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Trifluorosulfane Ligand as an Analogue of the Nitrosyl Ligand: Highly Exothermic Fluorine Transfer Reactions from Sulfur to Metal in the Chemistry of SF_3 Metal Carbonyls of the First Row Transition Metals

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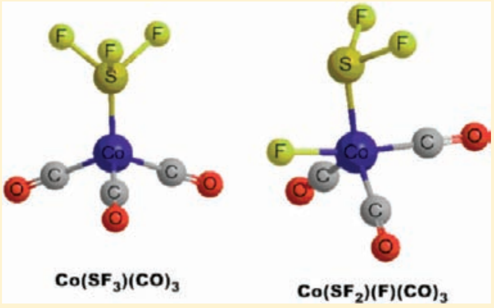
S *Supporting Information*



ABSTRACT: The variety of known very stable PF_3 metal derivatives analogous to metal carbonyls suggests the synthesis of SF_3 metal derivatives analogous to metal nitrosyls. However, the only known SF_3 metal complex is the structurally uncharacterized $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ synthesized by Cockman, Ebsworth, and Holloway in 1987 and suggested by electron counting to have a one-electron donor SF_3 group rather than a three-electron donor SF_3 group. In this connection, the possibility of synthesizing SF_3 metal derivatives analogous to metal nitrosyls has been investigated using density functional theory. The $[M]SF_3$ derivatives with $[M] = V(CO)_5$, $Mn(CO)_4$, $Co(CO)_3$, $Ir(CO)_3$, $(C_5H_5)Cr(CO)_2$, $(C_5H_5)Fe(CO)$, and $(C_5H_5)Ni$ analogous to known metal nitrosyl derivatives are all predicted to be thermodynamically disfavored with respect to the corresponding $[M](SF_2)(F)$ derivatives by energies ranging from 19.5 kcal/mol for $Mn(SF_3)(CO)_4$ to 5.4 kcal/mol for $Co(SF_3)(CO)_3$. By contrast, the isoelectronic $[M]PF_3$ derivatives with $[M] = Cr(CO)_5$, $Fe(CO)_4$, $Ni(CO)_3$, $(C_5H_5)Mn(CO)_2$, $(C_5H_5)Co(CO)$, and $(C_5H_5)Cu$ are all very strongly thermodynamically favored with respect to the corresponding $[M](PF_2)(F)$ derivatives by energies ranging from 64.3 kcal/mol for $Cr(PF_3)(CO)_5$ to 31.6 kcal/mol for $(C_5H_5)Co(PF_3)(CO)$. The known six-coordinate $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ is also predicted to be stable relative to the seven-coordinate $(Et_3P)_2Ir(CO)(Cl)(F)_2(SF_2)$. Most of the metal SF_3 complexes found in this work are singlet structures containing three-electron donor SF_3 ligands with tetrahedral sulfur coordination. However, two examples of triplet spin state metal SF_3 complexes, namely, the lowest energy $(C_5H_5)Fe(SF_3)(CO)$ structure and a higher energy $Co(SF_3)(CO)_3$ structure, are found containing one-electron donor SF_3 ligands with pseudo square pyramidal sulfur coordination with a stereochemically active lone electron pair.

1. INTRODUCTION

The chemistry of strong π-acceptor ligands is an important area of coordination chemistry, particularly since such ligands stabilize otherwise inaccessible low formal oxidation states. The classical example of a strong π-acceptor ligand is carbon monoxide, which forms a variety of stable transition metal carbonyls with the metal in a formal zerovalent oxidation state.[1] Some of these metal carbonyls are very stable. Thus $Cr(CO)_6$ is so robust that it can be steam-distilled in air without decomposition.

Another important class of ligands in coordination chemistry are tricoordinate phosphorus derivatives, PX_3. Among such ligands PF_3 plays a special role, since the electron-withdrawing properties of the fluorine atoms allows PF_3 to stabilize the low formal oxidation states of metals at least as effectively as carbon monoxide.[2,3] This is particularly true for the tetrahedral $M(PF_3)_4$ derivatives (M = Ni,[4,5] Pt[6,7]), which are more stable than their metal carbonyl counterparts.

The nitrosonium ion, NO^+, is isoelectronic with carbon monoxide and is the basis for the extensive chemistry of metal nitrosyls.[8,9] The neutral NO ligand is formally regarded as a three-electron donor to the metal atom, where one electron is given up in oxidation to NO^+ followed by electron pair donation to the metal atom. The NO ligand, like CO, is also effective at stabilizing low formal oxidation states. For example the manganese atom in the stable compound $Mn(NO)_3CO$ is formally in the -3 oxidation state (considering the NO ligand as NO^+).

The final member of this series of ligands potentially capable of stabilizing low formal oxidation states is the SF_3 (trifluorosulfane) ligand, which bears the same relationship to the NO ligand as PF_3 bears to the CO ligand. Although the neutral SF_3 radical is not a stable species like the NO radical (the familiar nitric oxide), the SF_3^+ cation, isoelectronic with the neutral PF_3, is obtained by abstraction of fluoride from SF_4 with strongly Lewis acidic fluorides.[10] Examples of SF_3^+ salts[11] include $[SF_3^+][BF_4^-]$, $[SF_3^+][EF_6^-]$ (E = P, As, Sb), and

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$[SF_3^+]_2[GeF_6^{2-}]$; the last has been structurally characterized by X-ray crystallography.[10] However, metal SF_3 complexes analogous to metal nitrosyls are almost unknown experimentally. The only well-documented example of a transition metal SF_3 complex in the literature is the iridium derivative[12] $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, which is obtained from the reaction of *trans*-$(Et_3P)_2Ir(CO)Cl$ with SF_4. Even in this known SF_3 iridium complex, the SF_3 is not a formal three-electron donor ligand like the normal linear nitrosyl ligand in metal carbonyl nitrosyls, but instead a formal donor of only a single electron. This gives the central iridium atom in $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ the favored 18-electron configuration, by receiving a pair of electrons from each of the two Et_3P ligands and the single CO ligand and single electrons from the Cl, F, and SF_3 ligands, all considered formally as neutral species.

