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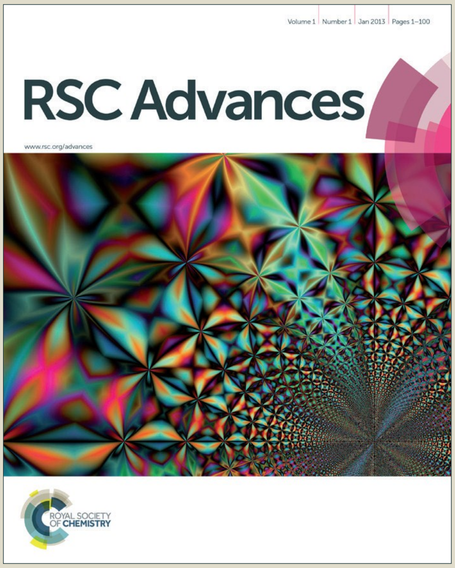

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# Fluorine Shifts From Sulfur to Metal in Difluorosulfane Complexes of Cyclopentadienyl Iron Carbonyl: Incompatibility of Sulfur-Fluorine Bonds with Iron-Iron Bonds

Huaiyu Jiang,[a] Nan Li[a,b]*, R.Bruce King[c]*

[a]School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, China
[b]State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, PR China
[d]Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

## Abstract

The structures and energetics of the cyclopentadienyliron difluorosulfane carbonyls $Cp_2Fe_2(SF_2)_m(CO)_n$ ($m = 1$, $n = 4, 3, 2$; $m = 2$, $n = 3, 2$) have been investigated using density functional theory. None of the low-energy such structures are found to have short enough Fe-Fe distances to suggest a direct iron-iron bond. This suggests the incompatibility of metal-metal bonds in such structures with sulfur-fluorine bonds. Thus the low energy structures with one $SF_2$ unit are of the type $Cp_2Fe_2(SF)(F)(CO)_n$ ($n = 3, 2$) in which either the SF or F unit bridges the iron atoms. For the $Cp_2Fe_2(SF_2)_2(CO)_n$ systems ($n = 3, 2$), fluorine atoms can migrate from an $SF_2$ group either to an iron atom or to the other $SF_2$ group forming an $SF_3$ ligand. Low-energy structures are found in which an $SF_2$ group has lost both fluorine atoms in these ways leaving a bare sulfur atom bridging the two iron atoms. However, fluorine migration does not occur in the lowest energy $Cp_2Fe_2(SF_2)(CO)_4$ structure, which has an intact $SF_2$ group bridging the iron atoms in two $CpFe(CO)_2$ units in a structure closely related to $SF_4$. A related structure with one bridging $SF_2$ group and one terminal $SF_2$ group is found for $Cp_2Fe_2(SF_2)_2(CO)_3$. However, the lowest energy isomer is a structure of the type $Cp_2Fe_2(\mu\text{-}SF)(SF_3)(CO)_3$ in which a fluorine atom has migrated from the bridging $SF_2$ group to the terminal $SF_2$ group to give a bridging SF ligand and a terminal $SF_3$ ligand.

**Keywords:** Iron; sulfur fluorides; fluorine migration; cyclopentadienylmetal carbonyls; density functional theory.

E-mail addresses: leen04@163.com (N. Li); rbking@chem.uga.edu (R. B King).

# 1. Introduction

The chemistry of strong back-bonding ligands is an important area of coordination chemistry in view of the ability of such ligands to stabilize low formal oxidation states. Carbon monoxide is the best known and among the most effective back-bonding ligands leading to thousands of metal carbonyl derivatives exhibiting relatively low formal oxidation states of the central metal atom.[1] The back-bonding in such metal carbonyl derivatives involves dπ→pπ* donation of metal d electrons into the π* antibonding orbitals of carbon monoxide. The chemistry of such metal carbonyls dates back more than a century to the 1890 discovery of nickel tetracarbonyl as a stable volatile liquid formally zerovalent nickel derivative.[2]

A more recent development is the recognition of the strong back-bonding properties of phosphorus trifluoride, $PF_3$, leading to stable zerovalent metal trifluorophosphine derivatives.[3] The first of these to be discovered was $Ni(PF_3)_4$, which is a volatile liquid like $Ni(CO)_4$ but even more stable thermally and oxidatively despite the formally zerovalent nickel.[4,5] The development of experimental methods for handling $PF_3$ under pressure, particularly in the laboratory of Kruck and co-workers,[6] led to the discovery of other stable zerovalent binary metal trifluorophosphine complexes such as $Cr(PF_3)_6$ (ref. 7) and $Fe(PF_3)_5$ (refs. 8, 9). The greater stability of zerovalent metal trifluorophosphine complexes allowed such complexes to be prepared without stable metal carbonyl counterparts. For example, $Pt(PF_3)_4$ is a liquid stable under ambient conditions[10,11] in contrast to the analogous $Pt(CO)_4$. The strong back-bonding ability of $PF_3$ arises from the donor properties of the phosphorus lone pair combined with the strong electron withdrawing properties of the fluorine atoms. For metal-$PF_3$ complexes the back-bonding involves donation of metal d electrons into π* antibonding orbitals of the P–F bonds.

Sulfur difluoride (difluorosulfane) is another potential strong back-bonding ligand to transition metals owing to the combination of the donor properties of the two sulfur lone pairs and the electron withdrawing properties of the two fluorine atoms. However, unlike phosphorus trifluoride, which is stable even at high pressures, sulfur difluoride exists only in low temperature matrices[12] or highly diluted in the gas phase.[13,14] Therefore the syntheses of difluorosulfane metal complexes is considerably more challenging than syntheses of trifluorophosphine metal complexes, requiring indirect methods. For this reason difluorosulfane metal complexes have not yet been synthesized. However, in order to explore the potential of difluorosulfane metal complexes, theoretical studies have been performed on difluorosulfane iron carbonyl complexes of the type

$Fe_m(SF_2)_m(CO)_n$ ($m = 1$, $n = 4, 3$; $m = 2$, $n = 7$).[15] In general, $SF_2$ complexes were found to be disfavored with respect to fluorine migration from sulfur to the metal to give metal complexes containing separate SF and F ligands. It thus appears that the fluorinating properties of the $SF_2$ ligand, like those of the $SF_3$ ligand, are too strong to be compatible with many transition metal systems.

