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# Unsaturation in Binuclear Iron Carbonyl Complexes of the Split (3 + 2) Five-electron Donor Hydrocarbon Ligand Bicyclo[3.2.1]octa-2,6-dien-4-yl (bcod): Role of Agostic Hydrogen Atoms

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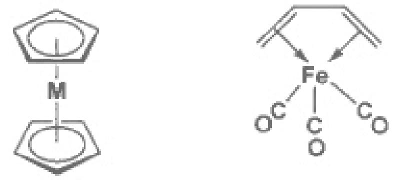
# Abstract

The experimentally known split (3 + 2) five-electron donor bicyclo[3.2.1]-octa-2,6-dien-4-yl (bcod) ligand provides a flexible alternative to the rigid planar cyclopentadienyl (Cp) ligand. In this connection the structures and energetics of the binuclear iron carbonyl complexes $(bcod)_2Fe_2(CO)_n$ ($n$ = 4, 3, 2, 1) have been investigated by density functional theory for comparison with the corresponding $Cp_2Fe_2(CO)_n$ derivatives. The *cis* and *trans* doubly CO-bridged $(bcod)_2Fe_2(\mu\text{-}CO)_2(CO)_2$ structures are the lowest energy tetracarbonyl structures, similar to the $Cp_2Fe_2(CO)_4$ system. However, an unbridged $(bcod)_2Fe_2(CO)_4$ isomer lies only ~1 kcal/mol in energy above the doubly bridged isomers. The flexibility of the bcod ligand leads to low-energy singlet and triplet spin state structures with agostic hydrogen atoms for the unsaturated $(bcod)_2Fe_2(CO)_n$ ($n$ = 3, 2, 1) systems. Analogous structures are not found in the corresponding $Cp_2Fe_2(CO)_n$ systems with the rigid cyclopentadienyl ligand. Such structures, effectively involving donation of an electron pair from an olefinic C–H bond to an iron atom through 3-center 2-electron C-H-Fe bonding, are energetically competitive with isomeric structures with metal-metal multiple bonds.

# 1. Introduction

Two of the iconic molecules in organometallic chemistry are ferrocene and butadieneiron tricarbonyl (Figure 1). The serendipitous discovery of ferrocene by two independent research groups in 1951[1,2] and the subsequent elucidation of its sandwich structure by X-ray crystallography[3] demonstrated for the first time that a planar cyclopentadienyl ring could bond through all of its carbon atoms so that a neutral $C_5H_5$ unit can be considered as a formal five-electron donor. The discovery of butadiene iron tricarbonyl in 1930 by Reihlen and coworkers[4] predates the discovery of ferrocene by approximately two decades. However, the nature of butadiene iron tricarbonyl was elucidated by Hallam and Pauson in 1958[5] only after the discovery of ferrocene. Its structure with the butadiene ligand complexed to the central iron atom through all four carbon atoms was subsequently established by Mills and Robinson in 1963.[6] The structural feature common to both ferrocene and butadiene iron tricarbonyl is the connected set formed by the group of ligand carbon atoms bonded to the central iron atom, namely a closed ring in ferrocene and a pair of conjugated double bonds in butadiene iron tricarbonyl.

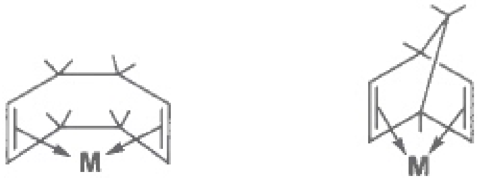


$(\eta^5\text{-}C_5H_5)_2Fe$ $(\eta^4\text{-}C_4H_6)Fe(CO)_3$

**Figure 1.** The structures of ferrocene and butadiene iron tricarbonyl.

The subsequent development of the chemistry of metal complexes of diolefins led to the discovery of two types of complexes, namely those of conjugated diolefins such as butadiene where the two ligating C=C double bonds form a connected set and those of non-conjugated diolefins such as 1,5-cyclooctadiene and norbornadiene where the two ligating C=C double bonds are separated by atoms not within bonding distance of the central metal atom (Figure 2). The development of the chemistry of metal complexes of non-conjugated diolefins was facilitated by the ready availability of two important chelating diolefins, namely 1,5-cyclooctadiene obtained from the metal-catalyzed dimerization of butadiene and norbornadiene obtained from the Diels-Alder reaction of cyclopentadiene with acetylene.

In metal complexes of non-conjugated diolefins the donation of the four electrons from the neutral ligands is split into two separate two-electron donor units, namely the two C=C double bonds isolated from each other through various types of saturated bridging units. Thus in 1,5-cyclooctadiene, the two C=C double bonds are separated by two electronically inactive $-CH_2CH_2-$ bridges (Figure 2). Norbornadiene has a non-bonded pair of saturated carbon atoms bridged by three different moieties. Two of these are –C=C– units thereby providing the two double bonds for complexation with transition metals. The third bridging unit is an electronically inactive –$CH_2$– unit.



**1,5-cyclooctadiene** **norbornadiene**

**Figure 2.** The non-conjugated chelating diolefin ligands 1,5-cyclooctadiene and norbornadiene.

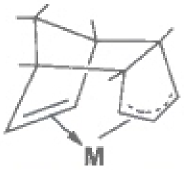
In contrast to the metal coordination chemistry of non-conjugated diolefins, such as 1,5-cyclooctadiene and norbornadiene, in which the four electrons from the ligand to the metal come from split (2 + 2) π-donation of the two isolated C=C double bonds, neutral ligands providing split (3 + 2) π-donation of five electrons to the metal atom are much less accessible. However, such ligands are of interest since they provide more flexibility than the rigid planar cyclopentadienyl ligand or even the acyclic pentadienyl ligand as a means of formally donating five electrons to a central transition metal. These split (3 + 2) five-electron donor ligands may be regarded as homoaromatic analogues of the aromatic cyclopentadienyl anion.[11,7]

The key paper on the chemistry of metal complexes of (3 + 2) split five-electron donor ligands was published by Köhler and coworkers in 1993.[8] They consider three such ligands related to the norbornadiene ligand but with one of the norbornadiene C=C double bonds replaced by an allylic bridge of three carbon atoms (Figure 3). Their bicyclo[3.2.1]octa-2,6-dien-4-yl ligand, abbreviated as bcod, is a direct analogue of norbornadiene with one C=C double bond replaced by a three-carbon allylic unit. Their bicyclo[3.2.1]nona-2,6,8-trien-4-yl ligand, abbreviated as bcnt, is related to bcod by replacing the –$CH_2$– bridge with a –C=C– bridge. They also included the tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dien-5-yl (dicp) ligand in their studies because of its accessibility from dicyclopentadiene. The first metal complexes of the (3 + 2) split five-electron donor ligands to be synthesized were the ferrocene analogues $(bcnt)_2Fe$ and $(dicp)_2Fe$.[9,10] However, the development of the chemistry of (3 + 2) split five-electron donor ligands is limited by the stability of the free ligands as well as the difficulties in their syntheses. Thus the bcnt ligand is subject to rearrangement to barbaralane[11,12] and the dicp ligand is prone to revert to a cyclopentadienyl ligand by a retro-Diels-Alder reaction.[10] In addition, the inherent low symmetry of the metal complexes leads to high solubility in organic solvents and difficulty in isolating crystalline products. Recently bicyclo[3.2.1]octa-3,6-dien-2-yl core structures have also attracted considerable attention for studying bishomoaromaticity and bishomoantiaromaticity owing to their unique structures.[13,14]

Since the monoanions of these ligands were used to synthesize their metal complexes, Köhler and coworkers considered them as (4 + 2) split six-electron donor monoanions. However, here we find it less confusing to do electron bookkeeping of transition metal organometallic complexes considering all ligands as neutral species. Therefore in this research we consider such ligands equivalently as (3 + 2) split five-electron donor neutral ligands. Also we abbreviate these cumbersomely named ligands in chemical formulas with lower case letters to avoid confusion since, for example, each letter in an upper case BCOD abbreviation is the chemical symbol of an element or isotope frequently found in chemical formulas.

**bicyclo[3.2.1]octa-2,6-dien-4-yl (bcod)**

**bicyclo[3.2.1]nona-2,6,8-trienyl (bcnt)**



**tricyclo[5.2.1.0$^{2,6}$]deca-3,8-dien-5-yl (dicp)**

**Figure 3**.The (3 + 2) split five-electron donor ligands studied by Köhler and coworkers.[8]

Most of the transition metal complexes of the (3 + 2) split five-electron donor neutral ligands synthesized by Köhler and coworkers are analogues of first row transition metal metallocenes.[11,8] These included the homoleptic derivatives $(\eta^{3,2}\text{-bcod})_2\text{Fe}$, $(\eta^{3,2}\text{-bcnt})_2\text{Fe}$, and $(\eta^{3,2}\text{-bcod})_2\text{Cr}$ containing two equivalent five-electron donor ligands. The structure of the ferrocene analogue $(\eta^{3,2}\text{-bcod})_2\text{Fe}$ was confirmed by X-ray crystallography, thereby establishing the (3 + 2) split five-electron donor donation of the bcod ligand. In addition the mixed sandwich compounds $(\eta^{3,2}\text{-bcod})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, $(\eta^{3,2}\text{-bcnt})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, and $(\eta^{3,2}\text{-bcod})\text{Ni}(\eta^5\text{-C}_5\text{Me}_5)$ were also synthesized by Köhler and coworkers. The metal carbonyl derivative $(\eta^{3,2}\text{-bcnt})\text{Mn(CO)}_3$ was obtained as an inseparable mixture with $\text{Mn}_2\text{(CO)}_{10}$.

