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Sulfur Difluoride and Sulfur Monofluoride as Ligands in Iron Carbonyl Chemistry

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Abstract

Density functional theory predicts a binuclear $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ octacarbonyl structure with two bridging SF_2 groups and a long Fe⋯Fe distance of ~3.5 Å indicating a lack of a direct iron-iron bond. In addition, three $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ stereoisomers of similar energies are found with one bridging SF_2 group and one terminal SF_2 group and an even longer Fe⋯ Fe distance of ~3.9 Å likewise indicating a lack of a direct iron-iron bond. In contrast to the binuclear $Fe_2(SF_2)_2(CO)_n$ (n = 8, 7) derivatives, the mononuclear $Fe(SF_2)(CO)_n$ (n = 4, 3) are disfavored by ~10 kcal/mol for n = 4 to ~30 kcal/mol for n = 3, respectively, with respect to fluorine shift from sulfur to iron to give the corresponding $Fe(SF)(F)(CO)_n$ derivatives. The SF ligands in the tetracarbonyls $Fe(SF)(F)(CO)_4$ are one-electron donor ligands with Fe–S distances of ~2.3 Å. However, the SF ligands in the tricarbonyls $Fe(SF)(F)(CO)_3$ are three-electron donor ligands with significantly shorter Fe=S distances of ~2.1 Å.

1. Introduction

The use of carbon monoxide as a ligand to stabilize low transition metal oxidation states dates back to the 1890 discovery of nickel tetracarbonyl as a volatile liquid containing nickel in the zerovalent oxidation state.[1] During the subsequent century a variety of other zerovalent binary metal carbonyls were discovered among which $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and $Co_2(CO)_8$ have become commercially available stable reagents frequently used in transition metal organometallic chemistry. The syntheses of such stable binary metal carbonyls typically involves reactions of suitably chosen transition metal systems with carbon monoxide, mostly at elevated pressures. A key to the stabilization of formally zerovalent transition metal derivatives is the removal of electron density from the metal atom by $d\pi \rightarrow p\pi^*$ back-bonding of filled metal d orbitals with empty CO antibonding orbitals.

The unusual properties of the CO ligand in stabilizing low oxidation states stimulated the search for other ligands with similar properties. In this connection Wilkinson and Irvine[2] in 1951 discovered that phosphorus trifluoride (trifluorophosphine) could stabilize low transition metal oxidation states even more effectively than CO. They thus discovered the binary zerovalent nickel trifluorophosphine complex $Ni(PF_3)_4$, as a volatile liquid considerably more stable than $Ni(CO)_4$. Subsequent work led to the extensive development of metal trifluorophosphine chemistry, particularly in the laboratories of Kruck et al., who routinely used phosphorus trifluoride under pressure to synthesize a variety of metal trifluorophosphine complexes.[3,4,5,6,7,8,9,10,11,12] The key to the effectiveness of phosphorus trifluoride as a strong acceptor ligand to stabilize low metal oxidation states is the combination of the phosphorus lone pair with the strong electron withdrawing properties of the fluorine atoms. In a number of cases such as the binary platinum complex[13] $Pt(PF_3)_4$, metal trifluorophosphine complexes could be isolated that do not have stable carbonyl analogues.

Another main group element fluoride that might be expected to function as a ligand to stabilize unusually low formal metal oxidation states is sulfur difluoride (difluorosulfane). In SF_2 there are two lone pairs available on the sulfur atom for donation to transition metals. In addition there are two fluorine atoms to enhance the acceptor properties of the SF_2 ligand. However, methods that are useful for the synthesis of metal carbonyls and metal trifluorophosphine complexes cannot be applied to the synthesis of metal difluorosulfane complexes owing to the instability of sulfur difluoride except either in low temperature matrices[14] or highly diluted in the gas phase.[15,16] Therefore metal difluorosulfane complexes have not been synthesized.

Another sulfur fluoride ligand of potential interest in transition metal chemistry is the trifluorosulfane ligand. The trifluorosulfane ligand bears the same relationship to the well-known nitrosyl (NO) ligand[17,18] as the trifluorophosphine ligand bears to the carbonyl ligand. Furthermore, trifluorosulfonium salts, such as $[SF_3^+][BF_4^-]$, and $[SF_3^+][EF_6^-]$ (E = P, As, Sb), are stable species obtained by abstraction of fluoride from SF_4 with strongly Lewis acidic fluorides.[19,20] Such trifluorosulfonium salts are potential reagents for the preparation of SF_3 transition metal complexes. However, the only metal SF_3 complex that has been isolated as a stable species is the octahedral iridium complex $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, which is obtained from the reaction of *trans*-$(Et_3P)_2Ir(CO)Cl$ with SF_4.[21] The neutral SF_3 ligand in this iridium complex is a pseudo trigonal bipyramidal one-electron donor ligand rather than a tetrahedral three-electron donor ligand analogous to the linear NO ligand found in the typical metal nitrosyl complexes. Theoretical studies suggest that metal carbonyl trifluorosulfane derivatives such as $M(CO)_n(SF_3)$ ($n = 5$, M = V, Ta; $n = 4$, M = Mn, Re; $n = 3$, M = Co) with tetrahedral three-electron donor SF_3 ligands are strongly disfavored thermochemically with respect to a fluorine shift from sulfur to metal to give isomeric $M(CO)_n(F)(SF_2)$ complexes.[22,23] Only $Ir(CO)_3(SF_3)$, in which the SF_3 group is a pseudo trigonal bipyramidal one-electron donor ligand rather than a tetrahedral three-electron donor ligand, has a chance of being viable toward fluorine shift to give the isomeric $Ir(CO)_3(F)(SF_2)$ derivative. These theoretical studies suggest that the SF_3 ligand, at least as a tetrahedral three-electron donor, is too strong a fluorinating agent for trifluorosulfane metal carbonyl complexes to be viable. This is consistent with the use of sulfur-fluorine compounds, notably SF_4, as fluorinating agents, particularly in organic chemistry.[24]

The predicted exothermic fluorine shift reactions of metal trifluorosulfane complexes $[M](SF_3)$ to give the isomeric metal difluorosulfane fluoride complexes $[M](F)(SF_2)$ suggests a method for the preparation of difluorosulfane complexes avoiding the need for the unstable sulfur difluoride. In fact, theoretical studies predict $[M](F)(SF_2)$ complexes to be viable towards SF_2 elimination to give the corresponding metal fluorides $[M](F)$.[23] In order to explore the scope of metal difluorosulfane complexes analogous to metal carbonyls we have used density functional theory to investigate the preferred structures and thermochemistry of iron carbonyl difluorosulfane complexes. Because the indirect methods required to introduce the SF_2 ligand into transition metal complexes, probably using SF_3^+ salts as the source of the SF_2 ligand, are not readily adapted to the synthesis of compounds with multiple SF_2 ligands, we have limited this initial study to difluorosulfane iron carbonyl derivatives of the types $Fe(SF_2)(CO)_n$ ($n = 4, 3$) and $Fe_2(SF_2)_2(CO)_n$ ($n = 8, 7$) containing only one SF_2 ligand per iron atom.