In order to explore further the possibility of synthesizing difluorosulfane metal complexes or fluorosulfane complexes formed by migration of fluorine from sulfur to metal, we turned to a study of $SF_2$ complexes of cyclopentadienylmetal carbonyls. There might appear to be the possibility that a tightly bound cyclopentadienyl ligand could block enough metal coordination sites to inhibit fluorine transfer from sulfur to metal thereby leading to viable difluorosulfane metal complexes. In addition, cyclopentadienylmetal carbonyl systems might provide more opportunities for indirect methods to synthesize difluorosulfane metal complexes thereby circumventing the problem of the instability of free $SF_2$. We chose the well-understood and readily available cyclopentadienyliron carbonyl system for this exploratory study.

The history of cyclopentadienyliron carbonyls dates back approximately 60 years to the original synthesis of $Cp_2Fe_2(CO)_4$ by Piper and Wilkinson reported in 1956.[16] The inexpensive starting materials required for this synthesis, namely $Fe(CO)_5$ and cyclopentadiene dimer, have made $Cp_2Fe_2(CO)_4$ a readily available reagent for the synthesis of numerous organoiron derivatives. In addition, photolysis of $Cp_2Fe_2(CO)_4$ under suitable conditions gives $Cp_2Fe_2(\mu\text{-}CO)_3$, which is of interest as a stable triplet state organometallic molecule.[17,18,19] A theoretical study[20] predicts a doubly bridged structure for $Cp_2Fe_2(CO)_2$, which is a possible intermediate in the preparation of $Cp_4Fe_4(CO)_4$ by the pyrolysis of $Cp_2Fe_2(CO)_4$ in a solvent such as toluene.[21]

This paper reports a theoretical study on cyclopentadienyliron carbonyl difluorosulfane complexes derived from the above cyclopentadienyliron carbonyl derivatives by replacing one or two CO groups with $SF_2$ ligands. Thus complexes of the types $Cp_2Fe_2(SF_2)(CO)_n$ ($n = 3, 2, 1$) and $Cp_2Fe_2(SF_2)_2(CO)_m$ ($m = 2, 1$) are included in this study.

## 2. Theoretical Methods

All calculations were performed with the Gaussian 09 program[22] using the two density functional theory (DFT) methods B3LYP* and M06L. The B3LYP* functional[23] is a reparametrised version of the hybrid functional B3LYP, which combining Becke's three parameter functional (B3)[24] with the Lee, Yang, and Parr (LYP)[25] correlation functional. After optimizing all of the structures using the B3LYP* method, we reoptimized 22 selected low-energy structures using the M06-L method. This method uses the local functional M06-L, which is based on the M05[26] and VSXC[27] functionals developed by Zhao and Truhlar.[28,29] A recent detailed study of 35 different DFT methods suggests that the M06-L method predicts structures consistent with experiment for transition metal organometallic and carbonyl derivatives provided suitable basis sets are used.[30]

All computations in this paper used the double- ζ plus polarization (DZP) basis sets. Pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.00$, and $\alpha_d(S) = 0.70$ were added to the Huzinaga-Dunning standard contracted DZ sets for carbon, oxygen, fluorine and sulfur, respectively.[31,32] For hydrogen, a set of p polarization functions ($\alpha_p(H) = 0.75$) was added to the standard Huzinaga-Dunning DZ sets. For iron, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses the Wachters primitive set[33] augmented by two sets of p functions and one set of d functions, and contracted following Hood, Pitzer, and Schaefer.[34] The harmonic vibrational frequencies were obtained at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The fine grid (75, 302) was the default for evaluating integrals numerically.[37] The tight ($10^{-8}$ hartree) designation was the default for self-consistent field (SCF) convergence. The finer grid (120, 974) was used for more precise resolution of small imaginary vibrational frequencies. All of the structures reported in this paper are genuine minima, with no imaginary vibrational frequencies.

The optimized structures are designated as **N(X)-nS/T**, where **N** and **X** are the numbers of carbonyl and $SF_2$ groups, respectively, **n** numbers the structures according to their relative energies by the B3LYP* method, and **S** (or **T**) represents singlet (or triplet) electronic state structures. For example, **2(1)-1T** is the lowest-lying triplet structure for $Cp_2Fe_2(SF_2)(CO)_2$. The bond distances in the figures were determined by the B3LYP* method. Unless otherwise indicated, the structures have long Fe···Fe distances greater than 3.6 Å indicating the lack of direct iron-iron bonds.

