}BH_4^-$ ligands.

5. Summary

Through our detailed structural and electronic analyses of a large number of transition-metal tetrahydroborato complexes, the following points can be made.

(1) Most of the transition-metal tetrahydroborato complexes conform to the 18-electron rule, especially those complexes with only one BH_4^- ligand.

(2) Usually, complexes with more than 18 valence electrons are considered as ionic complexes. Through our detailed analyses, both ionic and electronic effects are found to play important roles in the stereochemistry in these tetrahydroborato complexes. The ionic effect tends to maximize the coordination number while the electronic effect influences the orientation of bridging hydrogen atoms.

(3) Some complexes with two or more BH_4^- ligands are found to have more than 18 valence electrons. These complexes adopt structures allowing the extra electrons to be exclusively delocalized in the BH_4^- ligands. Although some complexes are formally 18-electron species, the number of electrons involved in the metal–ligand bonding is not necessarily 18.

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Appendix A. List of abbreviations

bdph	butyl-diphenylphosphine
bp	bisphenoxo dianion: $CH_2(C_5H_{12}PhO\ )_2$

^{t}Bu	tertiary butyl
Cp	η^5-C_5H_5 or its derivatives
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphino)ethane
dmph	2,9-dimethyl-1,10-phenanthroline
dppm	bis(dimethylphosphino)methane
hdmpb	hydrogen tris(3,5-dimethylpyrazolyl)borato anion
mphi	*N*-*p*-tolyl-*N*′-(*m*-methyl-*o*-phenylene)imidazolidine
N-N-N	*N*,*N*′,*N*″-tris(trimethylsilyl)diethylenetriamine dianion
$N(SiMe_2CH_2P^iPr_2)_2$	bis(di-isopropylphosphinaomethyl(dimethyl)silyl)amino
pcy_3	tricyclohexylphosphine
PMe_3	trimethylphosphine
phen	1,10-phenanthroline
P-N-P	bis(((dimethylphosphino)methyl)dimethylsilyl)amine-*P*,*N*,*P*′ anion
tripod	$CH_3C(CH_2PPh_2)_3$
thf	tetrahydrofuran
tmen	*N*,*N*,*N*′,*N*′-tetramethylenediamine

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