Bridging Hydrogen Atoms Versus Iron-Iron Multiple Bonding in Binuclear Borole Iron Carbonyls

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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 $(C_4H_4BH)_2Fe_2(CO)_{n+1} + (C_4H_4BH)_2Fe_2(CO)_{n-1}$.

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 $\text{B}_2\text{H}_4(\mu\text{-H})_2$ with four terminal and two bridging hydrogen atoms (Figure 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 (Figure 1). Dimerization of BH_3 to form the stable $\text{B}_2\text{H}_4(\mu\text{-H})_2$ 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.

Figure 1. (a) Monomeric BH_3 showing the empty p orbital; (2) The doubly bridged structure of diborane, $\text{B}_2\text{H}_4(\mu\text{-H})_2$; (3) The 3c-2e B_2H bond such as those involving the bridging hydrogens in diborane.

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 $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mo}_2(\text{CO})_4$, obtained by the thermal reaction of $\text{Mo}(\text{CO})_6$ with pentamethylcyclopentadiene (Figure 2) [3]. Consideration of the 18-electron rule suggested a formal $\text{Mo}\equiv\text{Mo}$ triple bond in this species. This suggestion was supported by a subsequent X-ray structural study indicating a short $\text{Mo}\equiv\text{Mo}$ distance of 2.488 Å as compared with the much longer $\text{Mo}-\text{Mo}$ single bond distance of 3.235 Å in the otherwise closely related $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ [4]. Binuclear cyclopentadienylmetal carbonyls subsequently proved to be a fertile source of stable species having multiple bonds between transition metals as exemplified by $(\eta^5\text{-R}_5\text{C}_5)_2\text{Cr}_2(\text{CO})_4$ ($\text{R} = \text{H}$ [5] Me [6, 7]), $(\eta^5\text{-C}_5\text{R}_5)_2\text{V}_2(\text{CO})_5$ [8, 9] and $(\eta^5\text{-C}_5\text{R}_5)_2\text{M}'_2(\text{CO})_3$ ($\text{M}' = \text{Mn}$ [10] Re [11]) with formal $\text{M}\equiv\text{M}$ triple bonds (Figure 2). In

addition, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_2$ [12] and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3$ [13] with formal $\text{M}=\text{M}$ double bonds have been synthesized and characterized structurally (Figure 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.

Figure 2. Known binuclear cyclopentadienylmetal carbonyls with $\text{M}\equiv\text{M}$ triple bonds or $\text{M}=\text{M}$ double bonds.

The unsubstituted borole ligand $\text{C}_4\text{H}_4\text{BH}$ is of interest in potentially forming transition metal complexes either with a terminal 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 B_2H 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, $\text{C}_4\text{H}_4\text{BH}$, 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 $(\eta^5\text{-C}_4\text{H}_4\text{BR})\text{M}(\text{CO})_3$ ($\text{M} = \text{Fe}$ [14], Ru [15], Os [15]; $\text{R} = \text{CH}_3$, C_6H_5), $(\eta^5\text{-C}_4\text{H}_4\text{BR})_2\text{Co}_2(\text{CO})_2(\mu\text{-CO})_2$ [16] and $(\eta^5, \eta^5\text{-}\mu\text{-}$

$C_4H_4BR[Mn(CO)_3]_2$ [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 $(\eta^5-C_4H_4BR)Fe(CO)_3$ are among the most stable and readily synthesized borole metal carbonyl complexes [18]. These are isoelectronic with both cymantrene $(\eta^5-C_5H_5)Mn(CO)_3$ [19, 20] and the very stable cyclobutadiene-iron tricarbonyl $(\eta^4-C_4H_4)Fe(CO)_3$ [21]. Both of these latter systems are known to undergo photolysis to form binuclear derivatives with metal-metal bonds. Among such derivatives, the binuclear tricarbonyls $(\eta^5-C_5H_5)_2Mn_2(CO)_3$ [22] and $(\eta^4-C_4H_4)_2Fe_2(CO)_3$ [23, 24] with formal metal-metal triple bonds appear to be the most stable and are readily synthesized. In a previous paper [25] we used density functional theory to explore the potential of analogous binuclear methylborole complexes $(\eta^5-C_4H_4BCH_3)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$). To our surprise the methyl hydrogens in the highly unsaturated $(\eta^5-C_4H_4BCH_3)_2Fe_2(CO)_n$ ($n = 2, 1$) were found to form agostic 3c-2e C-H-Fe bonds in low-energy structures (Figure 3). We then used the same theoretical methods to investigate analogous binuclear dimethylaminoborole iron carbonyl complexes $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) in order to explore possibilities of coordination of the pendant dimethylamino nitrogen group to the iron atom in unsaturated structures [26]. In this connection energetically competitive $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 4, 3, 2, 1$) structures were found in which the dimethylaminoborole ligand functions as a six-electron donor bridging the pair of iron atoms. Such a bridging dimethylaminoborole ligand functions as a four-electron donor to one iron atom through pentahapto bonding from its C_4B ring and a two-electron donor to the other iron atom through donation from the nitrogen lone pair (Figure 3).

