3964 *Inorg. Chem.* **1996,** *35,* 3964−3966

Theoretical Study of Metal−Tetrahydroborato Ligand Interactions in $[Y(THF)_4(BH_4)_2]^+$

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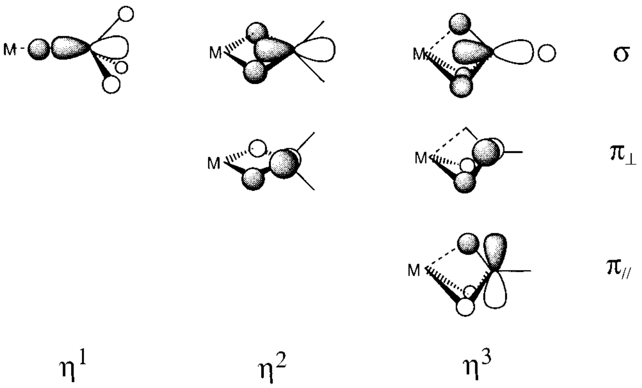
Received January 10, 1996[⊗]

Ab initio calculations for the $[Y(H_2O)_4(BH_4)_2]^+$ complex, a model of $[Y(THF)_4(BH_4)_2]^+$, have been carried out to study the metal−BH_4^- ligand interactions. Our calculations for various isomers with different BH_4^- coordination modes allow us to explore the electronic and electrostatic interactions in details. It is found that both electronic and electrostatic effects are of almost equal importance.

Introduction

The tetrahydroborato ion (BH_4^-, the simplest anionic boron hydride) forms unusual coordination complexes with transition metals through the η^1, η^2, and η^3 modes (see **1**). These different coordination modes have attracted considerable interest not only because they provide a variety of structure and bonding types but also because they provide models for studying the C−H bond activation involved in the industrially important dehydrogenation for a number of alkanes.[1−8] Recently, we surveyed comprehensively the current known and structurally characterized tetrahydroborato complexes of the transition metals.[8] In the survey, a general theoretical analysis based on orbital interaction argument was given to illustrate the relationship between their structures (BH_4^- coordination modes) and bonding characteristics. We have concluded that majority of tetrahydroborato complexes conform to the 18-electron rule when η^1-, η^2-, or η^3-BH_4^- is considered to donate two, four, or six electrons to the central metal atom. Those complexes, which have formally more than 18 valence electrons, adopt structures (coordination modes) allowing the extra electrons to be delocalized in the BH_4^- ligands as exclusively as possible. For example, the tetrahedral complexes $M(\eta^3\text{-}BH_4)_4$ (M = Ti, Zr, Hf) have formally 24 valence electrons. The six extra electrons occupy the t_1 nonbonding molecular orbitals in which no metal AOs are involved,[8] similar to the case of MO_4^{2-} (M = Mo, W) complexes.[9]



For the theoretical simplicity, the definition of σ or π interaction is based on the number of nodal planes passing through the M-B bond in the interaction orbials (zero nodal plane for σ and one for π)

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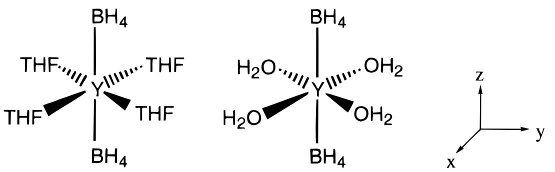
Due to the negative charge of BH_4^- ligand, the metal−BH_4^- interaction, for those complexes having formally more than 18 electrons, is often considered ionic. Recently, the excellent work of Parry and co-workers, who used some neutral borohydrides (e.g., $H_2(PR_3)B-B(PR_3)H_2$) as ligands in M−H−B complexes, provided an unequivocal evidence of electronic factor for the M and (B−H) interaction.[3] Our general survey also indicated that the electronic factor is also considerably important, as mentioned above for the tetrahedral 24-electron complexes.[8]

In this paper, *ab initio* quantum chemical calculations are used to study the structure and bonding of $[Y(H_2O)_4(BH_4)_2]^+$, as a model complex of $[Y(THF)_4(BH_4)_2]^+$ (see **2**).[10] The choice of this metal complex for study allows us to evaluate the electronic and electrostatic effects separately. In this study, the relative stability of various structures with different coordination modes of BH_4^- ligands in the mentioned complex were investigated.