## 3. Results

### 3.1 Systems with one $SF_2$ Ligand.

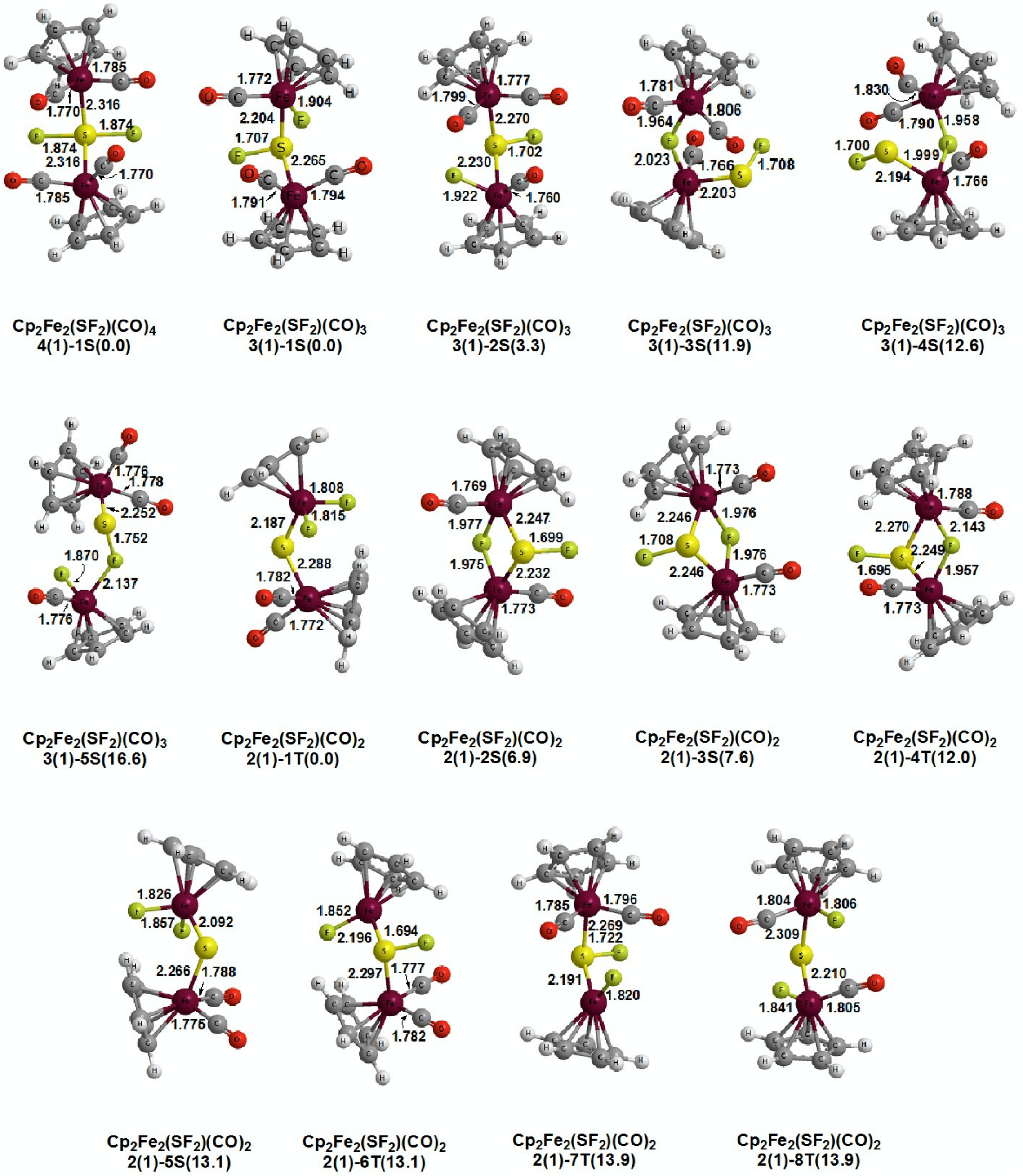
*3.1.1. $Cp_2Fe_2(SF_2)(CO)_4$ structures.* The single low-energy $Cp_2Fe_2(SF_2)(CO)_4$ structure **4(1)-1S** is predicted to have two terminal CO groups and a Cp ring bonded to each iron atom with the $SF_2$ ligand bridging the iron atoms (Figure 1 and Table 1). The linear F-S-F angle in the bridging $SF_2$ group suggests **4(1)-1S** to be a substitution product of $SF_4$ in which two fluorine atoms have been replaced by $CpFe(CO)_2$ moieties.

**Table 1.** Total energies E (Hartree), relative energies ΔE (kcal·mol$^{-1}$), and Fe···Fe distances (Å) for the $Cp_2Fe_2(SF_2)(CO)_n$ structures ($n$ = 2, 3, 4) by the B3LYP* method.

| Structures | E | ΔE | Fe···Fe |
|---|---|---|---|
| **4(1)-1S** | -3964.835532 | — | 4.105 |
| **3(1)-1S** | -3851.557302 | 0.0 | 3.753 |
| **3(1)-2S** | -3851.552037 | 3.3 | 3.886 |
| **3(1)-3S** | -3851.53827 | 11.9 | 3.727 |
| **3(1)-4S** | -3851.537291 | 12.6 | 3.709 |
| **3(1)-5S** | -3851.530823 | 16.6 | 4.762 |
| **2(1)-1T** | -3738.284538 | 0.0 | 3.693 |
| **2(1)-2S** | -3738.273574 | 6.9 | 3.146 |
| **2(1)-3S** | -3738.272424 | 7.6 | 3.154 |
| **2(1)-4T** | -3738.265342 | 12.0 | 3.176 |
| **2(1)-5S** | -3738.263628 | 13.1 | 3.614 |
| **2(1)-6T** | -3738.263627 | 13.1 | 3.658 |
| **2(1)-7T** | -3738.262444 | 13.9 | 3.692 |
| **2(1)-8T** | -3738.262351 | 13.9 | 3.745 |

*3.1.2 $Cp_2Fe_2(SF_2)(CO)_3$ structures***.** Many kinds of starting structures were tried for $Cp_2Fe_2(SF_2)(CO)_3$ including structures with a bridging SF groups and a terminal fluorine atom as well as structures with a bridging fluorine atom and a terminal SF group. The four lowest energy $Cp_2Fe_2(SF_2)(CO)_3$ structures correspond to two *cis/trans* isomer pairs (Figure 1 and Table 1). The first *cis/trans* isomer pair includes the global minimum **3(1)-1S** (*trans*) and the corresponding *cis* isomer **3(1)-2S**, lying 3.3 kcal·mol$^{-1}$ in energy above **3(1)-1S**. In these two structures, an SF group bridges $CpFe(CO)_2$ and CpFeF(CO) fragments through its sulfur atom. This pair of structures can be generated by transfer of a fluorine atom from a bridging $SF_2$ group to the iron atom connected to a single CO group to give a bridging SF group and a terminal fluorine atom. The other $Cp_2Fe_2(SF_2)(CO)_3$ *cis/trans* isomer pair includes structures **3(1)-3S** and **3(1)-4S**, lying 11.9 kcal·mol$^{-1}$ and 12.6 kcal·mol$^{-1}$, respectively, in energy above **3(1)-1S**. In this *cis/trans* isomer pair, a bridging fluorine atom connects CpFe(SF)(CO) and $CpFe(CO)_2$ fragments. Thus the $Cp_2Fe_2(SF)(F)(CO)_3$ isomers with a bridging SF group and a terminal fluorine atom are seen to be of lower energy than those containing a bridging fluorine atom and a terminal SF group.

The four lowest energy singlet $Cp_2Fe_2(SF_2)(CO)_3$ structures thus consist of two mononuclear units connected solely by a bridging SF group or F atom. The bridging SF groups or F atoms in these two *cis/trans* isomer pairs are each three-electron donors, thereby giving each iron atom the favored 18-electron configuration.



$Cp_2Fe_2(SF_2)(CO)_4$ 4(1)-1S(0.0)

$Cp_2Fe_2(SF_2)(CO)_3$ 3(1)-1S(0.0)

$Cp_2Fe_2(SF_2)(CO)_3$ 3(1)-2S(3.3)

$Cp_2Fe_2(SF_2)(CO)_3$ 3(1)-3S(11.9)

$Cp_2Fe_2(SF_2)(CO)_3$ 3(1)-4S(12.6)

$Cp_2Fe_2(SF_2)(CO)_3$ 3(1)-5S(16.6)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-1T(0.0)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-2S(6.9)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-3S(7.6)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-4T(12.0)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-5S(13.1)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-6T(13.1)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-7T(13.9)

$Cp_2Fe_2(SF_2)(CO)_2$ 2(1)-8T(13.9)

**Figure 1.** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level for the $Cp_2Fe_2(SF_2)(CO)_n$ structures ($n$ = 2, 3, 4) and their isomers. Relative energies (kcal/mol) are indicated in parentheses.