Figure 3. Six-electron donor borole ligands bridging a pair of iron atoms: involvement of the boron substituent in the ligand-metal bonding.

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 (Figure 3). The research reported

in this paper uses related theoretical methods to explore the formation of 3c-2e B-H-Fe bonds in unsaturated $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_n$ species ($n = 5, 4, 3, 2, 1$).

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [27, 28, 29, 30, 31, 32, 33]. Thus three DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method using the combination of the three parameter Becke functional with the Lee–Yang–Parr generalized gradient correlation functional [34, 35]. The other DFT method used in the present paper is BP86, which combines Becke’s 1988 exchange functional with Perdew’s 1986 gradient corrected correlation functional [36, 37]. Usually the B3LYP and BP86 methods predict consistent geometries and energy orders for the same spin states. However, these two DFT methods often predict different singlet-triplet splittings. The B3LYP method generally favors the high spin state, whereas the BP86 method favors the low spin state. This phenomenon has been thoroughly studied by Reiher and coworkers [38] and is reviewed by Harvey [39]. In order to solve this problem, Reiher et al. proposed a new parametrization for the B3LYP functional, named B3LYP*, which provides electronic state orderings in good agreement with experiment [40].

In the present study, we discuss the B3LYP* energy orderings and geometries in the text. The B3LYP and BP86 results are shown in the Supporting Information. For the $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_n$ ($n = 5, 4$) systems, the energy orderings from the three methods were in good agreement. For the energy orderings of the more highly unsaturated $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_n$ ($n = 3, 2, 1$) systems having low-energy triplet and quintet spin state structures, the B3LYP method favored the higher spin state structures, the BP86 method favored the lower spin state structures, and the B3LYP* method gave intermediate values in accord with expectation. Since the BP86 $\nu(\text{CO})$ vibrational frequencies are typically closest to the experimental values without any scaling factors [41, 42, 43], the BP86 method is used to predict the $\nu(\text{CO})$ frequencies of the species reported in this paper.

All computations were performed using the double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for boron, carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{B}) = 0.70$, $\alpha_d(\text{C}) = 0.75$, and $\alpha_d(\text{O}) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets [44, 45] and are

designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga–Dunning DZ set. For iron, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses the Wachters’ primitive set [46] augmented by two sets of p functions and one set of d functions, contracted following Hood et al. [47]. All optimizations were carried out using the Gaussian 09 program [48] with the fine grid option, i.e., the pruned (75, 302) grid, for evaluating integrals numerically.

3. Results

3.1 Molecular Structures

3.1.1. $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$. The potential energy surface of $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ is fluxional, since four different singlet local minima are found within 6.0 kcal/mol in energy. All four structures have one bridging CO group and four terminal groups, i.e., $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ (Figure 4). The C_2 *trans* structure **5S-1** is the global minimum. Two *cis* $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ structures, namely **5S-2**, and **5S-3**, lie 4.9 and 5.7 kcal/mol (B3LYP*), respectively, in energy above **5S-1**. A *trans* $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ structure **5S-4** with C_2 symmetry lies 6.0 kcal/mol (B3LYP*) in energy above **5S-1** (Figure 4). The Fe–Fe distances in all of these singlet singly bridged $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ structures range from 2.788 Å to 2.863 Å (B3LYP*), consistent with the formal Fe–Fe single bond, required to give each Fe atom the favored 18-electron configuration.