A special question of interest is how might the chemistry of these (3 + 2) split five-electron donor ligands differ from that of the five-electron donor cyclopentadienyl ligand. More specifically, splitting the ligand sites providing a net total of five electrons to the transition metal atom should provide more flexibility in coordination modes than the rigid planar pentagonal cyclopentadienyl ligand. The iron carbonyl system is of particular interest because of the richness of the iron carbonyl chemistry of the cyclopentadienyl ligand, as summarized below. In addition, reactions of the readily available $Fe(CO)_4I_2$ with lithium, tin, or zinc derivatives of the (3 + 2) split five-electron donor ligands (generically abbreviated as Q) provide entries into their iron carbonyl chemistry through $QFe(CO)_2I$ derivatives.

The key species in cyclopentadienyliron carbonyl chemistry is the binuclear complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$, readily obtainable in quantity from the thermal reaction of $Fe(CO)_5$ with dicyclopentadiene (Figure 4).[15,16,17] Both *trans* and *cis* isomers have been separated and shown by X-ray crystallography to have two bridging carbonyl groups and Fe–Fe bonds of length 2.54 Å thereby giving each iron atom the favored 18-electron configuration. Photolysis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ can lead to homolysis of the Fe–Fe bond to form two $(\eta^5\text{-}C_5H_5)Fe(CO)_2\bullet$ radicals[18,19] or loss of a carbonyl group with retention of the iron-iron bond to give the unsaturated derivative $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$.[20,21,22] The corresponding permethylated derivative $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$ was shown by X-ray diffraction to have three bridging CO groups and an iron-iron distance of 2.265 Å, consistent with the Fe=Fe formal double bond required to give each iron atom an 18-electron noble gas configuration.[23] However, $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$ is paramagnetic with a triplet ground state implying that the Fe=Fe double bond is of the $\sigma + \frac{2}{2}\pi$ type with unpaired electrons in two orthogonal one-electron π-bonds similar to the O=O double bond in triplet $O_2$ rather than the C=C double bond in singlet ethylene. The photochemical decarbonylation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ in a low-temperature matrix[24] can proceed further to give $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$, which was suggested to contain an unbridged Fe≡Fe triple bond on the basis of its ν(CO) frequencies.[25] A similar unsaturated species $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$ is a likely intermediate in the preparation of the very stable tetramer $(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4$ by the pyrolysis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ in a solvent such as toluene.[26] In addition to these experimental results, the $Cp_2Fe_2(CO)_n$ ($n$ = 4, 3, 2, 1) molecules have been the subject of extensive theoretical study using density functional methods.[27]

This paper describes our theoretical studies on the binuclear iron carbonyl derivatives of the bcod ligand $(bcod)_2Fe_2(CO)_n$ ($n$ = 4, 3, 2). In general, unsaturation in binuclear metal carbonyl derivatives can be accommodated by formation of metal-metal double or triple bonds such as those found in the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_n$ systems discussed above. Conversion of a two-electron donor bridging CO group to a four-electron donor $\eta^2\text{-}\mu\text{-}CO$ ligand bonding to the $M_2$ unit through oxygen as well as carbon is another possibility. However, such four-electron donor $\eta^2\text{-}\mu\text{-}CO$ groups generally require metals more oxophilic than iron and thus to the left of iron in the

Periodic Table, i. e., from groups 4 to 7. The unsaturated $(bcod)_2Fe_2(CO)_n$ ($n = 3, 2, 1$) derivatives introduced in this paper are found to exemplify a new way of accommodating unsaturation in binuclear metal carbonyl derivatives, namely by an agostic hydrogen atom within bonding distance of a metal atom coming from a hydrocarbon ligand (Figure 5). In this way a C–H two-center two-electron bond in the hydrocarbon ligand becomes a C–H–M three-center two-electron bond in its metal complex. This results in the effective donation of the electron pair in the ligand C–H bond to the central $M_2$ unit thereby compensating for the loss of a CO group in an unsaturated binuclear metal carbonyl derivative. Such agostic C–H–M hydrogen bonding is feasible for the flexible (3 + 2) split five-electron donor bcod ligand, but not for the rigid five-electron donor cyclopentadienyl ligand. Furthermore, such agostic interactions are potentially useful in protecting active metal sites involved in diverse types of metal-catalyzed reactions. Supplementing the (3 + 2) split donation of a ligand such as bcod with bonding of one of its hydrogens to a metal atom as an agostic hydrogen makes a neutral bcod ligand an effective donor of seven electrons to a pair of metal atoms.

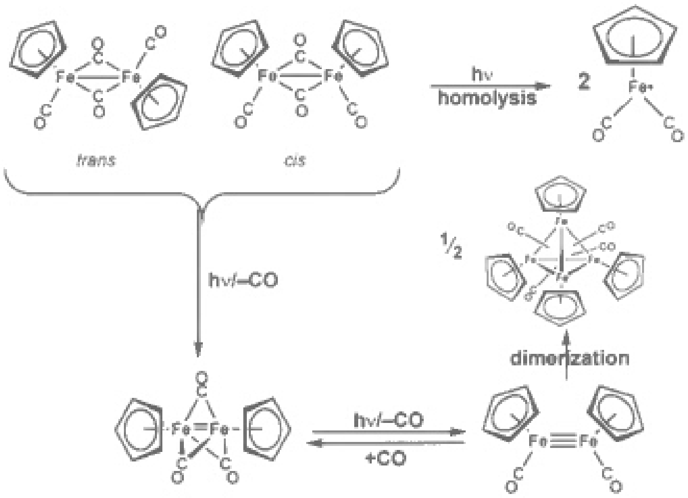


**Figure 4.** Processes involved in the decarbonylation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$.

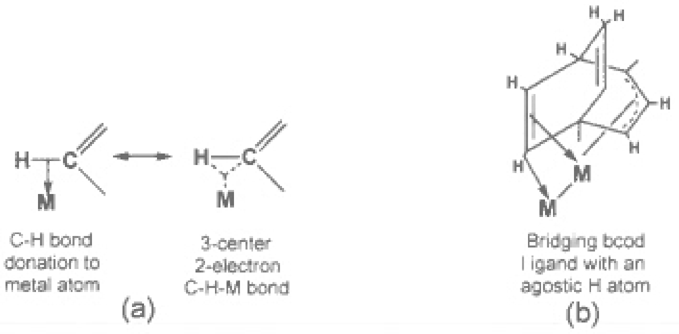


**Figure 5:**(a) Alternative representations of an agostic hydrogen atom as two-electron donation from the carbon-hydrogen bond to the metal atom and as a 3-center 2-electron C-H-M bond; (b) A seven-electron donor bcod ligand bridging an $M_2$ unit by donating five electrons to one metal atom and two electrons through an agostic C-H bond to the other metal atom.

## 2. Theoretical Methods

The computations were performed using the hybrid *meta*-GGA DFT method M06-L [28, 29] functional in the Gaussian09 program.[30] Work by Truhlar and coworkers[29] suggests that M06-L is one of the best functionals for the study of organometallic and inorganic thermochemistry, and perhaps the best current functional for transition metal energetics. The geometries of all structures were fully optimized using the M06-L functional with the (120, 974) integration grid.

