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Prospects for Making Organometallic Compounds with BF Ligands: Fluoroborylene Iron Carbonyls

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The fluoroborylene ligand (BF), isoelectronic with CO, was recently (2009) realized experimentally by Vidović and Aldridge in $Cp_2Ru_2(CO)_4(\mu\text{-BF})$. In this research the related iron carbonyl fluoroborylene complexes $Fe(BF)(CO)_n$ ($n = 4$, 3), $Fe_2(BF)(CO)_8$, and $Fe_2(BF)_2(CO)_n$ ($n = 7$, 6) are compared with the isoelectronic $Fe(CO)_{n+1}$ and $Fe_2(CO)_{n+2}$ as well as the thiocarbonyls $Fe(CS)(CO)_n$ and $Fe_2(CS)_2(CO)_n$ using density functional theory. For $Fe(BF)(CO)_4$ the axially and equatorially substituted trigonal bipyramidal structures are predicted to be nearly degenerate as is the case for $Fe(CS)(CO)_4$. The lowest energy structures for $Fe(BF)(CO)_3$ are derived from the trigonal bipyramidal $Fe(BF)(CO)_4$ structures by removal of CO groups. For the binuclear derivatives $Fe_2(BF)(CO)_8$ and $Fe_2(BF)_2(CO)_n$ ($n = 7$, 6) *structures with BF bridges are preferred energetically over structures with CO bridges*. However, no structures for the unsaturated $Fe_2(BF)_2(CO)_6$ are found with four-electron donor η^2-μ-BF groups. This differs from the corresponding $Fe_2(CS)_2(CO)_6$ where structures with η^2-μ-CS groups and formal Fe−Fe single bonds are preferred over structures with only two electron donor CO and CS groups and formal Fe═Fe double bonds. The lowest energy structure for $Fe_2(BF)_2(CO)_7$ is thus predicted to be similar to the well-known triply bridged $Fe_2(CO)_9$ structure but with two bridging BF groups and one bridging CO group. However, the dissociation energy of $Fe_2(BF)_2(CO)_7$ into mononuclear fragments is much higher than that of $Fe_2(CO)_9$. Removal of the bridging CO group from this lowest energy $Fe_2(BF)_2(CO)_7$ structure leads to the doubly BF-bridged global minimum structure for $Fe_2(BF)_2(CO)_6$.

1. Introduction

Simple two-atom ligands such as CO, NO, and N_2 containing only first row elements have played important roles in the development of transition metal coordination chemistry. The CO ligand is particularly important in stabilizing low formal transition metal oxidation states because of its strong π-acceptor strength, leading to the withdrawal of electron density from the central metal atom into the π^* antibonding orbitals of the CO ligand. For example, $Cr(CO)_6$, which contains chromium in the formal zero oxidation state, is stable enough toward oxidation that it can be steam-distilled in air, a purification method that can be used in its commercial manufacture. Furthermore, a critical factor in the extensive development of metal carbonyl chemistry since the original discoveries of the first metal carbonyl $[Pt(CO)Cl_2]_2$ in 1868[1] and the first binary metal carbonyl $Ni(CO)_4$ in 1890[2] has been the ready availability and high stability of carbon monoxide. For this reason carbon monoxide can often be used to introduce carbonyl groups into a variety of transition metal complexes, often by reactions at elevated pressures.

The transition metal chemistry of dinitrogen, isoelectronic with CO, developed much later despite the fact that N_2, like CO, is a readily available very stable gas. The difficulty with the synthesis of metal dinitrogen complexes is the much lower chemical reactivity of N_2 relative to CO. A highly reactive transition metal substrate is therefore required for the formation of metal dinitrogen complexes directly from N_2. Indeed the initial synthesis of the first transition metal dinitrogen complex, namely $[Ru(NH_3)_5(N_2)]^{2+}$ by Allen and Senoff in 1965[3] used hydrazine rather than gaseous N_2 as a source of the N_2 ligand. Only later were transition metal systems discovered, mainly containing early transition metals, which are reactive enough to form

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dinitrogen complexes directly with N_2 gas. In recent years the coordination chemistry of dinitrogen has developed extensively.[4,5]

Another ligand isoelectronic with CO and N_2 is the fluoroborylene ligand, BF. The free BF ligand (boron monofluoride) is obtained in high yield in the gas phase by passing BF_3 over crystalline boron at 2000°/1 mm.[6] However, BF is unstable even in the gas phase and condenses to a green uncharacterized polymer, even at −196 °C. Thus transition metal BF complexes need to be synthesized by indirect methods. In this connection the first mention of a metal BF complex is the synthesis of $Fe(BF)(CO)_4$ from $Fe(CO)_5$ and B_2F_4 reported in a 1968 conference proceedings.[7] However, the 1968 report of this synthesis has not apparently been repeated during the subsequent >40 years and thus must be regarded as doubtful until it is confirmed. Much more relevant, the fluoroborylene ruthenium complex $Cp_2Ru_2(CO)_4(\mu\text{-}BF)$ has been reported very recently (2009) by Vidović and Aldridge and characterized structurally by X-ray crystallography.[8] Despite the paucity of transition metal BF complexes, numerous transition metal complexes of other BR ligands have been synthesized.[9−11] These include the terminal borylene complexes $(\eta^5\text{-}Me_5C_5)B{\rightarrow}Fe(CO)_4$ (ref 12) and $(Me_3Si)_2NB{\rightarrow}M(CO)_5$ (M = Cr, W[13]) that are simple substitution products of the homoleptic metal carbonyls $Fe(CO)_5$ and $M(CO)_6$, respectively. In addition, the analogous complexes $[(CO)_nM\text{-}E(X)L_2]$ (E = Ga, Al), as Lewis base adducts of the transition metal, have been reported experimentally.[14] However, metal BF complexes are of particular interest owing to their potentially strong π-acceptor characteristics arising from the electron-withdrawing fluorine atom.

Metal fluoroborylene carbonyl complexes, particularly $Fe(BF)(CO)_4$, have been the subject of theoretical studies using density functional methods.[15,16] The general objective of these studies is to compare the bonding of BF in metal complexes to that of related ligands including $BNMe_2$, BNH_2, BO^-, and SiO. These studies predict BF to be both a better σ-donor and a better π-acceptor than CO. In addition, a variety of theoretical studies have been reported on the nature of the metal bonding to borylene ligands of various types[17−21] including the effect of bridging borylene ligands of various types on metal−metal bonding.[22,23]

The research discussed in the current paper explores possible structures for the binuclear $Fe_2(BF)_2(CO)_n$ (n = 7, 6) derivatives using density functional methods. In addition, $Fe_2(BF)(CO)_8$ has been included in this study. Of particular interest are the relative tendencies of BF and CO to function as bridging groups and the ability of BF to function as a four-electron donor ligand through Fe−F bonding in addition to Fe−B bonding. In this connection, a previously reported theoretical study[24] of the iron carbonyl thiocarbonyls $Fe_2(CS)_2(CO)_n$ (n = 7, 6) shows that the CS group has a greater tendency to function as a bridging group as well as a four-electron donor bridging ligand through Fe−S bonding and Fe−C bonding. This leads to distinctly different low energy structures for isovalent $Fe_2(CS)_2(CO)_n$ and isoelectronic $Fe_2(CO)_{n+2}$ species in many cases, particularly the more highly unsaturated systems.