A key issue in the development of the chemistry of difluorosulfane metal complexes is their viability towards further fluorine migration reactions from sulfur to the metal to give metal complexes of the SF (fluorosulfane) ligand. In fact, we predict most difluorosulfane iron carbonyls $Fe_m(SF_2)_m(CO)_n$ ($m = 1$, $n = 4, 3$; $m = 2$, $n = 7$) to be disfavored with respect to the isomeric $Fe_mF_m(SF)_m(CO)_n$ complexes. Only for $Fe_2(SF_2)(CO)_8$ does a genuine SF_2 complex appear to be viable. The SF ligands in the $Fe_mF_m(SF)_m(CO)_n$ complexes are of interest in their own right since as neutral SF ligands they can be either formal donors of one or three electrons to a metal atom analogous to the SF_3 ligand.

2. Theoretical Methods

All calculations were performed using the Gaussian 09 program package.[25] Three density functional theory (DFT) methods were used, namely B3LYP, BP86, and B3LYP*. The B3LYP method uses a hybrid functional combining Becke's three parameter functional (B3)[26] with the Lee, Yang, and Parr (LYP) correlation functional.[27] The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B)[28] with Perdew's 1986 correlation functional (P86).[29] In this study, some of the $Fe(SF_2)(CO)_3$/$Fe(SF)(F)(CO)_3$ structures optimized by the method of B3LYP favor the high-spin state, while those optimized with the BP86 method favor the low-spin state. In order to resolve this discrepancy we used the B3LYP* method, which is a reparametrised version of the B3LYP hybrid functional developed by Reiher providing electronic state orderings in agreement with experiment for the G2 test set.[30] In the present paper, only the B3LYP* results are reported. The B3LYP and BP86 results are listed in the Supporting Information.

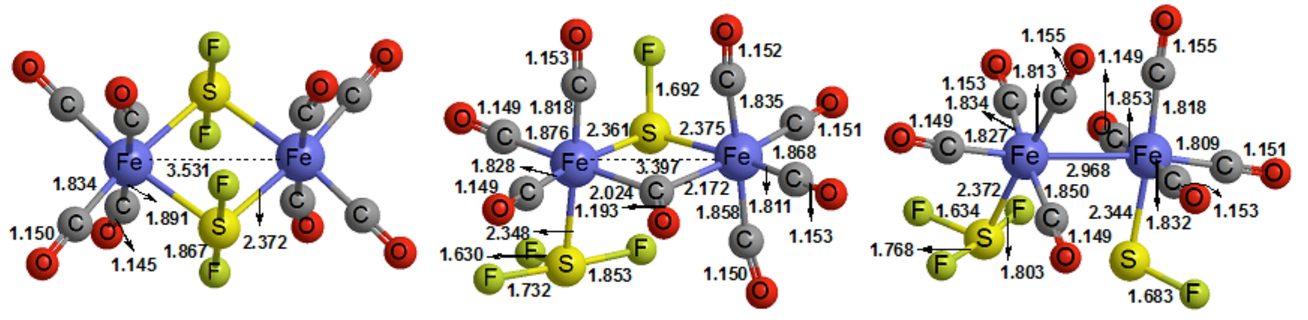
The double-ζ plus polarization (DZP) basis sets were used for all computations. For carbon, oxygen, fluorine and sulfur, these DZP basis sets were obtained by adding one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.00$, and $\alpha_d(S) = 0.70$, respectively, to the Huzinaga-Dunning standard contracted DZ sets.[31,32] For Fe, 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.[35] The finer grid (120, 974) was used for more precise resolution of small imaginary vibrational frequencies. Unless otherwise indicated, all of the structures reported in this paper are genuine minima, with only real vibrational frequencies. The tight (10^{-8} hartree) designation was the default for the self-consistent field (SCF) convergence.

The optimized structures are designated as **N-nS/T**, where **N** is the number of carbonyl groups, **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, **4-1S** is the lowest-lying singlet structure for $Fe(SF)(F)(CO)_4$. The bond distances in the figures were determined by the B3LYP* method.

3. Results

3.1 Molecular Structures of the Binuclear Derivatives

3.1.1 $Fe_2(SF_2)_2(CO)_8$ structures. Three $Fe_2(SF_2)_2(CO)_8$ structures were optimized (Figure 1). The lowest energy structure **8-1S** is predicted to be a C_{2h} structure with two bridging SF_2 groups and four terminal CO groups on each iron atom. The predicted long Fe⋯Fe distance of 3.531 Å obviously indicates the absence of a direct metal-metal bond. The nearly linear F-S-F angle of 178.8° in the bridging SF_2 groups suggests pseudo trigonal bipyramidal coordination of the sulfur atoms with a stereochemically active lone pair in an equatorial position. The SF_2 and CO ligands are two-electron donors leading to the favored 18-electron configuration for both Fe atoms in **8-1S**.