The $Cp_2Fe_2(CO)_3(F)(\mu\text{-}SF)$ structure **3(1)-5S**, lying 16.6 kcal·mol$^{-1}$ in energy above **3(1)-1S**, has a terminal fluorine atom and a bridging SF group just like the *cis*/*trans* isomer pair **3(1)1S**/**3(1)-2S** (Figure 1 and Table 1). However, the bridging SF group in **3(1)-5S**, unlike that in **3(1)1S**/**3(1)-2S**, bonds to one iron atom through its sulfur atom and to the other iron atom through its fluorine atom. This arrangement of the bridging SF group in **3(1)5S** leads to an extremely long non-bonding Fe···Fe distance of 4.762 Å, which is ~1.0 Å longer than the non-bonding Fe···Fe distances of ~3.7 Å in the *cis*/*trans* isomer pair **3(1)1S**/**3(1)-2S**. The sulfur atom of the bridging SF group in **3(1)5S** is a one-electron donor to the $CpFe(CO)_2$ unit, thereby giving that iron atom the favored 18-electron configuration. The fluorine atom of this bridging SF group is a two-electron donor to the CpFe(CO)(F) unit, thereby giving that iron atom also the favored 18-electron configuration.

*3.1.3.$Cp_2Fe_2(SF_2)(CO)_2$ structures.* We attempted to optimize various types of structures for $Cp_2Fe_2(SF_2)(CO)_2$ in both singlet and triplet spin states. Eight low-energy structures were found (Figure 1 and Table 1). Other structures were found to lie more than 15 kcal·mol$^{-1}$ in energy above the lowest energy structure **2(1)-1T** and thus are not considered in this paper.

The lowest-lying $Cp_2Fe_2(SF_2)(CO)_2$ structure is the triplet structure **2(1)-1T** with a bridging bare sulfur atom having two lone pairs (Figure 1 and Table 1). One iron atom bears two fluorine atoms as well as a Cp ring corresponding to a high-spin 16-electron configuration since this iron atom receives one electron from the bridging sulfur atom. The other iron atom in **2(1)-1T**, bearing two terminal CO groups as well as a Cp ring, has the favored 18-electron configuration after considering the electron that it gets from the bridging sulfur atom. The singlet analogue of **2(1)-1T** is **2(1)-5S**, lying 13.1 kcal·mol$^{-1}$ in energy above **2(1)-1T**. In **2(1)-5S** the $CpFeF_2$ iron atom is a low-spin iron atom with a 16-electron configuration.

The doubly bridged singlet $Cp_2Fe_2(SF_2)(CO)_2$ structures **2(1)-2S** and **2(1)-3S**, lying 6.9 and 11.9 kcal·mol$^{-1}$ in energy above **2(1)-1T**, correspond to a *trans*/*cis* isomer pair (Figure 1 and Table 1). The *trans* isomer **2(1)-2S** has a lower energy than the *cis* isomer **2(1)-3S** because of less steric hindrance between the two Cp rings. The relatively long Fe···Fe distances of ~3.15 Å in **2(1)-2S** and **2(1)-3S** suggest the lack of a direct iron-iron bond. Both the $SF_2$ group and a fluorine atom bridge the non-bonded pair of iron atoms in **2(1)-2S** and **2(1)-3S** with the $\mu\text{-}SF_2/\mu\text{-}F$ bridging system donating three electrons to each iron atom. This gives each iron atom the favored 18-electron configuration. The triplet spin-state structure **2(1)-4T**, lying 12.0 kcal mol$^{-1}$ in energy above **2(1)-1T**, is geometrically similar to **2(1)-2S**, but with a somewhat longer Fe⋯Fe distance of 3.176 Å. Based on the bond distances between the bridging $SF_2$/F groups and the iron atoms, we consider the upper iron atom in **2(1)-4T** (Figure 1) to have a high-spin 16-electron configuration. The lower iron atom in **2(1)-4T**, bearing a terminal CO group as well as the Cp ring, has the favored 18-electron configuration.