2. Theoretical Methods

Electron correlation effects were considered using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[25−39] Two DFT methods were used in this study. The popular B3LYP method combines the three-parameter Becke exchange functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[40,41] The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional (P86).[42,43] The BP86 method has been found to be somewhat more reliable than B3LYP for

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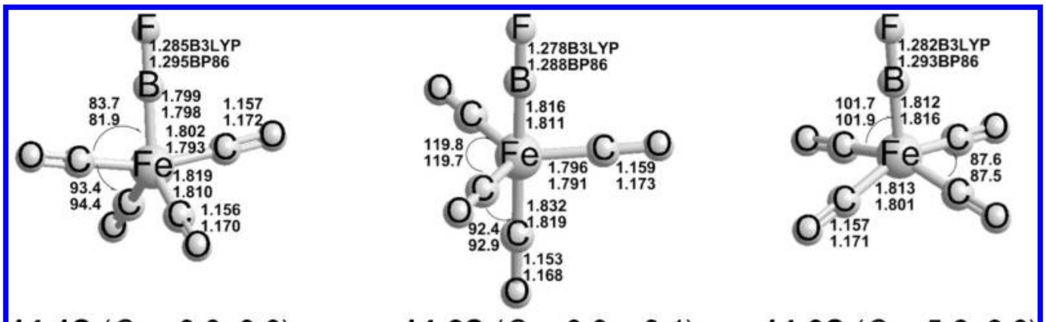

14-1S (C_{2v}, 0.0, 0.0) **14-2S** (C_{3v}, 0.9, –0.1) **14-3S** (C_{4v}, 5.6, 6.9)

Figure 1. Three optimized structures for Fe(BF)$(CO)_4$ indicating the relative energies (ΔE, in kcal/mol) by the B3LYP and BP86 methods, respectively.

the type of organometallic systems considered in this paper, especially for the prediction of vibrational frequencies.[44−46]

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 $\alpha_d(B) = 0.7$, $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(F) = 1.0$ for boron, carbon, oxygen, and fluorine, respectively, was added to the standard Huzinaga−Dunning contracted DZ sets,[47−49] designated as (9s5p1d/4s2p1d). The loosely contracted DZP basis set for iron is the Wachters primitive set[50] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[51] 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. All calculations were performed with the Gaussian 03 program package.[52] The fine grid (75, 302) was the default for the numerical evaluation of the integrals, while the finer grid (120, 974) was only used to evaluate the small imaginary vibrational frequencies. All of the predicted triplet structures in the present study are found to have negligible spin contamination, with the $S(S+1)$ values close to the ideal outcome value of 2.0.

A given $Fe_a(BF)_a(CO)_b$ structure is designated as **ab-cA** where **a** is the number of iron atoms (the same as the number of BF groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies using the B3LYP method. **A** indicates whether the structure is a singlet (**S**) or triplet (**T**). Thus the lowest energy structure of singlet $Fe_2(BF)_2(CO)_7$ is designated **27-1S**. The $Fe_2(BF)(CO)_8$ structures are anomalously named as **28-cA**, which is unambiguous since $Fe_2(BF)_2(CO)_8$ is not discussed in this paper. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (Nimag), and spin expectation values ($\langle S^2 \rangle$) for all of the optimized structures within ~30 kcal/mol are listed in the Supporting Information, Tables S1, S2, and S5−S7. Figures 1−4 give the optimized structures, listing in parentheses the relative energies (ΔE, in kcal/mol) using the B3LYP and BP86 methods, respectively.

3. Results

3.1. Mononuclear Derivatives.

3.1.1. Fe(BF)$(CO)_4$. Three singlet structures are predicted for Fe(BF)$(CO)_4$ (Figure 1 and Supporting Information, Table S1). The global minimum **14-1S** may be a C_{2v} symmetry singlet trigonal bipyramidal structure with the linear BF group in an equatorial position. A C_{3v} trigonal bipyramidal Fe(BF)$(CO)_4$ structure **14-2S**, with the BF group in an axial position, lies energetically above **14-1S** by 0.9 kcal/mol (B3LYP) or below **14-1S** by 0.1 kcal/mol (BP86), indicating that **14-1S** and **14-2S** are nearly degenerate in energy. This is analogous to the previously reported results for Fe(CS)$(CO)_4$ for which singlet C_{2v} and C_{3v} structures were found with almost the same energies.[24]

The C_{4v} singlet Fe(BF)$(CO)_4$ structure **14-3S** with a linear BF group in the apical position of a square pyramid lies above the global minimum **14-1S** by 5.6 kcal/mol (B3LYP) or 6.9 kcal/mol. Structure **14-3S** has a small imaginary vibrational frequency at 72i cm^{-1} (B3LYP) or 79i cm^{-1} (BP86). Following the corresponding normal mode leads to **14-1S**.

3.1.2. Fe(BF)$(CO)_3$. Four low-lying structures (two singlets and two triplets) were found for Fe(BF)$(CO)_3$ (Figure 2 and Supporting Information, Table S2). The global minimum of Fe(BF)$(CO)_3$ is either a singlet or a triplet structure, depending upon the theoretical method. The B3LYP method predicts a C_s triplet structure **13-1T** to be the global minimum at 3.4 kcal/mol below the singlet structure **13-1S**. However, the BP86 method predicts **13-1S** to be the global minimum, at 4.3 kcal/mol below **13-1T**.

The other triplet structure **13-2T** of Fe(BF)$(CO)_3$ lies 8.6 kcal/mol (B3LYP) or 11.3 kcal/mol (BP86) above **13-1T**. In **13-2T** the coordination of the iron atom is distorted square planar, with the pairs of opposite ligands slightly tilted in the same direction. The underlying skeleton of **13-2T** thus has ideal D_{2d} symmetry, which is reduced to C_s by the non-equivalence of the CO and BF ligands.

The other singlet structure **13-2S** of Fe(BF)$(CO)_3$ has C_{3v} symmetry and is predicted to lie higher in energy above **13-1S**, by 2.0 kcal/mol (B3LYP) or 1.5 kcal/mol (BP86). Structure **13-2S** is predicted to be a genuine minimum by B3LYP, but with a tiny degenerate imaginary frequency (9i cm^{-1}) by BP86 (Supporting Information, Table S2). Structures **13-1S** and **13-2S** can be derived from the

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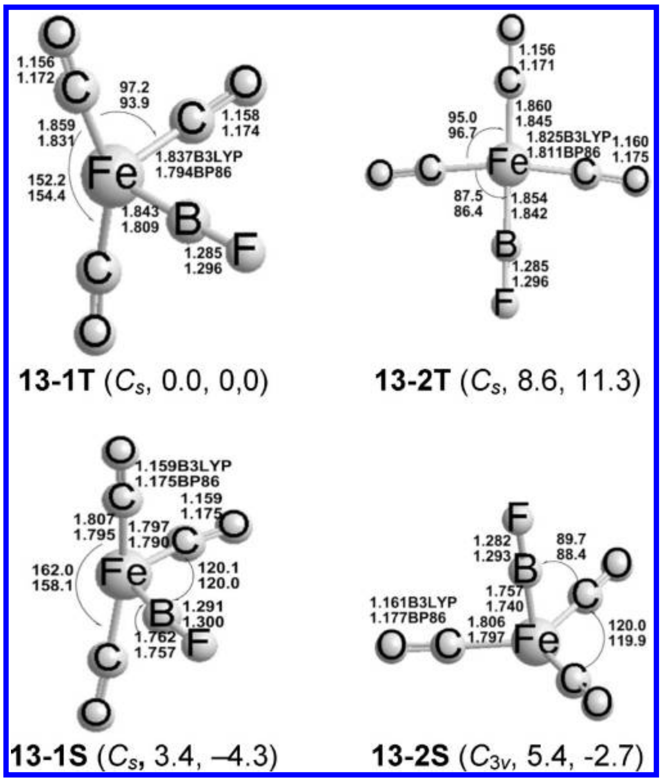

13-1T (C_s, 0.0, 0,0) **13-2T** (C_s, 8.6, 11.3)

13-1S (C_s, 3.4, –4.3) **13-2S** (C_{3v}, 5.4, -2.7)

Figure 2. Four optimized structures for Fe(BF)$(CO)_3$ indicating the relative energies (ΔE, in kcal/mol) by the B3LYP and BP86 methods, respectively.

Fe(BF)$(CO)_4$ structure **14-1S** by removing a CO group either from an axial or an equatorial position, respectively.