The relationship of SF_3 to NO analogous to the relationship of PF_3 to CO raises the question as to whether SF_3 metal carbonyls can be synthesized analogous to some of the well-known metal carbonyl nitrosyls. In this connection the first row transition metal SF_3 complexes $M(SF_3)(CO)_n$ ($M = V$, $n = 5$; $M = Mn$, $n = 4$; $M = Co$, $n = 3$) and $CpM(SF_3)(CO)_n$ ($Cp = \eta^5$-C_5H_5: $M = Cr$, $n = 2$; $M = Ni$, $n = 0$) analogous to the known metal nitrosyl derivatives[13−15,15,16] $M(NO)(CO)_n$ and $CpM(NO)(CO)_n$ have been investigated by density functional theory (DFT). The related iron SF_3 complex $CpFe(SF_3)(CO)$ was included in this study even though the analogous nitrosyl $CpFe(NO)(CO)$ has not yet been reported. In addition, since the one known example of a metal-SF_3 complex contains the third row transition metal iridium, the iridium complexes $Ir(SF_3)(CO)_3$ analogous to $Co(SF_3)(CO)_3$ as well as the known[12] $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ were also included in this study.

The present research suggests that none of these first row transition metal $[M]SF_3$ complexes ([M] = central metal atom with CO and/or Cp ligands) are thermodynamically viable with respect to fluorine shift reactions from sulfur to the metal atom to give the $[M](F)(SF_2)$ complexes. This is consistent with the use of sulfur−fluorine compounds, notably SF_4, as fluorinating agents, particularly in organic chemistry.[17] In addition, this theoretical prediction of the thermal instability of metal SF_3 complexes raises the question as to the thermodynamic stability of isoelectronic $[M]PF_3$ complexes, many of which have been synthesized. Accordingly we have used similar theoretical methods to investigate the thermodynamic stability of the $[M]PF_3$ complexes isoelectronic with the SF_3 complexes mentioned above with respect to the fluorine shift reactions to give the corresponding $[M](F)(PF_2)$ complexes. Thus the PF_3 complexes investigated in this research were $M(PF_3)(CO)_n$ ($M = Cr$, $n = 5$; $M = Fe$, $n = 4$; $M = Ni$, $n = 3$) and $CpM(PF_3)(CO)_n$ ($M = Mn$, $n = 2$; $M = Cu$, $n = 0$).

The general conclusion for this theoretical study is that all of the first row transition metal $[M]SF_3$ complexes are thermodynamically disfavored with respect to formation of the corresponding $[M](F)(SF_2)$ complexes. However, all of the isoelectronic first row transition metal $[M]PF_3$ complexes are thermodynamically viable with respect to the formation of the corresponding $[M](F)(PF_2)$ complexes. This suggests that whereas very stable metal PF_3 complexes can be prepared analogous to metal carbonyls, the prospects of synthesizing stable metal SF_3 complexes analogous to metal nitrosyls are not promising.

2. THEORETICAL METHODS

Electron correlation effects were considered by using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[18−32] Two DFT methods were used in this study. The B3LYP method is an HF/DFT hybrid method using Becke's three-parameter functional (B3)[33] and the Lee−Yang−Parr generalized gradient correlation functional (LYP).[34] The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B)[35] with Perdew's 1986 gradient correlation functional (P86).[36]

In this work all computations were performed using double-ζ plus polarization (DZP) basis sets. For carbon, oxygen, fluorine, phosphorus, chlorine, and sulfur, these DZP basis sets are obtained by adding one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.00$, $\alpha_d(P) = 0.60$, $\alpha_d(Cl) = 0.75$, and $\alpha_d(S) = 0.70$ to the standard Huzinaga−Dunning contracted DZ sets.[37,38] The loosely contracted DZP basis sets for transition metals are the Wachters primitive sets[39] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[40] and designated as (14s11p6d/10s8p3d). For $Co(SF_3)(CO)_3$, $Mn(SF_3)(CO)_4$, $V(SF_3)(CO)_5$, $(C_5H_5)Ni(SF_3)$, $(C_5H_5)Fe(SF_3)(CO)$, $(C_5H_5)Cr(SF_3)(CO)_2$, $Ni(PF_3)(CO)_3$, $Fe(PF_3)(CO)_4$, $Cr(PF_3)(CO)_5$, $(C_5H_5)Cu(PF_3)$, $(C_5H_5)Co(PF_3)(CO)$, and $(C_5H_5)Mn(PF_3)(CO)_2$, there are 207, 237, 267, 217, 247, 277, 207, 237, 267, 217, 247, and 277 contracted Gaussian functions, respectively. The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. For the third-row transition metal iridium, effective core potentials (ECPs) were used. In the present research we adopted the Stuttgart/Dresden double-ζ (SDD) ECP basis sets.[41] Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program,[42] exercising the fine grid option (75, 302) for evaluating integrals. The finer integration grid (99, 590) was used to investigate small imaginary vibrational frequencies. Unless otherwise indicated, all of the structures reported in this paper were genuine minima, with only real vibrational frequencies.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations.[43] Thus all imaginary vibrational frequencies with a magnitude less than $50i$ cm^{-1} are considered questionable, and are given less weight in the analysis.[43−45] Therefore, we do not always follow such low imaginary vibrational frequencies.