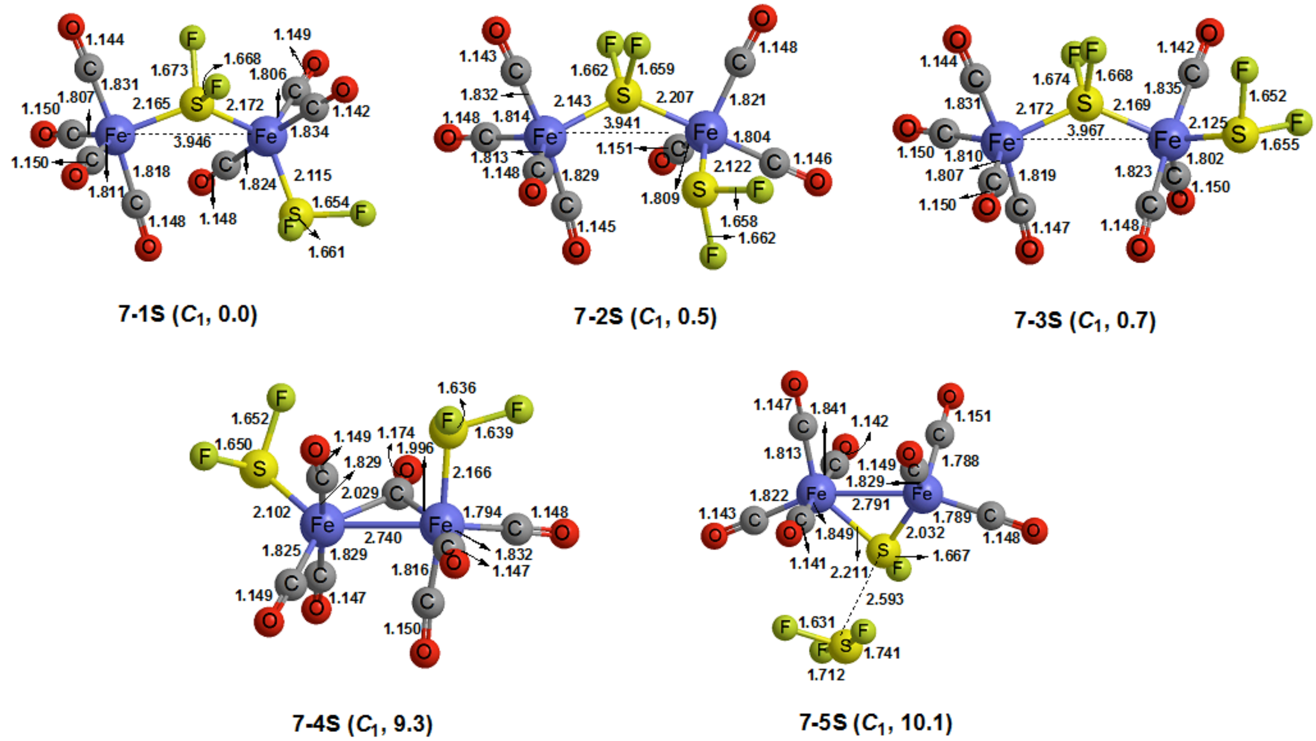
8-1S (D_{2h}, 0.0) **8-2S** (C_1, 16.5) **8-3S** (C_1, 20.5)

Figure 1. Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe_2(SF_2)_2(CO)_8$ structures. The numbers in the parentheses are the relative energies (ΔE in kcal/mol). The subsequent figures have the same arrangement.

The $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S** is obviously a very favorable structure since it lies a large 16.5 kcal/mol in energy below the next lowest energy $Fe_2(SF_2)_2(CO)_8$ structure **8-2S** (Figure 1). Structure **8-1S** thus appears to be an interesting synthetic objective. Structure **8-2S** is a fascinating $Fe_2(\mu\text{-}SF)(\mu\text{-}CO)(SF_3)(CO)_7$ structure with one bridging SF group, one bridging CO group, one terminal SF_3 group, and seven terminal CO groups. The sulfur atom in the terminal SF_3 group of **8-2S** has pseudo trigonal bipyramidal geometry with an Fe–S distance of 2.348 Å implying a formal single bond and a stereochemically active lone pair in an equatorial position. This terminal SF_3 group is thus a one-electron donor when considered as a neutral ligand. The predicted Fe···Fe distance of 3.397 Å in **8-2S**, is shorter than that in **8-1S** but nevertheless indicates the lack of a direct iron-iron bond. This makes **8-2S** a relatively rare example of a metal carbonyl derivative with a bridging CO group not accompanied by a metal-metal bond. However, the existence of the bridging CO group in **8-2S** shortens the non-bonded distance between the two iron atoms such as typically occurs with CO groups bridging metal-metal bonds. The bridging SF group is a three-electron donor considered as a neutral ligand and the terminal SF_3 group is a one-electron donor leading to the favored 18-electron configuration for each Fe atom in **8-2S**.

The third $Fe_2(SF_2)_2(CO)_8$ structure **8-3S**, lying 20.5 kcal/mol above **8-1S**, has eight terminal CO groups, one terminal SF group, and one terminal SF_3 group (Figure 1). The predicted Fe–S distances of ~2.3 Å to both the terminal SF and SF_3 groups imply formal single bonds and thus one-electron donors when considered as neutral ligands. The interpretation of the SF_3 ligand in **8-3S** as a one-electron donor rather than a three-electron donor is also supported by its pseudo trigonal bipyramidal geometry with a stereochemically active lone pair in an equatorial position. The predicted Fe–Fe distance of 2.968 Å can be considered as a formal single bond, thereby giving each iron atom the favored 18-electron configuration.

3.1.2 $Fe_2(CO)_7(SF_2)_2$ structures. Five $Fe_2(CO)_7(SF_2)_2$ structures were found (Figure 2). The three lowest energy structures **7-1S**, **7-2S**, and **7-3S** lie within ~1 kcal/mol of each other implying a fluxional system. Each of these three structures has four terminal CO groups bonded to one iron atom, three terminal CO groups and one terminal SF_2 group bonded to the other iron atom, a bridging SF_2 group, and a long $Fe\cdots Fe$ distance of ~3.9 Å indicating the lack of a direct iron-iron bond. These three $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ stereoisomers differ only in the position of the terminal SF_2 group. The predicted bridging Fe-S distances in the three structures are ~2.17 Å, while the terminal Fe-S bond distances are somewhat shorter at ~2.11 Å. Formulating all of the iron-sulfur bonds as S→Fe dative bonds corresponds to five dative bonds from CO and SF_2 groups to each iron atom so that the local environment of each iron atom is trigonal bipyramidal similar to that in $Fe(CO)_5$. This gives the iron atoms in all three structures the favored 18-electron configuration. In **7-1S** and **7-3S** the axial positions of both iron trigonal bipyramids are occupied by pairs of CO groups. However, in **7-2S** the axial positions of one iron trigonal bipyramid are occupied by a CO group and the sulfur atom of the bridging SF_2 group.



7-1S (C_1, 0.0)

7-2S (C_1, 0.5)

7-3S (C_1, 0.7)

7-4S (C_1, 9.3)

7-5S (C_1, 10.1)

Figure 2. Optimized geometries for the $Fe_2(SF_2)_2(CO)_7$ structures.