3.2. Binuclear Derivatives. **3.2.1. Fe_2(BF)$(CO)_8$.** Five singlet structures are found for Fe_2(BF)$(CO)_8$ (Figure 3, Supporting Information, Figure S3 and Table S5) within 30 kcal/mol. Here, only the first three structures within 15 kcal/mol of the global minimum are discussed in detail. The global minimum structure of Fe_2(BF)$(CO)_8$ is a C_2 singly bridged singlet structure **28-1S** (Figure 3 and Supporting Information, Table S5), which is very different from the experimental triply bridged structure $Fe_2(CO)_6$(μ-CO$)_3$[53] for $Fe_2(CO)_9$. Except for the metal−metal bond, the Fe_2(BF)$(CO)_8$ structure **28-1S** is very analogous to the experimentally known[8] ruthenium complex $Cp_2Ru_2(CO)_4$(μ-BF). The Fe−Fe distance of 2.760 Å (B3LYP) or 2.631 Å (BP86) in **28-1S** is longer than the experimental Fe−Fe distance of 2.523 Å in the triply bridged structure $Fe_2(CO)_6$(μ-CO$)_3$,[53] but suggests the single Fe−Fe bond required to give both iron atoms the favored 18-electron configuration. The longer Fe−Fe single bond distance in the Fe_2(BF)$(CO)_8$ structure **28-1S** relative to the known $Fe_2(CO)_6$(μ-CO$)_3$ can be related to the effect of three bridging CO groups in the latter structure shortening the iron−iron distance relative to the single bridging BF group in **28-1S**.

The second Fe_2(BF)$(CO)_8$ structure **28-2S** with C_{2v} symmetry, with a bridging BF group, lies 1.1 kcal/mol (B3LYP) or 2.9 kcal/mol (BP86) above the global minimum **28-1S**. Structure **28-2S** is a transition state with one imaginary frequency at 20*i* cm^{-1} (B3LYP) or 21*i* cm^{-1} (BP86), which cannot be removed by the finer integration grid (120,974). Following the normal mode of this imaginary frequency leads to **28-1S**.

The C_{2v} triply bridged Fe_2(BF)$(CO)_8$ structure **28-3S**, with one bridging BF group and two bridging CO groups, is predicted to lie in energy above **28-1S** by 5.3 kcal/mol (B3LYP) or below **28-1S** by 0.1 kcal/mol (BP86). Structure **28-3S** has an imaginary frequency at 70*i* cm^{-1} by the B3LYP method. However, **28-3S** is a genuine minimum with all real frequencies by the BP86 method. Following the normal mode of the imaginary frequency predicted for **28-3S** by the B3LYP method leads to **28-1S**. The Fe−Fe distance of 2.530 Å (B3LYP) or 2.523 Å (BP86) in **28-3S** is close to the experimental Fe−Fe distance of 2.523 Å for the triply bridged structure $Fe_2(CO)_6$(μ-CO$)_3$[53] and corresponds to the formal single bond required to give both iron atoms the favored 18-electron configuration.

3.2.2. $Fe_2(BF)_2(CO)_7$. Seven singlet structures are found for $Fe_2(BF)_2(CO)_7$ (Figure 4, Supporting Information, Figure S4 and Table S6) within 30 kcal/mol. Here, only the four structures within 15 kcal/mol of the global minimum structure **27-1S** as well as the highest lying structure **27-7S** of a different type for comparison, are discussed in detail (see Figure 4). Structures **27-1S** and **27-7S** have three bridging groups (either CO or BF groups), structure **27-2S** has two bridging BF groups, and the remaining two structures **27-3S** and **27-4S** have only one bridging BF group.

The singlet triply bridged C_{2v} global minimum $Fe_2(BF)_2(CO)_7$ structure **27-1S** (Figure 4 and Supporting Information, Table S6) with two bridging BF groups and one bridging CO group is predicted to be a genuine minimum by both the B3LYP and the BP86 methods. The Fe−Fe distance in **27-1S** is 2.545 Å (B3LYP) or 2.540 Å (BP86), which is close to the experimental Fe−Fe distance of 2.523 Å, determined by X-ray diffraction[53] for the homoleptic carbonyl analogue $Fe_2(CO)_6$(μ-CO$)_3$, also with three bridging groups.

The next low-lying C_s singlet $Fe_2(BF)_2(CO)_7$ structure **27-2S**, with two bridging BF groups and seven terminal CO groups, lies above the global minimum **27-1S** by 5.7 kcal/mol (B3LYP) or 8.3 kcal/mol (BP86). Structure **27-2S** has a small imaginary frequency at 16*i* cm^{-1} (B3LYP) or 22*i* cm^{-1} (BP86). This small imaginary frequency remains when a finer integration grid (120, 974) is used. Following the corresponding normal mode leads to **27-1S**. The Fe−Fe distance in **27-2S** is 2.691 Å (B3LYP) or 2.657 Å by BP86, which is longer than that in **27-1S** by ~0.15 Å in accord with the presence of three bridging groups in **27-1S** but only two bridging groups in **27-2S**.

Two singly bridged $Fe_2(BF)_2(CO)_7$ structures **27-3S** and **27-4S** have one bridging BF group, one terminal BF group, and seven terminal CO groups. Structure **27-3S** is a genuine minimum by both the B3LYP and the BP86 methods, lying 12.0 kcal/mol (B3LYP) or 17.4 kcal/mol (BP86) in energy above structure **27-1S**. The singlet C_s $Fe_2(BF)_2(CO)_7$ structure **27-4S** is predicted to lie at 12.4 kcal/mol (B3LYP) or 17.1 kcal/mol (BP86) in energy above **27-1S**. Structure **27-4S** is predicted to be a genuine minimum by BP86 but has a small imaginary vibrational frequency at 14*i* cm^{-1} by B3LYP. This small imaginary frequency remains when the finer integration grid (120, 974) is used. Following the corresponding

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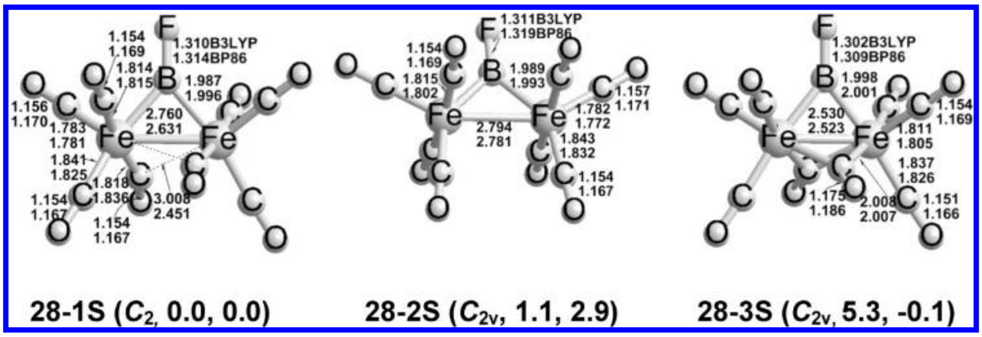


Figure 3. Optimized $Fe_2(BF)(CO)_8$ structures indicating the relative energies (ΔE, in kcal/mol) by the B3LYP and BP86 methods, respectively.