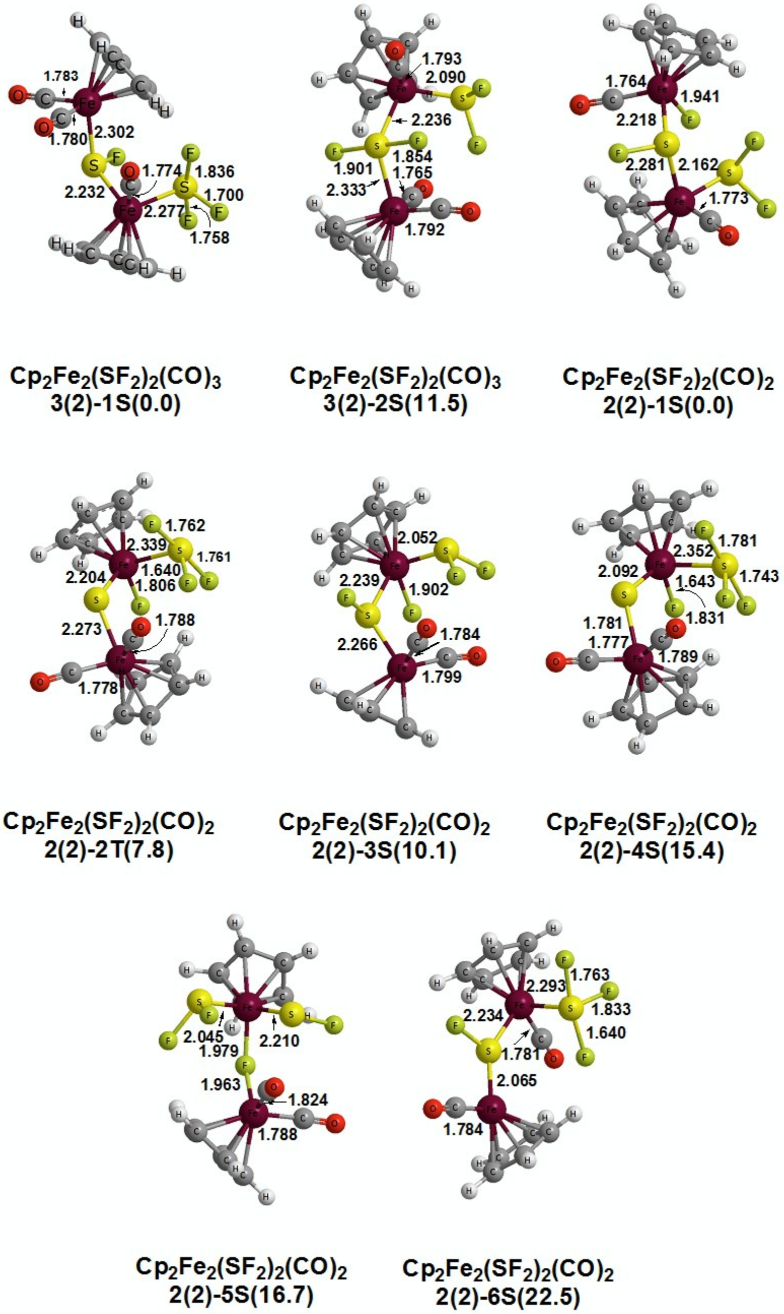
Another *cis/trans* $Cp_2Fe_2(SF_2)(CO)_2$ isomer pair **2(1)-6T** and **2(1)-7T**, lying 13.1 and 13.9 kcal·mol$^{-1}$, respectively, in energy above the global minimum, has an SF group bridging CpFeF and $CpFe(CO)_2$ fragments with non-bonding Fe⋯Fe distances of 3.658 and 3.692 Å (Figure 2 and Table 1). The iron atoms bearing a fluorine atom and a Cp ring in **2(1)-6T** and **2(1)-7T** receive two electrons from the SF bridge and thus have a high-spin 16-electron configuration thereby accounting for the triplet spin state. The other iron atoms in **2(1)-6T** and **2(1)-7T** have the favored 18-electron configuration after receiving one electron from the SF bridge.

The next $Cp_2Fe_2(SF_2)(CO)_2$ structure **2(1)-8T**, lying 13.9 kcal·mol$^{-1}$ in energy above **2(1)-1T**, has a sulfur atom bridging two CpFeF(CO) fragments with a non-bonding Fe⋯Fe distance of 3.745 Å (Figure 1 and Table 1). This gives each iron atom a 17-electron configuration for a binuclear triplet.

### 3.2 Systems with two $SF_2$ ligands

*3.2.1 $Cp_2Fe_2(SF_2)_2(CO)_3$.* Only two low-energy $Cp_2Fe_2(SF_2)_2(CO)_3$ structures were found (Figure 2 and Table 2). Both $Cp_2Fe_2(SF_2)(CO)_3$ structures have long Fe⋯Fe distances of 3.992 and 4.186 Å in **3(2)-1S** and **3(2)-2S**, respectively, indicating the absence of a direct metal-metal bond**.** The lower energy structure **3(2)-1S** is actually a $Cp_2Fe_2(\mu\text{-}SF)(CO)_3(SF_3)$, structure consisting of $CpFe(CO)_2$ and $CpFe(CO)(SF_3)$ fragments bridged by an SF group. Thus in **3(2)-1S** a fluorine atom has migrated from one $SF_2$ group to the other $SF_2$ group to give an $SF_3$ group and an SF group. The terminal $SF_3$ group is a one-electron donor with a nearly linear F-S-F angle of 170.6° similar to the bridging $SF_2$ group in **4(1)-1S**. The bridging SF group in **3(2)-1S** is a three-electron donor by donating one electron to the $CpFe(CO)_2$ unit and two electrons to the $CpFe(CO)(SF_3)$ unit so that each iron atom has the favored 18-electron configuration**.** The Fe–S bond of the bridging SF group to the $CpFe(CO)(SF_3)$ unit of length 2.232 Å is appreciably shorter than the Fe–S bond of the bridging SF group to the $CpFe(CO)_2$ unit of length 2.302 Å.

The higher energy $Cp_2Fe_2(SF_2)_2(CO)_3$ structure **3(2)-2S**, lying 11.5 kcal/·mol$^{-1}$ in energy above **3(1)-1S**, has two intact $SF_2$ ligands so that no fluorine migration has taken place. One of the $SF_2$ groups bridges $CpFe(CO)(SF_2)$ and $CpFe(CO)_2$ fragments donating one electron to each fragment thereby giving each iron atom the favored 18-electron configuration. A nearly linear F-S-F angle suggests this bridging $SF_2$ group to be a substitution product of $SF_4$. Structure **3(2)-2S** can be derived from the unique $Cp_2Fe_2(SF_2)(CO)_4$ structure **4(1)-1S** by replacing a terminal CO ligand with a terminal $SF_2$ ligand.



$Cp_2Fe_2(SF_2)_2(CO)_3$
3(2)-1S(0.0)

$Cp_2Fe_2(SF_2)_2(CO)_3$
3(2)-2S(11.5)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-1S(0.0)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-2T(7.8)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-3S(10.1)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-4S(15.4)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-5S(16.7)

$Cp_2Fe_2(SF_2)_2(CO)_2$
2(2)-6S(22.5)

**Figure 2.** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level for the $Cp_2Fe_2(SF_2)_2(CO)_n$ structures ($n$ = 3, 2). Relative energies (kcal/mol) are indicated in parentheses.

3.*2.2.* *$Cp_2Fe_2(SF_2)_2(CO)_2$*. Five singlet structures and one triplet structure were found for $Cp_2Fe_2(SF_2)_2(CO)_2$ (Figure 2 and Table 2). The lowest lying singlet $Cp_2Fe_2(SF_2)_2(CO)_2$ structure **2(1)-1S** and another low-lying singlet structure **2(2)-3S** at 10.1 kcal·mol$^{-1}$ in energy above **2(1)-1S**, correspond to a *trans/cis* isomer pair. The *trans* structure **2(1)-1S** is the lower energy structure because of less steric hindrance between the Cp rings. In these two structures, a SF group bridges CpFeF(CO) and CpFe($SF_2$)(CO) fragments by donating two electrons to the former fragment and an additional electron to the latter fragment. In **2(2)-1S** and **2(2)-2S** the long Fe⋯Fe distances of 3.699 and 3.990 Å, respectively, indicate the absence of direct iron-iron bonds. Nevertheless, both iron atoms in both of these complexes have the favored 18-electron configuration.