Structures are designated as **M-nS/T**, where **M** is the transition metal, **n** is the number to order the structures according to their relative energies (BP86 method), and **S** (or **T**) represents singlet (or triplet) electronic state structures. For example, **V-1S** is the lowest-lying singlet structure for $V(SF_2)(F)(CO)_5$ or $V(SF_3)(CO)_5$. The isomers of the known triethylphosphine iridium SF_3 complex $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ are designated as **P2Ir-nS**.

3. RESULTS

3.1. $M(SF_2)(F)(CO)_n$ and $M(SF_3)(CO)_n$ Derivatives.

3.1.1. $V(SF_2)(F)(CO)_5$ and $V(SF_3)(CO)_5$. The $V(SF_2)(F)(CO)_5$ equilibrium structure **V-1S** with separate SF_2 and F ligands is of lower energy than the $V(SF_3)(CO)_5$ isomer **V-2S** with an intact SF_3 ligand (Figure 1 and Table 1). The V−S distance in **V-1S** is predicted to be ∼2.4 Å. The SF_2 ligand is a two-electron donor, and the F atom is a one-electron donor leading to the favored 18-electron configuration for the vanadium atom.

The only $V(SF_3)(CO)_5$ structure (**V-2S**, C_s symmetry) found by the DFT methods lies 16.9 kcal/mol (B3LYP) or 10.4 kcal/mol (BP85) above the $V(SF_2)(F)(CO)_5$ structure **V-1S** (Figure 1 and Table 1). The B3LYP method predicts **V-2S** to have no imaginary vibrational frequencies. However, the BP86 method predicts a very small imaginary vibrational frequency for **V-2S** of 21*i* cm^{-1}, which decreases to the negligible value of 0.7*i* cm^{-1} when the finer integration grid (99, 590) is used. The SF_3 group in **V-2S** can be considered to be a three-electron donor, so that the vanadium in structure **V-2S**, like that in **V-1S**, has the favored 18-electron configuration.

3.1.2. $Mn(SF_2)(F)(CO)_4$ and $Mn(SF_3)(CO)_4$. The $Mn(SF_2)(F)(CO)_4$ structures, with separate SF_2 and F ligands, also have lower energies than their $Mn(SF_3)(CO)_4$ isomer. Two $Mn(SF_2)(F)(CO)_4$ structures **Mn-1S** and **Mn-2S** with C_s symmetry were found (Figure 2). The geometrical difference between these structures is only the position of the Mn—F bond relative to the SF_2 ligand. Thus **Mn-1S** has the SF_2 and F groups in *cis* positions whereas **Mn-2S** has the SF_2 and F groups in *trans* positions. Their energies are within 1.0 kcal/mol of each other (Table 2). Like the analogous vanadium structure **V-1S**, the Mn atoms in both **Mn-1S** and **Mn-2S** achieve the favored 18-electron configuration.

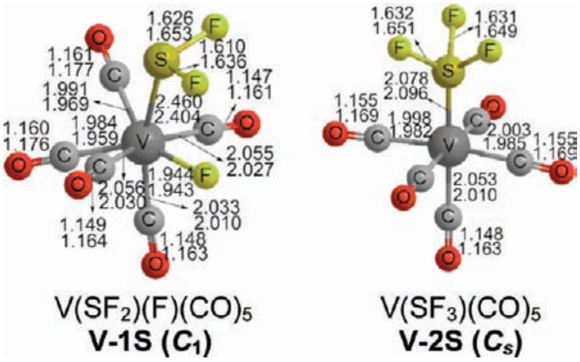

Figure 1. Optimized geometries for $V(SF_2)(F)(CO)_5$ and $V(SF_3)(CO)_5$. Bond distances are given in Å with the B3LYP values on top and the BP86 values on the bottom.

Table 1. Total Energies (*E* in Hartree), Relative Energies (Δ*E* in kcal/mol), and Numbers of Imaginary Vibrational Frequencies (Nimg) for $V(SF_2)(F)(CO)_5$ and $V(SF_3)(CO)_5$

	B3LYP			BP86		
	−*E*	Nimg	Δ*E*	−*E*	Nimg	Δ*E*
V-1S (C_1)	2208.59585	none	0.0	2208.81091	none	0.0
V-2S (C_s)	2208.56892	none	16.9	2208.79441	0.7*i*	10.4

The optimized intact $Mn(SF_3)(CO)_4$ structure **Mn-3S** is a distorted square pyramid structure with the SF_3 group in the apical position. The $Mn(SF_3)(CO)_4$ structure **Mn-3S** lies significantly higher in energy above **Mn-1S** by 34.1 kcal/mol (B3LYP) or 19.5 kcal/mol (BP86). The Mn—S distance in **Mn-3S** (1.957 Å by B3LYP and 1.961 Å by BP86) is much shorter than that in **Mn-1S** (2.259 Å by B3LYP and 2.221 Å by BP86) and **Mn-2S** (2.154 Å by B3LYP and 2.125 Å by BP86). This suggests much stronger back-bonding of the SF_3 ligand to the Mn atom relative to the SF_2 ligand. The SF_3 group in **Mn-3S** is a three-electron donor, leading to the favored 18-electron configuration for the Mn atom.

3.1.3. $Co(SF_2)(F)(CO)_3$ and $Co(SF_3)(CO)_3$. Three $Co(SF_2)(F)(CO)_3$ structures and two $Co(SF_3)(CO)_3$ structures were obtained (Figure 3). The three $Co(SF_2)(F)(CO)_3$ structures have related geometries with C_s symmetry, and similar energies within 8 kcal/mol. Structures **Co-1S** and **Co-2S** have a *cis* orientation of the SF_2 and F groups, whereas **Co-3S** has a *trans* orientation of the SF_2 and F groups. Both **Co-1S** and **Co-2S** are genuine minima. The geometrical difference between **Co-1S** and **Co-2S** lies only in the relative positions of the Co—F group and the fluorine atoms of the SF_2 ligand. Structure **Co-2S** lies 5.3 kcal/mol (B3LYP) or 5.8 kcal/mol (BP86) above **Co-1S**, while structure **Co-3S** lies 7.0 kcal/mol (B3LYP) or 7.5 kcal/mol (BP86) above **Co-1S**. The *trans* structure **Co-3S** is predicted by B3LYP to be a genuine minimum, while the BP86 method predicts a very small imaginary vibrational frequency (12*i* cm^{-1}) for **Co-3S**. The Co—S distances in these structures fall in the range 2.1 to 2.2 Å (Figure 3). Similar to the vanadium and manganese analogues, the cobalt atom in each of the three $Co(SF_2)(F)(CO)_3$ structures has the favored 18-electron configurations.