The $\nu(\text{CO})$ frequencies of the bridging CO groups fall in the fairly typical range 1807 to 1828 cm^{-1} (Table 1), which is about 120 cm^{-1} below the terminal $\nu(\text{CO})$ frequencies (1948 to 2030 cm^{-1}).

Figure 4. Optimized geometries for the $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ structures. Bond distances are in Å.

Table 1. The $\nu(\text{CO})$ vibrational frequencies (cm^{-1}) and the infrared intensities (km/mol) by the BP86 method for $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ derivatives. Bridging $\nu(\text{CO})$ frequencies are in **bold**.

5S-1 (C_2)	5S-2 (C_1)	5S-3 (C_1)	5S-4 (C_2)
1812(344)	1807(350)	1826(314)	1828(322)
1967(18)	1967(119)	1948(306)	1966(12)
1981(765)	1987(516)	1984(400)	1981(846)
1994(1222)	1995(595)	2000(514)	2001(1252)
2018(99)	2030(970)	2030(993)	2019(11)

3.1.2. $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$. The potential energy surface of $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ is also fluxional, since no less than twelve different structures (including different conformers) have been obtained within 20 kcal/mol. Six selected structures (Figure 5) are discussed here as representatives of the different structural types. All of these structures are found to be genuine minima with no imaginary vibrational frequencies.

Figure 5. Optimized geometries for six representative $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ structures. Bond distances are in Å.

The lowest energy $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ structure **4T-1** has two bridging CO groups and two terminal CO groups in *trans* positions relative to the iron-iron bond, i.e., $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (Figure 5). The Fe=Fe distance in **4T-1** of 2.472 Å (B3LYP*) suggests the formal double bond required to give each iron atom the favored 18-electron configuration. The two unpaired electrons of the triplet spin state reside in two π orthogonal “half-bond” components of the formal $\sigma + \frac{1}{2}\pi$ double bond. A similar $\sigma + \frac{1}{2}\pi$ Fe=Fe double bond is found in the stable triplet spin state cyclopentadienyliron carbonyl derivatives $(\eta^5\text{-R}_5\text{C}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ (R = H, CH₃), which have been synthesized and structurally characterized by X-ray crystallography [49, 50, 51]. A similar triplet doubly bridged structure **4T-2**, with the two terminal CO groups in *cis* positions, lies only ~1.3 kcal/mol above **4T-1** (Figure 5). The Fe=Fe distances of 2.502 Å (B3LYP*) in **4T-2** are almost identical to those in **4T-1** suggesting a similar type of $\sigma + \frac{1}{2}\pi$ double bond with the two unpaired electrons of the triplet spin state in the two π “half-bonds.”

The triplet $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ structure **4T-3**, lying 7.3 kcal/mol (B3LYP*) above **4T-1**, has one bridging CO group and three terminal CO groups (Figure 5). The Fe–Fe distance of 2.607 Å (B3LYP*) in **4T-3** corresponds to a formal single bond, thereby giving each iron atom a 17-electron configuration corresponding to a binuclear triplet.

The lowest energy singlet $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ structure **4S-1** (C_i) is a *trans* doubly bridged structure lying 2.3 kcal/mol (B3LYP*) above the triplet global minimum (Figure 5). The iron-iron distance of 2.538 Å (B3LYP*) in **4S-1** can be interpreted as the formal Fe=Fe double bond required to give each Fe atom the favored 18-electron configuration.

The singlet $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ structures **4S-2** and **4S-3** are a pair of *trans/cis* doubly bridged isomers with similar geometries and predicted to have energies within ~1 kcal/mol of the lowest energy singlet **4S-1** (Figure 5). In both **4S-2** and **4S-3**, one of the bridging CO groups has a relatively short Fe–O distance of ~2.4 Å, suggesting a four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ group. The second bridging CO group in either **4S-2** or **4S-3** is a normal two-electron donor. The predicted Fe–Fe distances of 2.608 Å (B3LYP*) in **4S-2** and 2.621 Å (B3LYP*) in **4S-3** correspond to formal single bonds, thereby giving each iron atom the favored 18-electron configuration in these structures with a four-electron donor $\eta^2\text{-}\mu\text{-CO}$ group.

Similar to $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ structures, the $\nu(\text{CO})$ frequencies for the bridging CO groups in $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ fall in the fairly typical range from 1831 to 1891 cm^{-1} (Table 2), which is ~120 cm^{-1} below the $\nu(\text{CO})$ frequencies (1969 to 2005 cm^{-1}) for the terminal CO groups in accord with expectation.