Double-$\zeta$ plus polarization (DZP) basis sets were used in this research. For carbon and oxygen one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ was added to the standard Huzinaga-Dunning contracted DZ sets. This basis set is designated (9s5p1d/4s2p1d).[31,32] For hydrogen, a set of p polarization functions $\alpha_p(H) = 0.75$ was added to the Huzinaga-Dunning DZ sets. For iron, in our loosely contracted DZP (14s11p6d/10s8p3d) basis sets, the Wachters' primitive sets were used, but augmented by two sets of p functions and one set of d functions and contracted following Hood *et al.*[33,34]

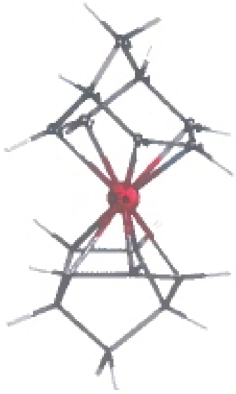


**Figure 6.** Experimental structure of singlet $(bcod)_2Fe$ with $C_2$ symmetry.

In order to validate the effectiveness of the M06-L method for studying transition metal bcod derivatives the experimentally[8] known $(bcod)_2Fe$ and $(bcod)_2Cr$ structures (Figure 6) were optimized. The M06-L method was found to predict the singlet $(bcod)_2Fe$ with $C_2$ symmetry as the global minimum consistent with experiment. The predicted bonding Fe-C distances, C-C distances, and C-C-C angles were found to close to the values determined by X-ray crystallography (Table 1). In addition the M06-L method also predicts the triplet spin state for $(bcod)_2Cr$ to be the global minimum, consistent with the experimental magnetic moment of $\mu_{eff} = 2.85$.[8]

**Table. 1** Comparison between the experimental results and the theoretical predictions of the bond distances and angles for $(bcod)_2Fe$.

| | Exp. | M06-L | | Exp. | M06-L |
|---|---|---|---|---|---|
| Fe-C2 | 2.176(2) | 2.151 | Fe-C3 | 2.059(2) | 2.064 |
| Fe-C4 | 2.128(2) | 2.117 | Fe-C6 | 2.139(2) | 2.112 |
| Fe-C7 | 2.162(2) | 2.120 | C1-C2 | 1.514(3) | 1.520 |
| C1-C7 | 1.517(3) | 1.515 | C1-C8 | 1.530(3) | 1.533 |
| C2-C3 | 1.397(3) | 1.411 | C3-C4 | 1.414(3) | 1.141 |
| C4-C5 | 1.521(3) | 1.517 | C5-C6 | 1.531(3) | 1.526 |
| C5-C8 | 1.530(3) | 1.532 | C6-C7 | 1.374(3) | 1.397 |
| C2-C1-C7 | 100.9(2) | 99.3 | C2-C1-C8 | 110.2(2) | 111.1 |
| C7-C1-C8 | 101.6(2) | 101.9 | C1-C2-C3 | 117.9(2) | 117.0 |
| C2-C3-C4 | 118.1(6) | 117.6 | C3-C4-C5 | 118.4(2) | 118.7 |
| C4-C5-C6 | 100.8(2) | 100.2 | C4-C5-C8 | 109.1(2) | 109.2 |
| C6-C5-C8 | 102.1(2) | 102.7 | C5-C6-C7 | 107.8(2) | 107.1 |
| C1-C7-C6 | 109.7(2) | 109.8 | C1-C8-C5 | 100.7(2) | 100.7 |

## 3. Results

### 3.1 Iron-iron interactions in the $(bcod)_2Fe_2(CO)_n$ derivatives

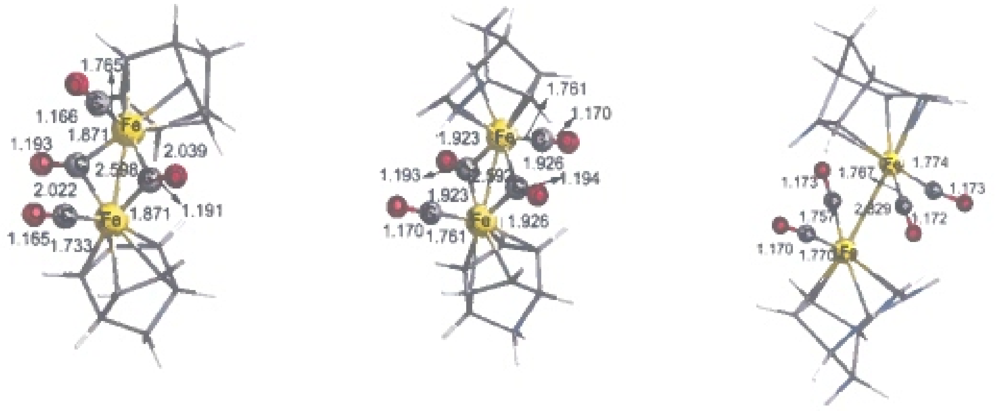
In order to provide some insight into the Fe-Fe interactions in the $(bcod)_2Fe_2(CO)_n$ derivatives, their Wiberg bond indices (WBIs) were determined using NBO analysis (Table 2).[35] In singlet structures unbridged Fe–Fe single bonds have WBI values ranging from 0.38 to 0.42 whereas doubly bridged Fe–Fe single bonds have somewhat lower WBIs of 0.28 to 0.35. This is consistent with previous studies[36] showing typical WBI values for single bonds between d-block metals around 0.3. The WBIs for Fe=Fe double bonds in singlet spin state structures range from 0.38 to 0.70 depending on the bridging groups, and those for Fe≡Fe triple bonds are even higher around ~0.9. In some systems the WBIs for a given Fe-Fe bond order are lower for triplet spin state structures than for similar singlet structures.

### 3.2 The $(bcod)_2Fe_2(CO)_n$ ($n = 4, 3, 2, 1$) structures

*3.2.1*$(bcod)_2Fe_2(CO)_4$*.* The energetically nearly degenerate three lowest energy $(bcod)_2Fe_2(CO)_4$ structures include a doubly bridged *cis-trans* isomer pair **4S-1** and **4S-2** based on the orientation of the terminal CO groups analogous to the *cis-trans* isomer pair of the well-known $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ as well as the unbridged structure **4S-3** intermediate between the two doubly bridged structures (Figure 7). The Fe–Fe distances of ~2.59 Å in either **4S-1** or **4S-2** are only slightly longer than the experimental ~2.54 Å Fe–Fe distances in the $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ isomers[15,16,17] and thus likewise correspond to single bonds thereby giving the iron atoms the favored 18-electron configurations. The WBI values of ~0.29 for the Fe–Fe bonds in **4S-1** and **4S-2** are in a typical range for single bonds between two d-block metals.[36]

**Table 2**. The Fe-Fe distances (Å), Wiberg bond indices (WBIs), and the corresponding bond orders for the $(bcod)_2Fe_2(CO)_n$ structures.

| Structure | Fe-Fe | WBIs | Bondorder | Bridging Groups |
|---|---|---|---|---|
| **4S-1** | 2.598 | 0.29 | 1 | 2 CO |
| **4S-2** | 2.592 | 0.28 | 1 | 2 CO |
| **4S-3** | 2.829 | 0.38 | 1 | none |
| **3T-1** | 2.444 | 0.31 | 2 | 2 CO |
| **3S-2** | 2.608 | 0.42 | 1 | agostic C-H |
| **3T-3** | 2.579 | 0.35 | 1 | agostic C-H |
| **3S-4** | 2.527 | 0.35 | 1 | 2 CO |
| **2T-1** | 2.449 | 0.35 | 2 | 2 CO |
| **2S-2** | 2.172 | 0.86 | 3 | 2 CO |
| **2T-3** | 2.418 | 0.42 | 2 | CO |
| **2S-4** | 2.345 | 0.70 | 2 | CO |
| **2S-5** | 2.359 | 0.38 | 2 | 2 agostic C-H |
| **2T-6** | 2.617 | 0.39 | 1 | $\eta^2$-μ-CO + CO |
| **1T-1** | 2.372 | 0.31 | 2 | none |
| **1S-2** | 2.436 | 0.48 | 2 | 2 |
| **1T-3** | 2.181 | 0.74 | 3 | CO |
| **1S-4** | 2.151 | 0.93 | 3 | CO |



