Prospects for Three-Electron Donor Boronyl (BO) Ligands and Dioxodiborene (B₂O₂) Ligands as Bridging Groups in Binuclear Iron Carbonyl Derivatives

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S *Supporting Information*

ABSTRACT: Recent experimental work (2010) on $(Cy_3P)_2Pt(BO)Br$ indicates that the oxygen atom of the boronyl (BO) ligand is more basic than that in the ubiquitous CO ligand. This suggests that bridging BO ligands in unsaturated binuclear metal carbonyl derivatives should readily function as three-electron donor bridging ligands involving both the oxygen and the boron atoms. In this connection, density functional theory shows that three of the four lowest energy singlet $Fe_2(BO)_2(CO)_7$ structures have such a bridging η^2-μ-BO group as well as a formal Fe−Fe single bond. In addition, all four of the lowest energy singlet $Fe_2(BO)_2(CO)_6$ structures have two bridging η^2-μ-BO groups and formal Fe−Fe single bonds. Other $Fe_2(BO)_2(CO)_n$ (n = 7, 6) structures are found in which the two BO groups have coupled to form a bridging dioxodiborene (B_2O_2) ligand with B−B bonding distances of ~1.84 Å. All of these $Fe_2(\mu\text{-}B_2O_2)(CO)_n$ structures have long Fe···Fe distances indicating a lack of direct iron−iron bonding. One of the singlet $Fe_2(BO)_2(CO)_7$ structures has such a bridging dioxodiborene ligand with cis stereochemistry functioning as a six-electron donor to the pair of iron atoms. In addition, the lowest energy triplet structures for both $Fe_2(BO)_2(CO)_7$ and $Fe_2(BO)_2(CO)_6$ have bridging dioxodiborene ligands with trans stereochemistry functioning as a four-electron donor to the pair of iron atoms.

$Fe_2(BO)_2(CO)_7$
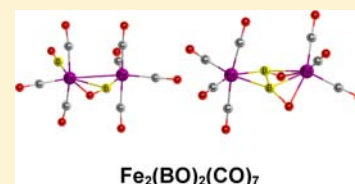
1. INTRODUCTION

The chemistry of metal carbonyls[1] dates back to the discovery of $Ni(CO)_4$ in 1890. However, until 1975 the carbonyl ligands in metal carbonyl derivatives, whether terminal or bridging, functioned as two-electron donors bonding to one, two, or three metal atoms through only the carbon atoms. The first example of a metal carbonyl derivative with a four-electron donor carbonyl ligand involving the oxygen atom as well as the carbon atom was the compound $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4$-$(\eta^2$-$\mu$-CO) (Figure 1), shown by Colton and collaborators[2,3] to have an unusual bridging CO group. Thus the short Mn−O distance of 2.29 Å in this complex suggests direct manganese−

oxygen bonding as well as the usual manganese−carbon bonding to both manganese atoms expected for a bridging carbonyl group. A bridging carbonyl group of this type can donate two electrons to a transition metal through a σ-bond and another two electrons coming from a CO π-bond. The π-bonding lowers the effective carbon−oxygen bond order consistent with the very low bridging infrared $\nu(CO)$ frequency of 1645 cm^{-1} found experimentally for this metal complex.

Replacement of the two bidentate phosphine ligands in $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) with four carbonyl groups gives the homoleptic carbonyl $Mn_2(CO)_8(\eta^2$-μ-CO), that is, $Mn_2(CO)_9$. However, the stable homoleptic carbonyl of manganese is $Mn_2(CO)_{10}$. Photolysis of $Mn_2(CO)_{10}$ in a frozen alkane matrix below 100 K[4,5] or in an argon matrix at 12 K[6] results in the loss of a single CO group. The observation of a very low $\nu(CO)$ frequency of 1764 cm^{-1} suggests that the isomer of $Mn_2(CO)_9$ produced in the matrix has the $Mn_2(CO)_8(\eta^2$-μ-CO) structure with a four-electron donor bridging carbonyl group (Figure 1). This $Mn_2(CO)_9$ isomer is also generated as a transient species by the flash photolysis of $Mn_2(CO)_{10}$ in hydrocarbon solution at room temperature.[7] More prolonged low-temperature photolysis of $Mn_2(CO)_{10}$
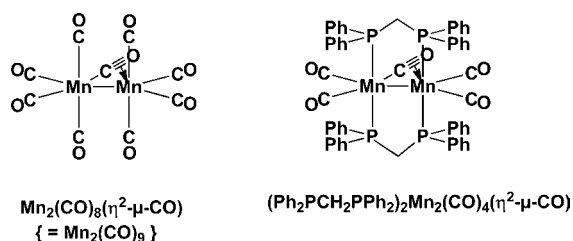

Figure 1. Analogy between the presumed structure of $Mn_2(CO)_9$ [= $Mn_2(CO)_8(\eta^2$-μ-CO)] observed in low temperature matrixes and stable $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) structurally characterized by X-ray crystallography.

gives a more highly unsaturated product $Mn_2(CO)_8$, shown by infrared spectroscopy to have only terminal carbonyls.[5]

Simple diatomic ligands related to the carbonyl ligand in these manganese derivatives mentioned above have been of interest for more than a century. Thus, metal complexes of the cyanide (CN),[8−10] nitrosyl (NO),[11,12] and carbonyl (CO)[13] ligands were already known by the end of the 19th century, and an extensive coordination chemistry of each of these ligands has developed during the 20th century. In addition, the first metal complex of the dinitrogen ligand, namely, $[Ru(NH_3)_5N_2]^{+2}$, was discovered by Allen and Senoff in 1965,[14] and the coordination chemistry of dinitrogen has developed extensively since then.[15,16] However, metal complexes containing the related diatomic boron ligands BO and BF were synthesized for the first time only very recently owing to synthetic difficulties arising from the instability of the free ligands. Thus only in 2009 the first structurally characterized fluoroborylene (BF) complex, namely, $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4(\mu\text{-}BF)$, was synthesized by Vidović and Aldridge and structurally characterized by X-ray diffraction.[17] Even more recently (2010) Braunschweig and co-workers.[18,19] synthesized the first stable boronyl (BO) complex, namely, $(Cy_3P)_2Pt(BO)Br$ (Cy = cyclohexyl).

The neutral boronyl ligand (BO) found in this experimentally known platinum complex has one less electron than the carbonyl (CO) ligand and thus functions as a net one-electron donor ligand to a transition metal atom. Alternatively stated, the BO^- anion is isoelectronic with the neutral CO group. Thus $(Cy_3P)_2Pt(BO)Br$ is an example of a planar four-coordinate d^8 metal complex, which is a common feature of platinum(II) chemistry.

Direct boronyl analogues of the homoleptic metal carbonyls remain unknown experimentally but have been investigated theoretically. Thus a theoretical study on cobalt carbonyl boronyls[20] focused on $Co(BO)(CO)_4$ and $Co_2(BO)_2(CO)_7$ as isoelectronic analogues of the well-known $Fe(CO)_5$ and $Fe_2(CO)_9$, respectively. Similarly $Fe_2(BO)_2(CO)_8$ is an isoelectronic analogue of $Mn_2(CO)_{10}$. A recent theoretical study[21] on $Fe_2(BO)_2(CO)_8$ predicts an unbridged structure consisting of two $Fe(BO)(CO)_4$ units linked by an unbridged Fe−Fe bond. An earlier theoretical study by Baerends and co-workers[22] of transition metal complexes comparing the isolobal ligands BF, BNH_2, $BN(CH_3)_2$, and BO predating the discovery of $(Cy_3P)_2Pt(BO)Br$ led to the general conclusion that the BO ligand, considered as a monoanion isoelectronic with CO, is an unusually strong σ donor but a very poor π-acceptor because of the very high energy of its π^* lowest unoccupied molecular orbital (LUMO).

An interesting property of the coordinated BO ligand in $(Cy_3P)_2Pt(BO)Br$ is the basicity of its oxygen atom. Thus reactions of $(Cy_3P)_2Pt(BO)Br$ with boron Lewis acids lead to adducts of the type $(Cy_3P)_2Pt(Br)(BO{\rightarrow}BR^f_3)$ (e.g., $R^f = C_6H_3\text{-}3,5\text{-}(CF_3)_2$).[23] This basicity of the oxygen atom in a coordinated BO ligand suggests the possibility of a three-electron donor bridging $\eta^2\text{-}\mu\text{-}BO$ ligand in binuclear metal complexes analogous to the four-electron donor bridging $\eta^2\text{-}\mu\text{-}CO$ ligand such as that in the $L_4Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$ structures $(2\ L = Ph_2PCH_2PPh_2$ or $L = CO)$ depicted in Figure 1. Two such three-electron donor bridging $\eta^2\text{-}\mu\text{-}BO$ ligands are found in the lowest energy $Co_2(BO)_2(CO)_6$ structure predicted in the previous theoretical study.[20] However, related structures are not predicted to be low energy structures of the isoelectronic $Fe_2(CO)_8$ in a similar density functional theory (DFT) study.[24] This is consistent with higher

basicity of the oxygen atom in coordinated BO relative to coordinated CO in metal complexes.