Table 2. The $\nu(\text{CO})$ frequencies by the BP86 method for $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ derivatives. Bridging $\nu(\text{CO})$ frequencies are in **bold**.

4T-1	4S-1	4T-2	4S-2	4S-3
1846(788)	1884(0)	1834(771)	1831(504)	1831(595)
1848(0)	1891(657)	1835(23)	1842(119)	1839(34)
1972(1230)	1973(1278)	1969(183)	1974(1075)	1975(224)
1985(0)	1986(0)	2005(1065)	1987(160)	2005(1137)

3.1.3 $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$. Four low-energy $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ structures have been found, including structures with one, two, or three bridging CO groups (Figure 6). All of these structures are genuine minima. Since the B3LYP* method found significant spin contamination for the triplet structures ($\langle S^2 \rangle = 2.55$ or 2.44 versus the ideal 2.00), a quintet spin state $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ structure was also explored. However, the energy of this quintet structure was so high (~ 30 kcal/mol) that it is not discussed in this paper.

Figure 6. Optimized geometries for the $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ structures. Bond distances are in Å.

The lowest energy $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ structure is **3S-1** (B3LYP*) with three bridging CO groups (Figure 6). The short $\text{Fe}=\text{Fe}$ distance in **3S-1** of 2.166 Å (B3LYP*) is consistent with a formal triple bond, thereby giving each iron atom the favored 18-electron configuration. Structure **3T-1**, lying only 0.5 kcal/mol in energy above **3S-1**, has one bridging CO group. The $\text{Fe}=\text{Fe}$ distance in **3T-1** of 2.389 Å (B3LYP*) is ~ 0.2 Å longer than the $\text{Fe}=\text{Fe}$ distance in **3S-1** and thus suggests a $\text{Fe}=\text{Fe}$ double bond. This gives each iron atom in **3T-1** a 17-electron configuration, consistent with a binuclear triplet.

Two doubly bridged $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})(\mu\text{-CO})_2$ structures were found, namely the triplet *trans* structure **3T-2** (C_s) and the singlet *cis* structure **3S-2** (C_1), lying 4.1 and

4.5 kcal/mol, respectively, in energy above **3S-1** (Figure 6). The Fe=Fe distance in **3T-2** of 2.341 Å (B3LYP*) can correspond to a formal double bond, thereby giving each iron atom a 17-electron configuration, corresponding to a binuclear triplet. The Fe=Fe distance in the singlet **3S-2** of 2.251 Å (B3LYP*) is ~0.1 Å shorter than that in triplet **3T-2**. This suggests a formal Fe≡Fe triple bond in **3S-2** thereby giving each iron atom the favored 18-electron configuration. Because of the asymmetry of the CO distribution in **3S-2** this Fe≡Fe triple bond is polarized with four of the six electrons from the iron atom bearing the terminal CO group (the “bottom” iron in Figure 6) and the other two electrons from the iron atom bonded only to the two bridging CO groups (the “top” iron in Figure 6).

Similar to $(C_4H_4BH)_2Fe_2(CO)_5$ and $(C_4H_4BH)_2Fe_2(CO)_4$, the $\nu(CO)$ frequencies of the bridging CO groups range from 1839 to 1912 cm^{-1} (Table 3), while the terminal $\nu(CO)$ frequencies range from 1962 to 2005 cm^{-1} .

Table 3. The $\nu(CO)$ frequencies by the BP86 method for $(C_4H_4BH)_2Fe_2(CO)_3$ derivatives. Bridging $\nu(CO)$ frequencies are in **bold**.

3S-1	3T-1	3T-2	3S-2
1879(729)	1875(366)	1839(840)	1900(710)
1884(735)	1962(482)	1852(111)	1910(110)
1912(11)	2005(919)	1976(540)	1989(1010)

3.1.4. $(C_4H_4BH)_2Fe_2(CO)_2$. Three low-energy $(C_4H_4BH)_2Fe_2(CO)_2$ structures were found (Figure 7). All three structures are predicted to be genuine minima with no imaginary vibrational frequencies. Singlet structures are not discussed here, since they lie at least 40 kcal/mol higher in energy than the global minimum.