**4S-1**
0.0 kcal/mol

**4S-2**
0.5 kcal/mol

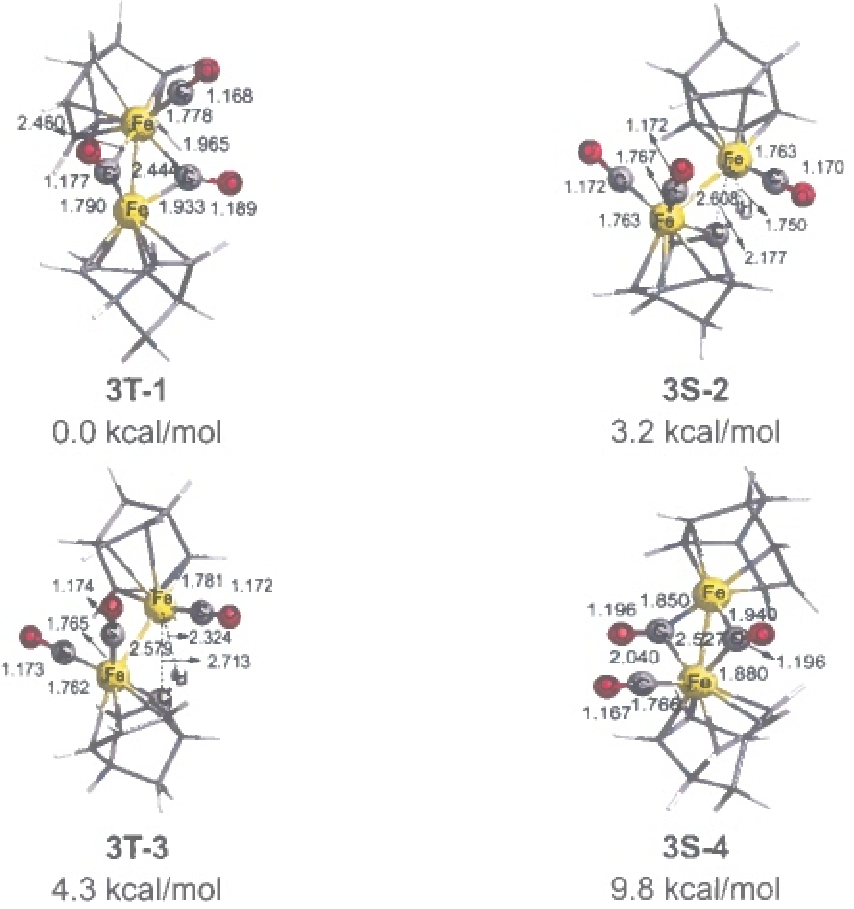
**4S-3**
1.0 kcal/mol

**Figure 7.** Three optimized $(bcod)_2Fe_2(CO)_4$ structures.

The unbridged $(bcod)_2Fe_2(CO)_4$ structure **4S-3** (Figure 7) lies only 1.0 kcal/mol in energy above the lowest energy doubly bridged $(bcod)_2Fe_2(CO)_2$ (μ-CO)$_2$ structure **4S-1**. This suggests a highly fluxional system with rapid interconversion of the *cis* and *trans* doubly bridged isomers **4S-1** and **4S-2** through the unbridged intermediate **4S-3**. The unbridged Fe–Fe distance of 2.829 Å in **4S-3** is ~0.23 Å longer than the doubly bridged Fe–Fe distances of ~2.60 Å in **4S-1** and **4S-2.** This reflects the effect of the two bridging carbonyl groups in shortening the Fe–Fe distances in **4S-1** and **4S-2** relative to that in the unbridged isomer **4S-3**. However, the WBI for the Fe–Fe interaction of 0.38 in **4S-3** is ~0.1 higher than those in **4S-1** and **4S-2** despite the longer Fe–Fe distance in **4S-3** relative to **4S-1** and **4S-2**. This can be viewed as a consequence of weakening the direct Fe-Fe interaction in **4S-1** and **4S-2** by three-center two-electron $Fe_2C$ bonding involving the bridging carbonyl groups, as discussed by Ponec, Lindvay, and Chaves[37] for $Fe_2(CO)_9$ and $Co_2(CO)_8$ and by Green, Green, and Parkin[38] for other related bridged metal-metal bonds.

*3.2.2 (bcod)$_2$Fe$_2$(CO)$_3$.* Four low-energy structures are found for the tricarbonyls $(bcod)_2Fe_2(CO)_3$ (Figure 8). In all four structures the bcod ligand is a split pentahapto ligand using both the olefinic and the allylic units. The lowest energy $(bcod)_2Fe_2(CO)_3$ structure is the doubly bridged triplet structure **3T-1** with three different types of carbonyl groups, namely a nearly symmetrical bridging carbonyl group, a very unsymmetrical semibridging carbonyl group, and a terminal carbonyl group. The symmetrical bridging carbonyl group in **3T-1** has nearly equivalent Fe–C distances of 1.933 and 1.965 Å. However, the unsymmetrical semibridging carbonyl group in **3T-1** has a very short Fe–C distance of 1.790 Å to the iron atom without the terminal carbonyl group and a long Fe–C distance of 2.460 Å to the iron atom with the terminal carbonyl group. The Fe–Fe distance of 2.444 Å in **3T-1** with a corresponding WBI value of 0.31 (Table 2) suggests a formal single bond between the two iron atoms. This corresponds to a 17-electron configuration of each iron atom in accord with a binuclear triplet structure.

The triplet $(bcod)_2Fe_2(CO)_3$ structure **3T-3**, lying 4.3 kcal/mol in energy above **3T-1**, is related to **3T-1** except all three carbonyl groups are terminal carbonyl groups with two on one iron atom and one on the other iron atom (Figure 8). The Fe–Fe distance of 2.579 Å is ~0.14 Å longer than that in **3T-1** reflecting the absence of bridging carbonyl groups in **3T-3**. Despite this significantly longer Fe–Fe distance in **3T-3** relative to **3T-1**, the WBI value of 0.35 for the Fe–Fe interaction in **3T-3** is actually slightly higher than that in **3T-1**, also reflecting the absence of the bridging carbonyl groups in **3T-3**. This can be related to the formal Fe–Fe bond in **3T-1** effectively being a multicenter interaction involving the bridging carbonyl groups, thereby lowering the effective direct interaction between the iron atoms similar to the situation in $Fe_2(CO)_9$ and $Co_2(CO)_8$.[37] This contrasts with the Fe–Fe interaction in3T-3 being a true two-center iron-iron direct interaction. The shortest Fe···H distance of 2.324 Å in **3T-3** is too long to imply a significant agostic interaction.



**3T-1**
0.0 kcal/mol

**3S-2**
3.2 kcal/mol

**3T-3**
4.3 kcal/mol

**3S-4**
9.8 kcal/mol

**Figure 8.** Four optimized $(bcod)_2Fe_2(CO)_3$ structures.

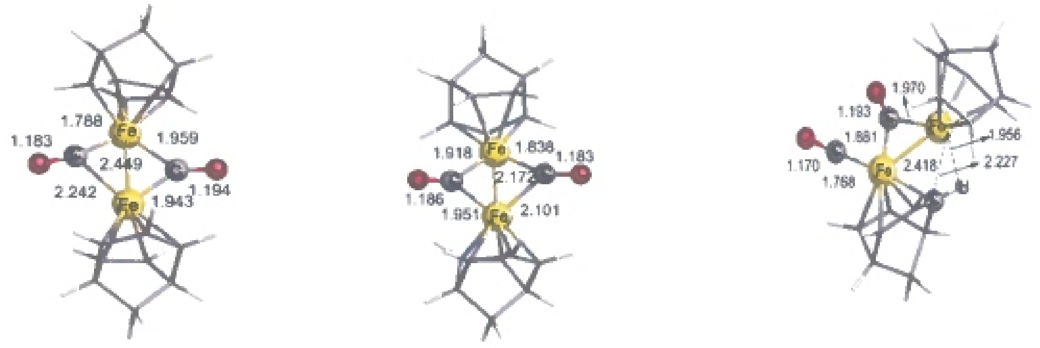
The lowest energy $(bcod)_2Fe_2(CO)_3$ singlet structure **3S-2**, lying 3.2 kcal/mol in energy above **3T-1**, has two terminal carbonyl groups bonded to one iron atom and the remaining terminal carbonyl group bonded to the other iron atom (Figure 8). In **3S-2** the predicted Fe-Fe distance of 2.608 Å with a WBI of 0.42 suggests a formal single bond. Structure **3S-2** has an agostic C–H–Fe interaction with an Fe–H distance of 1.750 Å, which is not much longer than the experimental value of 1.62 Å for diatomic FeH, which clearly incorporates a genuine single bond.[39] This agostic interaction effectively provides two electrons to the iron atom through donation of the two electrons of that C–H bond to the iron atom (Figure 8). This represents an initial stage of C–H bond activation by lengthening this C–H bond to ~1.14 Å. In **3S-2** the agostic C–H–Fe interaction combined with the Fe–Fe single bond gives each iron atom the favored 18-electron configuration. This agostic C–H interaction with the iron atom in **3S-2** bearing a single terminal carbonyl group effectively replaces a carbonyl group lost in going from the $(bcod)_2Fe_2(CO)_4$ structure **4S-3** to the $(bcod)_2Fe_2(CO)_3$ structure **3S-2**.

The other low-energy $(bcod)_2Fe_2(CO)_3$ structure **3S-4** is a doubly bridged singlet structure lying 9.8 kcal/mol in energy above **3T-1** (Figure 8). Structure **3S-4** can be derived from the $(bcod)_2Fe_2(CO)_4$ structure **4S-1** by loss of a terminal carbonyl group. This loss of the carbonyl group to give **3S-4** reduces the Fe–Fe distance from 2.598 Å in **4S-1** to 2.527 Å in **3S-4** with a corresponding increase in the WBI from 0.29 to 0.45. Because of the relatively small change in the Fe–Fe distance in going from **4S-1** to **3S-4**, we still consider the Fe–Fe bond in **3S-4** as a formal single bond, leading to an 18-electron configuration for the iron atom bearing the terminal carbonyl group, but only a 16-electron configuration for the iron atom missing a terminal carbonyl group.