The binuclear manganese carbonyl $Mn_2(CO)_9$, although not stable under ambient conditions, is an apparently unique example of an experimentally observable homoleptic metal carbonyl having a four-electron donor $\eta^2\text{-}\mu\text{-}CO$ group, albeit in a low-temperature matrix.[4−6] The isoelectronic $Fe_2(BO)_2(CO)_7$ provides an example of a molecule where the abilities of BO and CO groups to function as $\eta^2\text{-}\mu\text{-}EO$ (E = B, C) ligands can be compared. We therefore undertook a DFT study of both $Fe_2(BO)_2(CO)_7$ and $Fe_2(BO)_2(CO)_6$ to see what examples of bridging $\eta^2\text{-}\mu\text{-}BO$ and $\eta^2\text{-}\mu\text{-}CO$ groups involving both oxygen and carbon coordination could be found in low-energy structures.

This theoretical study, discussed in this paper, shows that most of the lowest energy $Fe_2(BO)_2(CO)_n$ $(n = 7, 6)$ structures have three-electron donor $\eta^2\text{-}\mu\text{-}BO$ groups. Furthermore, such three-electron donor $\eta^2\text{-}\mu\text{-}BO$ groups are shown to be favored over four-electron donor $\eta^2\text{-}\mu\text{-}CO$ groups consistent with the relatively high basicity of the BO oxygen. In other low-energy $Fe_2(BO)_2(CO)_n$ $(n = 7, 6)$ structures the two BO groups were found to couple to form a novel and unprecedented dioxodiborene (B_2O_2) ligand., which was observed in both cis and trans stereochemistry. Free B_2O_2 can be generated by the vaporization of B_2O_3 in a reducing environment[25] or by heating MgO with elemental boron to 1275 °C.[26] However, it is only available in the gas phase and not in concentrations where it can be used as an effective reagent for the synthesis of metal complexes. The coupling of two BO ligands on a metal site to form a coordinated B_2O_2 ligand is at least superficially similar to the coupling on metal sites of two CF ligands to form a coordinated $FC{\equiv}CF$ (difluoroacetylene) ligand[27,28] or two BF ligands to form a coordinated $FB{=}BF$ (difluorodiborene) ligand,[29] predicted in previous theoretical studies but not yet realized experimentally.

2. THEORETICAL METHODS

Electron correlation effects were considered by employing density functional theory (DFT), which has evolved as a practical and effective computational tool, especially for organometallic compounds.[30−36] Two DFT methods were used in this study. The first functional is the popular B3LYP method, which is the hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3)[37] with the Lee−Yang−Parr (LYP)[38] generalized gradient correlation functional. The other DFT method used in this paper is BP86, which combines Becke's 1988 exchange functional (B)[39] with Perdew's 1986 gradient corrected correlation functional (P86).[40]

For comparison with our previous research, the same double-ζ plus polarization (DZP) basis sets were adopted in the present study. Thus one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(B) = 0.7$, $\alpha_d(C) = 0.75$, and $\alpha_d(O) = 0.85$ for boron, carbon, and oxygen, respectively, was added to the standard Huzinaga−Dunning contracted DZ sets,[41,42] designated as (9s5p1d/4s2p1d). The loosely contracted DZP basis set for iron is the Wachters primitive set,[43] augmented by two sets of p functions and one set of d functions, and then contracted following Hood, Pitzer, and Schaefer,[44] designated as (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the two DFT methods. Harmonic vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program package,[45] using the fine grid option, that is, the pruned (75, 302) grid, as the default to evaluate integrals numerically, while the tight designation is the default for the self-consistent field (SCF) convergence.
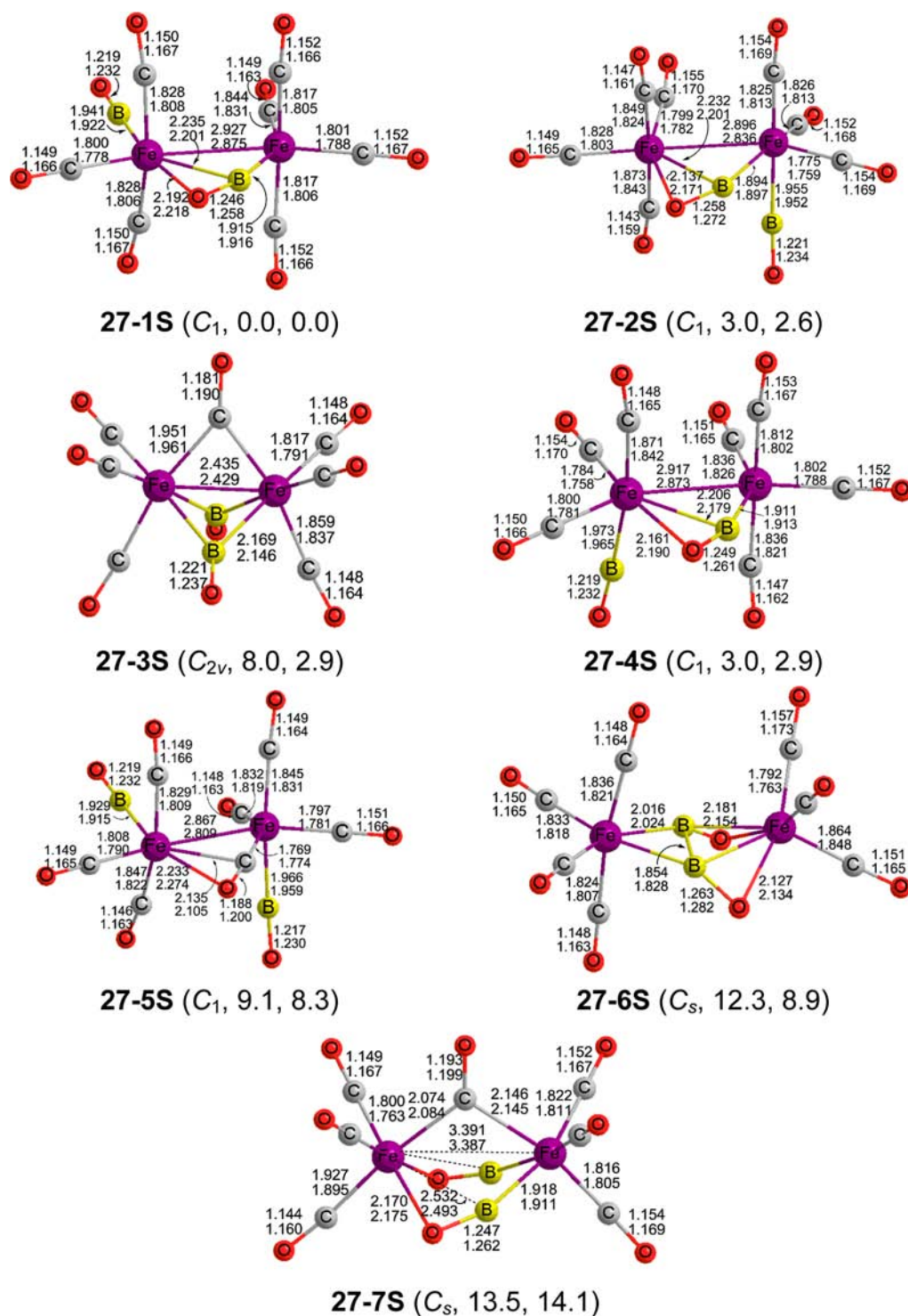
Figure 2. Seven optimized singlet $Fe_2(BO)_2(CO)_7$ structures. In Figures 2 to 8 the top numbers refer to distances obtained by the B3LYP and the bottom numbers refer to distances obtained by the BP86 method. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

A given $Fe_a(BO)_a(CO)_b$ structure is designated as **ab-cA** where **a** is the number of iron atoms (the same as the number of BO groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies. **A** indicates whether the structure is a singlet (**S**), doublet (**D**), triplet (**T**), or quartet (**Q**). Thus the lowest energy structure of singlet $Fe_2(BO)_2(CO)_6$ is designated **26−1S**. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin expectation values ($\langle S^2 \rangle$) for all of the optimized structures within 20 kcal/mol are listed in Supporting Information, Tables S67−S71.