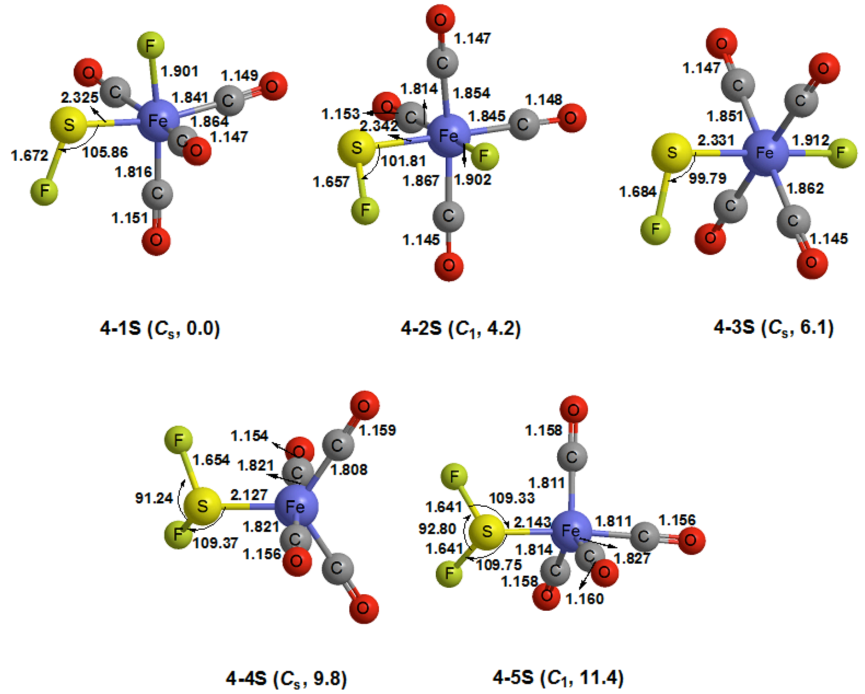
The next higher energy $Fe_2(SF_2)_2(CO)_7$ structure **7-4S**, lying 9.3 kcal/mol in energy above **7-1S**, has three terminal CO groups and one terminal SF_2 group bonded to each iron atom (Figure 2). The Fe–Fe distance of 2.740 Å in **7-4S** suggests a formal single bond. This Fe–Fe bond is bridged by the seventh CO group. Considering each of the nine ligands in **7-4S** as formal two-electron donors gives each iron atom the favored 18-electron configuration.

The next $Fe_2(SF_2)_2(CO)_7$ structure **7-5S**, lying 10.1 kcal/mol in energy above **7-1S**, can be considered as an ion pair with an SF_3^+ cation and an $[Fe_2(CO)_7(\mu\text{-}SF)]^-$ anion (Figure 2). The SF_3^+ cation has pseudo square planar geometry with a stereochemically active lone pair leading to a T-shaped configuration. The $[Fe_2(CO)_7(\mu\text{-}SF)]^-$ anion has a bridging SF ligand, four terminal CO groups bonded to one iron atom, three CO groups bonded to the other iron atom, and a predicted Fe–Fe distance of 2.791 Å implying a formal single bond. Considering the bridging μ-SF group in **7-5S** to be a three-electron donor to the Fe_2 unit gives each iron atom the favored 18-electron configuration. An S···S distance of 2.593 Å between the sulfur of the SF_3^+ cation and the sulfur of the bridging μ-SF group in **7-5S** suggests a weak electrostatic attraction.

3.2 Molecular Structures of the Mononuclear Derivatives

3.2.1 $Fe(SF)(F)(CO)_4$ and $Fe(SF_2)(CO)_4$ structures. Three $Fe(SF)(F)(CO)_4$ and two $Fe(SF_2)(CO)_4$ structures were optimized (Figure 3). The three $Fe(SF)(F)(CO)_4$ structures **4-1S**, **4-2S**, and **4-3S** with separate SF and F ligands are lower energy structures than the two $Fe(SF_2)(CO)_4$ isomers **4-4S** and **4-5S** with intact SF_2 ligands. The Fe-S distances in the $Fe(SF)(F)(CO)_4$ and $Fe(SF_2)(CO)_4$ structures are predicted to be ~2.3 Å and ~2.1 Å, suggesting formal Fe–S single and Fe=S double bonds, respectively. This is consistent with NBO analysis suggesting Fe–S single bonds in the $Fe(SF)(F)(CO)_4$ structures. Structure **4-1S** as well as **4-2S**, lying 4.2 kcal/mol in energy above **4-1S**, have their SF and F groups in *cis* positions of octahedrally coordinated iron atoms. They differ only in the orientation of the fluorine atom of the SF group relative to the fluorine atom directly bonded to iron. The $Fe(SF)(F)(CO)_4$ structure **4-3S**, lying 6.1 kcal/mol in energy above **4-1S**, has the SF and F ligands in *trans* positions of the octahedrally coordinated iron atom. The predicted Fe-F distances are ~1.9 Å in the $Fe(SF)(F)(CO)_4$ structures. The predicted Fe-S-F angle of ~100° in the $Fe(SF)(F)(CO)_4$ structures suggest two stereochemically active lone pairs on the sulfur atoms corresponding to pseudotetrahedral sulfur coordination. In the $Fe(SF)(F)(CO)_4$ structures **4-1S**, **4-2S**, and **4-3S** the SF and F ligands are one-electron donors, and the CO ligands are two-electron donors leading to the favored 18-electron configuration for the Fe atoms.

The two $Fe(SF_2)(CO)_4$ structures **4-4S** and **4-5S** with an intact SF_2 ligand, lying ~10 kcal/mol in energy above **4-1S**, exhibit approximate trigonal bipyramidal coordination for their central iron atoms (Figure 3). In **4-4S**, the SF_2 ligand occupies an equatorial position, while in **4-5S** the SF_2 ligand occupies an axial position. The SF_2 ligand can be regarded as a two-electron donor thereby giving the Fe atoms in **4-4S** and **4-5S** the favored 18-electron configuration.