*3.1.3 $(bcod)_2Fe_2(CO)_2$.* Six low-energy $(bcod)_2Fe_2(CO)_2$ structures were found (Figure 9). The lowest energy such structure is the triplet structure **2T-1** with two bridging carbonyl groups and an Fe=Fe distance of 2.449 Å, interpreted as a formal double bond. This gives each iron atom in **2T-1**a 17-electron configuration corresponding to a binuclear triplet. The singlet $(bcod)_2Fe_2(CO)_2$ structure **2S-2**, lying only 3.3 kcal/mol in energy above **2T-1**, is similar to the triplet structure **2T-1**, also with two bridging carbonyl groups. However, in **2S-2** the Fe≡Fe distance of 2.172 Å is ~0.27 Å shorter than that in **2T-1**. This combined with the (relatively) very high WBI of 0.86 for the iron-iron bond suggests a formal Fe≡Fe triple bond in **2S-2** thereby giving each iron atom the favored 18-electron configuration. Neither **2T-1** nor **2S-2** has any agostic hydrogen atoms.

Despite the lack of agostic hydrogen atoms in the lowest energy $(bcod)_2Fe_2(CO)_2$ structures **2T-1** and **2S-2**, two only slightly higher energy isomers of the dicarbonyl have agostic hydrogen atoms. The triplet structure **2T-3**, predicted to lie 4.2 kcal/mol in energy above **2T-1**, has one terminal carbonyl group and one bridging carbonyl group (Figure 9). There is an agostic hydrogen atom in **2T-3** with an Fe–H distance of 1.956 Å. The Fe=Fe distance of 2.418 Å in **2T-3** is similar to that in **2T-1**, and it can likewise be interpreted as a formal double bond. In **2T-3** each iron atom acquires the 18-electron configuration after considering the donation of two electrons to the $Fe_2$ unit by the agostic hydrogen atom forming a three-center two-electron C–H–Fe bond. In **2T-3** the triplet spin state can arise from two unpaired electrons within the Fe=Fe double bond, interpreted as the $\sigma + \frac{2}{2}\pi$ type with unpaired electrons in orthogonal $\pi$ orbitals. Such an Fe=Fe double bond in **2T-3** is similar to the Fe=Fe double bond in the stable triplet state $Cp_2Fe_2(\mu\text{-}CO)_3$ structure known experimentally.[22,23] The geometry of the singlet $(bcod)_2Fe_2(CO)_2$ structure **2S-4**, lying

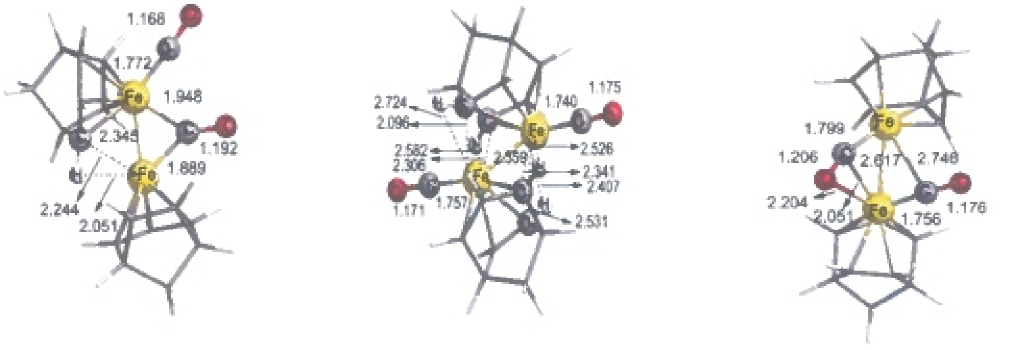
7.2 kcal/mol in energy above **2T-1**, is similar to that of the triplet structure **2T-3**, including an agostic hydrogen with an Fe–H distance of 2.051 Å, as well as one bridging carbonyl group and one terminal carbonyl group. The Fe=Fe distance of 2.345 Å coupled with a WBI of 0.70 (Table 2) in **2S-4**, suggests a formal double bond, thereby giving each iron atom the favored 18-electron configuration.



**2T-1**
0.0 kcal/mol

**2S-2**
3.3 kcal/mol

**2T-3**
4.2 kcal/mol



**2S-4**
7.2 kcal/mol

**2S-5**
8.7 kcal/mol

**2T-6**
11.1 kcal/mol

**Figure 9.** Six optimized $(bcod)_2Fe_2(CO)_2$ structures.

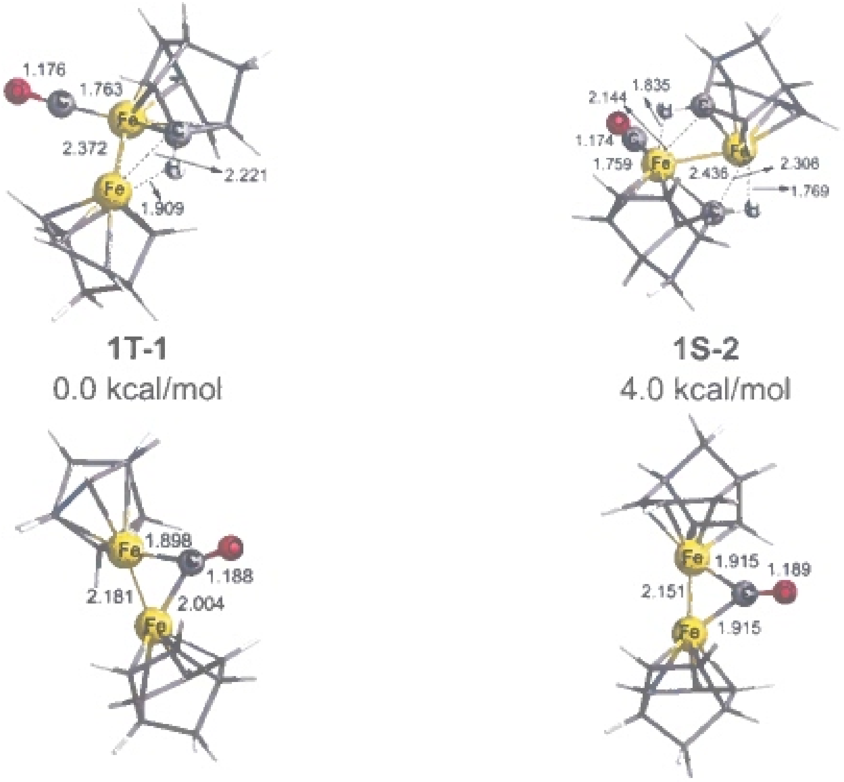
The fifth $(bcod)_2Fe_2(CO)_2$ structure **2S-5**, lying 8.7 kcal/mol in energy above **2T-1**, is a singlet structure with a terminal carbonyl group bonded to each iron atom (Figure 9). In **2S-5** the C=C double bond of one of the bcod ligands (the upper one in Figure 9) bridges the $Fe_2$ unit by being located within bonding distance to both iron atoms. This bridging C=C double bond is thus effectively an electron pair donor to each iron atom. In addition this bcod ligand is bonded to one of the iron atoms as an $\eta^3$-ligand, thereby becoming a seven-electron donor to the central $Fe_2$ unit. The Fe=Fe distance of 2.359 Å combined with a WBI of 0.38 suggests the formal double bond required to give each iron atom the favored 18-electron configuration. The much lower WBI for a formal Fe=Fe double bond in **2S-5** than that of 0.70 for the Fe=Fe double bond in **2S-4** can be related to the delocalization of the Fe-Fe interaction through multicenter bonding involving the C=C double bond of the bridging bcod ligand.

The sixth lowest energy $(bcod)_2Fe_2(CO)_2$structure, namely the triplet structure **2T-6** lying 11 kcal/mol above **2T-1**, is a doubly bridged structure with one of its two carbonyl groups functioning as a four-electron donor bridging $\eta^2$-μ-CO ligand with Fe–C distances of 1.799 and 2.051 Å and an Fe–O distance of 2.204 Å (Figure 8). The other carbonyl group in **2T-6** is a highly unsymmetrical semibridging two-electron donor μ-CO ligand with a short Fe–C distance of 1.756 Å and a long Fe–C distance of 2.746 Å. The predicted Fe–Fe distance in **2T-6** of 2.617 Å is consistent with a formal single bond, thereby giving each iron atom a 17-electron configuration consistent with a binuclear triplet.

*3.1.4 $(bcod)_2Fe_2(CO)$.* Four low-energy structures were found for the monocarbonyl $(bcod)_2Fe_2(CO)$ (Figure 10). The lowest energy such structure is the triplet **1T-1** having an agostic hydrogen atom with an Fe–H distance of 1.909 Å and an Fe–C distance of 2.263 Å in the resulting three-center two-electron C–H–Fe bond. The Fe–Fe distance of 2.345 Å coupled with a WBI of 0.31 (Table 2) in **1T-1** is interpreted as a formal double bond thereby giving each iron atom a 17-electron configuration for a binuclear triplet.