Table 2. Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $Mn(SF_2)(F)(CO)_4$ and $Mn(SF_3)(CO)_4$

	B3LYP		BP86	
	−*E*	Δ*E*	−*E*	Δ*E*
Mn-1S (C_s)	2302.26053	0.0	2302.51662	0.0
Mn-2S (C_s)	2302.25861	1.0	2302.51546	0.7
Mn-3S (C_s)	2302.20754	34.1	2302.48561	19.5

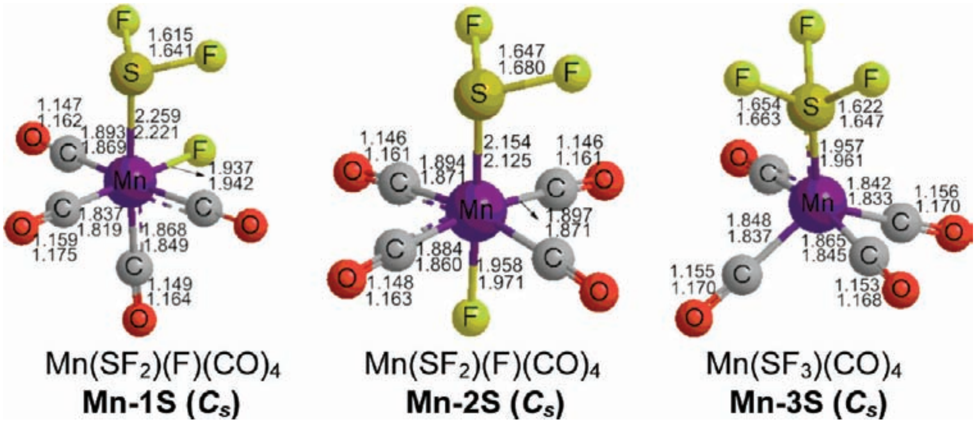

Figure 2. Optimized geometries for $Mn(SF_2)(F)(CO)_4$ and $Mn(SF_3)(CO)_4$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

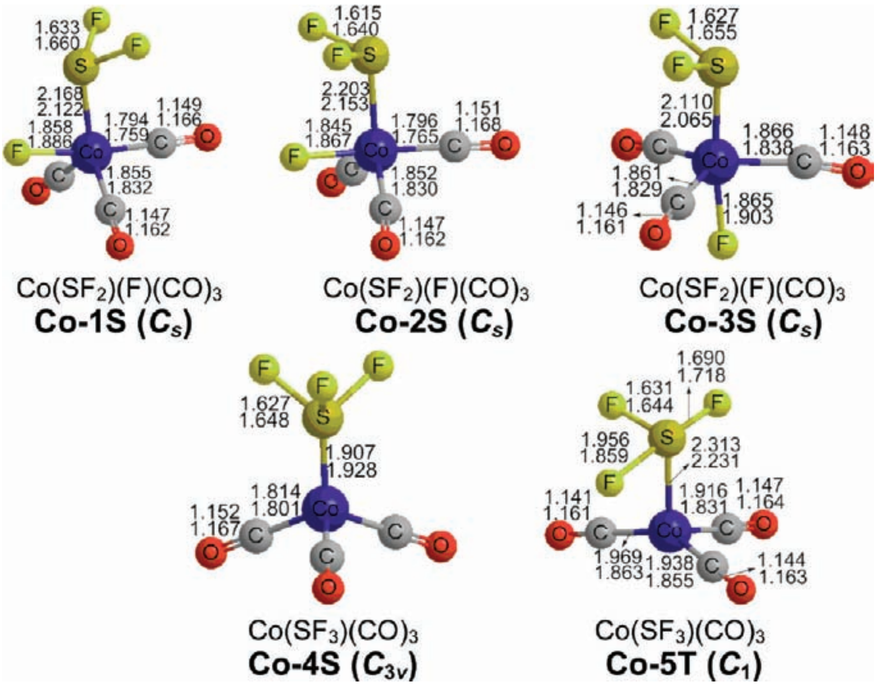

Figure 3. Optimized geometries for $Co(SF_2)(F)(CO)_3$ and $Co(SF_3)(CO)_3$. Bond distances are given in Å with the B3LYP values on top and the BP86 values on the bottom.