Figure 7. Optimized geometries for the $(C_4H_4BH)_2Fe_2(CO)_2$ structures. Bond distances are in Å.

The lowest-energy $(C_4H_4BH)_2Fe_2(CO)_2$ structure is the quintet singly-bridged structure **2Q-1**, in which a boron atom bridges both iron atoms (Figure 7). In **2Q-1** the long B-H distance 1.231 Å (B3LYP*) leads to an unusually low $\nu(BH)$ frequency of 2237 cm^{-1} (BP86). This hydrogen atom is also within bonding distance of the iron atom with a short Fe-H distance of 1.980 Å (B3LYP*). Thus this hydrogen atom bridges an Fe–B bond to form a three-center two-electron (3c-2e) B-H-Fe bond. The Fe=Fe distance in **2Q-1** of 2.485 Å (B3LYP*) suggests a formal Fe=Fe double bond to give one iron atom a 17-electron configuration and the other iron atom a 15-electron configuration, consistent with a binuclear quintet with four unpaired electrons.

The two triplet $(C_4H_4BH)_2Fe_2(CO)_2$ structures, i.e., doubly-bridged **2T-1** (C_2), and singly-bridged **2T-2** (C_1), have similar energies, lying ~15 kcal/mol above **2Q-1**. The Fe≡Fe distances of 2.219 Å (B3LYP*) in **2T-1** and 2.267 Å (B3LYP*) in **2T-2** suggest formal triple bonds to give the metal atoms 17-electron configurations for the binuclear triplet state. The $\nu(CO)$ frequencies for the bridging CO groups in $(C_4H_4BH)_2Fe_2(CO)_2$ fall in the fairly typical range of 1851 to 1869 cm^{-1} , while the terminal $\nu(CO)$ frequencies are significantly higher in the narrow range from 1973 to 1977 cm^{-1} (Table 4).

Table 4. The $\nu(CO)$ frequencies by the BP86 method for $(C_4H_4BH)_2Fe_2(CO)_2$ derivatives. Bridging $\nu(CO)$ frequencies are in **bold**.

2Q-1	2T-1	2T-2
1851(570)	1859(846)	1862(477)
1977(912)	1869(63)	1973(958)

3.1.5. $(C_4H_4BH)_2Fe_2(CO)$. Singlet, triplet, and quintet $(C_4H_4BH)_2Fe_2(CO)$ structures were found. However, the singlet structures were found to lie at least 40 kcal/mol above the global minimum so they are not discussed in this paper. In the two lowest energy structures **1Q-1** and **1T-1**, the single CO group bridges the central Fe_2 unit, i.e., $(C_4H_4BH)_2Fe_2(\mu-CO)$ (Figure 8). The iron-iron distances in these two $(C_4H_4BH)_2Fe_2(\mu-CO)$ structures fall in a fairly narrow range from 2.382 Å to 2.422 Å despite the different spin states.

The $(C_4H_4BH)_2Fe_2(CO)$ structure **1Q-1** is the global minimum, while **1T-1** lies 7.3 kcal/mol (B3LYP*) above **1Q-1** (Figure 8). Both **1Q-1** and **1T-1** exhibit some interesting features. Thus, in both structures the planes of the two $\eta^4-C_4H_4B$ rings planes are nearly perpendicular to each other. As a result, the boron atom in one of the C_4H_4BH rings bridges the two iron atoms as indicated by the short Fe–B distances of 2.263 and 2.313 Å (B3LYP*) in **1Q-1** and **1T-1**, respectively, involving this boron atom. In

addition, there are short Fe-H distances of 1.884 and 1.790 Å (B3LYP*) in **1Q-1** and **1T-1**, respectively. These short Fe-H distances are accompanied by relatively long B-H distances of 1.243 and 1.242 Å (B3LYP*) for **1Q-1** and **1T-1**, respectively, which are ~0.05 Å longer than normal B-H single bond distances. This leads to unusually low $\nu(\text{BH})$ vibrational frequencies (2135 cm^{-1} and 2188 cm^{-1} by BP86) by ~400 cm^{-1} relative to typical values. This agostic hydrogen atom thus bridges the boron atom and the iron atom leading to a 3c-2e B-H-Fe bond.

Figure 8. Optimized geometries for the two $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})$ structures. Bond distances are in Å.