The lowest energy singlet $(bcod)_2Fe_2(CO)$ structure **1S-2**, lying only 4.0 kcal/mol in energy above **2T-1**, has two agostic hydrogen atoms with short Fe–H distances of ~1.8 Å (Figure 10). Each bcod ligand in **1S-2** functions as a bridging seven-electron donor ligand with three electrons coming from the allylic unit, two electrons from the C=C double bond, and the remaining two electrons through the C–H–Fe three-center two-electron bonding of the agostic hydrogen atom. The Fe=Fe distance of 2.436 Å in **1S-2** coupled with a WBI of 0.48 suggests the formal double bond required to give each iron atom the favored 18-electron configuration.

The remaining predicted two low-energy $(bcod)_2Fe_2(CO)$ structures are the triplet structure **1T-3** and the singlet structure **1S-4**, lying 4.4 and 8.6 kcal/mol, respectively, in energy above **1T-1** (Figure 10). In each structure the carbonyl group bridges the central $Fe_2$ unit. The predicted Fe≡Fe distances of 2.181 and 2.151 Å coupled with WBIs of 0.74 and 0.93, respectively, suggest formal triple bonds. This gives each iron atom in **1T-3** a 17-electron configuration for a binuclear triplet. The singlet spin state in **1S-4** can correspond to the favored 18-electron configuration for one iron atom and a 16-electron configuration for the other iron atom. Neither **1T-3** nor **1S-4** has an agostic hydrogen atom.



**1T-1**
0.0 kcal/mol

**1S-2**
4.0 kcal/mol

**1T-3**
4.4 kcal/mol

**1S-4**
8.6 kcal/mol

**Figure 10.** Four optimized (bcod)$_2$Fe$_2$(CO) structures.

### 3.3Thermochemistry

The carbonyl dissociation energies for the reactions (bcod)$_2$Fe$_2$(CO)$_n$ → (bcod)$_2$Fe$_2$(CO)$_{n-1}$ + CO are reported in Table 3. The predicted dissociation energy of one CO group from (bcod)$_2$Fe$_2$(CO)$_4$ (**4S-1**) to give (bcod)$_2$Fe$_2$(CO)$_3$ (**3S-2**) is substantial at 27.2 kcal/mol. Further dissociation of a CO group from the singlet or triplet tricarbonyl (bcod)$_2$Fe$_2$(CO)$_3$ to give the dicarbonyl (bcod)$_2$Fe$_2$(CO)$_2$in the same spin state requires ~23 kcal/mol. Subsequent dissociation of a CO group from the singlet or triplet dicarbonyl (bcod)$_2$Fe$_2$(CO)$_2$ to give the monocarbonyl (bcod)$_2$Fe$_2$(CO) in the same spin state requires significantly higher energy of ~43 kcal/mol. Thus the dissociations of singlet or triplet (bcod)$_2$Fe$_2$(CO)$_n$ ($n$ = 3, 2) to (bcod)$_2$Fe$_2$(CO)$_{n-1}$ in the same spin state with the same number of carbonyl groups are predicted to be essentially the same for the singlet and triplet spin states.

Table 3 also shows the energies for the disproportionation reactions 2(bcod)$_2$Fe$_2$(CO)$_n$ → (bcod)$_2$Fe$_2$(CO)$_{n+1}$+ (bcod)$_2$Fe$_2$(CO)$_{n-1}$. Such disproportionation of the tricarbonyl (bcod)$_2$Fe$_2$(CO)$_3$ **3S-2** is endothermic by 4.2 kcal/mol, suggesting **3S-2** to be marginally viable. However, a similar disproportionation of the dicarbonyl (bcod)$_2$Fe$_2$(CO)$_2$ is endothermic by 19.9 kcal/mol for the singlet **2S-2** or by 19.3 kcal/mol for the triplet **2T-1**. This suggests that the dicarbonyl (bcod)$_2$Fe$_2$(CO)$_2$

is viable. Also the disproportionation energies of the singlet and triplet spin states of the dicarbonyl (bcod)$_2$Fe$_2$(CO)$_2$ are very similar.

**Table 3.** Bond dissociation energies (kcal/mol) with and without Gibbs free energies for removal of one carbonyl group and disproportionation energies of the (bcod)$_2$Fe$_2$(CO)$_n$ derivatives.

| Reaction Energy | ΔE | ΔG |
|---|---|---|
| (bcod)$_2$Fe$_2$(CO)$_4$ (**4S-1**) → (bcod)$_2$Fe$_2$(CO)$_3$ (**3S-2**) + CO | 40.6 | 27.2 |
| (bcod)$_2$Fe$_2$(CO)$_3$ (**3S-2**)→ (bcod)$_2$Fe$_2$(CO)$_2$ (**2S-2**)+ CO | 37.8 | 23.0 |
| (bcod)$_2$Fe$_2$(CO)$_3$ (**3T-1**)→ (bcod)$_2$Fe$_2$(CO)$_2$ (**2T-1**)+ CO | 37.7 | 23.8 |
| (bcod)$_2$Fe$_2$(CO)$_2$ (**2S-2**)→ (bcod)$_2$Fe$_2$(CO) (**1S-2**) + CO | 54.6 | 43.0 |
| (bcod)$_2$Fe$_2$(CO)$_2$ (**2T-1**)→ (bcod)$_2$Fe$_2$(CO) (**1T-1**) + CO | 53.9 | 43.1 |
| 2(bcod)$_2$Fe$_2$(CO)$_3$ (**3S-2**)→(bcod)$_2$Fe$_2$(CO)$_2$ (**2S-2**)+ (bcod)$_2$Fe$_2$(CO)$_4$ (**4S-1**) | –2.8 | 4.2 |
| 2(bcod)$_2$Fe$_2$(CO)$_2$ (**2S-2**)→ (bcod)$_2$Fe$_2$(CO)$_3$ (**3S-2**)+ (bcod)$_2$Fe$_2$(CO) (**1S-2**) | 16.8 | 19.9 |
| 2(bcod)$_2$Fe$_2$(CO)$_2$ (**2T-1**)→ (bcod)$_2$Fe$_2$(CO)$_3$ (**3T-1**)+ (bcod)$_2$Fe$_2$(CO) (**1T-1**) | 16.2 | 19.3 |

**Table 4**. Energy gaps between the lowest unoccupied and the highest occupied molecular orbitals (in kcal/mol) and the spin values ⟨S$^2$⟩ for the (bcod)$_2$Fe$_2$(CO)$_n$ structures.

| Structure | ΔE(LUMO-HOMO) | ⟨S$^2$⟩ |
|---|---|---|
| **4S-1** | 47.7 | 0.00 |
| **4S-2** | 52.7 | 0.00 |
| **4S-3** | 48.6 | 0.00 |
| **3T-1** | 52.6 | 2.14 |
| **3S-2** | 44.2 | 0.00 |
| **3T-3** | 53.7 | 2.19 |
| **3S-4** | 31.6 | 0.00 |
| **2T-1** | 30.4 | 3.01 |
| **2S-2** | 23.9 | 0.00 |
| **2T-3** | 34.0 | 2.19 |
| **2S-4** | 33.9 | 0.00 |
| **2S-5** | 44.3 | 0.00 |
| **2T-6** | 44.3 | 2.24 |
| **1T-1** | 33.7 | 2.22 |
| **1S-2** | 33.1 | 0.00 |
| **1T-3** | 32.2 | 2.57 |
| **1S-4** | 20.1 | 0.00 |

The energy gaps between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for the $(bcod)_2Fe_2(CO)_n$ structures are given in Table 4. The predicted energy gaps ranging from 20.1 kcal/mol to 47.7 kcal/mol are large enough to stabilize these compounds. Table 4 also lists the $\langle S^2 \rangle$ values for most structures. These are close to the ideal $\langle S^2 \rangle = S(S + 1)$ values ($= \langle S^2 \rangle = 2$ for triplet structures) except for **2T-1** and **1T-3.** These two triplet structures have significantly larger $\langle S^2 \rangle$ values of 3.01 and 2.57, respectively, relative to the ideal $\langle S^2 \rangle = 2$ suggesting significant spin contamination.

### 3.4 Carbonyl vibrational frequencies

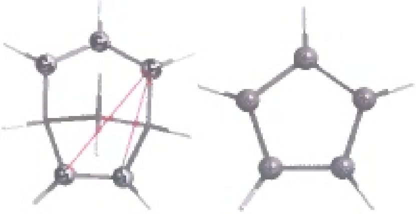
The terminal CO groups in the $(bcod)_2Fe_2(CO)_n$ structures exhibit ν(CO) frequencies from 1989 to 2059 $cm^{-1}$, which lie in the typical region for terminal CO groups (Table 5). The ν(CO) frequencies for the two-electron donor bridging carbonyl groups ranging from 1827 to 1925 $cm^{-1}$ are significantly lower in accord with expectation. The four-electron donor bridging $\eta^2$-μ-CO group in **2T-6** exhibits a much lower ν(CO) frequency than the two-electron donor bridging carbonyl groups at 1787 $cm^{-1}$.