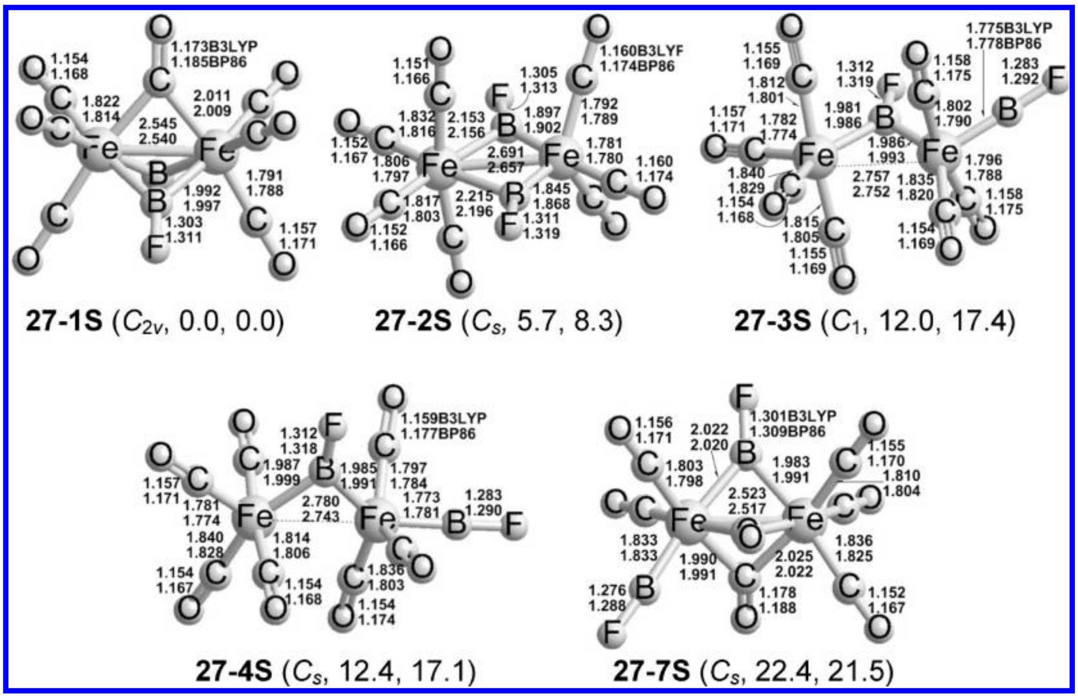


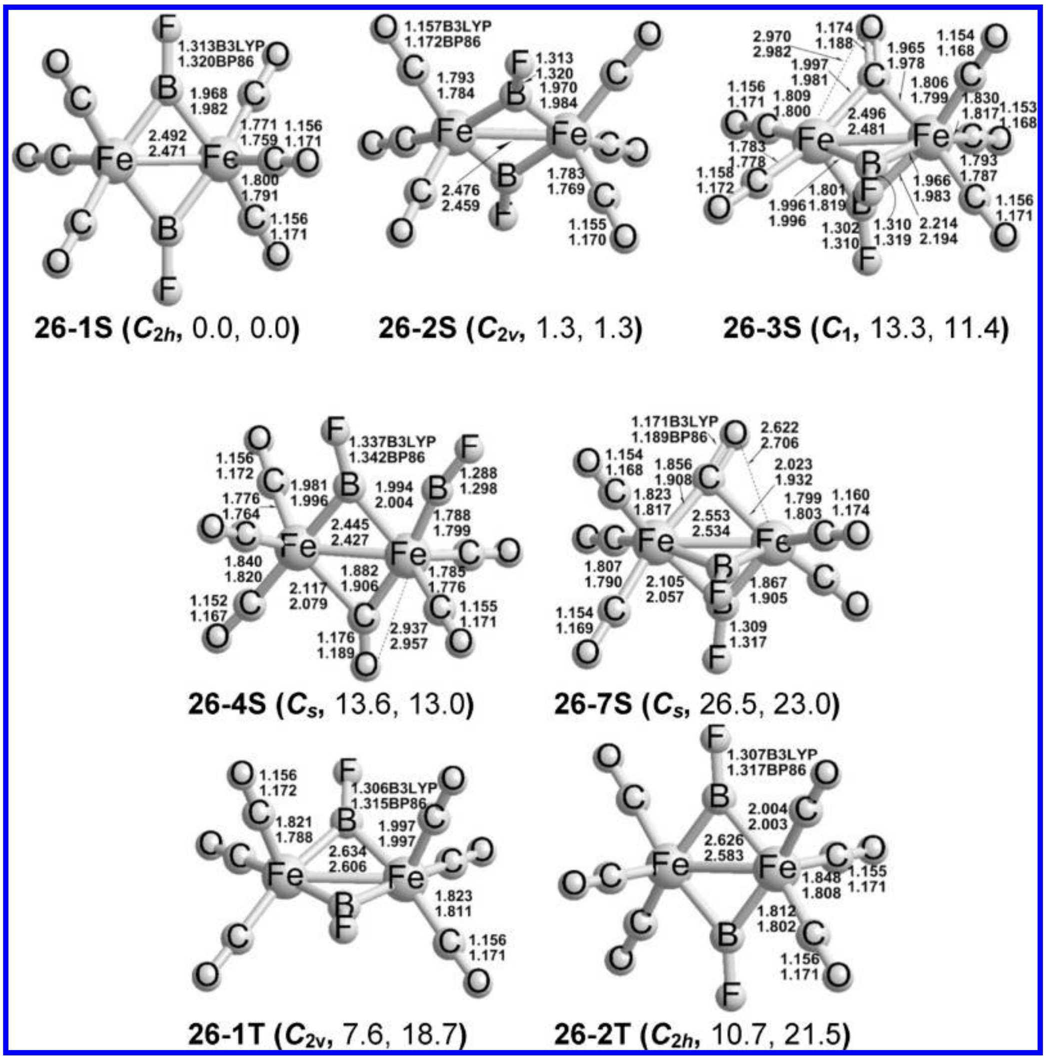
Figure 4. Optimized $Fe_2(BF)_2(CO)_7$ structures indicating the relative energies (ΔE, in kcal/mol) by the B3LYP and BP86 methods, respectively.

normal mode leads to **27-3S**. The Fe−Fe bond distances in the $Fe_2(BF)_2(CO)_7$ structures **27-3S** and **27-4S** are in the range of 2.76 to 2.78 Å (B3LYP) or 2.74 to 2.75 Å (BP86). These Fe−Fe distances of the singly bridged $Fe_2(BF)_2(CO)_7$ structures are ~0.1 Å longer than that in the doubly bridged structure **27-2S**, again indicating the shortening of a formal Fe−Fe bond by increasing the number of bridging groups.

The relatively higher energy $Fe_2(BF)_2(CO)_7$ structure **27-7S** with two bridging CO groups and one bridging BF group lies 22.4 kcal/mol (B3LYP) or 21.5 kcal/mol (BP86) above that of the favored triply bridged structure **27-1S**. The Fe−Fe bond distance of 2.523 Å (B3LYP) or 2.517 Å (BP86) is slightly shorter than that in **27-1S**, but it is close to the Fe−Fe distance (2.523 Å) obtained from X-ray diffraction[53] for the carbonyl analogue $Fe_2(CO)_6(\mu\text{-}CO)_3$. The much higher energy of **27-7S** with one BF bridge and two CO bridges relative to that of **27-1S** with two BF bridges and one CO bridge suggests that BF bridges are *much more favorable* than CO bridges in otherwise equivalent structures.

3.2.3. $Fe_2(BF)_2(CO)_6$. Seven singlet structures and four triplet structures within 30 kcal/mol were found for $Fe_2(BF)_2(CO)_6$ (Figure 5, Supporting Information, Figure S5 and Table S7). The plethora of $Fe_2(BF)_2(CO)_6$ structures, including structures with one, two and three bridging groups, indicates a very complicated potential energy surface. Among these twelve structures of $Fe_2(BF)_2(CO)_6$, except for the highest singlet structure **26-7S** of a different type, the five structures with energies more than 15 kcal/mol above the global minimum structure **26-1S** are not discussed, but are reported in the Supporting Information.

A C_{2h} doubly bridged singlet $Fe_2(BF)_2(CO)_6$ structure **26-1S**, with two bridging BF groups and six terminal CO groups, is the global minimum predicted by both B3LYP and BP86 methods. However, the next lowest lying $Fe_2(BF)_2(CO)_6$ structure **26-2S** is a C_{2v} structure lying only 1.3 kcal/mol (B3LYP and BP86) above **26-1S**. Structure **26-2S** has one small imaginary vibrational frequency ($27i$ cm^{-1}) by B3LYP or two small imaginary frequencies ($25i$ and $11i$ cm^{-1}) by BP86. A finer integration grid (120,974) does not remove these imaginary frequencies. Following the corresponding normal mode leads to **26-1S**. The Fe═Fe bond distances are 2.492 Å (B3LYP) or 2.471 Å (BP86) in **26-1S** and 2.476 Å (B3LYP) or 2.459 Å (BP86) in **26-2S**. These Fe═Fe distances are ~0.2 Å shorter than the doubly bridged



26-1S (C_{2h}, 0.0, 0.0) **26-2S** (C_{2v}, 1.3, 1.3) **26-3S** (C_1, 13.3, 11.4)

26-4S (C_s, 13.6, 13.0) **26-7S** (C_s, 26.5, 23.0)

26-1T (C_{2v}, 7.6, 18.7) **26-2T** (C_{2h}, 10.7, 21.5)

Figure 5. Five singlet and two triplet optimized structures of $Fe_2(BF)_2(CO)_6$ indicating the relative energies (ΔE, in kcal/mol) by the B3LYP and BP86 methods, respectively.