3. RESULTS

3.1. Binuclear Derivatives. *3.1.1. $Fe_2(BO)_2(CO)_7$.* Both singlet and triplet $Fe_2(BO)_2(CO)_7$ structures were optimized. Twelve structures (seven singlets and five triplets) were found within 20 kcal/mol of the global minimum, indicating a very complicated potential energy surface (Figure 2). The seven singlet $Fe_2(BO)_2(CO)_7$ structures lying within 20 kcal/mol of the global minimum **27−1S** include the four singly bridged
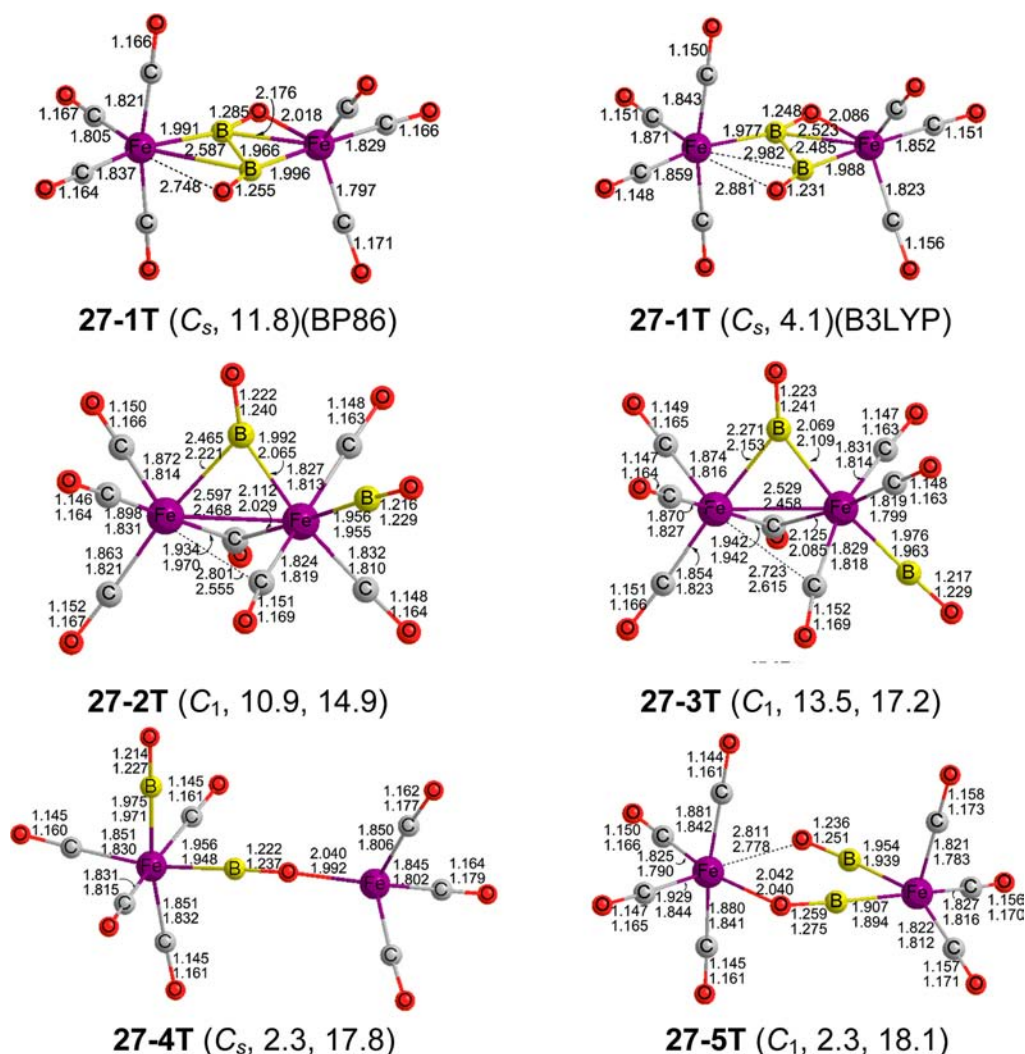
Figure 3. Five optimized structures of triplet Fe(BO)$_2$(CO)$_7$. The energies relative to **27−1S** (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

Fe$_2$(BO)$_2$(CO)$_7$ structures **27−1S**, **27−2S**, **27−4S**, and **27−5S**, one doubly bridged Fe$_2$(BO)$_2$(CO)$_7$ structure **27−6S**, and two triply bridged Fe$_2$(BO)$_2$(CO)$_7$ structures **27−3S** and **27−7S** (Figure 2 and Supporting Information, Table S67). Thus all of the singlet Fe$_2$(BO)$_2$(CO)$_7$ structures have one or more CO and/or BO groups bridging the Fe$_2$ unit. Unbridged Fe$_2$(BO)$_2$(CO)$_7$ structures (singlet and triplet) are all found to lie at least 30 kcal/mol above the global minimum **27−1S** and thus are not discussed in the present paper.

The Fe$_2$(BO)$_2$(CO)$_7$ structures **27−1S**, **27−2S**, and **27−4S** each have one bridging BO group (Figure 2 and Supporting Information, Table S67). All seven CO groups in each of these three structures are terminal CO groups. These three structures differ only in the positions of their terminal BO groups relative to the singly BO-bridged Fe$_2$ unit. The short Fe−O distances of 2.1 to 2.2 Å to the bridging BO group in each of these three structures indicate three-electron donor bridging BO groups. These bridging BO groups donate one electron as a σ-donor to the "right" iron atom and an additional two electrons as a π-donor to the "left" iron atom through the BO bond. The π-bonding of these bridging BO groups in **27−1S**, **27−2S**, and **27−4S** reduce the effective B−O bond order leading to longer B−O distances in the bridging BO group of ∼1.25 Å relative to the typical terminal B−O distances.

and **27−4S** have similar energies within only ∼3.0 kcal/mol thereby suggesting a fluxional Fe$_2$(BO)$_2$(CO)$_7$ system. The Fe−Fe distances of 2.927 Å (B3LYP) or 2.875 Å (BP86) in **27−1S**, 2.896 Å (B3LYP) or 2.836 Å (BP86) in **27−2S**, and 2.917 Å (B3LYP) or 2.873 Å (BP86) in **27−4S** all correspond to formal single bonds thereby giving each iron atom the favored 18-electron configuration, assuming that the Fe−Fe bond in **27−2S** is polarized.

The Fe$_2$(BO)$_2$(CO)$_7$ structure **27−3S** is a fascinating C_{2v} singlet structure with two bridging BO groups and one bridging CO group. This geometry is related to the known Fe$_2$(CO)$_6$(μ-CO)$_3$ structure determined by X-ray crystallography,[46] also with three bridging groups. Structure **27−3S** lies 8.0 kcal/mol (B3LYP) or 2.9 kcal/mol (BP86) above **27−1S**. The BP86 method predicts all real vibrational frequencies, while the B3LYP method predicts a small imaginary frequency of 63i cm^{-1} (Supporting Information, Table S67), which cannot be removed using a finer integration grid. Following the corresponding normal mode leads to a slightly different structure with C_s symmetry. The predicted Fe=Fe distance in **27−3S** of 2.435 Å (B3LYP) or 2.429 Å (BP86) is ∼0.1 Å shorter than the experimental distance of 2.523 Å for a Fe−Fe single bond in the known Fe$_2$(CO)$_6$(μ-CO)$_3$ structure.[46] This
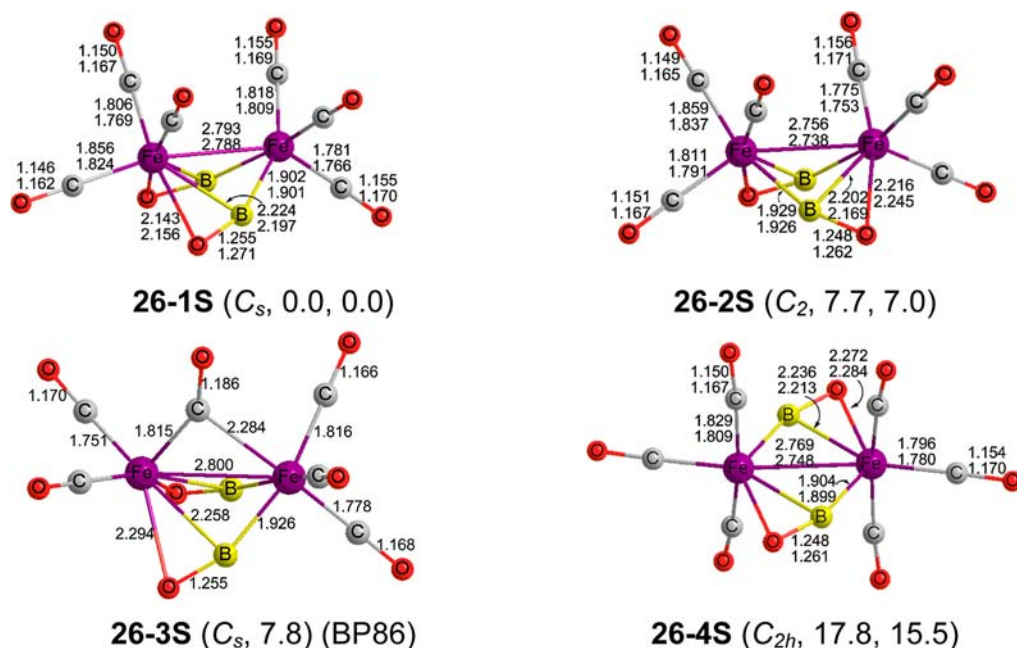
Figure 4. Four optimized singlet $Fe_2(BO)_2(CO)_6$ structures. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

suggests a formal Fe=Fe double bond in **27−3S** thereby giving each iron atom the favored 18-electron configuration.