Table 3. Total Energies (*E* in Hartree), Relative Energies (Δ*E* in kcal/mol), and Numbers of Imaginary Vibrational Frequencies (Nimag) for $Co(SF_2)(F)(CO)_3$, $Co(SF_3)(CO)_3$, $Ir(SF_2)(F)(CO)_3$, $Ir(SF_3)(CO)_3$, and $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ [Ir(C_1)-1S-trans, Ir(C_1)-2S-cis]

	B3LYP				BP86			
	$-E$	Nimg	ΔE	$\langle S^2\rangle$	$-E$	Nimg	ΔE	$\langle S^2\rangle$
Co-1S (C_s)	2420.67286	none	0.0	0.00	2420.95650	none	0.0	0.00
Co-2S (C_s)	2420.66444	none	5.3	0.00	2420.94720	none	5.8	0.00
Co-3S (C_s)	2420.66165	none	7.0	0.00	2420.94456	12*i*	7.5	0.00
Co-4S (C_{3v})	2420.64525	none	17.3	0.00	2420.94784	none	5.4	0.00
Co-5T (C_1)	2420.66348	none	5.9	2.04	2420.92681	none	18.6	2.01
Ir-1S (C_s)	1142.28342	none	0.0	0.00	1142.45770	none	0.0	0.00
Ir-2S (C_s)	1142.24237	none	25.8	0.00	1142.42860	none	18.3	0.00
P2Ir-1S (C_1-trans)	2633.90681	none	0.0	0.00	2634.10667	none	0.0	0.00
P2Ir-2S (C_1-cis)	2633.88077	none	16.3	0.00	2634.07932	none	17.2	0.00

Two $Co(SF_3)(CO)_3$ structures **Co-4S** and **Co-5T** are obtained using either DFT method (Figure 3 and Table 3). The energetically lower structure **Co-4S** is a singlet C_{3v} structure, while the other $Co(SF_3)(CO)_3$ structure **Co-5T** is a triplet. Neither $Co(SF_3)(CO)_3$ structure has any imaginary vibrational frequencies. The singlet $Co(SF_3)(CO)_3$ structure **Co-4S** is predicted to lie 17.3 kcal/mol (B3LYP) or 5.4 kcal/mol (BP86) above **Co-1S**. The Co—S distance in the singlet **Co-4S** structure is much shorter (~1.9 Å) than the Co—S distances (~2.1 to 2.2 Å) in the three $Co(SF_2)(F)(CO)_3$ structures. This again indicates much stronger back-bonding from the Co atom to the SF_3 ligand than to the SF_2 ligand. The cobalt atom in **Co-4S** has the favored 18-electron configuration.

The triplet structure **Co-5T** for $Co(SF_3)(CO)_3$ is predicted to lie only 5.9 kcal/mol above **Co-1S** by the B3LYP method, whereas the BP86 method predicts a much larger energy difference, with **Co-5T** lying 18.6 kcal/mol above **Co-1S** (Figure 3 and Table 3). This is consistent with the observation made by Reiher et al.,[46] that the B3LYP method favors high spin states relative to the BP86 method. The sulfur coordination of the SF_3 group in the triplet **Co-5T** is pseudo square pyramidal with a stereochemically active lone pair, in contrast to the tetrahedral coordination of the SF_3 sulfur in all of the $M(SF_3)(CO)_n$ structures discussed above. The stereochemical activity of the sulfur lone pair in **Co-5T** means that this SF_3 group is a one-electron donor rather than a three-electron donor. This gives the cobalt atom in **Co-5T** only a 16-electron configuration, consistent with the triplet spin multiplicity.

3.1.4. $Ir(SF_2)(F)(CO)_3$, $Ir(SF_3)(CO)_3$, and $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$.

To see whether there are significant differences in the relative stabilities of [M]SF_3 versus [M]$(SF_2)(F)$ derivatives for third row transition metals versus first row transition metals the relative energies of $Ir(SF_2)(F)(CO)_3$ and $Ir(SF_3)(CO)_3$ were examined (Figure 4 and Table 3). As for the cobalt analogues, the $Ir(SF_2)(F)(CO)_3$ structure **Ir-1S** was found to be the global minimum with the corresponding $Ir(SF_3)(CO)_3$ structure **Ir-2S** lying 25.8 kcal/mol (B3LYP) or 18.3 kcal/mol (BP86) above **Ir-1S** in energy. In addition, two structures were found for the known compound $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ (Figure 4). Both of them have C_1 symmetry. The *cis* isomer **P2Ir-2S** was found to lie significantly higher in energy above than the corresponding *trans* isomer **P2Ir-1S** by 16.3 kcal/mol (B3LYP) or 17.2 kcal/mol (BP86), possibly owing to steric hindrance between the Et_3P ligands in the *cis* isomer. An attempt to optimize the corresponding $(Et_3P)_2Ir(CO)(Cl)(F)_2(SF_2)$ structure, which would have seven-coordinate iridium, led instead to loss of the chlorine atom. Thus the key factors determining the stability of $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ appears to be the hexacoordinate central iridium atom and the one-electron donor SF_3 group rather than the third row transition metal iridium versus the first row transition metal cobalt.

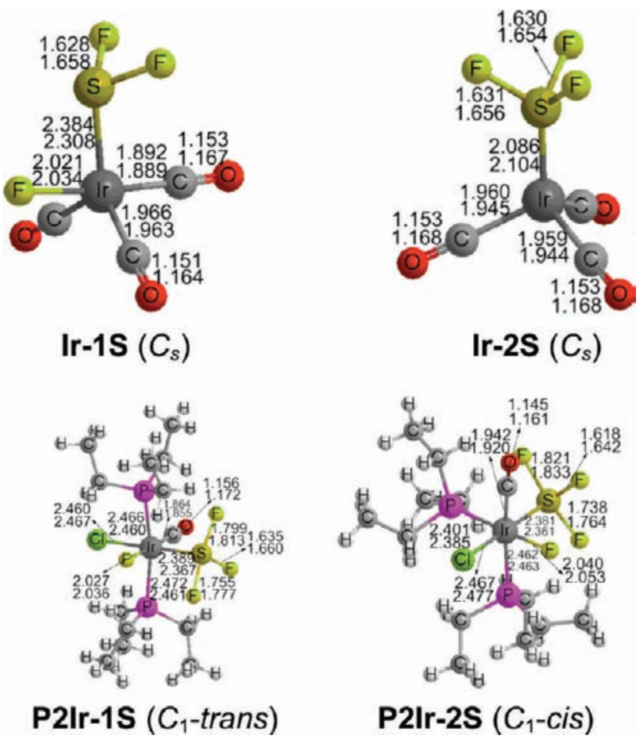

Figure 4. Optimized geometries for $Ir(SF_3)(CO)_3$ and $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$. Bond distances are given in Å with the B3LYP values on top and the BP86 values on the bottom.