**Table 5**. Harmonic vibrational frequencies(in $cm^{-1}$) and infrared intensities (in parentheses, in km/mol) for the $(bcod)_2Fe_2(CO)_n$ structures. Bridging carbonyl frequencies are in **bold.**

| Structure | ν(CO), $cm^{-1}$ |
|---|---|
| **4S-1** | **1851**(***832***), **1877**(***24***), 2026(*171*), 2059(*1458*) |
| **4S-2** | **1831**(***818***), **1866**(***12***), 2011(*1273*), 2021(*54*) |
| **4S-3** | 1970(*86*), 1988(*1149*), 1998(*844*), 2030(*126*) |
| **3T-1** | **1870**(***510***), 1959(*432*), 2031(*1111*) |
| **3S-2** | 1982(*304*), 2003(*1198*), 2029(*594*) |
| **3T-3** | 1968(*280*), 1995(*1252*), 2021(*541*) |
| **3S-4** | **1827**(***843***), **1854**(***43***), 2034(*991*) |
| **2T-1** | **1847** (***500***), **1921** (***468***) |
| **2S-2** | **1894**(***823***), **1925**(***369***) |
| **2T-3** | **1853**(***462***), 2017(*1262*) |
| **2S-4** | **1858**(***402***), 2031(*1272*) |
| **2S-5** | 1989(*1825*), 2009(*271*) |
| **2T-6** | **1787**(***473***), 1976(*659*) |
| **1T-1** | 1977(*822*) |
| **1S-2** | 1988(*896*) |
| **1T-3** | **1889**(***582***) |
| **1S-4** | **1888**(***520***) |

### 3.5 Ligand planarity

The cyclopentadienyl anion $C_5H_5^-$ is coplanar with all five carbon atoms in exactly the same plane. However, in the bcod ligand the olefinic part and the allylic part are not in the same plane. The planarity of the five donor carbon atoms in the bcod ligand can be referenced from a plane determined by three of the five donor carbon atoms, namely the two olefinic carbon atoms ($C_1$ and $C_2$), and a terminal carbon atom of the allylic part ($C_3$) (light red lines in Figure 11). The deviations from this plane of the remaining two donor carbon atoms ($C_4$ and $C_5$) in the allylic part (Table 6) can determine the non-planarity of the pentahapto bcod ligand. The results indicate that the other terminal allylic carbon atom ($C_5$) is located nearly in the $C_1$-$C_2$-$C_3$ plane (within 0.06 Å) except for the unique structure **2S-5** in which one of the bcod ligands bridges the central $Fe_2$ unit rather than bonds exclusively to one of the iron atoms as in the other $(bcod)_2Fe_2(CO)_n$ structures. This leads to considerable distortion of the bcod ligand. Thus in **2S-5** the $C_5$ carbon of the bridging bcod ligand lies ~0.6 Å out of the $C_1$-$C_2$-$C_3$ plane. In some of the structures containing agostic C-H-Fe bonds (e.g., **3S-2** and **1T-1**) the deviations of the $C_5$ atom from the $C_1$-$C_2$-$C_3$ plane are larger than those in other structures and exceed 0.1 Å. Also, the deviation of one of the $C_5$ atoms from the $C_1$-$C_2$-$C_3$ plane in **2T-6** containing the four-electron donor $\eta^2$-$\mu$-CO ligand is significantly larger at 0.172 Å. The distances of the central allylic carbon $C_4$ to the $C_1$-$C_2$-$C_3$ plane (typically ~0.2 Å) are much larger than those of the terminal allylic carbon $C_5$ to the $C_1$-$C_2$-$C_3$ plane.



bcod$C_5H_5$

**Figure 11.** The $C_1$-$C_2$-$C_3$ plane in the bcod ligand (red lines) as compared with the planarcyclopentadienyl ($C_5H_5$) ligand.

## 4. Discussion

There are major differences between the split five-electron donor bcod ligand and the cyclopentadienyl (Cp) ligand even though both ligands may be considered as neutral species functioning as five-electron donors to a transition metal atom. Thus the Cp ligand, consisting of a single planar pentagonal $C_5$ ring, is much more compact than the bcod ligand where the two-electron donor olefinic site is separated from the three-electron donor allylic site by carbon bridges. Bending the carbon bridges also makes the bcod ligand more flexible than the rigid planar pentagonal Cp ligand. This flexibility moves the central allylic carbon of the bcod ligand (designated as $C_4$ in Table 4) significantly out of the plane determined by the remaining four donor carbon atoms. Thus, in the $(bcod)_2Fe_2(CO)_n$ complexes studied in this work, this central allylic bcod carbon atom typically lies ~0.2 Å out of the plane determined by the two olefinic carbon atoms $C_1$ and $C_2$ and one of the end allylic carbon atoms ($C_3$).

**Table 6.** The distances (in Å) of $C_4$ and $C_5$ from the $C_1$-$C_2$- $C_3$ plane.

| Structures | $C_4(1)$ | $C_4(2)$ | $C_5(1)$ | $C_5(2)$ | Comments |
|---|---|---|---|---|---|
| **4S-1** | 0.194 | 0.208 | 0.033 | 0.003 | — |
| **4S-2** | 0.176 | 0.176 | 0.030 | 0.030 | — |
| **3T-1** | 0.180 | 0.187 | 0.030 | 0.006 | — |
| **3S-2** | 0.319 | 0.176 | 0.113 | 0.032 | Agostic C–H |
| **3T-3** | 0.228 | 0.166 | 0.010 | 0.007 | Agostic C–H |
| **3S-4** | 0.178 | 0.238 | 0.048 | 0.065 | — |
| **2T-1** | 0.280 | 0.226 | 0.040 | 0.015 | — |
| **2S-2** | 0.241 | 0.225 | 0.011 | 0.004 | — |
| **2T-3** | 0.202 | 0.194 | 0.020 | 0.011 | Agostic C–H |
| **2S-4** | 0.248 | 0.286 | 0.022 | 0.043 | Agostic C–H |
| **2S-5** | 0.268 | 0.647 | 0.020 | 0.583 | Bridging bcod |
| **2T-6** | 0.374 | 0.220 | 0.172 | 0.031 | Bridging $\eta^2$-$\mu$-CO |
| **1T-1** | 0.312 | 0.277 | 0.140 | 0.079 | Agostic C–H |
| **1S-2** | 0.219 | 0.258 | 0.021 | 0.011 | 2 ×Agostic C–H |
| **1T-3** | 0.198 | 0.209 | 0.075 | 0.027 | — |
| **1S-4** | 0.219 | 0.219 | 0.027 | 0.027 | — |

The flexibility of the bcod ligand can also move one of its olefinic hydrogen atoms within bonding distance of the metal atom thus generating systems with agostic hydrogen atoms (Figure 6).The M–H interactions involving such agostic hydrogen atoms become part of 3-center 2-electron C-H-M bonds, thereby effectively donating the two electrons of the C–H σ-bond to the transition metal atom. Thus a bcod ligand bonding to a metal atom through its C=C double bond, its $C_3$ allylic subunit, and a C-H-M agostic interaction can become, in principle, a seven-electron donor ligand to a metal atom or an $M_2$ unit (Figure 5). This is a way of relieving unsaturation in binuclear bcod metal carbonyl derivatives that is not available in the corresponding cyclopentadienylmetal carbonyl derivatives.

The tetracarbonyls $(bcod)_2Fe_2(CO)_4$ and $Cp_2Fe_2(CO)_4$ are saturated systems, requiring only a formal Fe–Fe single bond to give each iron atom the favored 18-electron configuration. For both systems, *cis* and *trans* doubly CO-bridged stereoisomers (e.g., **4S-1** and **4S-2** in Figure 7 for bcod) are the lowest energy structures with a slightly higher energy unbridged isomer (**4S-3** in Figure 7 for bcod).

The doubly bridged structures have been realized experimentally for the $Cp_2Fe_2(CO)_4$ system.[15,16,17] However, for $(bcod)_2Fe_2(CO)_4$ the unbridged isomer is found to lie only ~1 kcal/mol in energy above the doubly bridged isomers implying a highly fluxional system. The Fe–Fe distances are somewhat longer in the $(bcod)_2Fe_2(CO)_4$ isomers than in the $Cp_2Fe_2(CO)_4$ isomers by ~0.05 Å for the doubly bridged structures and by ~0.1 Å for the slightly higher energy unbridged structures. This may relate to the greater steric requirements of the bcod ligand relative to the Cp ligand. Furthermore, for both the $(bcod)_2Fe_2(CO)_4$ and the $Cp_2Fe_2(CO)_4$ systems the Fe–Fe bonds in the unbridged isomers are ~0.2 Å longer than those in the bridged isomers.