**Table 2.** Total energies E (Hartree), relative energies ΔE (kcal·mol$^{-1}$), and Fe⋯Fe distances (Å) for the $Cp_2Fe_2(SF_2)_2(CO)_n$ structures ($n = 3, 2$) by the B3LYP* method.

| | E | ΔE | Fe–Fe |
|---|---|---|---|
| **3(2)-1S** | -4449.252207 | 0.0 | 3.992 |
| **3(2)-2S** | -4449.233859 | 11.5 | 4.186 |
| **2(2)-1S** | -4335.975764 | 0.0 | 3.699 |
| **2(2)-2T** | -4335.963298 | 7.8 | 3.913 |
| **2(2)-3S** | -4335.959741 | 10.1 | 3.990 |
| **2(2)-4S** | -4335.951219 | 15.4 | 3.829 |
| **2(2)-5S** | -4335.949222 | 16.7 | 3.705 |
| **2(2)-6S** | -4335.939875 | 22.5 | 4.082 |

The only triplet low-energy $Cp_2Fe_2(SF_2)_2(CO)_2$ structure **2(2)-2T**, lying 7.8 kcal·mol$^{-1}$ in energy above the lowest energy structure **2(2)-1S**, has a bridging sulfur atom connecting two mononuclear units, CpFeF($SF_3$) and CpFe$(CO)_2$ by donating one electron to each iron atom (Figure 2 and Table 2). Thus one fluorine from this sulfur atom has migrated to the other sulfur atom and the other fluorine from this sulfur atom has migrated to the iron atom. The long Fe⋯Fe distance of 3.913 Å in **2(2)-2T** indicates the lack of a direct iron-iron bond. The iron atom bearing a fluorine atom and a one-electron donor $SF_3$ group as well as a Cp ring has a high-spin 16-electron configuration corresponding to the triplet spin state. The other iron atom in **2(2)-2T**, bearing two terminal CO groups as well as the Cp ring, has the favored 18-electron configuration. The singlet analogue of **2(2)-2T**, namely **2(2)-4S**, is a higher energy structure lying 15.4 kcal·mol$^{-1}$ above **2(2)-1S**, indicating that for a 16-electron

$CpFeF(SF_3)$ unit a high-spin configuration is energetically preferred over a low-spin configuration. This may relate to fluorine being a weak-field ligand.

The singlet $Cp_2Fe_2(SF_2)_2(CO)_2$ structure **2(2)-5S**, lying 16.7 kcal·mol$^{-1}$ in energy above **2(2)-1S**, is predicted to have a fluorine atom bridging a $CpFe(CO)_2$ unit to a $CpFe(SF_2)(SF)$ unit by donating one electron to the former and two electrons to the latter (Figure 2 and Table 2). The long Fe···Fe distance of 3.705 Å in **2(2)-5S** indicates the lack of a direct iron-iron bond thereby giving each iron atom the favored 18-electron configuration.

The singlet $Cp_2Fe_2(SF_2)_2(CO)_2$ structure **2(2)-6S**, lying 22.5 kcal·mol$^{-1}$ in energy above **2(2)-1S**, has an SF group bridging a $CpFe(F)(SF_3)$ unit to a CpFe(CO) unit (Figure 2 and Table 2). The relatively long Fe···Fe distance of 4.082 Å indicates the lack of a direct iron-iron bond. Each iron atom in **2(2)-6S** has the favored 18-electron configuration assuming that the terminal $SF_3$ group is a three-electron donor, the iron atom in the $CpFe(F)(SF_3)$ unit has a formal positive charge, and the iron atom in the CpFe(CO) unit has a formal negative charge.

### 3.3 Thermochemistry

Table 3 lists the CO dissociation energies of $Cp_2Fe_2(SF_2)(CO)_n$ and $Cp_2Fe_2(SF_2)(CO)_n$ derivatives, considering the lowest energy structures. The CO dissociation energy for $Cp_2Fe_2(SF_2)(CO)_4$ to give $Cp_2Fe_2(SF_2)(CO)_3$ and CO is only modestly endothermic at 11.2 kcal·mol$^{-1}$ (B3LYP*) or 15.7 kcal·mol$^{-1}$ (M06L). Further dissociation of CO from $Cp_2Fe_2(SF_2)(CO)_3$ to give $Cp_2Fe_2(SF_2)(CO)_2$ requires less energy at 7.8 kcal·mol$^{-1}$ (B3LYP*) or 6.7 kcal·mol$^{-1}$ (M06L). This suggests that $Cp_2Fe_2(SF_2)(CO)_3$ is not a viable species. The dissociation of $Cp_2Fe_2(SF_2)_2(CO)_3$ to $Cp_2Fe_2(SF_2)_2(CO)_2$ + CO is only modestly endothermic at 10.1 kcal·mol$^{-1}$ (B3LYP*) or 12.8 kcal·mol$^{-1}$ (M06L) similar to that of $Cp_2Fe_2(SF_2)(CO)_4$.

**Table 3.** Carbonyl dissociation energies of difluorosulfane derivatives of cyclopentadienyliron carbonyl.

| | ΔE (kcal·mol$^{-1}$) | |
|---|---|---|
| Reaction | B3LYP* | M06L |
| $Cp_2Fe_2(SF_2)(CO)_4 \rightarrow Cp_2Fe_2(SF_2)(CO)_3 + CO$ | 11.2 | 15.7 |
| $Cp_2Fe_2(SF_2)(CO)_3 \rightarrow Cp_2Fe_2(SF_2)(CO)_2 + CO$ | 7.8 | 6.7 |
| $Cp_2Fe_2(SF_2)_2(CO)_3 \rightarrow Cp_2Fe_2(SF_2)_2(CO)_2 + CO$ | 10.1 | 12.8 |

### 3.4 Infrared ν(CO) frequencies.

The ν(CO) frequencies and intensities of the lowest energy $Cp_2Fe_2(SF_2)_m(CO)_n$ structures are listed in Table 3 as determined by the B3LYP* method. They are in the expected 2103 to 2029 cm$^{-1}$ range for terminal ν(CO) frequencies. They are potentially useful for identifying any $Cp_2Fe_2(SF_2)_m(CO)_n$ derivatives that might be synthesized in future studies.