The $Fe_2(BO)_2(CO)_7$ structure **27−7S** is another triply bridged structure, lying 13.5 kcal/mol (B3LYP) or 14.1 kcal/mol (BP86) above the global minimum **27−1S** (Figure 2 and Supporting Information, Table S67). In **27−1S** two $Fe(CO)_3$ units are linked by one bridging CO group and two bridging BO groups. The two bridging BO groups are three-electron donor η^2-μ-BO groups, which are bonded to one iron atom through the boron atom and to the other iron atom through the oxygen atom. These two η^2-μ-BO groups in **27−7S** exhibit unusually low ν(BO) frequencies at 1653 and 1680 cm^{-1}. The long Fe⋯Fe distances of 3.391 Å (B3LYP) or 3.387 Å (BP86) indicate the lack of a direct iron−iron bond. However, since **27−7S** has two three-electron donor BO groups, each iron atom has the favored 18-electron configuration.

The $Fe_2(BO)_2(CO)_7$ structure **27−6S**, at 12.3 kcal/mol (B3LYP) or 8.9 kcal/mol (BP86) in energy above **27−1S**, is an unusual structure since the two BO groups have coupled to form a novel *cis*-dioxodiborene (*cis*-B_2O_2) ligand with a B−B distance of 1.854 Å (B3LYP) or 1.828 Å (BP86) (Figure 2 and Supporting Information, Table S67). This *cis*-dioxodiborene ligand is bonded to the Fe_2 unit through not only the boron atoms but also the oxygen atoms as indicated by Fe−O distances of ∼2.13 Å. It therefore is a six-electron donor ligand to the Fe_2 unit in **27−6S**. The ν(BO) frequencies in the *cis*-dioxodiborene ligand are very low at 1550 and 1575 cm^{-1} (BP86). The Fe⋯Fe distance of 3.703 Å (B3LYP) or 3.695 Å (BP86) in **27−6S** is too long for a direct interaction between the two iron atoms. Thus both the iron atoms have the favored 18-electron configurations.

The lowest-lying triplet $Fe_2(BO)_2(CO)_7$ structure **27−1T** lies 4.1 kcal/mol (B3LYP) or 11.8 kcal/mol (BP86) above **27−1S** (Figure 3 and Supporting Information, Table S67). The B3LYP and BP86 methods predict somewhat different energies and geometries for **27−1T**. The singlet−triplet splitting discrepancy in $Fe_2(BO)_2(CO)_7$ predicted by these two DFT

methods is not surprising in view of the work by Reiher et al.[47] The B3LYP method predicts **27−1T** to have one three-electron donor bridging BO group and one terminal BO group, while the BP86 method predicts two bridging BO groups. The three-electron donor bridging BO group predicted by the B3LYP method exhibits a short Fe−O distance of 2.086 Å. The long B⋯B distance of 2.485 Å implies very weak interaction between the bridging and the terminal BO groups in the B3LYP **27−1T** structure. Thus in the B3LYP **27−1T** structure the two BO groups can be considered as separate ligands. However, the BP86 method predicts a **27−1T** structure with a much shorter B−B distance of 1.966 Å indicating coupling of the two BO ligands to form a *trans*-dioxodiborene ligand. The dioxodiborene ligand in **27−1T** is different from that in **27−6S** not only because of its trans rather than cis stereochemistry but also because only one of its oxygen atoms is within bonding distance (2.018 Å) of an iron atom. The other oxygen atom of the *trans*-dioxodiborene ligand in **27−1T** is 2.748 Å from the nearest iron atom. This suggests that the bridging *trans*-dioxodiborene ligand in **27−1T** is a four-electron donor rather than the six-electron donor ligand found in **27−6S**. Both ν(BO) frequencies in the *trans*-dioxodiborene ligand of **27−1T** are very low, namely, 1561 cm^{-1} and 1687 cm^{-1}. The lowest ν(BO) frequency can be assigned to the BO group of the *trans*-B_2O_2 ligand bonded to an iron atom through its oxygen atom whereas the other ν(BO) frequency can be assigned to the other BO group with a long Fe⋯O distance. The Fe⋯Fe distance in **27−1T** is clearly too long for a direct iron−iron bond. Each iron atom in **27−1T** has the 17-electron configuration for a binuclear triplet assuming that the bridging *trans*-dioxodiborene is a four-electron donor.

Both triply bridged triplet $Fe_2(BO)(CO)_5(\mu$-BO$)(\mu$-CO$)_2$ structures **27−2T** and **27−3T** have one bridging BO group, one bridging CO group, and one semibridging CO group, and they lie at 11 to 14 kcal/mol (B3LYP) or 14 to 17 kcal/mol (BP86) above **27−1S** (Figure 3 and Supporting Information, Table S67). The two structures **27−2T** and **27−3T** are related

26-1T (C_{2h}, −1.6, 5.4)　　　　　　**26-2T** (C_s, −3.2, 13.7)

26-3T (C_1, 0.4, 15.6)

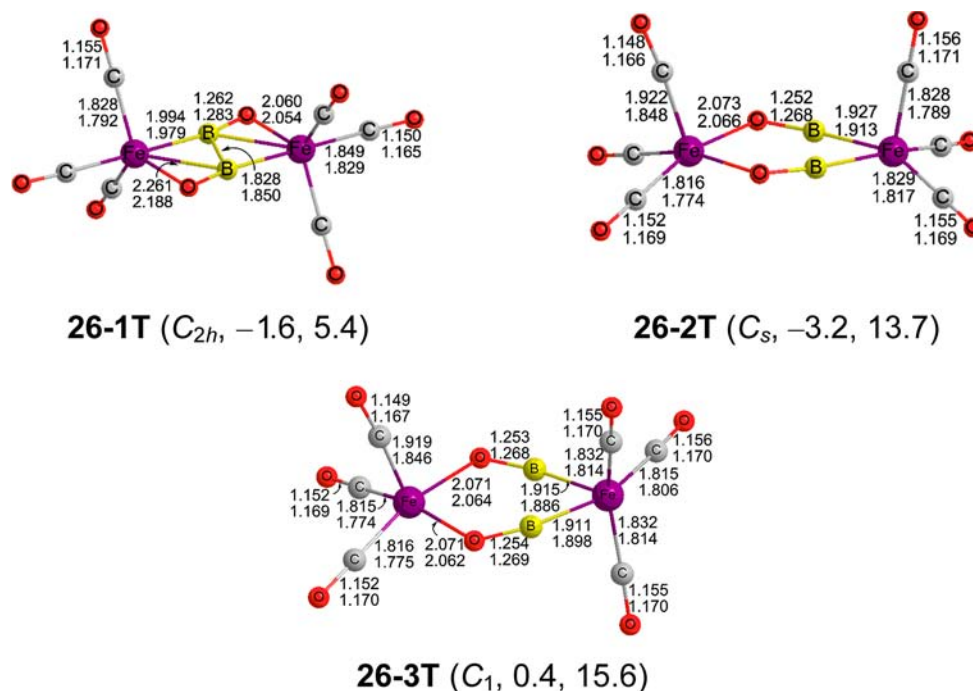**Figure 5.** Three optimized triplet $Fe_2(BO)_2(CO)_6$ structures. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

to the triply bridged $Fe_2(CO)_6(\mu\text{-}CO)_3$ structure determined by X-ray crystallography.[46] The structural difference between structures **27−2T** and **27−3T** mainly lies in the position of the terminal BO group relative to the central $Fe_2(\mu\text{-}BO)(\mu\text{-}CO)_2$ unit. The Fe−Fe distances of ~2.5 Å for structures **27−2T** and **27−3T** are similar to the experimental triply bridged Fe−Fe single bond distance[46] for $Fe_2(CO)_6(\mu\text{-}CO)_3$ and thus likewise can be interpreted as single bonds. This gives each iron atom in both **27−2T** and **27−3T** a 17-electron configuration, consistent with a binuclear triplet.

Two triplet bridged "end-to-end" **27−4T** and **27−5T** lie energetically 2.3 kcal/mol (B3LYP) or ~18.0 kcal/mol (BP86) above **27−1S** (Figure 3 and Supporting Information, Table S67). The discrepancy between the energies of these two triplet $Fe_2(BO)_2(CO)_7$ structures relative to the singlet global minimum obtained by the B3LYP and BP86 methods is another example of the observation by Reiher and co-workers of the tendency for the B3LYP method to favor triplet spin states.[47] In structure **27−4T** a three-electron donor end-on bridging BO group links the $Fe(BO)(CO)_4$ unit through its boron atom to the $Fe(CO)_3$ unit through its oxygen atom. Similarly in structure **27−5T** the two end-on bridging BO groups link the $Fe(CO)_4$ unit through the oxygen atoms to the $Fe(CO)_3$ unit through the boron atoms. The B3LYP method gives all real vibrational frequencies for both **27−4T** and **27−5T**, while the BP86 method obtains a negligible imaginary frequency 8i cm^{-1} (Supporting Information, Table S67) for **27−4T**. The very long Fe···Fe distances of 5.206 Å (B3LYP) or 5.171 Å (BP86) in **27−4T** and 4.484 Å (B3LYP) or 4.472 Å (BP86) in **27−5T** indicate the absence of a direct iron−iron bond.