Fe−Fe single bond in **27-2S** (Figure 4) and thus can correspond to the formal double bonds needed to give both iron atoms in **26-1S** and **26-2S** the favored 18-electron configurations. The $Fe_2(BF)_2(CO)_6$ structures **26-1S** and **26-2S** can be derived from the triply bridged $Fe_2(BF)_2(CO)_7$ structure **27-1S** by removing the bridging CO group.

The lowest-lying triply bridged singlet $Fe_2(BF)_2(CO)_6$ structure **26-3S** has C_1 symmetry and lies 13.3 kcal/mol (B3LYP) or 11.4 kcal/mol (BP86) in energy above the global minimum **26-1S**. Structure **26-3S** is a genuine minimum by both B3LYP and BP86 methods and can be derived from the global minimum $Fe_2(BF)_2(CO)_7$ structure **27-1S** by removing a terminal CO group. The Fe−O distance to the bridging CO group of 2.970 Å (B3LYP) or 2.982 Å (BP86) is too long for a four-electron donor bridging η^2-μ-CO group and suggests only a relatively weak interaction. The triply bridged Fe═Fe distance of 2.496 Å (B3LYP) or 2.481 Å (BP86) in **26-3S** is ~0.05 Å shorter than the triply bridged Fe−Fe distance in the $Fe_2(BF)_2(CO)_7$ structure **27-1S**. This is consistent with the formal Fe═Fe double bond needed to give both iron atoms in **26-3S** the favored 18-electron configuration in the presence of only two-electron donor BF and CO groups.

The singlet C_s $Fe_2(BF)_2(CO)_6$ structure **26-4S** with one bridging BF group and one bridging CO group is predicted to lie 13.6 kcal/mol (B3LYP) or 13.0 kcal/mol (BP86) in energy above **26-1S**. Structure **26-4S** has one imaginary frequency at $15i$ cm^{-1} (B3LYP) or $10i$ cm^{-1} (BP86). However, this small imaginary frequency is removed by using a finer integration grid (120,974).

The predicted highest-lying singlet $Fe_2(BF)_2(CO)_6$ structures, namely **26-7S** with two bridging CO groups and one bridging BF group, lies 26.5 kcal/mol (B3LYP) or 23.0 kcal/mol (BP86) in energy above the global minimum **26-1S**. Structure **26-7S** has a substantial imaginary frequency at $110i$ cm^{-1} (B3LYP) or $109i$ cm^{-1} (BP86). Following the corresponding normal mode leads to **26-3S**. The Fe−Fe distance in **26-7S** is 2.553 Å (B3LYP) and 2.534 Å (BP86), very similar to the Fe−Fe single bond distance in the triply bridged $Fe_2(BF)_2(CO)_7$ structure **27-1S** and suggests only a formal Fe−Fe single bond in **26-7S**. The Fe−O bond distance to the bridging CO group in **26-7S** is 2.622 Å (B3LYP) or 2.706 Å (BP86), suggesting a four electron-donor bridging η^2-μ-CO group. This four-electron donor bridging CO group combined with seven two electron donor CO and BF groups and the Fe−Fe single bond gives

Table 1. Dissociation Energies (kcal/mol) for Successive Removal of Carbonyl and BF Groups from $Fe_2(BF)(CO)_m$ (m = 4, 3) and $Fe_2(BF)_2(CO)_n$ (n = 7, 6) Based on the Lowest Energy Structures[a]

	B3LYP	BP86
$Fe(BF)(CO)_4 \rightarrow Fe(BF)(CO)_3 + CO$	41.1	50.9
$Fe(BF)(CO)_4 \rightarrow Fe(CO)_4 + BF$	59.3[c]	75.8[c]
$Fe(BF)(CO)_3 \rightarrow Fe(BF)(CO)_2 + CO$	34.0	49.5
$Fe(BF)(CO)_3 \rightarrow Fe(CO)_3 + BF$	49.4[c]	62.5[c]
$Fe_2(BF)_2(CO)_7 \rightarrow Fe(BF)_2(CO)_6 + CO$	23.1	29.3
$Fe_2(BF)_2(CO)_7 \rightarrow Fe_2(BF)(CO)_7 + BF$	67.4	72.5
$Fe_2(BF)_2(CO)_6 \rightarrow Fe_2(BF)_2(CO)_5 + CO$	35.4	47.6
$Fe_2(BF)_2(CO)_6 \rightarrow Fe_2(BF)(CO)_6 + BF$	71.4[c]	77.8[c]
$Fe_2(CO)_9 \rightarrow Fe_2(CO)_8 + CO$	29.4[b]	35.1[b]
$Fe_2(CO)_8 \rightarrow Fe_2(CO)_7 + CO$	25.4[b]	37.6[b]
$Fe_2(CS)_2(CO)_7 \rightarrow Fe(CS)_2(CO)_6 + CO$	30.6[b]	35.2[b]
$Fe_2(CS)_2(CO)_6 \rightarrow Fe(CS)_2(CO)_5 + CO$	14.9[b]	24.3[b]

[a] All results reported here refer to the global minima. [b] Dissociation energies of $Fe_2(CS)_2(CO)_m$ and $Fe_2(CO)_n$ are taken from refs 24 and 55. [c] The global minimum structures for $Fe(CO)_4$, $Fe(CO)_3$, $Fe(BF)(CO)_7$, and $Fe_2(BF)(CO)_6$ used to calculate these energies are given in the Supporting Information, Figure S6 and Table S8.

both iron atoms in **26-7S** the favored 18-electron configuration.

The two lowest-lying triplet structures, namely **26-1T** and **26-2T**, found for $Fe_2(BF)_2(CO)_6$, are doubly bridged structures with two bridging BF groups. Structure **26-1T** lies at 7.6 kcal/mol (B3LYP) or 18.7 kcal/mol (BP86) in energy above **26-1S**, whereas structure **26-2T** lies at 10.7 kcal/mol (B3LYP) or 21.5 kcal/mol (BP86) above **26-1S**. The two structures **26-1T** and **26-2T** with two bridging BF groups are similar to structures **26-1S** and **26-2S** in geometry, except for longer Fe−Fe distances in **26-1T** and **26-2T** of 2.61 ± 0.03 Å corresponding to single rather than double bonds. Consequently, the iron atoms in **26-1T** and **26-2T** have 17-electron configurations, consistent with a binuclear triplet structure.

3.3. Dissociation Energies. Table 1 reports the dissociation energies for removing one carbonyl group from the global minima of the mononuclear $Fe(BF)(CO)_m$ and binuclear $Fe_2(BF)_2(CO)_n$ structures according to the following equations:

$$Fe(BF)(CO)_m \rightarrow Fe(BF)(CO)_{m-1} + CO \qquad (m = 4, 3)$$

$$Fe_2(BF)_2(CO)_n \rightarrow Fe_2(BF)_2(CO)_{n-1} + CO \quad (n = 7, 6)$$

In addition, Table 1 also reports the dissociation energies of one BF group from the global minima of the monouclear $Fe(BF)(CO)_m$ (m = 4, 3) and binuclear $Fe_2(BF)_2(CO)_n$ (n = 7, 6) according to the following equations:

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

$$Fe_2(BF)_2(CO)_n \rightarrow Fe_2(BF)(CO)_n + BF \qquad (n = 7, 6)$$

For comparison, the experimental dissociation energies[54] for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.

Table 1 shows that our theoretical result for the loss of one CO group from mononuclear $Fe(BF)(CO)_4$ is very close to the experimental CO dissociation energy[54] for $Fe(CO)_5$. However, the dissociation energy of $Fe(BF)(CO)_3$ is larger than the experimental value for $Ni(CO)_4$.