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Theoretical Details

Complex $[Y(THF)_4(BH_4)_2]^+$ was modeled by replacing the THF ligands with water molecules. All *ab initio* molecular orbital calcula-

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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S0020-1669(96)00026-2 CCC: $12.00

tions were carried out using the Gausian94 package[11] on SGI and HP workstations. Full geometry optimizations (in Cartesian coordinates) using 6-31g basis sets[12] for O, B, and H atoms were performed for all calculated structures (basis set I). Effective core potential (ECP) with an associated double-ζ basis set (using the LANL2DZ option) for the valence electrons [8s6p2s/3s3p2d] was used for the metal atom Y in all calculations.[11,13] To examine the effect of polarization functions in the metal$-BH_4^-$ interaction, a better basis set, 6-31g**,[12] was also used for the two BH_4^- ligands to do full geometry optimization again for all studied isomers (basis set II). Frequency calculations using basis set I were done to determine the characteristics of the optimized stationary geometries. Single-reference configuration interaction calculations using single- and double-excitations (CISD) and Møller−Plesset perturbation (MP2 and MP3) calculations using basis set I were carried out to examine the importance of electron correlation. To further test the accuracy of LANL2DZ basis set, polarization functions ($\zeta_f = 0.835$)[14] were added to LANL2DZ for the transition metal atom in basis set II to form a new basis set (basis set III). Using this new basis set, single-point HF and MP2 energy calculations were performed.

Results and Discussion

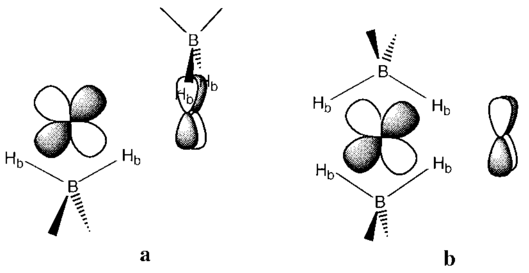
General Considerations. In our previous study,[8] each BH_4^- ligand was taken as occupying only one coordinate site. The difference among the three coordination modes is distinguished by considering η^1, η^2, and η^3 as having zero, one, and two π components, respectively, in addition to the metal$-BH_4^-$ σ interaction (see **1** for details). In $[Y(H_2O)_4(BH_4)_2]^+$, the yttrium atom is coordinated in a pseudooctahedral geometry. Besides the six atomic orbitals used to form the six σ MOs with the six ligands, the metal atom has three π symmetry d orbitals (the so called "t_{2g}" set in octahedral complexes). Two of the three d_π orbitals, *xz* and *yz*, are available to interact with π symmetry orbitals of BH_4^- ligands along the *z* axis (see **2** for the Cartesian coordinate system) while the other can only interact with the p_π orbitals of oxygens in the equatorial plane.

To maximize the electronic interaction between the metal atom and the two axial BH_4^- ligands, both *xz* and *yz* orbitals should be fully utilized in the metal$-BH_4^-$ π bonding. To achieve this maximization, both BH_4^- ligands are expected to coordinate to the central atom either through an η^3 mode or through an η^2 mode by having the two bridging units perpendicular to each other. For the η^3 mode, each BH_4^- ligands uses its two π orbitals to interact with both *xz* and *yz* orbitals. In this case, the two BH_4^- ligands have four orbitals involved in the metal$-BH_4^-$ π bonding. Two of the four linear combinations cannot find symmetry-adapted d_π orbitals for π interaction, and therefore they are nonbonding and delocalized exclusively in the two BH_4^- ligands. For the η^2 mode, when the two bridging units are perpendicular to each other, each BH_4^- ligand uses its π symmetry orbital to interact with one of the two metal d orbitals (*xz* or *yz*) to form a π molecular orbital (see **3a** and **4c**). In summary, both structures (η^2 and η^3) discussed here can achieve the optimal metal$-BH_4^-$ electronic interaction. Therefore their energy difference can be approximately considered as resulting from the different electrostatic interactions between these two modes (η^2 and η^3).

Table 1. Calculated Geometrical Parameters (Å, deg) Using Basis Set I and Basis Set II (in Parentheses) for Various Structures of $[Y(H_2O)(BH_4)]^+$ and Their Relative Energies (kcal/mol)[a]

	4a	4b	4c	4d	exptl
		Geometrical Parameters			
Y−O	2.37 (2.37)	2.37 (2.37)	2.35 (2.35)	2.35 (2.36)	2.32 av
Y−B	2.58 (2.56)	2.58 (2.56)	2.75 (2.73)	2.75 (2.73)	2.52 av
B−Y−B	180 (180)	174 (173)	180 (180)	180 (180)	167
		Relative Energy			
HF	0.0 (0.0)	0.1 (0.0)	4.5 (5.1)	11.2 (11.9)	
MP2	0.0	0.2	8.2	15.4	
MP3	0.0	0.0	8.1	15.3	
CISD	0.0	0.1	6.8	13.8	

[a] See Theoretical Details for basis sets.



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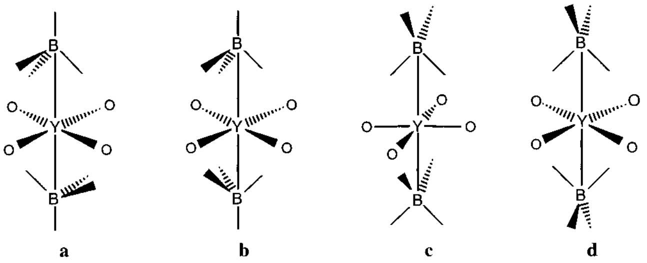

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When the two η^2-BH_4^- bridging units are parallel to each other (see **3b** and **4d**), the two π orbitals from both BH_4^- ligands can only interact with one of the two d orbitals of the metal atom, and thus, the optimal electronic interaction is not satisfied (see **3b**). Therefore, the energy difference between **4c** and **4d** mainly comes from the different electronic interactions since the coordination modes of the two BH_4^- ligands in these two structures are not different.