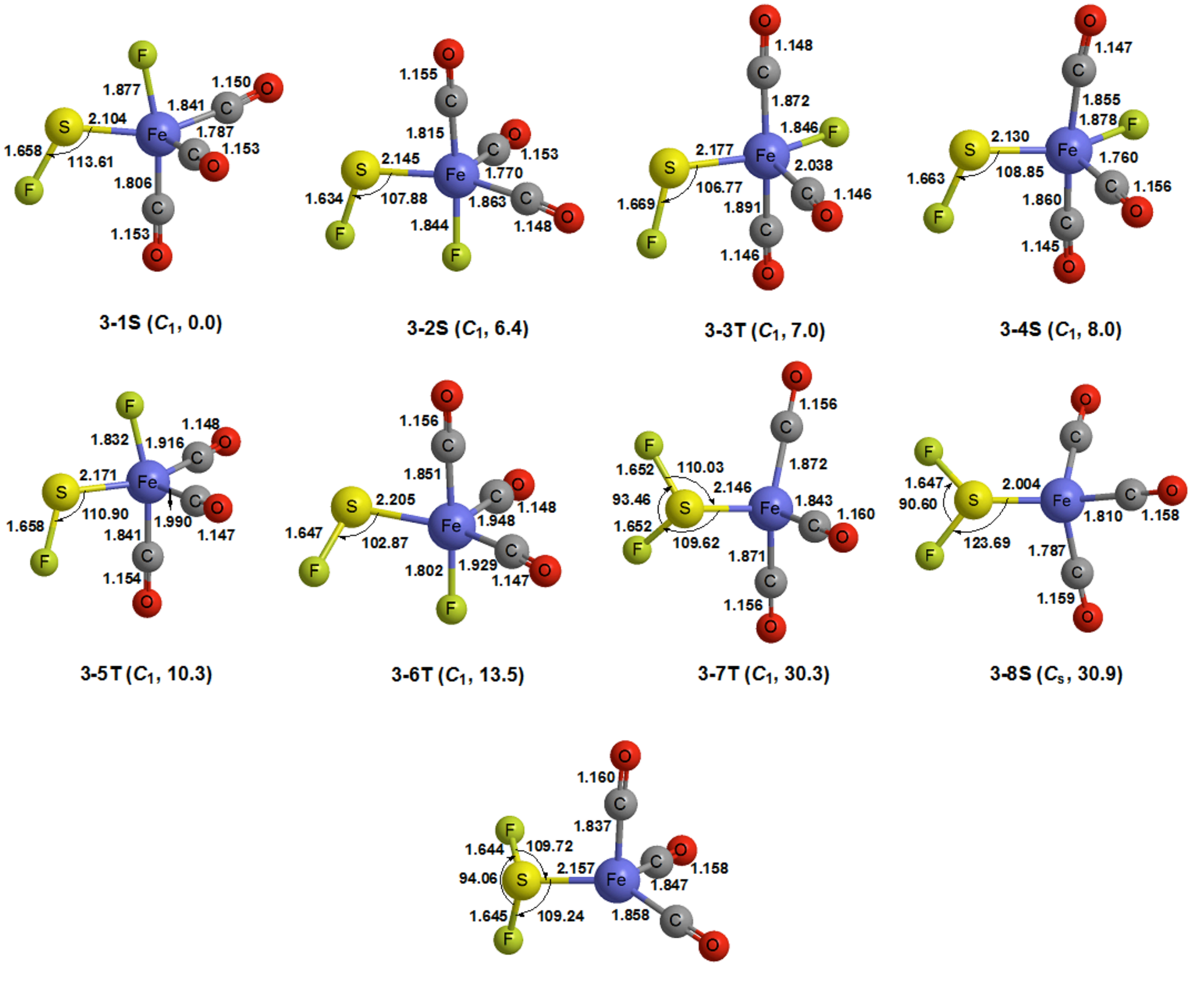


4-1S (C_s, 0.0) **4-2S** (C_1, 4.2) **4-3S** (C_s, 6.1)

4-4S (C_s, 9.8) **4-5S** (C_1, 11.4)

Figure 3. Optimized geometries for the $Fe(SF)(F)(CO)_4$ and $Fe(SF_2)(CO)_4$ structures.

3.2.2 $Fe(SF)(F)(CO)_3$ and $Fe(SF_2)(CO)_3$ structures. The $Fe(SF)(F)(CO)_3$ isomers with separate SF and F ligands are lower energy structures than their $Fe(SF_2)(CO)_3$ isomers with intact SF_2 ligands(Figure 4) similar to the tetracarbonyl structures discussed above The Fe-S distances in the $Fe(SF)(F)(CO)_3$ and $Fe(SF_2)(CO)_3$ isomers are both predicted to be ~2.1 Å suggesting multiple bonding for both structure types. The $Fe(SF)(F)(CO)_3$ structure **3-1S** as well as **3-2S**, lying 6.4 kcal/mol in energy above **3-1S**, both have trigonal bipyramidal coordination of the central iron atom with the fluorine atom in an axial position. They differ only in the orientation of the SF fluorine atom relative to the fluorine atom bonded directly to iron. The $Fe(SF)(F)(CO)_3$ structure **3-4S**, lying 8.0 kcal/mol in energy above **3-1S**, is similar to **3-1S** and **3-2S** except that both the SF and F ligands are in equatorial positions of the trigonal bipyramid. NBO analyses suggest the Fe=S bonds in **3-1S, 3-2S**, and **3-4S** to be formal double bonds consisting of a normal Fe–S single bond combined with a S→Fe dative bond. Thus the neutral SF ligands in **3-1S, 3-2S**, and **3-4S** can be regarded as three-electron donors thereby giving their iron atoms the favored 18-electron configuration. The triplet spin state $Fe(SF)(F)(CO)_3$ structure **3-3T**, lying 7.0 kcal/mol in energy above **3-1S**, has similar geometry to the singlet spin state structure **3-4S**. In addition, the higher energy triplet structures **3-5T** and **3-6T**, lying 10.3 and 13.5 kcal/mol in energy above **3-1S**, respectively, have geometries similar to the singlet structures **3-1S** and **3-2S**, respectively. The predicted Fe-F distances of under 1.9 Å in the $Fe(SF)(F)(CO)_3$ isomers are comparable to those in the Fe(SF)(F)$(CO)_4$ structures. The predicted Fe-S-F angles in the Fe(SF)(F)$(CO)_3$ structures of ~105° relate to the stereochemically active lone pairs on the sulfur atoms.