Table 1 also shows that the dissociation energies of one BF group from the $Fe(BF)(CO)_m$ (m = 4, 3) and $Fe_2(BF)_2(CO)_n$ (n = 7, 6) are much larger than the corresponding dissociation energies of one CO group. This indicates that the bonding ability of BF group to Fe is stronger than that of CO group to Fe, consistent with the reported results on other borylene complexes.[14,22] The CO dissociation energy of binuclear $Fe_2(BF)_2(CO)_7$ is predicted to be slightly smaller than those of the analogous compounds[24,55] $Fe_2(CS)_2(CO)_7$ and $Fe_2(CO)_9$, while that of the unsaturated derivative $Fe_2(BF)_2(CO)_6$ is significantly larger than those of analogous compounds $Fe_2(CS)_2(CO)_6$ or $Fe_2(CO)_8$.

Table 2 reports the dissociation energies of the binuclear $Fe_2(BF)_2(CO)_n$ into mononuclear fragments by the following reactions:

$$Fe_2(BF)_2(CO)_n \rightarrow Fe(BF)(CO)_x + Fe(BF)(CO)_y$$
$$(n = x + y)$$

The dissociation energies of $Fe_2(BF)_2(CO)_n$ (n = 7, 6) are obviously larger than those of $Fe_2(CS)_2(CO)_n$ (n = 7, 6) and $Fe_2(CO)_n$ (n = 9, 8). Experiments have shown that many aspects of the chemistry of $Fe_2(CO)_9$ are related to facile rupture of the iron−iron bond to give stable relatively unreactive $Fe(CO)_5$ and an unsaturated reactive $Fe(CO)_4$ fragment.[56] However, the energy required for dissociation of $Fe_2(BF)_2(CO)_7$ into $Fe(BF)(CO)_4$ + $Fe(BF)(CO)_3$ is much larger than that of $Fe_2(CO)_9$ into $Fe(CO)_5$ + $Fe(CO)_4$. Thus decarbonylation of $Fe_2(BF)_2(CO)_7$ to give $Fe_2(BF)_2(CO)_6$ + CO is favored greatly over dissociation of $Fe_2(BF)_2(CO)_7$ into the mononuclear $Fe(BF)(CO)_4$ and $Fe(BF)(CO)_3$ fragments, in contrast to $Fe_2(CO)_9$ chemistry.

3.4. Vibrational Frequencies. The predicted ν(CO) and ν(BF) frequencies for the optimized structures for $Fe(BF)(CO)_n$ (n = 4, 3), $Fe_2(BF)(CO)_8$, and $Fe_2(BF)_2(CO)_n$ (n = 7, 6) using the BP86 method are listed in Tables 3 and 4, which has been shown to be more reliable for ν(CO) frequencies than the B3LYP method.[57,58] From these Tables it can be seen that for all of the fluoroborylene iron carbonyls, $Fe(BF)(CO)_n$, $Fe_2(BF)(CO)_8$, and $Fe_2(BF)_2(CO)_n$, the terminal ν(CO) frequencies fall in the range 2080 to 1939 cm^{-1}. All of these terminal ν(CO) frequencies are below the ν(CO) frequency for free CO. Furthermore, the ν(CO) frequencies predicted for $Fe(BF)(CO)_4$ are 10 ± 5 cm^{-1} lower than the corresponding ν(CO) frequencies for the analogous $Fe(CS)(CO)_4$ structures.[24] This implies that the terminal BF ligand is a slightly weaker π-acceptor than the terminal CS ligand. For the bridging CO groups in the binuclear

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Table 2. Dissociation Energies ($D_{\mathrm{Fe-Fe}}$, in kcal/mol) of the Binuclear Complexes $Fe_2(BF)_2(CO)_n$ into Two Mononuclear Fragments[a,b]

		B3LYP		BP86	
reaction	bridging groups	$D_{\mathrm{Fe-Fe}}$	$R_{\mathrm{Fe-Fe}}$	$D_{\mathrm{Fe-Fe}}$	$R_{\mathrm{Fe-Fe}}$
$Fe_2(BF)_2(CO)_7 \rightarrow Fe(BF)(CO)_4 + Fe(BF)(CO)_3$	di-μ-BF, μ-CO	45.8	2.545	60.6	2.540
$Fe_2(BF)_2(CO)_6 \rightarrow 2\ Fe(BF)(CO)_3$	di-μ-BF	63.7	2.492	82.1	2.471
$Fe_2(BF)_2(CO)_6 \rightarrow Fe(BF)(CO)_4 + Fe(BF)(CO)_2$		56.6		80.7	
$Fe_2(CS)_2(CO)_7 \rightarrow Fe(CS)(CO)_4 + Fe(CS)(CO)_3$	di-μ-CS, μ-CO	24.9	2.494	36.8	2.491
$Fe_2(CS)_2(CO)_6 \rightarrow 2\ Fe(CS)(CO)_3$	μ-CS,η^2-μ-CS	44.9	2.503	57.1	2.462
$Fe_2(CS)_2(CO)_6 \rightarrow Fe(CS)(CO)_4 + Fe(CS)(CO)_2$		42.4		56.0	
$Fe_2(CO)_9 \rightarrow Fe(CO)_5 + Fe(CO)_4$	tri-μ-CO	4.6	2.525	28.3	2.519
$Fe_2(CO)_8 \rightarrow 2Fe(CO)_4$	di-μ-CO	9.0	2.443	43.0	2.447
$Fe_2(CO)_8 \rightarrow Fe(CO)_5 + Fe(CO)_3$		8.4		35.1	

[a] The related structures here refer to the lowest-energy structures. Dissociation energies of $Fe_2(CS)_2(CO)_n$ and $Fe_2(CO)_n$ are from refs 24 and 55. [b] The global minimum structure **12-1T** for the highly unsaturated $Fe(BF)(CO)_2$ complex can be found in Supporting Information. The Fe−Fe distances ($R_{\mathrm{Fe-Fe}}$ in Å) are listed as well.

Table 3. ν(CO) and ν(BF) Stretching Frequencies (cm^{-1}) and the Infrared Intensities (in km/mol, in parentheses) for $Fe(BF)(CO)_n$ (n = 4, 3) Derivatives Predicted by the BP86 Method

	ν(CO)	ν(BF)[a]
14-1S (C_{2v})	2060(113),2000(293),1993(1011),1984(1310),	1465(628)
$Fe(CS)(CO)_4$ (C_{2v})	2070 (191), 2008 (331), 2008 (1239), 1990 (1047)	
14-2S (C_{3v})	2058(211),2003(390), 1978(1116),1978(1116),	1497(564)
$Fe(CS)(CO)_4$ (C_{3v})	2063(346),2010(367),1991(1067),1991(1067)	
14-3S (C_{4v})	2065(132), 1996(0),1989(1269),1989(1269)	1447(619)
13-1T (C_s)	2013(97), 1963(738),1957(1489)	1441(510)
13-2T (C_s)	2025(251), 1970(558),1951(1496)	1450(637)
13-1S (C_s)	2024(72), 1963(790),1950(1439)	1468(555)
13-2S (C_{3v})	2008(23), 1943(1133),1943(1133),	1513(430)

[a] For comparison, the corresponding stretching frequencies of free BF, CO, and CS from the BP86 method are 1314 cm^{-1}, 2091 cm^{-1}, and 1238 cm^{-1}, respectively.