The ν(CO) and ν(SF) vibrational frequencies for the $M(SF_2)(F)(CO)_n$ and $M(SF_3)(CO)_n$ structures predicted by the BP86 method are listed in Table 4. The terminal ν(CO) stretching frequencies fall in the range 1929 to 2102 cm^{-1}. The ν(SF) stretching frequencies fall in the range 618 to 793 cm^{-1} for all of the transition metal derivatives except for $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$. There are no significant differences between the ν(SF) stretching frequencies in the SF_3 and SF_2 ligands. The ν(SF) frequencies are significantly lower for both the *trans* and *cis* $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ isomers. These include a single unusually low ν(SF) frequency at ~450 cm^{-1}. This may be a consequence of the stronger donor properties of the Et_3P ligands relative to cyclopentadienyl and carbonyl ligands.

3.2. $(C_5H_5)M(SF_2)(F)(CO)_n$ and $(C_5H_5)M(SF_3)(CO)_n$.

3.2.1. $(C_5H_5)Cr(SF_2)(F)(CO)_2$ and $(C_5H_5)Cr(SF_3)(CO)_2$. Only one structure **Cr-1S** for $(C_5H_5)Cr(SF_2)(F)(CO)_2$ and one structure **Cr-2S** for

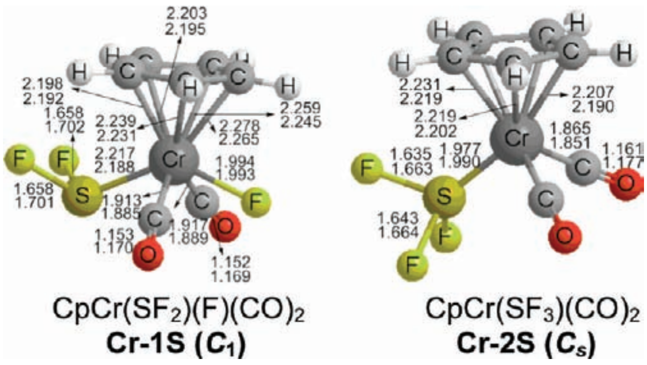

Figure 5. Optimized geometries for $(C_5H_5)Cr(SF_2)(F)(CO)_2$ and $(C_5H_5)Cr(SF_3)(CO)_2$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 4. Harmonic Vibrational Frequencies (in cm^{-1}) for $M(SF_2)(F)(CO)_n$ and $M(SF_3)(CO)_n$, with the BP86 Method[a]

structures	ν(CO)	ν(SF)	ν(MF)
V-1S (C_1)	2062(258),2020(520),2003(1147), 1948(817),1929(605)	722(219),695(141)	507(23)
V-2S (C_s)	2057(435), 2014(381), 1983(33), 1974(1633),1974(1598)	758(905),652(199),650(201)	
Mn-1S (C_s)	2089(182),2031(456),2024(1222), 1970(751)	724(187),721(119)	527(26)
Mn-2S (C_s)	2102(106),2054(44),2033(1196), 2019(1232)	663(227),655(188)	505(14)
Mn-3S (C_s)	2065(317),2000(48), 2000(1255), 1987(1192)	786(908), 682(226), 618(19)	
Co-1S (C_s)	2079(317),2032(831),2028(581)	699(288),666(116)	599(12)
Co-2S (C_s)	2076(312),2032(852),2018(591)	737(229),711(100)	600(1)
Co-3S (C_s)	2082(110),2040(763),2030(844)	697(238),678(112)	536(50)
Co-4S (C_{3v})	2063(348),2013(826),2013(825)	793(797),661(164),661(164)	
Co-5T (C_1)	2062(284),2022(879),2015(955)	729(129),629(234),461(6)	
Ir-1S (C_s)	2083(346), 2026(637), 2022(964)	705(275),665(116)	511(25)
Ir-2S (C_s)	2060(343), 2011(876), 2010(876)	772(814), 648(177),648(178)	
P2Ir-1S (C_1-*trans*)	2026(490)	698(113), 552(151),451(3)	493(11)
P2Ir-1S (C_1-*cis*)	2070(446)	724(145), 577(242), 450(30)	479(62)

[a] Infrared intensities are given in parentheses in km/mol.

Table 5. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $(C_5H_5)Cr(SF_2)(F)(CO)_2$ and $(C_5H_5)Cr(SF_3)(CO)_2$