3.1.2. $Fe_2(BO)_2(CO)_6$. Four singlet structures and three triplet structures were found for $Fe_2(BO)_2(CO)_6$ within 20 kcal/mol of the global minimum (Figures 4 and 5 and Supporting Information, Table S68). Six of these structures are doubly bridged structures with two bridging BO groups. The seventh

$Fe_2(BO)_2(CO)_6$ structure is a triply bridged structure with two bridging BO groups and one semibridging CO group. All of the bridging BO groups in all of the $Fe_2(BO)_2(CO)_6$ structures are three-electron donor μ-BO groups, as indicated by the relatively short Fe−O distances within 2.3 Å.

The B3LYP and the BP86 methods differ significantly in the relative energy ordering of these structures. The B3LYP method predicts the two triplet structures **26−1T** and **26−2T** to lie below the singlet structure **26−1S**. However, the BP86 method predicts the energies of three of the singlet $Fe_2(BO)_2(CO)_6$ structures, **26−1S**, **26−2S**, and **26−3S**, to lie below that of the triplet structure **26−2T**. As mentioned above, Reiher and collaborators[47] have found that B3LYP always overestimates the energies of the high-spin states, and the BP86 method overestimates the energies of the low-spin states. In such cases, the real singlet−triplet splittings should lie between the B3LYP and BP86 predictions.[47]

The $Fe_2(BO)_2(CO)_6$ global minimum by BP86 is the C_s doubly bridged structure **26−1S** (Figure 4 and Supporting Information, Table S68). The two bridging BO groups are three-electron donor $\eta^2\text{-}\mu\text{-}BO$ groups, as indicated by the relatively short Fe−O distances of 2.143 Å (B3LYP) or 2.156 Å (BP86). The Fe−Fe distance in **26−1S** of 2.793 Å (B3LYP) or 2.788 Å (BP86) corresponds to a formal single bond, thereby giving both iron atoms the favored 18-electron configuration.

The $Fe_2(BO)_2(CO)_6$ structure **26−2S** with C_2 symmetry lies 7.7 kcal/mol (B3LYP) or 7.0 kcal/mol (BP86) above **26−1S** (Figure 4 and Supporting Information, Table S68). Structure **26−2S**, like **26−1S**, has two three-electron donor bridging $\eta^2\text{-}\mu\text{-}BO$ groups. However, in **26−1S** both short Fe−O distances are to the same iron atom (the "left" iron atom in Figure 4), whereas in **26−2S** each short Fe−O distance goes to a different iron atom. The dihedral angle B−Fe−Fe−B of 98.1° in **26−2S** is ~5° larger than that of 92.7° in **26−1S**. The Fe−Fe distance of 2.756 Å (B3LYP) or 2.738 Å (BP86) in **26−2S** is ~0.04 Å shorter than that in **26−1S**. However, it is still within the range
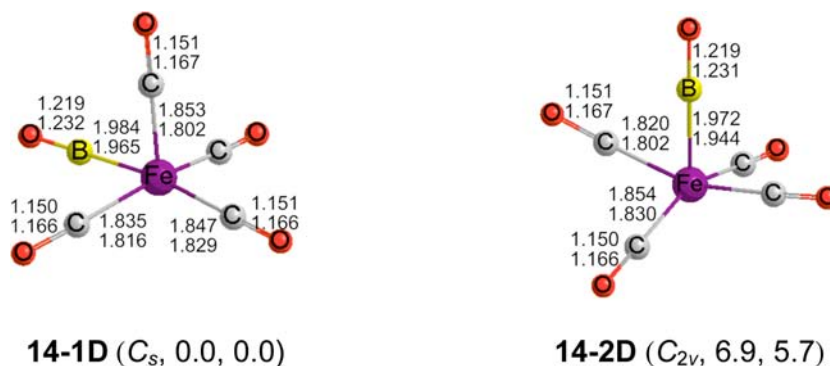
14-1D (C_s, 0.0, 0.0)   **14-2D** (C_{2v}, 6.9, 5.7)

Figure 6. Two optimized $Fe(BO)(CO)_4$ structures. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.
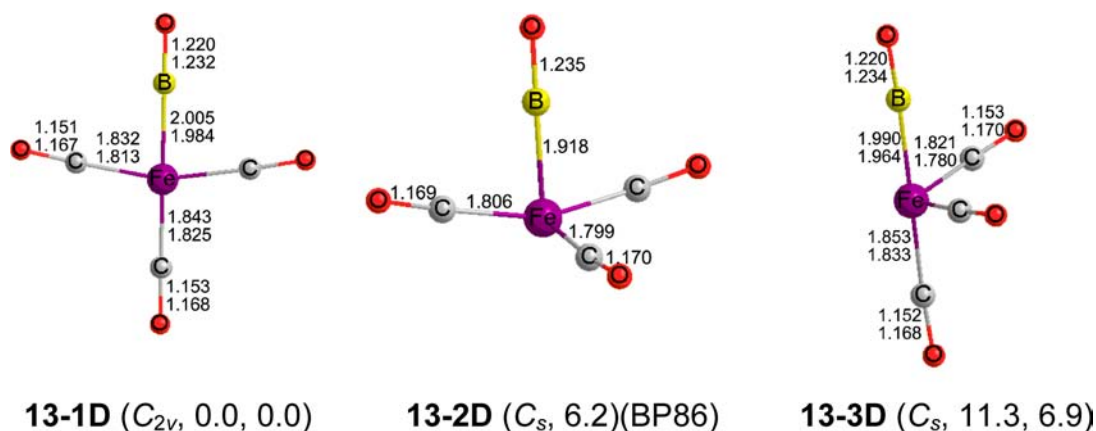

13-1D (C_{2v}, 0.0, 0.0)   **13-2D** (C_s, 6.2)(BP86)   **13-3D** (C_s, 11.3, 6.9)

Figure 7. Three optimized $Fe(BO)(CO)_3$ structures. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

of the formal single bond required to give both iron atoms the favored 18-electron configuration.

The triply bridged $Fe_2(BO)_2(CO)_6$ structure **26−3S** with one semibridging CO group and two bridging BO groups is a stationary point predicted by the BP86 method, lying 7.8 kcal/mol above **26−1S** (Figure 4 and Supporting Information, Table S68). The two bridging BO groups in **26−3S** are indicated to be three-electron donor η^2-μ-BO groups by the short Fe−O distances of 2.294 Å and the low $\nu(BO)$ vibrational frequencies of 1711 and 1691 cm^{-1}. The Fe−Fe distance in **26−3S** of 2.800 Å corresponds to a formal single bond thereby giving each iron atom the favored 18-electron configuration. The BP86 method predicts **26−3S** to be a transition state with one small imaginary frequency of 44i cm^{-1}. Following the corresponding normal mode leads to **26−1S**. An attempt to optimize **26−3S** with the B3LYP method starting from the BP86 structure leads directly to **26−1S.**

The C_{2h} $Fe_2(BO)_2(CO)_6$ structure **26−4S** has a relatively high energy of 17.8 kcal/mol (B3LYP) or 15.5 kcal/mol (BP86) above **26−1S** (Figure 4 and Supporting Information, Table S68). Structure **26−4S** has two three-electron donor bridging BO groups, as indicated by the short Fe−O distances of 2.272 Å (B3LYP) or 2.284 Å (BP86) and the unusually low $\nu(BO)$ frequency at 1671 and 1666 cm^{-1}. The Fe−Fe distance of 2.769 Å (B3LYP) or 2.748 Å (BP86) is similar to those in **26−1S, 26−2S,** and **26−3S** and consistent with a formal single bond to give each iron atom in **26−4S** the favored 18-electron configurations.

The triplet $Fe_2(BO)_2(CO)_6$ structures differ from the singlet structures by having very long (>3.7 Å) Fe$\cdots$Fe distances, indicating no direct interaction between the iron atoms in the triplet structures (Figure 5 and Supporting Information, Table S68). The C_{2h} triplet structure **26−1T** lies 1.6 kcal/mol *below* **26−1S** by B3LYP or 5.4 kcal/mol *above* **26−1S** by BP86. In **26−1T** the two BO ligands have coupled to form a dioxodiborene (B_2O_2) ligand with a B−B distance of 1.828 Å (B3LYP) or 1.850 Å (BP86). The short Fe−O distances of 2.060 Å (B3LYP) or 2.054 Å (BP86) in **26−1T** indicate that this dioxodiborene is a six-electron donor to the Fe_2 unit. The BP86 method predicts **26−1T** to be a genuine minimum, but the B3LYP method predicts it to have two tiny imaginary frequencies (16i and 9i cm^{-1}) (Supporting Information, Table S68), which cannot be removed by a finer integration grid. Following the normal mode leads to a C_2 structure having similar energy and geometry.