3-1S (C_1, 0.0) **3-2S** (C_1, 6.4) **3-3T** (C_1, 7.0) **3-4S** (C_1, 8.0)

3-5T (C_1, 10.3) **3-6T** (C_1, 13.5) **3-7T** (C_1, 30.3) **3-8S** (C_s, 30.9)

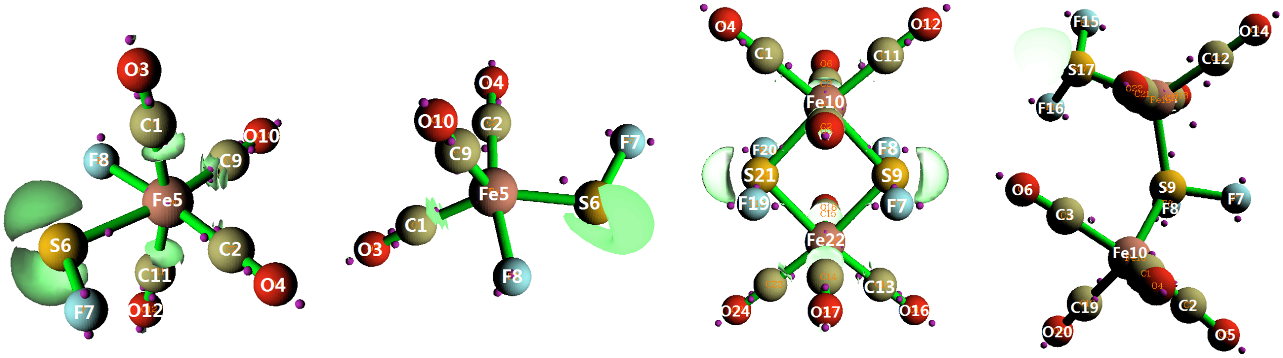
3-9T (C_1, 31.8)

Figure 4. Optimized geometries for the Fe(SF)(F)$(CO)_3$ and Fe$(SF_2)(CO)_3$ structures.

Three Fe$(SF_2)(CO)_3$ isomers with intact SF_2 ligands were found including one singlet spin state structure and two triplet spin state structures (Figure 4). However, all of three of these Fe$(SF_2)(CO)_3$ isomers lie more than 30 kcal/mol in energy above the global minimum Fe(SF)(F)$(CO)_3$ structure **3-1S**. The predicted Fe-S bond lengths in Fe$(SF_2)(CO)_3$ isomers are ~2.00 Å and ~2.15 Å for the singlet and triplet spin state structures, respectively, suggesting higher formal Fe-S bond orders for the singlet Fe$(SF_2)(CO)_3$ structures than for the triplet Fe$(SF_2)(CO)_3$ structures.

3.3 ELF and NBO Analysis of the Ligand-Iron and Iron-Iron Bonding

In electron-rich molecules, lone pairs of electrons are significant since they are often stereochemically active.[36] The ELF (electron localization function) is a simple method[37] for analysis of electron localization in molecular systems. Thus the three-dimensional (3D) ELF isosurface can provide information on the bond and lone pair localization,[38] in which the non-bonded ELF isosurface corresponds to regions occupied by lone pairs.[39] In this study, 3D ELF isosurfaces (ELF = 0.920) were determined using Multiwfn[40] for the most stable predicted structures **4-1S**, **3-1S**, **8-1S**, and **7-1S** (Figure 5). For the Fe(SF)(F)$(CO)_4$ structure **4-1S** two non-bonded ELF regions were found corresponding to the two lone pairs of the sulfur atom. This is consistent with the neutral SF ligand in **4-1S** functioning as a one-electron donor, which leaves two non-bonding sulfur lone pairs. For both the Fe(SF)(F)$(CO)_3$ structure **3-1S** and the $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S,** only one lone pair region was found around each sulfur atom. In **3-1S** this is consistent with the neutral SF ligand being a three-electron donor leaving only a single lone pair. In **8-1S** this is consistent with each bridging SF_2 group forming single Fe–S bonds to each iron atom as well as the two S–F single bonds. This leaves two of the original six sulfur valence electrons as a non-bonding lone pair. In **7-1S**, only one lone pair region is found around the sulfur atom in the terminal SF_2 group and no lone pair region around the sulfur atom of the bridging SF_2 group. This is consistent with the terminal SF_2 group using four of the six sulfur valence electrons for the two S–F bonds and a dative S→Fe bond to the iron atom. The bridging SF_2 group uses all six sulfur valence electrons in forming two S–F bonds and a dative S→Fe bond to each iron atom thereby leaving no electrons for non-bonding lone pairs.



4-1S **ELF=0.920** **3-1S** **ELF=0.920** **8-1S** **ELF=0.920** **7-1S** **ELF=0.920**

Figure 5. ELF isosurfaces (ELF=0.920) for the most stable structures **4-1S**, **3-1S**, **8-1S**, and **7-1S**.

The 3D ELF of **8-1S** indicates that there is a lone pair of each bridging S atom. For the central Fe_2S_2 unit in **8-1S**, each bridging S atom provides one lone pair to the two Fe atoms to form a four-center four-electron delocalized bond, thereby giving each Fe atom the favored 18-electron configuration. For **7-1S,** the NBO analysis shows all three S→Fe bonds to be single dative bonds consistent with the 3D ELF isosurface with only one lone pair (Figure 5). These three S→Fe dative bonds help each Fe atom to satisfy the 18-electron configuration.

Table 1. Wiberg Bond Indices (WBI) of the Fe−S bonds in the mononuclear Fe(SF)(F)(CO)$_n$ and Fe(SF$_2$)(CO)$_n$ singlet structures (n = 3, 4) from NBO analysis

Structures	Fe-S bond length (Å)	WBI	Bond order
4-1S (C_s)	2.325	0.81	1
4-2S (C_1)	2.342	0.83	1
4-3S (C_s)	2.331	0.85	1
4-4S (C_s)	2.127	1.05	1
4-5S (C_1)	2.143	1.06	1
3-1S (C_1)	2.104	1.42	2
3-2S (C_1)	2.145	1.29	2
3-4S (C_1)	2.130	1.35	2
3-8S (C_s)	2.004	1.43	2

Table 2. Wiberg Bond Indices (WBI) of the Fe−S and Fe–Fe Bonds in the Fe$_2$(SF$_2$)$_2$(CO)$_n$ (n = 7, 8) structures from NBO Analysis

