

Theoretical study on interaction of different coordination modes of BH_4 ligand with transition metal in $[\text{TM}(\text{BH}_4)(\text{CO})_4]^-$ (TM = Cr, Mo)

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Abstract

Density functional calculations were performed on bonding and structural features of $[(\eta^n\text{-BH}_4)\text{TM}(\text{CO})_4]^-$ ($n = 1, 2, 3$; TM = Cr, Mo) complexes. Calculations show that the ground state is bidentate which is in good agreement with experimental results. It has been found that the bridge and terminal hydrogen atoms will interchange by two pathways: (i) twist of BH_4 about one of the bridge B–H and (ii) twist of BH_4 about one of the terminal B–H. The molecular orbital calculations and natural bond orbital methodologies for different isomers of these complexes have been evaluated. The final results indicate that case (i) is more preferable relative to another case.

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1. Introduction

In recent decades, there has been considerable amount of interest in transition metal tetrahydroborate (BH_4) complexes. Several complexes have been synthesized and characterized by X-ray, neutron diffraction or by IR and NMR spectroscopies [1,2]. Besides their importance in homogenous catalysis, tetrahydroborates are of great interest due to the unusual coordination modes with transition metals through the η^1 , η^2 and η^3 modes (Fig. 1). Most of these compounds contain metals in positive formal oxidation states [3,4].

Generally, the ^1H NMR spectra of metal tetrahydroborate complexes exhibit a single BH_4 resonance at room temperature. This situation has been reported regardless of whether the ground state metal tetrahydroborate coordination geometry is bidentate or tridentate, and this is due to the exceedingly rapid intramolecular interchange of bridge and terminal hydrogen atoms [5]. Various possible pathways have been proposed. The first pathway suggested stereochemical nonrigidity in tetrahydroborate complexes and involves permutation of bridge and terminal hydrogens via a monodentate intermediate or transition state [5] (Fig. 2).

Certain empirical observations as well as ab initio calculations [5–9] have suggested that, at least for the early transition metals, bidentate and tridentate structures do not differ much in energy. The second suggested pathway which is a concerted process for tetrahydroborates having bidentate reactant geometries twists the BH_4 ligand about

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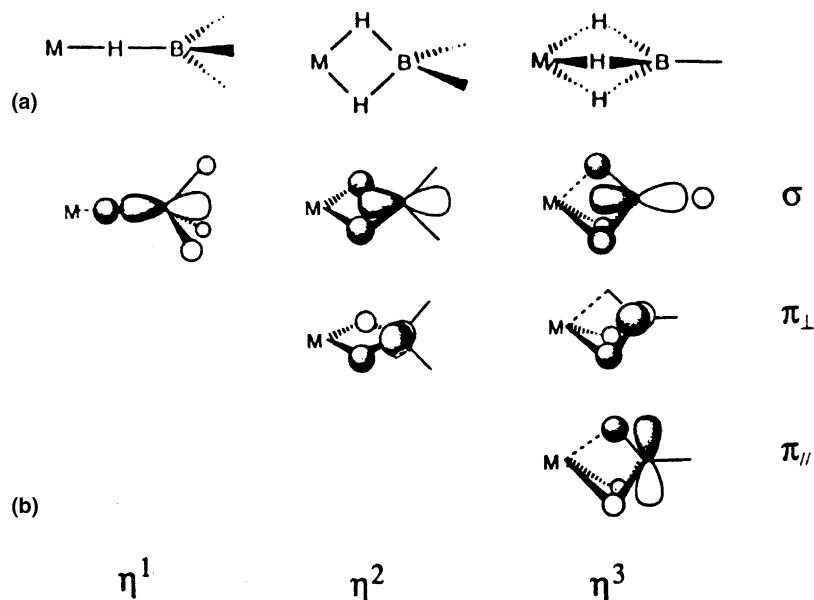


Fig. 1. (a) Three different coordination modes of BH₄. (b) BH₄ orbitals involve d orbitals in the η¹, η² and η³ coordination modes.

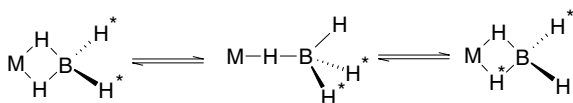


Fig. 2. Suggested pathway for interchange of bridge and terminal hydrogens through a monodentate intermediate or transition state.

one of the B–H^b bonds. The twisting process can be drawn for a complex with a tridentate reactant structure [5,10].

The aim of this work is to investigate the stability and possible structures of two examples of borohydride zero-valent metal complexes, [Cr(CO)₄(BH₄)][−] [11] and [Mo(CO)₄(BH₄)][−] [12] with the aid of density functional calculations. On the other hand, we have offered some insights into hydrogen exchange mechanism and also investigated relative stability of them through natural bonding orbital (NBO) and molecular orbital (MO) calculations.

2. Computational details

All geometries were fully optimized using the B3LYP (Becke three parameter exchange functional (B3) [13] and Lee–Yang–Parr correlation functional LYP [14]) density functional theory [15] as implemented in GAUSSIAN 98 [16]. In all tests the fine grid (75-302) was employed for a numerical evaluation of integrals. Mo and Cr atoms were described by effective core potentials (ECP's) of Wadt and Hay [17] with a double- ζ valance using the LANL2DZ. Carbons and oxygens are described with standard 6-31G basis set and polarization function is also added for carbon atoms, i.e.,

$\zeta_d(\text{C}) = 0.8$ [18]. The 6-31G** [19] is used for BH₄ ligand.

The natural bond orbital (NBO) analysis was performed using the NBO program [20] as implemented in GAUSSIAN 98. This program was also used to obtain Wiberg bond indexes (bond orders) [21], which is a measure of bond strength and occupancies. NBO occupancies were used to quantitatively evaluate the occupation number of given localized bonding orbitals, which give information regarding the strengths of interactions among different units within a molecule [22]. Frequency calculations were performed to determine the characteristics of optimized stationary geometries.

3. Results and discussion

The synthesis BH₄ adducts of TM(CO)₄ (TM = Cr, Mo) have been reported through a mixture of PPN⁺TM(CO)₅I[−] with PPN⁺BH₄[−] in THF [11,12]. Here, we focus on the structural isomers and bonding studies of the BH₄ adducts of TM(CO)₄ using the density functional theory (DFT) method as described in Section 2.

3.1. Effect of computational methods

The HF, DFT-B3LYP and MP2 fully optimized geometries of [(η²-BH₄)TM(CO)₄][−] (TM = Cr, Mo) (see 1) with C_{2v} symmetry are given in Tables 1 and 2. Frequency calculations of three methods showed no imaginary frequency for these complexes.

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