The $Fe_2(BO)_2(CO)_6$ structures **26−2T** and **26−3T** have two $Fe(CO)_3$ units connected by two bridging BO groups (Figure 5 and Supporting Information, Table S68). Both structures can be dissected into a bidentate $Fe(BO)_2(CO)_3$ unit chelating to the iron atom of the $Fe(CO)_3$ unit through the oxygen atoms of the two BO groups thereby leading to a six-membered $Fe_2B_2O_2$ chelate ring. The long Fe−Fe distances of ∼4.3 Å in **26−2T** and **26−3T** indicate no direct Fe−Fe interaction. Thus the iron atom in this bidentate $Fe(BO)_2(CO)_3$ unit has a 16-electron configuration, and the iron atom in the $Fe(CO)_3$ unit has the 18-electron configuration by receiving two electrons from each BO

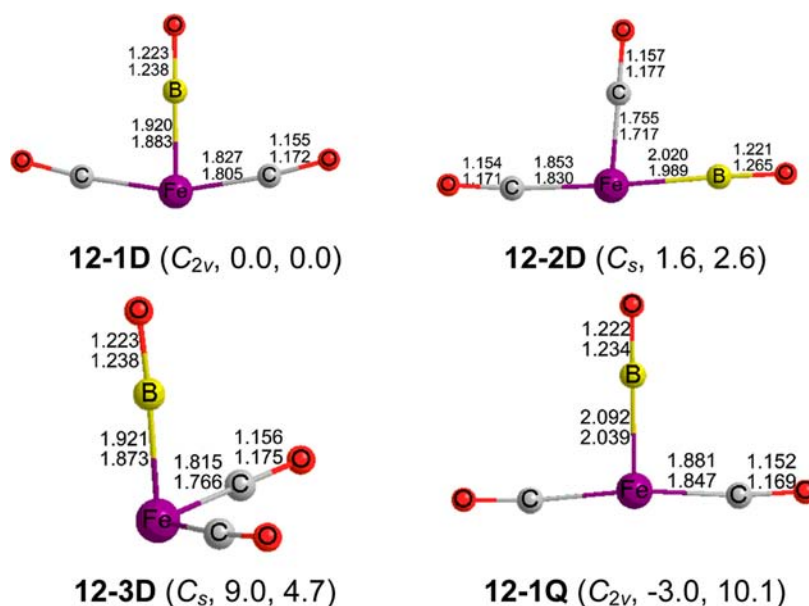**Figure 8.** Four optimized Fe(BO)(CO)$_2$ structures. The relative energies (in kcal/mol) by B3LYP and BP86, respectively, are shown under each structure.

group. The BP86 method predicts **26−2T** to lie 13.7 kcal/mol above **26−1S**. However, the B3LYP method predicts **26−2T** to be the lowest energy structure, lying 3.2 kcal/mol below **26−1S**. Structure **26−3T** lies 3.6 kcal/mol (B3LYP) or 1.9 kcal/mol (BP86) in energy above **26−2T**.

3.2. Mononuclear Derivatives. *3.2.1. Fe(BO)(CO)$_4$.* Both DFT methods predict two doublet structures for Fe(BO)-(CO)$_4$ (Figure 6 and Supporting Information, Table S69). These two structures are genuine minima without any imaginary frequencies. The C_s global minimum **14−1D** is a square pyramid with a BO group in a basal position. Another doublet Fe(BO)(CO)$_4$ structure **14−2D** (C_{2v} symmetry) is also a square pyramid, but the BO group is in the apical position. Structure **14−2D** lies 5.7 kcal/mol (BP86) or 6.9 kcal/mol (B3LYP) in energy above **14−1D**. The iron atoms in **14−1D** and **14−2D** each have 17 electron configurations.

3.2.2. Fe(BO)(CO)$_3$. Three low lying doublet structures are predicted for Fe(BO)(CO)$_3$ (Figure 7 and Supporting Information, Table S70). The global minimum **13−1D** (C_{2v} symmetry) is a square planar structure with a trans pair of CO ligands both slightly tilted toward the BO ligand. Structure **13−1D** can be generated by removing the apical CO group from the Fe(BO)(CO)$_4$ structure **14−1D**. The C_s structure **13−2D**, predicted only by BP86, lies 6.2 kcal/mol above the global minimum **13−1D**. Structure **13−2D** has a trigonal pyramid configuration with the BO group in the apical position. Attempted optimization of **13−2D** using the B3LYP method leads instead to **13−1D**. The Fe(BO)(CO)$_3$ structure **13−3D** has a "sawhorse" geometry, which can be derived from a trigonal bipyramid by removing an equatorial ligand. Structure **13−3D** is predicted to lie 11.3 kcal/mol (B3LYP) or 6.9 kcal/mol (BP86) in energy above **13−1D**. The iron atoms in **13−1D**, **13−2D**, and **13−3D** all have a 15 electron configuration assuming a one-electron donor terminal BO ligand.

3.2.3. Fe(BO)(CO)$_2$. Four low-lying structures (three doublets and one quartet) are found for Fe(BO)(CO)$_2$ (Figure 8 and Supporting Information, Table S71). The global minimum of Fe(BO)(CO)$_2$ is either **12−1D** or **12−1Q**, depending upon the theoretical method.[47] Both **12−1D** and **12−1Q** have planar

T-shaped geometries (C_{2v} symmetry) with the BO group in the middle. The B3LYP method predicts the quartet structure **12−1Q** to be the global minimum, lying 3.0 kcal/mol below **12−1D**, while the BP86 method predicts the doublet structure **12−1D** to lie 10.1 kcal/mol below **12−1Q**. Another doublet structure **12−2D**, lying 1.6 kcal/mol (B3LYP) or 2.6 kcal/mol (BP86) above **12−1D**, has an unsymmetrical planar T-shaped configuration with C_s symmetry and a CO group in the middle (Figure 8). The C_s doublet pyramidal structure **12−3D** lies 9.0 kcal/mol (B3LYP) or 4.7 kcal/mol (BP86) above **12−1D**. The Fe atoms in all four structures have a 13-electron configuration.

3.3. Dissociation Energies. Table 1 reports the dissociation energies for removing one carbonyl group from the global minima of the mononuclear Fe(BO)(CO)$_m$ and binuclear

Table 1. Energies (kcal/mol) for Successive Removal of CO or BO Groups from the Lowest-Lying Fe(BO)(CO)$_m$ (m = 4, 3) and Fe(BO)(CO)$_n$ (n = 7, 6) Complexes and for the Dissociation of the Lowest-Lying Binuclear Fe$_2$(BO)$_2$(CO)$_n$ (n = 7, 6) Complexes into Mononuclear Fragments

	B3LYP	BP86
Fe(BO)(CO)$_4$ → Fe(BO)(CO)$_3$ + CO	28.5	41.3
Fe(BO)(CO)$_3$ → Fe(BO)(CO)$_2$+ CO	42.5	48.6
Fe$_2$(BO)$_2$(CO)$_7$ → Fe$_2$(BO)$_2$(CO)$_6$ + CO	13.6	22.2
Fe$_2$(CO)$_9$ → Fe$_2$(CO)$_8$ + CO	29.4[a]	35.1[a]
Fe$_2$(BO)$_2$(CO)$_6$ → Fe$_2$(BO)$_2$(CO)$_5$ + CO	12.7	40.8
Fe(BO)(CO)$_4$ → Fe(CO)$_4$ + BO	75.6	81.9
Fe(BO)(CO)$_3$ → Fe(CO)$_3$+ BO	78.3	82.4
Fe$_2$(BO)$_2$(CO)$_7$ → Fe$_2$(BO)(CO)$_7$ + BO	84.6	81.3
Fe$_2$(BO)$_2$(CO)$_6$ → Fe$_2$(BO)(CO)$_6$ + BO	75.1	83.4
Fe$_2$(BO)$_2$(CO)$_7$ → Fe(BO)(CO)$_3$ + Fe(BO)(CO)$_4$	20.5	40.1
Fe$_2$(BO)$_2$(CO)$_7$ → Fe$_2$(BO)$_2$(CO)$_3$ + Fe(CO)$_4$	32.9	47.7
Fe$_2$(CO)$_9$ → Fe(CO)$_5$ + Fe(CO)$_4$	28.3[a]	13.1[a]
Fe$_2$(BO)$_2$(CO)$_6$ → 2Fe(BO)(CO)$_3$	35.3	59.2
Fe$_2$(BO)$_2$(CO)$_6$ → Fe(BO)$_2$(CO)$_3$ + Fe(CO)$_3$	50.4	67.3

[a]Data from reference 24.

