



Bridging hydrogen atoms versus iron–iron multiple bonding in binuclear borole iron carbonyls



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ARTICLE INFO

Article history:

Received 26 February 2016

Received in revised form 19 March 2016

Accepted 21 March 2016

Available online 26 March 2016

Keywords:

Iron

Borole

Metal–metal multiple bonding

Metal carbonyls

Bridging hydrogen atoms

Density functional theory

ABSTRACT

The geometries and energetics of the binuclear unsubstituted borole iron carbonyls $(C_4H_4BH)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) have been studied by density functional theory for comparison with the previously studied related substituted borole iron carbonyls $(C_4H_4BR)_2Fe_2(CO)_n$ [$R = CH_3, (CH_3)_2N$] having different substituents on the boron atoms. The lowest energy $(C_4H_4BH)_2Fe_2(CO)_n$ ($n = 5, 4, 3$) structures have terminal borole ligands related to those in the $(C_4H_4BR)_2Fe_2(CO)_n$ [$R = CH_3, (CH_3)_2N$] systems as well the isoelectronic $(\eta^5-C_5H_5)_2Mn_2(CO)_n$ systems. However, the lowest energy structure of the dicarbonyl $(C_4H_4BH)_2Fe_2(CO)_2$ is an unusual quintet spin state structure with one of the borole ligands bridging the central Fe_2 unit by forming a three-center two-electron $B-H-Fe$ bond to one iron atom as well as functioning as a pentahapto ligand to the other iron atom. For the $(C_4H_4BR)_2Fe_2(CO)_n$ [$R = CH_3, (CH_3)_2N$] systems the tricarbonyls ($n = 3$) having formal $Fe\equiv Fe$ triple bonds of lengths ~ 2.2 Å analogous to the experimentally known $(\eta^5-Me_5C_5)_2Mn_2(\mu-CO)_3$ structure appear to be favorable structures. An analogous $(C_4H_4BH)_2Fe_2(\mu-CO)_3$ structure is found for the unsubstituted borole ligand. However, this structure appears to be disfavored relative to disproportionation into $(C_4H_4BH)_2Fe_2(CO)_{n+1} + (C_4H_4BH)_2Fe_2(CO)_{n-1}$.

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1. Introduction

One of the central concepts of modern inorganic chemistry is that of a three-center two-electron (3c-2e) bond. Such bonding was first recognized in diborane after the structure of diborane was shown to be $B_2H_4(\mu-H)_2$ with four terminal and two bridging hydrogen atoms (Fig. 1) [1]. The bonding of each bridging hydrogen to the central B_2 unit of diborane is the prototypical 3c-2e bond involving overlap of an orbital from the bridging hydrogen with an orbital from each of the two boron atoms [2]. The boron atom in the unstable monomeric borane (BH_3) may be considered as electron deficient or unsaturated since it has only six electrons in its sp^3 manifold thereby leaving an empty p orbital (Fig. 1). Dimerization of BH_3 to form the stable $B_2H_4(\mu-H)_2$ involves overlap of the empty p orbital of one BH_3 unit with the $B-H$ σ -bonding orbital of a second BH_3 unit to form the 3c-2e B_2H bond.

In unsaturated molecules without potentially bridging hydrogens to form multicenter bonds, multiple bonding is another