The lowest energy structure for the tricarbonyl $Cp_2Fe_2(CO)_3$ is a triply bridged triplet spin state structure with a short 2.265 Å formal Fe=Fe double bond in an experimentally realized permethylated structure.[23] An analogous $(bcod)_2Fe_2(\mu\text{-}CO)_3$ structure is not found as a low-energy species. The lowest energy $(bcod)_2Fe_2(CO)_3$ structure **3T-1** (Figure 8) is indeed a triplet spin state structure, but with only two bridging carbonyl groups. We suspect that the greater steric requirements of the bcod ligand relative to the Cp ligand limits the number of bridging carbonyl groups to two across the central $Fe_2$ unit.

The lowest energy singlet structure **3S-2** (Figure 8) for the tricarbonyl $(bcod)_2Fe_2(CO)_3$ relieves its unsaturation by an agostic olefinic hydrogen atom from one of the bcod ligands binding to an iron atom with a very short Fe–H distance of 1.75 Å. Thus this bcod ligand functions as a bridge across the $Fe_2$ unit by being a (3 + 2) split five-electron donor to one iron atom and bonding as a two-electron donor to the other iron atom through the agostic hydrogen atom (Figure 8). The Fe–Fe distance of 2.608 Å with a WBI of 0.45 can be interpreted as a formal single bond shortened by the bridging bcod ligand.

The lowest energy structures for the dicarbonyl $(bcod)_2Fe_2(CO)_2$ do not have agostic hydrogen atoms despite their unsaturation. Instead they resemble the lowest energy $Cp_2Fe_2(CO)_2$ structures[27] in having two bridging CO groups and multiple iron-iron bonds relating to their spin state. Thus the Fe=Fe bond in the lowest energy $(bcod)_2Fe_2(CO)_2$ structure **2T-1** (Figure 9) of length 2.449 Å with a WBI of 0.35 can be interpreted as a formal double bond to give each iron atom a 17-electron configuration for a binuclear triplet. This Fe=Fe double bond is significantly longer than the Fe=Fe double bond of length ~2.3 Å in the corresponding triplet doubly bridged $Cp_2Fe_2(\mu\text{-}CO)_2$ structure.[27] In the lowest energy singlet $(bcod)_2Fe_2(CO)_2$ structure **2S-2** (Figure 7) the Fe≡Fe bond of length 2.172 Å with a WBI of 0.86 can be interpreted as the formal triple bond required to give each iron atom the favored 18-electron configuration. This Fe≡Fe distance is very close to the Fe≡Fe triple bond distance of ~2.13 Å predicted for the corresponding doubly bridged $Cp_2Fe_2(\mu\text{-}CO)_2$

structure.[27] Agostic hydrogen atoms are found in the higher energy $(bcod)_2Fe_2(CO)_2$ structures **2T-3** and **2S-4**, as discussed in detail above.

The still higher energy $(bcod)_2Fe_2(CO)_2$ structures **2S-5** and **2T-6** (Figure 9) exemplify other ways of accommodating the unsaturation in these systems. The singlet structure **2S-5** is the only $(bcod)_2Fe_2(CO)_n$ structure found in this work where a bcod ligand bridges the central $Fe_2$ unit by trihapto bonding of the allylic unit to one iron atom and the olefinic carbon atoms within bonding distance of both iron atoms. The triplet structure **2T-6** is the only $(bcod)_2Fe_2(CO)_n$ structure found in this work with a four-electron donor $\eta^2$-$\mu$-CO group.

The lowest energy structure by a substantial margin (~25 kcal/mol) predicted for the experimentally unknown monocarbonyl $Cp_2Fe_2(CO)$ is a triplet structure with the carbonyl group bridging the central $Fe_2$ unit.[27] The ultrashort Fe≣Fe distance of ~2.03 Å in this structure was interpreted as a formal quadruple bond to give each iron atom the favored 18-electron configuration. The two unpaired electrons of the triplet spin state were assumed to be located in the Fe≣Fe quadruple bond, interpreted as a $\sigma + 2\pi + \frac{2}{2}\delta$ bond with two single-electron $\delta$ bonds. The $(bcod)_2Fe_2(CO)$ system differs from the $Cp_2Fe_2(CO)$ system, since agostic hydrogen atoms rather than high order Fe-Fe bonds are found in both the lowest energy triplet and singlet $(bcod)_2Fe_2(CO)$ structures. The triplet $(bcod)_2Fe_2(CO)$ structure **1T-1** (Figure 10) has one agostic hydrogen atom. Interpreting the Fe=Fe distance of 2.372 Å with a WBI of 0.31 as a formal double bond gives each iron atom in **1T-1** the 17-electron configuration for a binuclear triplet. The singlet $(bcod)_2Fe_2(CO)$ structure **1S-2** has an agostic hydrogen atom from each bcod ligand. The Fe=Fe distance of 2.436 Å in **1S-2** is similar to that in **1T-1** but the WBI of the Fe=Fe interaction in **1S-2** is significantly larger at 0.48. Interpreting the Fe=Fe interaction in **1S-2** as a formal double bond coupled with the two agostic hydrogen atoms gives each iron atom the favored 18-electron configuration. The higher energy $(bcod)_2Fe_2(CO)$ structures **1T-3** and **2S-4** also have a bridging carbonyl group but do not have agostic hydrogen atoms. They therefore resemble the lowest energy $Cp_2Fe_2(CO)$ structures.

The C-H-Fe agostic interactions may play an essential role in stablizing the $(bcod)_2Fe_2(CO)_n$ compounds owing to the non-planarity and flexibility of the bcod ligand. In order to further confirm our results, the very recently developed DLPNO-CCSD(T) method with def2-SPV basis sets implented in the ORCA4 program[40,41] has been used to calculate the single point energies for the reported $(bcod)_2Fe_2(CO)$ structures. The energy order is changed for **1T-1** and **1S-2** at the DLPNO-CCSD(T)/def2-SPV level. The M06-L/DZP method predicted the triplet structure **1T-1** to be 4.2 kcal/mol lower than the singlet structure **1S-2**, however, the more accurate DLPNO-CCSD(T)/def2-SPV predictes **1S-1** to be 2.1 kcal/mol lower than **1T-1**. This may be due to the stronger interactions from the two pairs of C-H-Fe agostic bonds in the singlet **1S-2** structure. When compareing the relatvie energy beteween the two singlet structures **1S-2** and **1S-4** at the DLPNO-CCSD(T)/def2-SPV level, we found that the **1S-4** structure without C-H-M agostic interaction is much higher in energy, namely 27.7 kcal/mol, than the singlet structure **1S-2** with two pairs of C-H-Fe agostic interactions. We suspect that the M06-L DFT method may underestimate this kind of agostic interactions.

## 5. Summary

The lowest energy $(bcod)_2Fe_2(CO)_4$ structures are doubly bridged *cis* and *trans* isomers with Fe–Fe single bonds resembling the corresponding $Cp_2Fe_2(\mu\text{-}CO)_2$ structures. The corresponding unbridged $(bcod)_2Fe_2(CO)_4$ isomer lies only ~1 kcal/mol in energy above these doubly bridged isomers.

For the tricarbonyl $(bcod)_2Fe_2(CO)_3$ a low-energy triply bridged structure analogous to the experimentally known triplet $Cp_2Fe_2(\mu\text{-}CO)_3$ structure is not found. Instead the lowest energy $(bcod)_2Fe_2(CO)_3$ structure is a triplet doubly bridged structure. Lying within 4 kcal/mol of this lowest energy $(bcod)_2Fe_2(CO)(\mu\text{-}CO)_2$ structure are both singlet and triplet isomers with agostic olefinic hydrogen atoms forming 3-center two-electron C-H-Fe bonds. Such agostic hydrogen atoms are also found in the lowest energy singlet and triplet structures of the monocarbonyl $(bcod)_2Fe_2(CO)$. However, related structures with agostic hydrogen atoms are not found in the corresponding $Cp_2Fe_2(CO)_n$ derivatives owing to the rigidity of the cyclopentadienyl ring.

The lowest energy structures for the dicarbonyl $(bcod)_2Fe_2(CO)_2$ are triplet and singlet doubly bridged structures without agostic hydrogen atoms resembling the corresponding $Cp_2Fe_2(CO)_2$ structure. However, slightly higher energy singlet and triplet $(bcod)_2Fe_2(CO)_2$ structures within 7 kcal/mol of the lowest energy structures are found containing agostic hydrogen atoms.

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The authors declare no competing financial interests.

**Supporting Information**

Tables S1 to S17: Optimized coordinates of the $(bcod)_2Fe_2(CO)_n$ structures ($n$ = 1 to 4); Tables S18 to S34: Harmonic vibrational frequencies (in cm$^{-1}$) and infrared intensities (in km/mol) for $(bcod)_2Fe_2(CO)_n$ structures ($n$ = 1 to 4); Complete Gaussian09 reference (Reference 30). Separate concatenated xyz file containing the coordinates of the optimized structures.

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