**Table 3.** CO stretching frequencies (cm$^{-1}$) of the lowest energy $Cp_2Fe_2(SF_2)_m(CO)_n$ structures by the B3LYP* method. Infrared intensities in km/mol are given in parentheses.

| Structures | CO stretching frequencies (cm$^{-1}$) |
|---|---|
| $Cp_2Fe_2(SF_2)(CO)_4$ (**4(1)-1S**) | 2044(173), 2051(462), 2081(767), 2103(786) |
| $Cp_2Fe_2(SF_2)(CO)_3$ (**3(1)-1S**) | 2044(334), 2065(872), 2096(527) |
| $Cp_2Fe_2(SF_2)(CO)_2$ (**2(1)-1T**) | 2045(809), 2084(800) |
| $Cp_2Fe_2(SF_2)_2(CO)_3$ (**3(2)-1S**) | 2038(141), 2059(989), 2091(743) |
| $Cp_2Fe_2(SF_2)_2(CO)_2$ (**2(2)-1S**) | 2029(716), 2061(741) |

## 4. Discussion

The $Cp_2Fe_2(SF_2)_m(CO)_n$ systems discussed in this paper are of two general types. The species $Cp_2Fe_2(SF_2)(CO)_4$ and $Cp_2Fe_2(SF_2)_2(CO)_3$ may be derived from the unknown $Cp_2Fe_2(CO)_5$ by replacing one or two CO ligands with $SF_2$ groups. The 18-electron rule suggests a singly bridged $Cp(CO)_2Fe–C(O)–Fe(CO)_2Cp$ structure for $Cp_2Fe_2(CO)_5$ without an iron-iron bond assuming that both Cp rings remain as pentahapto ligands. However, the tendency to form Fe-Fe bonds in $Cp_2Fe_2(CO)_n$ derivatives is so strong that $Cp_2Fe_2(CO)_5$ is not a viable species, although it has been postulated as one of several species formed in the flash photolysis of $Cp_2Fe_2(CO)_4$.[35] The species $Cp_2Fe_2(SF_2)(CO)_n$ ($n$ = 3, 2) and $Cp_2Fe_2(SF_2)_2(CO)_2$ may be derived from the known $Cp_2Fe_2(CO)_n$ ($n$ = 4, 3) species by replacing one or two CO groups with $SF_2$ groups.

The unique $Cp_2Fe_2(\mu\text{-}SF_2)(CO)_4$ structure **4(1)-1S** (Figure 1) is the only $Cp_2Fe_2(SF_2)_m(CO)_n$ structure found in this work in which fluorine transfer of some type from an $SF_2$ unit has not occurred. Thus in **4(1)-1S**, an intact $SF_2$ group bridges two $CpFe(CO)_2$ units. Structure **4(1)-1S** can be related to the pseudo-trigonal bipyramidal structure of $SF_4$ (Figure 3)[36] in which the two equatorial fluorine atoms have been replaced by isolobal $CpFe(CO)_2$ units so that the fluorine atoms in **4(1)-1S** correspond to the axial fluorine atoms in $SF_4$ with a linear F–S–F angle. The axial S–F distances of

1.646 Å lengthen to 1.874 Å in **4(1)-1S**, presumably an effect of the CpFe(CO)$_2$ substituents. Also the equatorial F–S–F in SF$_4$ of 101.6° expands to 124.8 Å in **4(1)-1S** when the equatorial fluorine atoms are replaced by CpFe(CO)$_2$ units. The relationship of **4(1)-1S** to SF$_4$ suggests a stereochemically active sulfur lone pair in **4(1)-1S**.

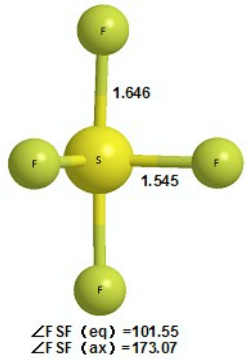


**Figure 3.** The structure of SF$_4$.

The two Cp$_2$Fe$_2$(SF$_2$)$_2$(CO)$_3$ structures can also be derived from the hypothetical Cp$_2$Fe$_2$(CO)$_5$, this time by replacing two CO groups with SF$_2$ groups. The higher energy of these two structures, namely **3(2)-2S** (Figure 2), has a bridging SF$_2$ group similar to that in **4(1)-1S** as well as a terminal SF$_2$ group (Figure 2). The lower energy Cp$_2$Fe$_2$(SF$_2$)$_2$(CO)$_3$ structure **3(2)-1S** is derived from **3(2)-2S** by migration of a fluorine atom from the bridging SF$_2$ group to the terminal SF$_2$ group to give a bridging μ-SF ligand and a terminal SF$_3$ ligand. This fluorine migration reaction lowers the energy by ~11 kcal/mol. An essentially linear F–S–F angle of ~171° in the terminal SF$_3$ ligand of **3(2)-1S** indicates a one-electron donor SF$_3$ ligand with a stereochemically active lone pair.

The lowest energy Cp$_2$Fe$_2$(CO)$_4$ structures have an iron-iron bond of length 2.54 Å bridged by two of the four CO groups. A higher energy unbridged Cp$_2$Fe$_2$(CO)$_4$ structure with a longer 2.73 Å Fe–Fe bond is found in the theoretical study of this system.[20] However, replacing a CO group in Cp$_2$Fe$_2$(CO)$_4$ with an SF$_2$ group leads only to low-energy Cp$_2$Fe$_2$(SF)(F)(CO)$_3$ structures with separate SF and F units. The four lowest energy such structures differ only in *trans* versus *cis* arrangement of the Cp rings and whether the iron atoms are bridged by a fluorine atom or by an SF unit forming Fe–S bonds with each iron atom. The higher energy Cp$_2$Fe$_2$(SF)(F)(CO)$_3$ structure **3(1)-5S** also has a bridging SF group but forming an Fe–F bond to one iron atom and an Fe–S bond to the other iron atom. None of these Cp$_2$Fe$_2$(SF)(F)(CO)$_3$ structures has an iron-iron bond. Formation of these Cp$_2$Fe$_2$(SF)(F)(CO)$_3$ structures can involve an internal oxidative addition reaction of an S–F bond in an initial $Cp_2Fe_2(CO)_3(SF_2)$ structure across an Fe–Fe bond thereby breaking the Fe–Fe bond and forming a new Fe–F bond. The net result of this process is a fluorine migration from sulfur to iron at the expense of the iron-iron bond.