Structures	Fe-S/Fe bond length (Å)		WBI	Bond order	Structures	Fe-S/Fe bond length (Å)		WBI	Bond order
8-1S (C_{2h})	Fe10-S9*	2.372	0.77	1	**7-2S** (C_1)	Fe10-S9*	2.143	0.95	1
	Fe10-S21*	2.372	0.77	1		Fe20-S9*	2.207	0.86	1
	Fe22-S9*	2.372	0.77	1		Fe20-S19	2.122	1.10	1
	Fe22-S21*	2.372	0.77	1		Fe-Fe	3.941	0.04	0
	Fe-Fe	3.531	0.03	0					
8-2S (C_1)	Fe18-S9*	2.361	0.76	1	**7-3S** (C_1)	Fe10-S9*	2.172	0.89	1
	Fe10-S9*	2.375	0.76	1		Fe18-S9*	2.169	0.89	1
	Fe18-S17	2.348	0.75	1		Fe18-S17	2.125	1.05	1
	Fe-Fe	3.397	0.07	0		Fe-Fe	3.967	0.04	0
8-3S (C_1)	Fe22-S21	2.372	0.75	1	**7-4S** (C_1)	Fe20-S19	2.102	1.02	1
	Fe10-S9	2.344	0.81	1		Fe10-S9	2.166	0.96	1
	Fe-Fe	2.968	0.36	1		Fe-Fe	2.740	0.27	1
7-1S (C_1)	Fe10-S9*	2.165	0.90	1	**7-5S** (C_1)	Fe10-S19*	2.211	0.77	1
	Fe18-S9*	2.172	0.87	1		Fe20-S19*	2.032	1.19	2
	Fe18-S17	2.115	1.07	1		Fe-Fe	2.791	0.37	1
	Fe-Fe	3.946	0.04	0					

* bridging Fe-S bond length

In order to investigate further the nature of the metal-ligand bonding in the SF$_2$ and SF iron carbonyl complexes, the Wiberg Bond indices (WBIs) of the Fe-S bonds in the singlet structures were determined using natural bond orbital (NBO) analyses (Tables 1 and 2).[41,42] The WBIs for the Fe–S bonds in the related $Fe(SF)(F)(CO)_4$ structures **4-1S**, **4-2S**, and **4-3S** of ~0.8 (Table 1) suggest normal single bonds consistent with the 3D ELF isosurface (Figure 5). For isomer **3-1S**, the higher WBI of ~1.4 for the Fe=S bond suggests a double bond. The ELF shows there is one lone pair of the S atom, which implies the Fe=S double bond consisting of normal two-electron two-center σ bond supplemented by an Fe←S dative bond. This corresponds to a three-electron donor SF ligand, thereby giving the iron atom in **3-1S** the favored 18-electron configuration.

3.4 Thermochemistry of Isomerization, Decarbonylation, and Fragmentation Reactions of the Iron Carbonyl Complexes

Table 3 lists the predicted energies for isomerization, decarbonylation, and fragmentation reactions for the iron carbonyl complexes of sulfur fluoride ligands based on the lowest energy structures. The conversions of the mononuclear $Fe(SF_2)(CO)_n$ (n = 4, 3) to the isomeric $Fe(SF)(F)(CO)_n$ derivatives by fluorine shift from sulfur to iron are predicted to be exothermic indicating the thermal stability of the $Fe(SF)(F)(CO)_n$ species. The decarbonylations of both isomers $Fe(SF)(F)(CO)_4$ and $Fe(SF_2)(CO)_4$ to the corresponding tricarbonyls are endothermic. This suggests the lower energy isomer $Fe(SF)(F)(CO)_4$ to be a reasonable synthetic objective. The thermochemistry (Table 3) suggests the binuclear octacarbonyl $Fe_2(SF_2)_2(CO)_8$ to be disfavored relative to two equivalent $Fe(SF)(F)(CO)_4$ fragments. However, the binuclear heptacarbonyl $Fe_2(SF)_2(CO)_7$ appears to be viable with respect to dissociation into mononuclear fragments.

Table 3. Isomerization Energies (kcal/mol) for $Fe(SF_2)(CO)_n \rightarrow Fe(SF)(F)(CO)_n$ (n = 3, 4), Decarbonylation Energies (kcal/mol) for $Fe(SF)(F)/(SF_2)(CO)_4 \rightarrow Fe(SF)(F)/(SF_2)(CO)_3$ and Fragmentation Reactions Based on the Lowest Energy Structures by the B3LYP* method

Isomerization Reactions	ΔE (kcal/mol)	ΔG (kcal/mol)
$Fe(SF_2)(CO)_4 \rightarrow Fe(SF)(F)(CO)_4$	–9.8	–10.2
$Fe(SF_2)(CO)_3 \rightarrow Fe(SF)(F)(CO)_3$	–30.3	–29.1
Decarbonylation Reactions		
$Fe(SF)(F)(CO)_4 \rightarrow Fe(SF)(F)(CO)_3 + CO$	14.7	4.4
$Fe(SF_2)(CO)_4 \rightarrow Fe(SF_2)(CO)_3 + CO$	35.3	23.4
Fragmentation Reactions		
$Fe_2(SF_2)_2(CO)_8 \rightarrow 2Fe(SF)(F)(CO)_4$	2.9	–14.2
$Fe_2(SF_2)_2(CO)_7 \rightarrow Fe(SF)(F)(CO)_4 + Fe(SF)(F)(CO)_3$	19.8	6.1

4. Discussion

This theoretical study predicts the existence of viable $Fe_2(SF_2)_2(CO)_n$ ($n = 8, 7$) structures having intact SF_2 ligands. The $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S** with two bridging SF_2 groups is particularly favorable since it lies more than 16 kcal/mol in energy below the next lowest energy isomer **8-2S** (Figure 1). This is a promising synthetic objective that might be obtainable by the reaction of the known[43] $(Me_3Si)_2Fe(CO)_4$ with SF_4 under mild conditions and with carefully controlled stoichiometries to prevent fluorination of the CO groups with excess SF_4. In addition, three low energy $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ stereoisomers having one terminal and one bridging SF_2 group are found with energies within ~1 kcal/mol (Figure 2). This closeness in energy of three stereoisomers suggest a highly fluxional system. The low-energy $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S** and the three low-energy $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ structures **7-1S**, **7-2S**, and **7-3S** all have long Fe⋯Fe distances ranging from ~3.5 Å in **8-1S** to ~3.9 Å in the three $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ structures indicating the absence of direct iron-iron bonds. This is confirmed by low WBIs of 0.03 to 0.04 for the Fe⋯Fe interactions in these structures.

The bridging SF_2 groups in these $Fe_2(SF_2)_2(CO)_n$ ($n = 8, 7$) structures are of two types (Figure 6). In the $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S** each of the bridging SF_2 groups is a one-electron donor to each iron atom with Fe–S distances of ~2.37 Å and WBIs of 0.77. The sulfur atoms in **8-1S** can be considered to have pseudo trigonal bipyramidal coordination forming two axial S–F bonds and two equatorial S–Fe two-electron two-center covalent bonds leaving a stereochemically active lone pair in an equatorial position. These stereochemically active lone pairs in the bridging SF_2 ligands can be recognized in the ELF isosurface of $Fe_2(\mu\text{-}SF_2)(CO)_8$ (Figure 5).