	B3LYP		BP86	
	$-E$	ΔE	$-E$	ΔE
Cr-1S (C_1)	2162.55810	0.0	2162.78800	0.0
Cr-2S (C_s)	2162.53576	14.0	2162.77616	7.4

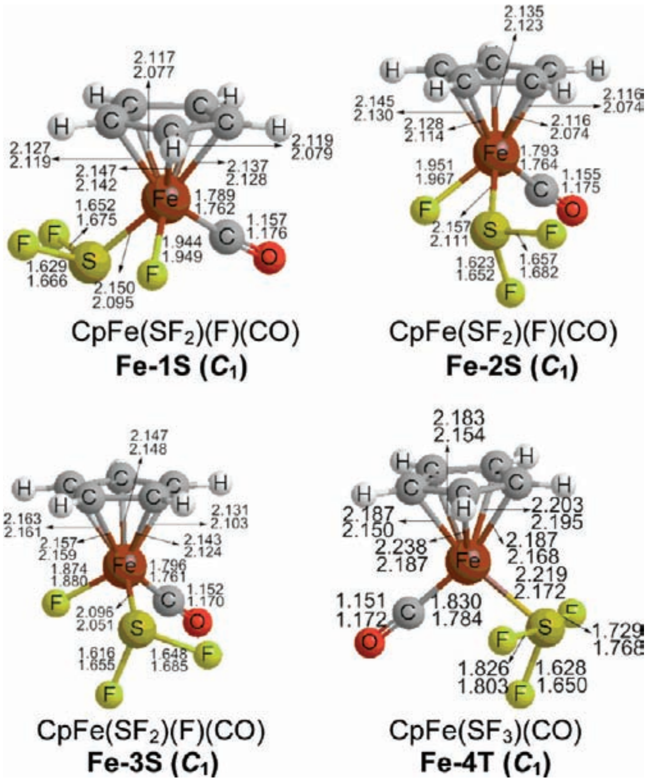

Figure 6. Optimized geometries for $(C_5H_5)Fe(SF_2)(F)(CO)$ and $(C_5H_5)Fe(SF_3)(CO)$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 6. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $(C_5H_5)Fe(SF_2)(F)(CO)$ and $(C_5H_5)Fe(SF_3)(CO)$

	B3LYP			BP86		
	$-E$	ΔE	$\langle S^2 \rangle$	$-E$	ΔE	$\langle S^2 \rangle$
Fe-1S (C_1)	2268.46054	0.0	0.00	2268.71628	0.0	0.00
Fe-2S (C_1)	2268.45959	0.6	0.00	2268.71403	1.4	0.00
Fe-3S (C_1)	2268.45331	4.5	0.00	2268.71290	2.1	0.00
Fe-4T (C_1)	2268.44666	8.7	2.32	2268.68644	18.7	2.03

$(C_5H_5)Cr(SF_3)(CO)_2$ were found (Figure 5 and Table 5). The structure **Cr-1S**, with separate SF_2 and F ligands, lies 14.0 kcal/mol (B3LYP) or 7.4 kcal/mol (BP86) below the structure **Cr-2S** with an intact SF_3 group. The Cr−S distance in **Cr-2S** (~2.0 Å) is shorter than that in **Cr-1S** (~2.2 Å), again indicating the stronger back-bonding capability of the SF_3 ligand relative to the SF_2 ligand. The Cr atom in each structures has the favored 18-electron configurations.

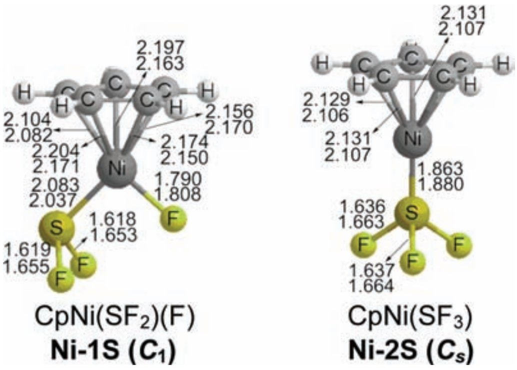

Figure 7. Optimized geometries for $(C_5H_5)Ni(SF_2)(F)$ and $(C_5H_5)Ni(SF_3)$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 7. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol for $(\eta^5\text{-}C_5H_5)Ni(SF_2)(F)$ Ni-1S and $(\eta^5\text{-}C_5H_5)Ni(SF_3)$ Ni-2S

	B3LYP		BP86	
	$-E$	ΔE	$-E$	ΔE
Ni-1S (C_1)	2399.68748	0.0	2399.95370	0.0
Ni-2S (C_s)	2399.65005	23.4	2399.93197	13.6

3.2.2. $(C_5H_5)Fe(SF_2)(F)(CO)$ and $(C_5H_5)Fe(SF_3)(CO)$. Three low-lying $(C_5H_5)Fe(SF_2)(F)(CO)$ singlet structures were found (Figure 6 and Table 6). However, the only $(C_5H_5)Fe(SF_3)(CO)$ structure is a triplet electronic state. The three singlet $(\eta^5\text{-}C_5H_5)Fe(SF_2)(F)(CO)$ structures **Fe-1S**, **Fe-2S**, and **Fe-3S** have related geometries, differing only in the orientations of the SF_2 group relative to the other ligands. Accordingly their energies are close to each other (within 5 kcal/mol). Thus structures **Fe-2S** and **Fe-3S** lie 0.6 and 1.4 kcal/mol (B3LYP) or 4.5 and 2.1 kcal/mol (BP86), respectively, above the global minimum **Fe-1S**. The Fe−S distances in these $(\eta^5\text{-}C_5H_5)Fe(SF_2)(F)(CO)$ structures are ~2.1 Å (Figure 5). The iron atoms in each of the three $(\eta^5\text{-}C_5H_5)Fe(SF_2)(F)(CO)$ structures **Fe-1S**, **Fe-2S**, and **Fe-3S** have the favored 18-electron configuration.

The only $(\eta^5\text{-}C_5H_5)Fe(SF_3)(CO)$ structure found was the triplet structure **Fe-4T**, which lies 8.7 kcal/mol (B3LYP) or 18.7 kcal/mol (BP86) in energy above **Fe-1S** (Figure 6 and Table 6). The SF_3 ligand in **Fe-4T** has pseudo square pyramidal coordination of the sulfur atom similar to that in the triplet $Co(SF_3)(CO)_3$ structure **Co-4T** (Figure 3). This indicates that the SF_3 ligand has a stereochemically active lone pair and therefore is a formal one-electron donor, in contrast to the three-electron donor pyramidal SF_3 ligands found in the singlet structures. The failure to find a singlet $(\eta^5\text{-}C_5H_5)Fe(SF_3)(CO)$ structure may relate to the fact that the corresponding nitrosyl $(\eta^5\text{-}C_5H_5)Fe(NO)(CO)$ has never been reported.[47]