Table 4. ν(CO) and ν(BF) Stretching Frequencies (cm^{-1}) and the Infrared Intensities (in km/mol, in parentheses) for the Binuclear $Fe_2(BF)(CO)_8$ and $(Fe_2(BF)_2(CO)_n$ (n = 7, 6) Derivatives Predicted by the BP86 Method[a]

	ν(CO)	ν(BF)
28-1S (**C_2**)	2073(18), 2030(1669), 2006(1325), 2002(6), 1999(1433), 1997(65), 1941(201), 1939(598)	**1341(389)**
28-2S (**C_{2v}**)	2082(19), 2035(1308), 2017(761), 2007(1989), 1998(651), 1996(139), 1985(146), 1974(0)	**1312(401)**
28-3S(**C_{2v}**)	2071(16), 2032(1646), 2010(1335), 2005(25), 2002(1366),1997(0), **1890(226)**,**1872(692)**	**1362(415)**
27-1S (**C_{2v}**)	2063(14),2027(1548), 2005(1452), 2000(0), 1998(1340), 1993(17), **1888(445)**	**1363(280), 1349(555)**
27-2S (**C_s**)	2080(140), 2023(573), 2015(700), 2013(1393), 2011(1001), 1978(548), 1966(420)	**1360(177), 1335(560)**
26-1S (**C_{2h}**)	2055(0), 2020(1660), 1994(1314), 1991(1776), 1991(0), 1987(0)	**1340(0), 1325(660)**
26-2S (**C_{2v}**)	2053(17), 2019(1541), 1994(1480), 1992(1349), 1988(0), 1982(271)	**1341(10), 1323(644)**
26-1T (**C_{2v}**)	2042(0), 1999(1990), 1987(1481), 1982(1450), 1980(0), 1974(8)	**1346(56), 1326(666)**
26-2T (**C_{2h}**)	2041(0), 1993(2431), 1986(1469), 1982(1344), 1981(0), 1979(0)	**1337(0), 1317(665)**

[a] The bridging ν(CO) and ν(BF) frequencies are in **bold face**.

fluoroborylene iron carbonyls, the bridging ν(CO) frequencies are predicted to fall in the range of 1890 to 1872 cm^{-1}. The lower bridging ν(CO) frequencies relative to terminal ν(CO) frequencies is a typical feature of metal carbonyl chemistry. It relates to the lower C=O bond order in the carbonyl group when bonded to two metal atoms rather than a single metal atom.

The terminal ν(BF) frequencies in the fluoroborylene iron carbonyls are predicted to fall in the range 1513 to 1441 cm^{-1}. These terminal ν(BF) frequencies are appreciably higher than the predicted ν(BF) frequency of 1314 cm^{-1} for free BF in contrast to the situation with terminal ν(CO) frequencies relative to the ν(CO) frequency of free CO. This suggests that the effect of Fe→B π back-bonding to the BF ligand on the B−F bond is very different than the effect of the well-known Fe→C π-back-bonding to the CO ligand on the C−O bond.

The ν(BF) frequencies for the bridging BF groups are significantly lower, in the range 1363 to 1317 cm^{-1}. In this respect BF groups are completely analogous to CO groups in that the bridging ν(BF) frequencies are 100 to 150 cm^{-1} lower than the terminal ν(BF) frequencies in similar types of compounds.

4. Discussion

4.1. Mononuclear Structures. The CS and BF ligands might be expected *a priori* to be similar ligands. Both are formal two-electron donors with strong π-acceptor properties similar to CO. Comparison of the ν(CO) frequencies predicted for $Fe(CS)(CO)_4$ and $Fe(BF)(CO)_4$ using the same DFT method (BP86) and basis set (Table 3) indicates that the terminal BF ligand is only a slightly weaker π-acceptor than the very strong π-acceptor CS ligand. The mononuclear $Fe(BF)(CO)_4$ and $Fe(CS)(CO)_4$ are predicted to be very similar in that the two possible trigonal bipyramidal structures, namely, structures with the unique ligand (BF or CS) in the axial or equatorial positions, are of nearly the same energy within ~1 kcal/mol. For the experimentally known thiocarbonyl $Fe(CS)(CO)_4$, this has been verified by the spectroscopic detection of two isomers in solution.[59]

For the unsaturated $Fe(BF)(CO)_3$, the two singlet structures **13-1S** and **13-2S** are slightly lower in energy than the triplet structures by the more reliable BP86 method.[44−46] Structures **13-1S** and **13-2S** may be derived by removal of a CO group from the equatorial and axial positions, respectively, of a trigonal pyramidal $Fe(BF)(CO)_4$ structure. Further removal of CO groups in various ways from an original trigonal bipyramidal $Fe(BF)(CO)_4$ structure can lead to the more highly unsaturated structures $Fe(BF)(CO)_n$ (n = 2, 1) predicted from this theoretical study (See Supporting Information, Figures S1 and S2).

4.2. Binuclear Structures. The lowest lying $Fe_2(BF)(CO)_8$ structure **28-1S** (Figure 3) is a singly bridged structure in which the bridging ligand is a BF group rather than a CO group. Structure **28-1S** is thus analogous to the experimental known singly bridged structure of $Os_2(CO)_9$.[61] The triply bridged structure **28-3S** (Figure 3), with two bridging CO groups and one bridging BF group, is analogous to the experimentally known[53] $Fe_2(CO)_6(\mu\text{-}CO)_3$ structure.

The lowest energy $Fe_2(BF)_2(CO)_7$ structure **27-1S** (Figure 4) is a triply bridged structure analogous to the experimentally known[53] structure for $Fe_2(CO)_9$ but with both BF groups in bridging positions in addition to one of the CO groups. The closely related triply bridged $Fe_2(BF)_2(CO)_7$ structure **27-7S** (Figure 4), with only one bridging BF group and two bridging CO groups, lies much higher in energy at ~27 kcal/mol above **27-1S**. The predicted triply bridged Fe−Fe single bond distances in **27-1S** and **27-7S** of ~2.53 Å are essentially identical to the experimental triply bridged Fe−Fe distance of 2.52 Å in the parent $Fe_2(CO)_9$ found by X-ray crystallography.[53]

Singly bridged $Fe_2(BF)_2(CO)_7$ structures, namely, **27-3S** and **27-4S** (Figure 4), are also found for $Fe_2(BF)_2(CO)_7$ but at energies at least 12 kcal/mol above the global minimum **27-1S**. These two singly bridged $Fe_2(BF)_2(CO)_7$ structures are closely related to the experimentally known[60,61] singly bridged structure for the isoelectronic $Os_2(CO)_9$.

A characteristic feature of the chemistry of $Fe_2(CO)_9$ is its easy dissociation into stable $Fe(CO)_5$ and a reactive coordinatively unsaturated $Fe(CO)_4$ fragment.[56] This makes $Fe_2(CO)_9$ a useful precursor for the synthesis of $LFe(CO)_4$ derivatives under mild conditions. This reactivity pattern of $Fe_2(CO)_9$ is supported by a relatively low predicted energy[24] of 4.6 kcal/mol (B3LYP) or 28.3 kcal/mol (BP86) for the dissociation of $Fe_2(CO)_9$ into $Fe(CO)_5$ + $Fe(CO)_4$ (Table 2). An analogous reactivity pattern for $Fe_2(BF)_2(CO)_7$ is not indicated by these theoretical studies since the predicted energy for the dissociation of $Fe_2(BF)_2(CO)_7$ into $Fe(BF)(CO)_4$ + $Fe(BF)(CO)_3$ is much higher at 45.8 kcal/mol (B3LYP) or 60.6 kcal/mol (BP86). The greater ability of a bridging BF group relative to a CO group to stabilize a bimetallic system is indicated by the recent discovery[11] of the stable $Cp_2Ru_2(CO)_4(\mu\text{-}BF)$, in which a pair of ruthenium atoms is linked by a bridging BF group without an accompanying Ru−Ru bond. The completely analogous cyclopentadienylruthenium carbonyl $Cp_2Ru_2(CO)_4(\mu\text{-}CO)$ (i.e, $Cp_2Ru_2(CO)_5$) is not known as a stable compound. The known stable cyclopentadienylruthenium carbonyl $Cp_2Ru_2(CO)_4$ has not only two bridging CO groups but also a Ru−Ru bond holding both halves of the molecular together.

The unsaturated binuclear derivative $Fe_2(BF)_2(CO)_6$ was found to have a complicated potential energy surface with 11 structures within 30 kcal/mol of the global minimum **26-1S** (Supporting Information, Table S7 and Figure S5 and Figure 5). The two lowest energy $Fe_2(BF)_2(CO)_6$ structures, namely, **26-1S** and **26-2S** (Figure 5) are predicted to be doubly bridged structures with two bridging BF groups and a short enough Fe=Fe distance for the formal double bond required to give both iron atoms the favored 18-electron configuration. A similar doubly bridged structure was previously[55] predicted for the parent $Fe_2(CO)_8$ using DFT. The predicted Fe=Fe double bond distance of ~2.47 Å in **26-1S** and **26-2S** is close to the previously predicted Fe=Fe double bond distance of ~2.48 Å for the doubly bridged $Fe_2(CO)_6(\mu\text{-}CO)_2$ structures using the same DFT method.