8-1S
pseudo trigonal bipyramidal
1 electron to each Fe

7-1S, 7-2S, 7-3S
tetrahedral
2 electrons to each Fe

Figure 6. Two different types of bridging $\mu\text{-}SF_2$ groups indicating the approximately sulfur coordination geometry and electron lone pairs. Two-electron two-center covalent bonds are indicated by solid lines (—), dative bonds are indicated by arrows (→), and non-bonding interactions by dashed lines (---).

The bridging SF_2 ligands in the three $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ structures **7-1S**, **7-2S**, and **7-3S** are of a different type than those in **8-1S**, since they donate two electrons to each iron atom (Figure 6). In these systems all six sulfur valence electrons are used to bond to iron or fluorine atoms leading to tetrahedral sulfur coordination without any stereochemically active lone pairs. The iron-sulfur bonding in **7-1S**, **7-2S**, and **7-3S** can be considered as S→Fe dative bonds leading to shorter iron-sulfur distances of ~2.15 Å. The absence of a stereochemically active lone pair on the bridging sulfur atom in **7-1S** can be recognized in its ELF isosurface (Figure 5). Note that loss of a CO group from the $Fe_2(\mu\text{-}SF_2)_2(CO)_8$ structure **8-1S** to give an $Fe_2(\mu\text{-}SF_2)(SF_2)(CO)_7$ structure **7-1S**, **7-2S**, or **7-3S** converts one of the bridging SF_2 groups in **8-1S** from a two-electron donor pseudo trigonal bipyramidal $\mu\text{-}SF_2$ group to a four-electron donor tetrahedral $\mu\text{-}SF_2$ group with other $\mu\text{-}SF_2$ group becoming a terminal SF_2 group.

The mononuclear $Fe(SF_2)(CO)_n$ (n = 4, 3) derivatives differ from the binuclear $Fe_2(SF_2)(CO)_n$ (n = 8, 7) derivatives in their susceptibility to fluorine shifts from sulfur to metal similar to the metal trifluorosulfane complexes previously studied theoretically.[22,23] Such processes generate $Fe(SF)(F)(CO)_n$ (n = 4, 3) derivatives predicted to have lower energies than the isomeric $Fe(SF_2)(CO)_n$ derivatives. The resulting terminal SF groups, considered as neutral ligands, can be either one- or three-electron donors to the central iron atom (Figure 7). Thus the tetracarbonyls $Fe(SF)(F)(CO)_4$ (Figure 3) require one-electron donor SF ligands to give the iron atom the favored 18-electron configuration. The Fe–S distances to such one-electron donor SF ligands are ~2.35 Å and can regarded as formal single bonds with WBIs of ~0.8. The sulfur atoms of such one-electron donor SF ligands have two stereochemically active lone pairs, which can be recognized in the ELF isosurface of the $Fe(SF)(F)(CO)_4$ structure **4-1S** (Figure 5). The F-S-Fe angles in these $Fe(SF)(F)(CO)_4$ structures with one-electron donor SF ligands range from 98° to 106°. However, the tricarbonyls $Fe(SF)(F)(CO)_3$ (Figure 4) require three-electron donor SF ligands to give each iron atom the favored 18-electron configuration. The Fe=S distances to such three-electron donor SF ligands at ~2.1 Å are significantly shorter than the Fe–S distances to one-electron donor SF ligands. Three-electron donor SF ligands have only one stereochemically active lone pair, which can be recognized in the ELF isosurface of the $Fe(SF)(F)(CO)_3$ structure **3-1S** (Figure 5). The F-S-Fe angles in in these $Fe(SF)(F)(CO)_3$ structures with three-electron donor SF ligands are slightly wider than those in the $Fe(SF)(F)(CO)_4$ structures with one-electron donor SF ligands ranging from 102° to 113°. This widening of the F-S-Fe angle in the iron complexes with a three-electron donor SF ligand relative to those in the iron complexes with a one-electron donor SF ligand may be a consequence of two stereochemically active lone pairs in the latter complexes but only one stereochemically active lone pair in the former complexes.

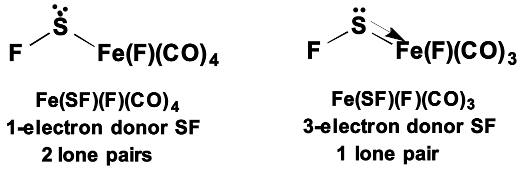


Figure 7. Comparison of the one-electron donor SF ligands in the $Fe(SF)(F)(CO)_4$ structures **4-1S**, **4-2S**, and **4-3S** with the three-electron donor SF ligands in the $Fe(SF)(F)(CO)_3$ structures.

5. Conclusions

This theoretical study of $Fe(SF_2)(CO)_n$ (n = 4, 3) and $Fe_2(SF_2)_2(CO)_n$ (n = 8, 7) derivatives indicates major differences between the PF_3 and SF_2 ligands even though both ligands have strongly electron withdrawing fluorine atoms and at least one lone electron pair on the donor atom. The known experimental chemistry of metal PF_3 complexes is almost exclusively limited to species with terminal PF_3 ligands. Many such metal complexes are analogous to metal carbonyls but often thermally more stable. On the other hand metal complexes with bridging PF_3 groups are very rare consistent with our previously reported theoretical studies on such complexes. In contrast to the PF_3 ligand the SF_2 ligand appears to have a high tendency to bridge two metal atoms as indicated by the predicted viability of $Fe_2(SF_2)_2(CO)_n$ (n = 8, 7) complexes with bridging SF_2 ligands. The much greater tendency of the SF_2 ligand to bridge two metal atoms relative to the PF_3 ligand can be related to the lower sulfur coordination number and the presence of two sulfur lone pairs for donation to different metal atoms.

Supporting Information

Table **S1 to S4** Coordinates of the $Fe(SF)(F)(CO)_4$/ $Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/ $Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively; Tables **S5 to S8** Harmonic vibrational frequencies of the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively; Table **S9 to S12** Optimized geometries (bond lengths in Å) at the B3LYP*/DZP level of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively; Table **S13 to S16** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively; Figures **S1 to S4** Optimized geometries (bond lengths in Å) at the BP86/DZP (the upper) and B3LYP/DZP (the lower) levels of theory for the $Fe(SF)(F)(CO)_4$/$Fe(SF_2)(F)(CO)_4$, $Fe(SF)(F)(CO)_3$/$Fe(SF_2)(F)(CO)_3$, $Fe_2(SF_2)_2(CO)_8$, $Fe_2(SF_2)_2(CO)_7$ derivatives, respectively.

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