Table 5. Bond distances in Å (B3LYP*) and the $\nu(\text{BH})$ frequencies in cm^{-1} (BP86) for the agostic hydrogen atoms in the $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})$ structures.

	r(Fe-H)	r(B-H)	$\nu(\text{BH})$
1Q-1	1.884	1.243	2135
1T-1	1.790	1.242	2188

3.2 Thermochemistry

Table 6 reports the dissociation energies for loss of a single carbonyl in the lowest energy $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_n$ structures, namely the following process:

In determining these dissociation energies, the fragments were allowed to relax.

The sequence of the predicted energies for the four stages of successive dissociation of CO groups from $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ leading ultimately to $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})$ is 32.8, 28.7, 29.4, and 46.4 kcal/mol. These values are similar to

the experimental bond dissociation energies for the simple metal carbonyls $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively [52].

The CO dissociation energies for the previously studied related binuclear borole iron carbonyl systems $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_n$ [25] and $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_n$ [26] were reported using the B3LYP and BP86 methods. However, as discussed above, the B3LYP* method is expected to predict more reliable relative energies for the different electronic spin states [38, 39, 40]. For a valid comparison between the three $(\text{C}_4\text{H}_4\text{BR})_2\text{Fe}_2(\text{CO})_n$ systems [$\text{R} = \text{CH}_3$, $(\text{CH}_3)_2\text{N}$, and H], we re-optimized the lowest energy structures for the $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_n$ and $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_n$ systems. The CO dissociation energies based on these B3LYP* structures are also listed in Table 6. The CO dissociation energies all of the structures are seen to be substantial and similar to the experimental results for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ [52].

Table 6. Dissociation energies (kcal/mol) for the successive removal of carbonyl groups for $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_n$ predicted by the B3LYP* method. Those for $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_n$ and $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_n$ are also listed for comparison.

	B3LYP*
$(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_5$ (5S-1) $\rightarrow$ $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ + CO	32.8
$(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_4$ (4T-1) $\rightarrow$ $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ + CO	28.7
$(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_3$ (3S-1) $\rightarrow$ $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_2$ + CO	29.4
$(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})_2$ (2Q-1) $\rightarrow$ $(\text{C}_4\text{H}_4\text{BH})_2\text{Fe}_2(\text{CO})$ (1Q-1) + CO	46.4
$(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_5$ $\rightarrow$ $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_4$ + CO	28.8
$(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_4$ $\rightarrow$ $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_3$ + CO	27.0
$(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_3$ $\rightarrow$ $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_2$ + CO	43.4
$(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})_2$ $\rightarrow$ $(\text{C}_4\text{H}_4\text{BCH}_3)_2\text{Fe}_2(\text{CO})$ + CO	31.8
$[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_5$ $\rightarrow$ $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_4$ + CO	30.7
$[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_4$ $\rightarrow$ $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_3$ + CO	26.4
$[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_3$ $\rightarrow$ $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_2$ + CO	36.4
$[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})_2$ $\rightarrow$ $[\text{C}_4\text{H}_4\text{BN}(\text{CH}_3)_2]_2\text{Fe}_2(\text{CO})$ + CO	30.9

In order to compare the relative stabilities for the $(\text{C}_4\text{H}_4\text{BR})_2\text{Fe}_2(\text{CO})_n$ structures [$\text{R} = \text{CH}_3$, $(\text{CH}_3)_2\text{N}$, and H] having different numbers of CO groups, we determined the energies for the following disproportionation reactions using the lowest energy structures (Table 7):

The $(C_4H_4BH)_2Fe_2(CO)_3$ structure is seen to be only marginally stable towards disproportionation whereas $(C_4H_4BH)_2Fe_2(CO)_2$ appears to be stable towards disproportionation. This contrasts with the $(C_4H_4BCH_3)_2Fe_2(CO)_n$ and $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ systems for which the tricarbonyls are viable with respect to disproportionation, whereas the dicarbonyls and tetracarbonyls are disfavored relative to disproportionation. This difference may relate to the stabilization of the lowest energy dicarbonyl $(C_4H_4BH)_2Fe_2(CO)_2$ structure **2Q-1** by formation of the 3c-2e B-H-Fe bond.