The other $Fe_2(BF)_2(CO)_6$ structures lie at least 10 kcal/mol in energy above the two lowest lying doubly BF-bridged $Fe_2(BF)_2(CO)_6$ structures **26-1S** and **26-2S**. This provides further evidence for BF groups being favored over CO groups as bridges in binuclear transition metal chemistry. In addition, no $Fe_2(BF)_2(CO)_6$ structures were found with short enough Fe−F distances to indicate four-electron donor η^2-μ-BF ligands analogous to η^2-μ-CO ligands found in a few unsaturated binuclear metal carbonyl derivatives. This contrasts with the analogous thiocarbonyl $Fe_2(CS)_2(CO)_6$ for which structures with four-electron donor bridging η^2-CS groups and thus short Fe−S distances and a formal Fe−Fe single bond are energetically favored over structures with exclusively two-electron donor CS (and CO) groups and a formal Fe=Fe double bond. However, a relatively high energy $Fe_2(BF)_2(CO)_6$ structure **26-7S** (Figure 5) with two bridging BF groups and a four-electron donor bridging η^2-μ-CO group with a short Fe−O distance of ~2.66 Å is found at ~25 kcal/mol above **26-1S**. In **26-7S** the Fe−Fe bond distance of ~2.54 Å is essentially identical to the experimental 2.52 Å Fe−Fe bond distance[56] in $Fe_2(CO)_9$, therefore confirming the formal single bond in **26-7S** required to give both iron atoms the favored 18-electron configuration. Structure **26-7S** was found to be not a genuine minimum but a transition state with a significant imaginary vibrational frequency at ~110 i cm^{-1}. Following the corresponding normal mode leads to structure **26-3S** (Figure 5) in which the four-electron donor bridging η^2-μ-CO group becomes a normal two-electron bridging CO group, with concurrent shortening of the iron−iron

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bond from a single bond distance to a double bond distance to maintain the favored 18-electron configuration of the iron atom.

4.3. Comparison of the BF, CO, and CS Ligands in Binuclear Iron Carbonyl Derivatives. Recent studies have shown that the borylene ligands in multinuclear transition metal complexes are very flexible varying from terminal to bridging two or three metal atoms.[20,21,62,63] Bridging borylene ligands can also have a significant effect on the metal−metal bond being bridged.[22,23] The results from this research on $Fe_2(BF)_2(CO)_n$ derivatives combined with previous studies on $Fe_2(CS)(CO)_n$ derivatives using analogous theoretical methods[24] demonstrate some important differences between the isovalent two-atom CO, CS, and BF ligands. This is seen at least in binuclear iron carbonyl complexes and presumably, by generalization, in other binuclear metal complexes. These differences relate to the relative tendencies for these isoelectronic XY ligands to bridge two metal atoms and to form four-electron donor η^2-μ-XY bridging groups.

The relative tendency of these three XY ligands to function as bridges between two metal atoms increases in the sequence CO < CS ~ BF. Thus, in the lowest energy structures of the $Fe_2(XY)_2(CO)_n$ complexes, the CS or BF ligand appears in the bridging positions in preference to the CO ligands. For example, in this research the lowest energy $Fe_2(BF)_2(CO)_7$ and $Fe_2(BF)_2(CO)_6$ structures (**27-1S** and **26-1S**, respectively) have both BF ligands in bridging positions. However, a direct comparison between CS and BF as bridging ligands is not yet possible since no $Fe_2(CS)_x(BF)_y(CO)_z$ complexes have yet been studied. The instability of both CS and BF as free ligands is likely to make the synthesis of complexes containing both CS and BF groups difficult, thereby discouraging experimental studies on such systems.

The great tendency of BF to serve as a bridge between two metal atoms is also indicated by the structure of the recently (2009) reported[8] $Cp_2Ru_2(CO)_4(\mu\text{-BF})$, which contains a bridging BF group between the two ruthenium atoms without an accompanying ruthenium−ruthenium bond. By contrast, similar metal carbonyl complexes containing a bridging carbonyl group without an accompanying metal−metal bond are essentially non-existent. In other words, a pair of metal atoms bridged by a carbonyl group is accompanied by a formal bond between the same pair of metal atoms as indicated by a short metal−metal distance. The ruthenium derivative $Cp_2Ru_2(CO)_4(\mu\text{-BF})$ (= $[CpRu(CO)_2]_2BF$) can be regarded as a derivative of BF_3 in which two of the fluorine atoms have been replaced by $CpRu(CO)_2$ groups. The ruthenium atoms in such a $[CpRu(CO)_2]_2BF$ structure already have the favored 18-electron configuration, without requiring a metal−metal bond.

The other major difference between the three XY ligands is their ability to function as four-electron donor bridging η^2-μ-XY groups, which clearly increases in the sequence BF < CO < CS. Thus no evidence was obtained in this work for any four-electron donor bridging η^2-μ-BF groups, even among the higher energy structures of the unsaturated $Fe_2(BF)_2(CO)_6$ (Figure 5). However, the $Fe_2(BF)_2(CO)_6$ structure **26-7S** (Figure 5) contains a four-electron donor bridging η^2-μ-CO group. In the unsaturated iron thiocarbonyl derivatives $Fe_2(CS)_2(CO)_n$ (n = 6, 5, 4) the structures with four-electron donor η^2-μ-CS groups and formal Fe−Fe single bonds are energetically preferred over structures with only two-electron donor CS and CO ligands and iron−iron multiple bonds.[24]

For an XY ligand to function as a four-electron donor bridging η^2-μ-XY group both the X atom (C or B) and the Y atom (O, S, or F) must be involved in the bonding to the pair of transition metals being bridged. However, in the BF ligand the electron deficiency of the boron atom withdraws sufficient electron density from the fluorine atom so that the fluorine atom cannot become involved in direct bonding to a metal atom. This can account for the reluctance of the BF ligand to function as a four-electron donor bridging η^2-μ-BF ligand in the binuclear iron carbonyl complexes studied in this research.

5. Conclusion

The iron carbonyl fluoroborylene complexes $Fe(BF)(CO)_n$ (n = 4, 3) and $Fe_2(BF)_2(CO)_n$ (n = 7, 6) have been compared with the isoelectronic $Fe(CO)_{n+1}$ and $Fe_2(CO)_{n+2}$, as well as the thiocarbonyls $Fe(CS)(CO)_n$ and $Fe_2(CS)_2(CO)_n$, using two density functional methods. For $Fe(BF)(CO)_4$ the axially and equatorially substituted trigonal bipyramidal structures are predicted to be nearly degenerate as for $Fe(CS)(CO)_4$. The lowest energy structures for $Fe(BF)(CO)_3$ are derived from the trigonal bipyramidal $Fe(BF)(CO)_4$ structures by removal of CO groups. The binuclear derivatives $Fe_2(BF)_2(CO)_n$ (n = 7, 6) prefer energetically to have structures with BF bridges rather than structures with CO bridges. However, for the unsaturated $Fe_2(BF)_2(CO)_6$, no structures are found with four-electron donor η^2-μ-BF groups. This differs from the corresponding $Fe_2(CS)_2(CO)_6$ where structures with η^2-μ-CS groups and formal Fe−Fe single bonds are energetically preferred over structures with only two electron donor CO and CS groups and formal Fe=Fe double bonds.

The lowest energy structure for $Fe_2(BF)_2(CO)_7$ is predicted to be similar to the well-known triply bridged $Fe_2(CO)_9$ structure[53] but with two bridging BF groups and one bridging CO group. However, the dissociation energy of $Fe_2(BF)_2(CO)_7$ into mononuclear fragments is much higher than that of $Fe_2(CO)_9$. Removal of the bridging CO group from this lowest energy triply bridged $Fe_2(BF)_2(CO)_7$ structure leads to the doubly BF-bridged global minimum structure for $Fe_2(BF)_2(CO)_6$.

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Supporting Information Available: Figures S1−S6 and Tables S1−S59 and the complete Gaussian 03 reference (reference 52). This material is available free of charge via the Internet at http://pubs.acs.org.

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