$Fe_2(BO)_2(CO)_n$ structures according to the following equations:

$$Fe(BO)(CO)_m \rightarrow Fe(BO)(CO)_{m-1} + CO$$

$$(m = 4, 3)$$

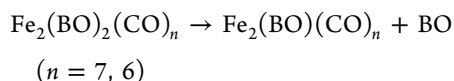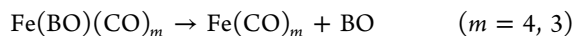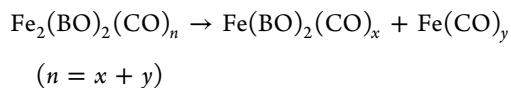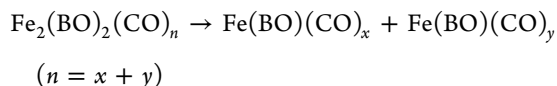$$Fe_2(BO)_2(CO)_n \rightarrow Fe_2(BO)_2(CO)_{n-1} + CO$$

$$(n = 7, 6)$$
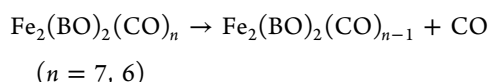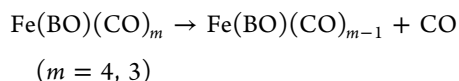
Table 1 also reports the dissociation energies of one BO group from the global minima of the mononuclear $Fe(BO)$-$(CO)_m$ and the binuclear $Fe_2(BO)_2(CO)_n$ according to the following equations:

$$Fe(BO)(CO)_m \rightarrow Fe(CO)_m + BO \qquad (m = 4, 3)$$

$$Fe_2(BO)_2(CO)_n \rightarrow Fe_2(BO)(CO)_n + BO$$

$$(n = 7, 6)$$

The theoretical dissociation energy for the loss of one CO group from mononuclear $Fe(BO)(CO)_4$ is seen to be 28.5 kcal/mol (B3LYP) or 41.3 kcal/mol (BP86). The BP86 result is very close to the experimental CO dissociation energy (41.5 kcal/mol) for $Fe(CO)_5$.[48] The loss of one CO group from the binuclear $Fe_2(BO)_2(CO)_7$ is much smaller, that is, 13.6 kcal/mol (B3LYP) or 22.2 kcal/mol (BP86). These are significantly below the experimental 28 kcal/mol CO dissociation energy[49] of $Fe_2(CO)_9$ to give $Fe_2(CO)_8$.

The dissociation energies of loss of one BO group from the $Fe(BO)(CO)_m$ ($m = 4, 3$) and $Fe_2(BO)_2(CO)_n$ ($n = 7, 6$) structures range from 75 to 85 kcal/mol (B3LYP) or 81 to 83 kcal/mol (BP86). These BO dissociation energies are much larger than the corresponding CO dissociation energies, suggesting that the Fe-BO bonds are stronger than the Fe-CO bonds. This is consistent with the reported results on other borylene complexes.[20] Furthermore, this can relate to the stability of free CO but the instability of free BO.

The dissociation of the binuclear $Fe_2(BO)_2(CO)_n$ ($n = 7, 6$) into mononuclear fragments according to the following reactions was also investigated (Table 1):

$$Fe_2(BO)_2(CO)_n \rightarrow Fe(BO)(CO)_x + Fe(BO)(CO)_y$$

$$(n = x + y)$$

$$Fe_2(BO)_2(CO)_n \rightarrow Fe(BO)_2(CO)_x + Fe(CO)_y$$

$$(n = x + y)$$

Such dissociation energies of the lowest energy binuclear $Fe_2(BO)_2(CO)_n$ structures into mononuclear fragments are large ranging from 20 to 50 kcal/mol (B3LYP) or 40 to 67 kcal/mol (BP86). The BP86 data suggest that the reaction chemistry of $Fe_2(BO)_2(CO)_7$ is not likely to involve dissociation into mononuclear fragments. This contrasts with the chemistry of $Fe_2(CO)_9$, which often involves dissociation into stable $Fe(CO)_5$ and a reactive $Fe(CO)_4$ fragment. This is the basis for the synthesis of various $LFe(CO)_4$ derivatives by reactions of $Fe_2(CO)_9$ with various ligands L under mild conditions.[50,51]

4. DISCUSSION

4.1. Structures with Bridging BO Groups.
The lowest energy $Mn_2(CO)_9$ structure has a single four-electron donor

bridging η^2-μ-CO group predicted (BP86) to have a very low $\nu(CO)$ frequency of 1767 cm^{-1} (Figure 1).[52] An analogous $Fe_2(BO)_2(CO)_7$ structure **27−5S** is found with two terminal BO groups and a similar η^2-μ-CO group (Figure 2). The predicted $\nu(CO)$ frequency for this bridging η^2-μ-CO group of 1819 cm^{-1} in **27−5S** (Supporting Information, Table S73) is significantly higher than that in the $Mn_2(CO)_8(\eta^2$-μ-CO) structure noted above. This can be relate to weaker backbonding to the η^2-μ-CO group when terminal CO groups are replaced by the more strongly electron withdrawing BO groups, which remove electron density from the metal atoms.

Structure **27−5S** is not the lowest energy $Fe_2(BO)_2(CO)_7$ structure but lies ∼9 kcal/mol above the global minimum **27−1S**, which has a single three-electron donor bridging η^2-μ-BO group (Figure 2). This is a clear demonstration that three-electron donor bridging η^2-μ-BO groups are more favorable than four-electron donor bridging η^2-μ-CO groups. This may relate to the higher basicity of the oxygen atom in a BO ligand relative to a CO ligand as observed by Braunschweig and co-workers[23] in the chemistry of $(Cy_3P)_2Pt(BO)Br$. The structures **27−2S** and **27−4S** likewise have single three-electron donor bridging η^2-μ-BO groups. The three $Fe_2(BO)_2(CO)_7$ structures **27−1S**, **27−2S**, **27−4S** lie within 3 kcal/mol of each other in energy and differ only in the location of the terminal BO group relative to the central $Fe_2(\eta^2$-μ-BO) unit. The $\nu(BO)$ frequencies for the bridging η^2-μ-BO groups are very low ranging from 1612 to 1691 cm^{-1} (Supporting Information, Table S73)

An $Fe_2(BO)_2(CO)_7$ structure with a single η^2-μ-CO or η^2-μ-BO group requires an Fe−Fe single bond to give both iron atoms the favored 18-electron configuration. The Fe−Fe distances in the structures **27−1S**, **27−2S**, **27−4S**, and **27−5S** range from 2.80 to 2.93 Å, which are reasonable for formal single bonds. A triply bridged $Fe_2(CO)_6(\mu$-BO)$_2(\mu$-CO) structure **27−3S** at a comparable energy is also found in which both BO groups are one-electron donors (considered as neutral ligands) and all CO groups are the usual two-electron donors. Such a structure requires a formal Fe=Fe double bond to give each iron atom the favored 18-electron configuration. The predicted Fe=Fe distance of ∼2.43 Å in **27−3S** is ∼0.4 Å shorter than the Fe−Fe single bond distances in **27−1S**, **27−2S**, **27−4S**, and **27−5S** noted above and thus can correspond to a formal double bond, even after allowing for some expected shortening of the Fe=Fe distance by the three bridging groups in **27−3S**. A similar singlet triply bridged $Mn_2(CO)_6(\mu$-CO)$_3$ was found in the previous theoretical study of binuclear manganese carbonyls[52] with a predicted Mn=Mn distance of ∼2.43 Å, which is essentially identical to the Fe=Fe distance in **27−3S**. This singlet $Mn_2(CO)_6(\mu$-CO)$_3$ structure is found to lie ∼18 kcal/mol above the $Mn_2(CO)_8(\eta^2$-μ-CO) global minimum.

An $Fe_2(BO)_2(CO)_7$ structure **27−7S** was found in which both BO groups are three-electron donor bridging η^2-μ-BO groups (Figure 2). No Fe−Fe bond is required in such a structure for each iron atom to attain the favored 18-electron configuration. This is consistent with the long nonbonding Fe···Fe distance of ∼3.39 Å in **27−7S**. Structure **27−7S** is a relatively high-energy structure, lying ∼14 kcal/mol above the global minimum **27−1S**. The two η^2-μ-BO groups in **27−7S** are predicted to exhibit the relatively low $\nu(BO)$ frequencies of 1653 and 1680 cm^{-1}.

A singlet hexacarbonyl $Fe_2(BO)_2(CO)_6$ structure requires a formal Fe≡Fe triple bond for each iron atom to attain the

favored 18-electron configuration if all BO groups are one-electron donors and all CO groups are two-electron donors. In fact, the two lowest energy structures of the analogous $Mn_2(CO)_8$ have only two-electron donor CO groups and $Mn\equiv Mn$ distances around 2.37 Å suggesting such formal triple metal−metal bonds.[52] Analogous $Fe_2(BO)_2(CO)_6$ structures with short $Fe\equiv Fe$ distances suggesting formal triple bonds were not found. Instead the lowest energy singlet $Fe_2(BO)_2(CO)_6$ structures all have two three-electron donor η^2-μ-BO groups and Fe−Fe distances ranging from 2.7 to 2.8 Å suggesting formal single bonds (Figure 4). This gives each iron atom in these structures the favored 18-electron configuration. Furthermore, in two of the three triplet $Fe_2(BO)_2(CO)_6$ structures (**26−2T** and **26−3T** in Figure 5) both BO groups are also three-electron donor bridging η^2-μ-BO groups. The long Fe⋯Fe distances of ~4.3 Å suggest the lack of iron−iron bonds thereby giving both iron atoms in each of these structures the 17-electron configuration for a binuclear triplet.