Table 7. Energies (kcal/mol) for the disproportionation reaction $2(C_4H_4BH)_2Fe_2(CO)_n \rightarrow (C_4H_4BH)_2Fe_2(CO)_{n+1} + (C_4H_4BH)_2Fe_2(CO)_{n-1}$ predicted by the B3LYP* method. Those for $(C_4H_4BCH_3)_2Fe_2(CO)_n$ and $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ are also listed for comparison.

	B3LYP*
$2(C_4H_4BH)_2Fe_2(CO)_4 \rightarrow (C_4H_4BH)_2Fe_2(CO)_5 + (C_4H_4BH)_2Fe_2(CO)_3$	-4.1
$2(C_4H_4BH)_2Fe_2(CO)_3 \rightarrow (C_4H_4BH)_2Fe_2(CO)_4 + (C_4H_4BH)_2Fe_2(CO)_2$	0.6
$2(C_4H_4BH)_2Fe_2(CO)_2 \rightarrow (C_4H_4BH)_2Fe_2(CO)_3 + (C_4H_4BH)_2Fe_2(CO)$	17.1
$2(C_4H_4BCH_3)_2Fe_2(CO)_4 \rightarrow (C_4H_4BCH_3)_2Fe_2(CO)_5 + (C_4H_4BCH_3)_2Fe_2(CO)_3$	-1.8
$2(C_4H_4BCH_3)_2Fe_2(CO)_3 \rightarrow (C_4H_4BCH_3)_2Fe_2(CO)_4 + (C_4H_4BCH_3)_2Fe_2(CO)_2$	16.4
$2(C_4H_4BCH_3)_2Fe_2(CO)_2 \rightarrow (C_4H_4BCH_3)_2Fe_2(CO)_3 + (C_4H_4BCH_3)_2Fe_2(CO)$	-11.6
$2[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_4 \rightarrow [C_4H_4BN(CH_3)_2]_2Fe_2(CO)_5 + [C_4H_4BN(CH_3)_2]_2Fe_2(CO)_3$	-4.3
$2[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_3 \rightarrow [C_4H_4BN(CH_3)_2]_2Fe_2(CO)_4 + [C_4H_4BN(CH_3)_2]_2Fe_2(CO)_2$	9.9
$2[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_2 \rightarrow [C_4H_4BN(CH_3)_2]_2Fe_2(CO)_3 + [C_4H_4BN(CH_3)_2]_2Fe_2(CO)$	-5.4

4. Discussion

The results reported in this paper allow a comparison of the preferred structures of binuclear borole iron carbonyls $(C_4H_4BR)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) having three different type of boron substituents [$R = CH_3, H, (CH_3)_2N$] with those of the isoelectronic binuclear cyclopentadienylmanganese carbonyls [53, 54] $(C_5H_5)_2Mn_2(CO)_n$. For the latter cyclopentadienyl derivatives all of the low energy structures have terminal pentahapto $\eta^5-C_5H_5$ cyclopentadienyl rings. The lowest energy structures for the highly unsaturated derivatives $(C_5H_5)_2Mn_2(CO)_n$ ($n = 2, 1$) have metal-metal multiple bonds of various orders with low energy triplet and higher spin state structures. No examples of agostic bonding of cyclopentadienyl ring hydrogens are found, even in the highly unsaturated $(C_5H_5)_2Mn_2(CO)$. The triply bridged singlet tricarbonyl $(\eta^5-C_5H_5)_2Mn_2(CO)_3$, which has a short $Mn \equiv Mn$ distance suggesting a formal triple bond, appears to be the

energy sink and has been realized experimentally [10]. The tetracarbonyl and dicarbonyl $(C_5H_5)_2Mn_2(CO)_n$ ($n = 4, 2$) are predicted to be disfavored relative to disproportionation into $(C_5H_5)_2Mn_2(CO)_{n+1} + (C_5H_5)_2Mn_2(CO)_{n-1}$, where one of the products is the very stable tricarbonyl $(\eta^5-C_5H_5)_2Mn_2(CO)_3$.