alternative. In metal carbonyl chemistry, the first unsaturated molecule to be synthesized with a metal–metal multiple bond was the pentamethylcyclopentadienylmolybdenum derivative $(\eta^5-Me_5C_5)_2Mo_2(CO)_4$, obtained by the thermal reaction of $Mo(CO)_6$ with pentamethylcyclopentadiene (Fig. 2) [3]. Consideration of the 18-electron rule suggested a formal $Mo\equiv Mo$ triple bond in this species. This suggestion was supported by a subsequent X-ray structural study indicating a short $Mo\equiv Mo$ distance of 2.488 Å as compared with the much longer $Mo-Mo$ single bond distance of 3.235 Å in the otherwise closely related $(\eta^5-C_5H_5)_2Mo_2(CO)_6$ [4]. Binuclear cyclopentadienylmetal carbonyls subsequently proved to be a fertile source of stable species having multiple bonds between transition metals as exemplified by $(\eta^5-R_5C_5)_2Cr_2(CO)_4$ ($R = H$ [5] Me [6,7]), $(\eta^5-C_5R_5)_2V_2(CO)_5$ [8,9] and $(\eta^5-C_5R_5)_2M'_2(CO)_3$ ($M' = Mn$ [10] Re [11]) with formal $M\equiv M$ triple bonds (Fig. 2). In addition, $(\eta^5-C_5H_5)_2Co_2(CO)_2$ [12] and $(\eta^5-C_5H_5)_2Fe_2(CO)_3$ [13] with formal $M=M$ double bonds have been synthesized and characterized structurally (Fig. 2). The metal–metal distances in all of these structures with metal–metal multiple bonds were all shown by X-ray crystallography to be significantly shorter than comparable structures clearly indicated to have metal–metal single bonds.

The unsubstituted borole ligand C_4H_4BH is of interest in potentially forming transition metal complexes either with a terminal

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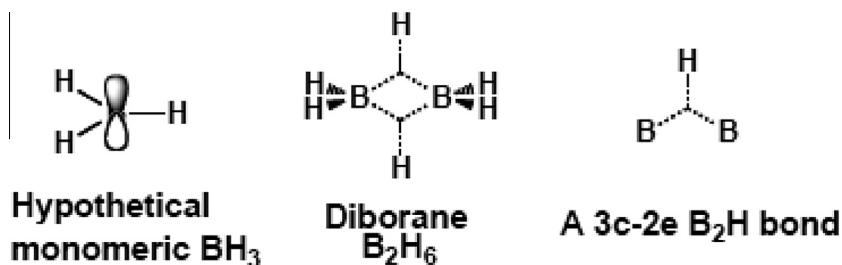


Fig. 1. (a) Monomeric BH₃ showing the empty p orbital; (2) the doubly bridged structure of diborane, B₂H₄(μ-H)₂; (3) The 3c-2e B₂H bond such as those involving the bridging hydrogens in diborane.

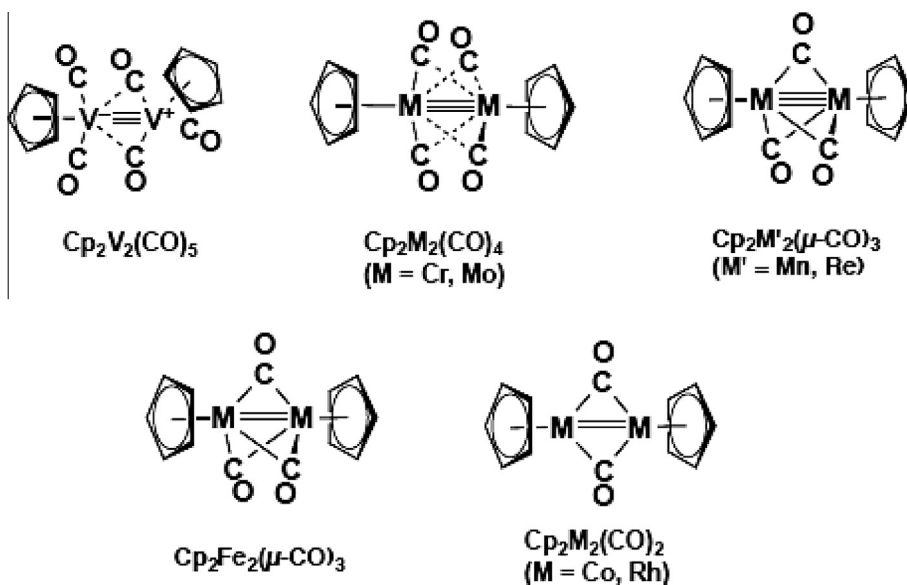


Fig. 2. Known binuclear cyclopentadienylmetal carbonyls with M=M triple bonds or M=M double bonds.