4.2. Coupling of Two BO Ligands Have Coupled to Form a Dioxodiborene (B_2O_2) Ligand. The first examples of metal complexes of the dioxodiborene (B_2O_2) ligand were found in this research, albeit not in the lowest energy structures. Free dioxodiborene is not a stable species but is found in the gas phase when B_2O_3 vapor is in a reducing environment.[25,26] Free OBBO was produced and identified by Andrews and co-workers[53] and found to have a ν(BO) frequency of be 1898.9 cm^{-1}. Free OBBO is found to have a linear geometry by both theory and experiment.[54,55] The isoelectronic cyanogen as a ligand retains its linearity in its metal complexes, such as $(\eta^1$-NCCN)[Nb(NRAr)$_3$]$_2$ (R = neopentyl, Ar = bulky aryl),[56] [Ag(NCCN)$_2$]$_n$[AsF$_6$]$_n$,[57] and [Zn(NCCN)$_6$][AsF$_6$]$_2$.[58] However, the B_2O_2 unit bridging the two iron atoms is not linear in the $Fe_2(B_2O_2)(CO)_n$ ($n = 7, 6$) derivatives but instead has bent cis or trans stereochemistry. Thus in the singlet structure **27−6S** the B_2O_2 ligand has cis stereochemistry (Figure 2). However, in the triplet structures **27−1T** (Figure 3) and **26−1T** (Figure 5) the B_2O_2 ligand has trans stereochemistry. The B−B distances of ~1.84 Å are not sensitive to whether the B_2O_2 ligand has cis or trans stereochemistry. These B−B distances in the $Fe_2(B_2O_2)(CO)_n$ dioxodiborene complexes are significantly shorter than the ~1.91 Å B−B distance predicted for the recently studied[29] difluorodiborene complex $(\eta^5$-C$_5$H$_5$)Fe(CO)(μ-B$_2$F$_2$). These B−B distances in complexed B_2F_2 and B_2O_2 ligands are significantly longer than the experimental B−B distance in B_2F_4 of 1.7219(4) Å determined by electron diffraction[59,60] and also longer than that of 1.590 Å in free B_2.[61] This apparent lengthening of the B−B bond upon complexation of a B_2X_2 (X = O, F) ligand to an Fe_2 unit may relate to back-donation of iron d electrons into antibonding orbitals of the B−B bond.

The bonding modes of difluorodiborene and dioxodiborene ligands to a pair of metal atoms are distinctly different (Figure 9). For the B_2F_2 ligand only the boron atoms are involved in the metal−ligand bonding so that the B_2F_2 ligand is a two-electron donor. In fact, the bonding of a B_2F_2 ligand can be considered as a π-bond of the B≡B double bond to the transition metal atoms. However, in the $Fe_2(\mu$-cis-$B_2O_2)(CO)_7$ structure **27−6S** (Figure 2) both oxygen atoms of the B_2O_2 ligand are within bonding distance (~2.13 Å) of one of the iron atoms. The long Fe⋯Fe distance of ~3.7 Å in **27−6S** indicates the absence of an iron−iron bond. The dioxodiborene ligand can be formally considered to be O≡B−B≡O with two B≡O double bonds. The iron atom within bonding distance of the
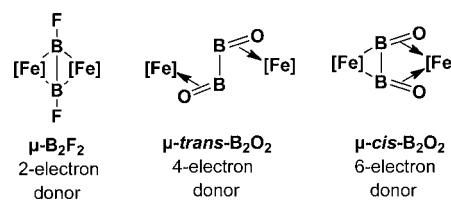

Figure 9. Bonding of bridging difluorodiborene and *trans-* and *cis-*B_2O_2 ligands to a pair of iron atoms. The designation [Fe] refers to an iron atom surrounded by its ligands other than the B_2F_2 or B_2O_2 ligand.

two oxygen atoms (the "right" iron in Figure 2) can be considered to be π bonded to each of the B≡O double bonds thereby receiving four electrons from the B_2O_2 ligand. This gives this iron atom the favored 18-electron configuration. The other iron atom in **27−6S** (the "left" iron atom in Figure 2) is within bonding distance of only the two boron atoms of the μ-B_2O_2 ligand. This iron atom can receive two electrons from the B−B σ-bond in the μ-B_2O_2 ligand by effectively forming a three-center two-electron FeB$_2$ bond. Thus the neutral bridging B_2O_2 ligand is a six-electron donor in the $Fe_2(\mu$-cis-$B_2O_2)$-$(CO)_7$ structure **27−6S**. This π-bonding of the B≡O double bonds of the cis-B_2O_2 ligand to the "right" iron atom in **27−6S** leads to very low ν(BO) frequencies of 1550 and 1575 cm^{-1}, as compared with the experimental ν(BO) frequencies of 1899 and 1895 cm^{-1} in free dioxodiborene.[57]

The bridging *trans-*B_2O_2 ligands in the lowest energy triplet structures **27−1T** (Figure 3) and **26−1T** (Figure 5) appear to be only four-electron donor ligands (Figure 9). In **26−1T** the B≡O double bonds each donate an electron pair to the Fe_2 system through π-bonding with one of the iron atoms as suggested by the short Fe−O distances of 2.06 Å to both B≡O units of the *trans-*B_2O_2 ligand. Because of the trans stereochemistry of the dioxodiborene ligand in **26−1T**, each B≡O double bond coordinates to a different iron atom in contrast to the cis-dioxodiborene ligand in the singlet structure **27−6S** (Figure 2) discussed above. Both of the BO groups in the *trans-*B_2O_2 ligand exhibit very low ν(BO) frequencies of 1576 and 1584 cm^{-1} (Supporting Information, Table S73). The four-electron donor *trans-*B_2O_2 ligand in **27−1T** is different from that in **26−1T**. Thus in **27−1T** only one of the B≡O units of the *trans-*B_2O_2 is π-bonded to an iron atom as indicated by one short Fe−O distance of ~2.02 Å and one long Fe⋯O distance of ~2.78 Å. The other iron atom in the BP86 structure **27−1T** is bonded to the B−B σ-bond in the *trans-*B_2O_2 ligand similar to the "left" iron atom (Figure 2) in the **27−6S** structure. In the *trans-*B_2O_2 ligand of **27−1T** the BO unit bonded to an iron atom exhibits a very low ν(BO) frequency of 1561 cm^{-1} whereas the BO unit not bonded to an iron atom exhibits a significantly higher, but still rather low, ν(BO) frequency of 1687 cm^{-1} (Supporting Information, Table S73).

5. SUMMARY

The boronyl (BO) ligand functions as a three-electron donor bridging η^2-μ-BO ligand in most of the unsaturated $Fe_2(BO)_2(CO)_n$ ($n = 7, 6$) structures. This appears to relate to the relatively high basicity of metal boronyl oxygen atoms compared, for example, with metal carbonyl oxygen atoms. Thus three of the four lowest energy singlet $Fe_2(BO)_2(CO)_7$ structures have such bridging η^2-μ-BO groups and formal Fe−Fe single bonds. They differ only in the location of the terminal BO group relative to the central $Fe_2(\eta^2$-μ-BO) unit. Similarly all

four of the low energy singlet $Fe_2(BO)_2(CO)_6$ structures have two such bridging $\eta^2\text{-}\mu\text{-BO}$ groups and formal Fe—Fe single bonds. In structures of these types, both iron atoms have the favored 18-electron configuration.

Bridging dioxodiborene (B_2O_2) ligands are found for the first time in these $Fe_2(BO)_2(CO)_n$ (n = 7, 6) structures. The number of electrons donated by the B_2O_2 ligand to the Fe_2 unit appears to depend on the dioxodiborene stereochemistry. Thus in the lowest energy triplet $Fe_2(B_2O_2)(CO)_n$ (n = 7, 6) structures, a *trans*-dioxodiborene ligand bonds to each iron atom through one of its B=O bonds and thus donates four electrons to the central Fe_2 unit. However, one of the singlet $Fe_2(B_2O_2)(CO)_7$ structures contains a six-electron donor *cis*-dioxodiborene ligand, which bonds to one iron atom through both of its B=O bonds and to the other iron atom through its B—B bond. In all of these binuclear dioxodiborene iron carbonyl complexes, the iron—iron distance is too long for a direct bond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details are given in Tables S1−S73, as well as the complete Gaussian 03 reference 45. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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