The binuclear borole iron carbonyls $(C_4H_4BR)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) differ from the corresponding $(C_5H_5)_2Mn_2(CO)_n$ derivatives since the pendant boron substituents $R [= H, CH_3, N(CH_3)_2]$ play a role in the bonding of the borole ligand to the Fe_2 system in the highly unsaturated derivatives. This makes the normally four-electron donor neutral borole ligand a six-electron donor ligand bridging both metal atoms (Figure 3). For the methylborole derivatives $(C_4H_4BCH_3)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) one of the hydrogens of the pendant methyl group forms an agostic C-H-Fe 3c-2e bond with the iron atom not involved in the bonding to the π system of the same borole ring. Such agostic C-H-Fe bonding is found in a higher energy triplet state structure of $(C_4H_4BCH_3)_2Fe_2(CO)_2$ and in the lowest energy triplet and singlet $(C_4H_4BCH_3)_2Fe_2(CO)$ structures. It does not play a significant role in the thermochemistry of the $(C_4H_4BCH_3)_2Fe_2(CO)_n$ ($n = 5, 4, 3, 2, 1$) system since the tricarbonyl $(C_4H_4BCH_3)_2Fe_2(CO)_3$ is viable with respect to disproportionation whereas the tetracarbonyl and dicarbonyl $(C_4H_4BCH_3)_2Fe_2(CO)_n$ ($n = 4, 2$) are disfavored with respect to such disproportionation.

The dimethylaminoborole ligand in unsaturated $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ derivatives can function as a net six-electron donor to the Fe_2 system by supplementing the four net electrons from the borole ring with two electrons from the dimethylamino group. These two additional electrons from the dimethylamino group can come either from the nitrogen lone pair or from an agostic C-H-Fe interaction with one of the methyl hydrogen atoms. Both dimethylaminoborole ligands in the lowest energy $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 4, 3$) structures function only as net four-electron donors involving only the five atoms of the C_4B borole ring. However, slightly higher energy $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 4, 3$) structures are found in which dimethylaminoborole is a six-electron donor bridging ligand using electron pairs from the nitrogen atom as well as from the two C=C double bonds. For the more highly unsaturated $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 2, 1$), low energy singlet ($n = 2$) and triplet ($n = 1$) perpendicular structures are also found with similar bridging six-electron donor dimethylaminoborole ligands. In addition, highly unsaturated $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ ($n = 3, 2, 1$) structures are found having agostic hydrogen atoms bridging an iron-carbon bond. However, these bonding possibilities for the pendant dimethylamino group in the $[C_4H_4BN(CH_3)_2]_2Fe_2(CO)_n$ systems do not lead to significant qualitative differences of

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their CO dissociation behavior and that of the methylborole systems $(C_4H_4BCH_3)_2Fe_2(CO)_n$. Thus in both systems the tricarbonyls $(C_4H_4BR)_2Fe_2(CO)_3$ [$R = CH_3$ and $(CH_3)_2N$] are viable with respect to disproportionation into $(C_4H_4BR)_2Fe_2(CO)_4$ and $(C_4H_4BR)_2Fe_2(CO)_2$ whereas the tetracarbonyls and dicarbonyls $(C_4H_4BR)_2Fe_2(CO)_n$ ($n = 4, 2$) are disfavored relative to disproportionation into $(C_4H_4BR)_2Fe_2(CO)_{n+1} + (C_4H_4BR)_2Fe_2(CO)_{n-1}$ (Table 7). Furthermore, the lowest-energy structures of the tricarbonyls $(C_4H_4BR)_2Fe_2(CO)_3$ are triply bridged structures with $Fe\equiv Fe$ distances of ~ 2.2 Å corresponding to formal triple bonds similar to the experimental structure $(\eta^5-Me_5C_5)_2Mn_2(\mu-CO)_3$ with an $Mn\equiv Mn$ distance of 2.17 Å as determined by X-ray crystallography [55].

The relative stabilities of the $(C_4H_4BH)_2Fe_2(CO)_n$ systems appear to be different from those of the previously reported $(C_4H_4BR)_2Fe_2(CO)_n$ systems [$R = CH_3, (CH_3)_2N$]. In particular, disproportionation of the tricarbonyl $(C_4H_4BH)_2Fe_2(CO)_3$ into $(C_4H_4BH)_2Fe_2(CO)_4 + (C_4H_4BH)_2Fe_2(CO)_2$ is essentially thermoneutral. However, the dicarbonyl $(C_4H_4BH)_2Fe_2(CO)_2$ appears to be viable towards an analogous disproportionation. We believe that this might relate to the stabilization of the lowest energy $(C_4H_4BH)_2Fe_2(CO)_2$ structure **2Q-2** by the B-H-Fe 3c-2e bond.

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