The low-energy structures for the disubstituted $Cp_2Fe_2(SF_2)_2(CO)_2$ include structures such as **2(2)-2T** and **2(2)-4S** in which both fluorine atoms of an $SF_2$ unit have migrated, one to an iron atom and the other to the other $SF_2$ group to make a $SF_3$ ligand (Figure 2). This leaves a central bare sulfur atom bridging the two iron atoms. The lowest energy $Cp_2Fe_2(SF_2)_2(CO)_2$ structure **2(2)-1S**, however, has one $SF_2$ group split into a bridging SF ligand and a terminal fluorine atom leaving a terminal $SF_2$ ligand on the iron atom not bearing the terminal fluorine atom. Structure **2(2)-1S** is closely related to the lowest energy $Cp_2Fe_2(SF_2)(CO)_3$ structure **3(1)-1S**.

The $Cp_2Fe_2(SF_2)(CO)_2$ structures are formally derived from the unsaturated $Cp_2Fe_2(CO)_3$ by replacing one of the CO groups with an $SF_2$ unit. However, whereas $Cp_2Fe_2(CO)_3$ has three bridging CO groups and a formal Fe=Fe double bond,[17,18,19] all of the low-energy $Cp_2Fe_2(SF_2)(CO)_2$ structures have long Fe···Fe distances indicating the lack of a direct iron-iron bond as well as only terminal CO groups. The lowest energy $Cp_2Fe_2(SF_2)(CO)_2$ structure is the triplet structure **2(1)-1T** in which the $SF_2$ group has split into a bare sulfur atom bridging the two iron atoms and two fluorine atoms bonded to the same iron atom. In the lowest energy singlet structures **2(1)-2S** and **2(1)-3S** the $SF_2$ group has split into SF and F units, each of which bridges the iron atoms by donating one electron to one iron atom and two electrons to the other iron atom. In this way each iron atom can get the favorable 18-electron configuration.

## 5. Summary

None of the low-energy $Cp_2Fe_2(SF_2)_m(CO)_n$ structures ($m = 1$, $n = 4, 3, 2$; $m = 2$, $n = 3, 2$) has short Fe-Fe distances suggesting a direct metal-metal bond. This suggests that metal-metal bonds in such structures are incompatible with sulfur-fluorine bonds. Thus the low energy structures with one $SF_2$ unit are of the type $Cp_2Fe_2(SF)(F)(CO)_n$ ($n = 3, 2$) in which either the SF or F unit can bridge the iron atoms. For the $Cp_2Fe_2(SF_2)_2(CO)_n$ systems ($n = 3, 2$), fluorine atoms can migrate from an $SF_2$ group either to an iron atom or to the other $SF_2$ group forming an $SF_3$ ligand. Low-energy structures are found in which an $SF_2$ group has lost both fluorine atoms in these ways leaving a bare sulfur atom bridging the two iron atoms.

The $Cp_2Fe_2(SF_2)(CO)_4$ and $Cp_2Fe_2(SF_2)_2(CO)_3$ systems are derived from a hypothetical $Cp_2Fe_2(CO)_5$ species, which does not require an Fe-Fe bond for each iron atom to have the favored 18-electron configuration. Fluorine migration does not occur in the lowest energy $Cp_2Fe_2(SF_2)(CO)_4$ structure, which has the $SF_2$ group bridging the iron atoms in two $CpFe(CO)_2$ units. A related structure with one bridging $SF_2$ group and one terminal $SF_2$ group is found for $Cp_2Fe_2(SF_2)_2(CO)_3$. However, the lowest energy isomer is a structure of the type $Cp_2Fe_2(\mu\text{-}SF)(SF_3)(CO)_3$ in which a fluorine atom has migrated from the bridging $SF_2$ group to the terminal $SF_2$ group to give a bridging SF ligand and a terminal $SF_3$ ligand.

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**Supporting Information.** Tables S1 to S14: Coordinates of the $Cp_2Fe_2(SF_2)(CO)_n$ structures ($n$ = 2, 3, 4); Tables S15 to S22: Coordinates of the $Cp_2Fe_2(SF_2)_2(CO)_n$ structures ($n$ = 2, 3); Tables S23 and S24: Harmonic vibrational frequencies of the $Cp_2Fe_2(SF_2)(CO)_n$ ($n$ = 2, 3, 4) complexes; Tables S25 and S26: Harmonic vibrational frequencies of the $Cp_2Fe_2(SF_2)_2(CO)_n$ ($n$ = 2,3) complexes; Figure S1: Optimized geometries (bond lengths in Å) at the M06-L/DZP levels of theory for $Cp_2Fe_2(SF_2)(CO)_n$ structures ($n$ = 2, 3, 4); Figure S2: Optimized geometries (bond lengths in Å) at the M06-L/DZP levels of theory for $Cp_2Fe_2(SF_2)_2(CO)_n$ structures ($n$ = 2, 3); Table S27: Total energies E (Hartree), relative energies ΔE (kcal/mol), Fe···Fe distances at the M06-L/DZP levels of theory for $Cp_2Fe_2(SF_2)(CO)_n$ structures ($n$ = 2, 3, 4); Table S28: Total energies E (Hartree), relative energies ΔE (kcal/mol), Fe···Fe distances at the M06-L/DZP levels of theory for $Cp_2Fe_2(SF_2)_2(CO)_n$ structures ($n$ = 2, 3); complete Gaussian reference.

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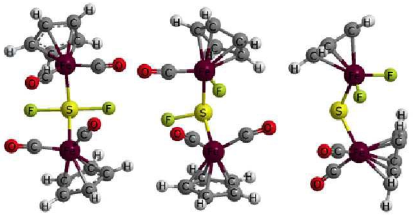
# Graphical Abstract

## Fluorine Shifts From Sulfur to Metal in Difluorosulfane Complexes of Cyclopentadienyl Iron Carbonyl: Incompatibility of Sulfur-Fluorine Bonds with Iron-Iron Bonds

Huaiyu Jiang, Nan Li*, R. Bruce King*

Density functional theory studies on $Cp_2Fe_2(SF_2)_m(CO)_n$ ($m$ = 1, $n$ = 4, 3, 2; $m$ = 2, $n$ = 3, 2) show that none of the low-energy such structures have short enough Fe-Fe distances suggesting a direct iron-iron bond. Instead fluorine transfer from an $SF_2$ group to an iron atom or another $SF_2$ group is observed.



$Cp_2Fe_2(SF_2)(CO)_4$ $Cp_2Fe_2(SF_2)(CO)_3$ $Cp_2Fe_2(SF_2)(CO)_2$