pentahapto borole ligand analogous to the ubiquitous pentahapto cyclopentadienylmetal complexes or species with B—H—M bridges exhibiting 3c-2e BHM bonding analogous to the 3c-2e B₂H bonding in diborane discussed above. Since the borole ligand can be generated by replacement of one of the five carbon atoms in the neutral cyclopentadienyl ligand with boron, the borole ligand, has one electron less than the cyclopentadienyl ligand. As a result, the neutral borole ligand is a net donor of four π electrons to a transition metal system, whereas a neutral cyclopentadienyl ligand is a net donor of five π electrons. Thus neutral borole is an antiaromatic 4n π-electron system similar to cyclobutadiene. For this reason unsubstituted borole, C₄H₄BH, is unstable in the free state and thus not available as a ligand to react directly with transition metal derivatives for the synthesis of its metal complexes. However, borole metal complexes have been synthesized using stable dihydroboroles as starting materials. Such reactions may involve direct thermal reactions of dihydroboroles with metal carbonyls to give complexes such as (η⁵-C₄H₄BR)M(CO)₃ (M=Fe [14], Ru [15], Os [15]; R = CH₃, C₆H₅), (η⁵-C₄H₄BR)₂Co₂(CO)₂(μ-CO)₂ [16] and (η⁵,η⁵-μ-C₄H₄BR)[Mn(CO)₃]₂ [14]. Alternatively, borole dianions, which can be obtained by the dilithiation of dihydroboroles [17], are also possible reagents for the synthesis of borole metal complexes.

The iron derivatives (η⁵-C₄H₄BR)Fe(CO)₃ are among the most stable and readily synthesized borole metal carbonyl complexes [14]. These are isoelectronic with both cymantrene (η⁵-C₅H₅)Mn(CO)₃ [18,19] and the very stable cyclobutadiene-iron tricarbonyl

(η⁴-C₄H₄)Fe(CO)₃ [20]. Both of these latter systems are known to undergo photolysis to form binuclear derivatives with metal-metal bonds. Among such derivatives, the binuclear tricarbonyls (η⁵-C₅H₅)₂Mn₂(CO)₃ [10] and (η⁴-C₄H₄)₂Fe₂(CO)₃ [21,22] with formal metal-metal triple bonds appear to be the most stable and are readily synthesized. In a previous paper [23] we used density functional theory to explore the potential of analogous binuclear methylborole complexes (η⁵-C₄H₄BCH₃)₂Fe₂(CO)_n (n = 5, 4, 3, 2, 1). To our surprise the methyl hydrogens in the highly unsaturated (η⁵-C₄H₄BCH₃)₂Fe₂(CO)_n (n = 2, 1) were found to form agostic 3c-2e C—H—Fe bonds in low-energy structures (Fig. 3). We then used the same theoretical methods to investigate analogous binuclear dimethylamino-borole iron carbonyl complexes [C₄H₄BN(CH₃)₂]₂Fe₂(CO)_n (n = 5, 4, 3, 2, 1) in order to explore possibilities of coordination of the pendant dimethylamino nitrogen group to the iron atom in unsaturated structures [24]. In this connection energetically competitive [C₄H₄BN(CH₃)₂]₂Fe₂(CO)_n (n = 4, 3, 2, 1) structures were found in which the dimethylaminoborole ligand functions as a six-electron donor bridging the pair of iron atoms. Such a bridging dimethylamino-borole ligand functions as a four-electron donor to one iron atom through pentahapto bonding from its C₄B ring and a two-electron donor to the other iron atom through donation from the nitrogen lone pair (Fig. 3).

These studies on binuclear methylborole and dimethylaminoborole iron carbonyl complexes demonstrate that the boron substituents, namely methyl and dimethylamino groups, can bond to the iron atom in unsaturated species (Fig. 3). The research

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