On the basis of the above considerations, four isomeric structures (see **4**) were designed and used as starting points for full geometry optimization. The results of these calculations (HF, MP2, MP3, CISD), together with the experimental data,[10] are summarized in Table 1.

Effects of Basis Set and Electron Correlation. It can be seen from Table 1 that both geometries and relative energies (between different isomers) do not change significantly from the medium-size basis set (6-31g) to the better basis set (6-31g**) used for the BH_4^- ligands. The MP2, MP3, and CISD calculation results also indicate that the electron correlation is not important when the relative energies are considered. To further test the accuracy of LANL2DZ basis set for the transition metal, we used basis set II geometries to perform single-point HF and MP2 energy calculations on the four isomers (**4a**−**4d**) with the largest basis set, Basis set III. The results, when

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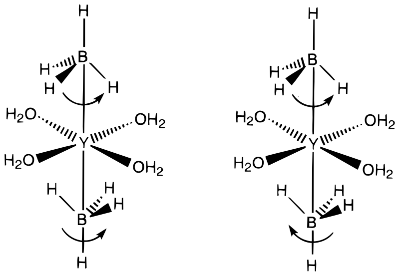
compared to those from basis set I and basis set II, indicated that no significant changes were found in the relative energies (**4a**, 0.0; **4b**, 0.0; **4c**, 5.0; **4d**, 11.7 kcal/mol at the HF level and **4a**, 0.0; **4b**, 0.2; **4c**, 8.7; **4d**, 15.8 kcal/mol at the MP2 level).

Structures and Stability. The relative energies of different structures together with their structural parameters for the yttrium complex are shown in Table 1. We can see from this table that the two η^3 isomeric structures (**4a**,**b**) are of almost equal energy. The frequency calculations for these two structures show that two harmonic motions, corresponding to the rotations of the two η^3-BH_4^- ligands (see **5**), have very small frequencies. These results indicate that the η^3-BH_4^- rotational barrier along the Y−B bond is very small. The calculation results (see Table 1) also indicate that the two η^3 isomeric structures (**4a**,**b**) are most stable while **4b** is slightly closer to the experimental structure. The calculated metal−ligand bond lengths agree quite well with the experimental ones (within 0.05 Å) for both **4a** and **4b**. For the **4b** structure, the calculated B−Y−B angle is slightly larger than the X-ray data but the B−Y−B bending reproduces the experimental observation.



a b

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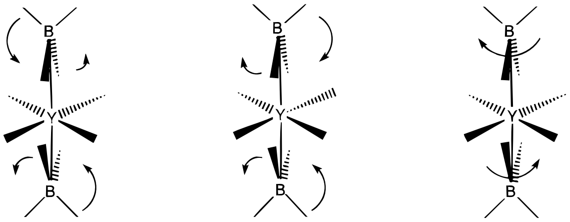
For the η^2 structures (**4c**,**d**), the metal−ligand bond lengths are close to each other. For **4c**, the bridging hydrogens eclipse the O−Y−O axes and the four oxygens bend away from the bridging hydrogen atoms. These bending allow maximum π interactions between the metal and BH_4^- ligands. For **4d**, the bridging hydrogens stagger the oxygen atoms. Frequency calculations reveal **4c** is a true local minimum while **4d** is not. For **4d**, three negative vibration frequencies correspond to harmonic motions that would lead the structure to **4c** and the two η^3 isomers (see **6**).



a b c

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Electrostatic and Electronic Interactions between the Metal Atom and BH_4^- Ligands. As discussed above, the energy difference between **4a** (or **4b**) and **4c** can be taken as resulting from the difference in their electrostatic interactions. Therefore, the electrostatic interaction energy difference between η^2 and η^3 can be approximately evaluated (6.8 kcal/mol at CISD). The energy difference between the two η^2 structures (**4c**,**d**) is viewed as the electronic interaction energy difference (7.0 kcal/mol at CISD). In conclusion, the electronic and electrostatic stabilizations in this yttrium complex are of almost equal importance. We should point out that the evaluation scheme presented here is only an approximate approach, which differs from the conventional energy partition method.

Conclusions

The conclusions can be summarized as follows: (a) In the studied complex, the BH_4^- ligands coordinate to the yttrium atom through a η^3 mode, a result consistent with the experimental data. (b) Both electronic and electrostatic effects are of almost equal importance in the interactions between the central metal atom and BH_4^- ligands. (c) The rotation barrier of η^3-BH_4 along the Y−B bond is very small.

Acknowledgment. This work was supported by the Research Grant Council of Hong Kong. The authors thank Dr. Yirong Mo for helpful discussions.

IC960026K