3.2.3. $(C_5H_5)Ni(SF_2)(F)$ and $(C_5H_5)Ni(SF_3)$. One $(\eta^5\text{-}C_5H_5)Ni(SF_2)(F)$ structure and one $(\eta^5\text{-}C_5H_5)Ni(SF_3)$ structure were found (Figure 7 and Table 7). The intact $(\eta^5\text{-}C_5H_5)Ni(SF_3)$ structure **Ni-2S** is a relatively high energy structure lying 23.4 kcal/mol (B3LYP) or 13.6 kcal/mol (BP86) above the $(\eta^5\text{-}C_5H_5)Ni(SF_2)(F)$ structure **Ni-1S**. Both structures have the expected pentahapto $\eta^5\text{-}C_5H_5$ rings as indicated by Ni−C

Table 8. Harmonic Vibrational Frequencies (in cm^{-1}) for $(C_5H_5)M(SF_2)(F)(CO)_n$ and $(C_5H_5)M(SF_3)(CO)_n$ (with the BP86 Method)[a]

structures	ν(CH)	ν(CO)	ν(SF)	ν(MF)
Ni-1S	3197(1),3189(0),3181(0), 3174(0),3157(1)		704(350),665(105)	507(23)
Ni-2S	3192(1),3180(1),3180(1), 3167(0),3167(0)		828(742),616(132), 616(132)	
Fe-1S	3199(0),3190(0),3183(0), 3176(0),3170(0)	1980(724)	683(251),660(134)	527(26)
Fe-2S	3194(0),3184(0),3180(0), 3170(0),3169(0),	1988(673)	700(218),666(211)	505(14)
Fe-3S	3202(1),3189(0), 3185(0), 3177(0),3165(0),	2011(634)	692(285),631(136)	
Fe-4T	3194(0),3184(1), 3181(0), 3172(0),3168(0),	1997(747)	793(50),713(174), 598(276),	599(12)
Cr-1S	3203(0),3196(3),3191(1), 3182(0),3179(0),	2013(407), 1972(972)	616(165),581(94)	600(1)
Cr-2S	3197(0),3187(0),3187(0), 3175(0),3174(0),	1986(686), 1944(811)	788(698),659(191), 629(158)	536(50)

[a] Infrared intensities are given in parentheses in km/mol.

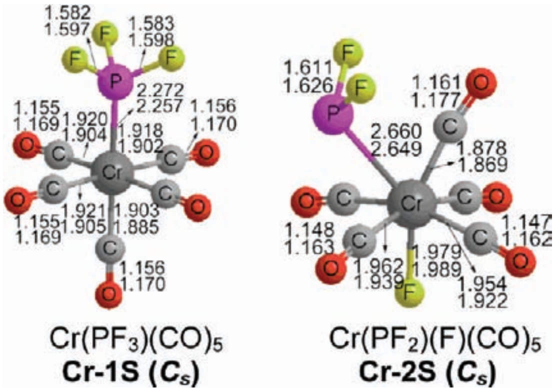

Figure 8. Optimized geometries for $Cr(PF_3)(CO)_5$ and $Cr(PF_2)(F)(CO)_5$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

distances of ~2.2 Å to all of the ring carbon atoms. The Ni—S distance of 2.04 Å (B3LYP) or 2.08 Å (BP86) in **Ni-1S** is appreciably longer than the Ni—S distance of 1.86 Å (B3LYP) or 1.88 Å (BP86) in **Ni-2S**, again consistent with the stronger back-bonding capability of the SF_3 ligand relative to the SF_2 ligand. The nickel atoms in both of the nickel complexes **Ni-1S** and **Ni-2S** have the favored 18-electron configuration.

The vibrational frequencies for $(C_5H_5)M(SF_2)(F)(CO)_n$ and $(C_5H_5)M(SF_3)(CO)_n$ predicted by the BP86 method are reported in Table 8. The terminal ν(CO) stretching frequencies fall in the usual range of 1944 to 2013 cm^{-1}. The ν(SF) stretching frequencies for SF_2 groups fall in the range of 581 to 704 cm^{-1}, and those for the SF_3 group fall in the range of 598 to 828 cm^{-1}. The ν(SF) frequencies for the SF_3 and SF_2 ligands thus fall in the same general region.

3.3. $M(PF_3)(CO)_n$ and $M(PF_2)(F)(CO)_n$. *3.3.1. $Cr(PF_3)(CO)_5$ and $Cr(PF_2)(F)(CO)_5$.* The trifluorophosphine complex $Cr(PF_3)(CO)_5$ has been isolated by chromatography from the mixture obtained by irradiating $Cr(CO)_6$ with PF_3 in a sealed Pyrex vessel.[48] In addition $Cr(PF_3)(CO)_5$ has been studied theoretically by several groups.[49−51] Our theoretical C_s structure (Figure 8 and Table 9) for $Cr(PF_3)(CO)_5$ is in qualitative agreement with the previous theoretical studies. The latter structure can be regarded as an octahedral $Cr(CO)_6$ structure in which one of the CO groups is replaced by a PF_3 group. The isomeric structure $Cr(PF_2)(F)(CO)_5$ is also a C_s genuine minimum. However, it is a very high energy structure, lying 66.7 kcal/mol (B3LYP) or 64.3 kcal/mol (BP86) above $Cr(PF_3)(CO)_5$.

Table 9. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Cr(PF_3)(CO)_5$ and $Cr(PF_2)(F)(CO)_5$

	B3LYP		BP86	
	$-E$	ΔE	$-E$	ΔE
Cr-1S (C_s)	2252.42319	0.0	2252.64949	0.0
Cr-2S (C_s)	2252.31693	66.7	2252.54700	64.3

3.3.2. $Fe(PF_3)(CO)_4$ and $Fe(PF_2)(F)(CO)_4$. The $Fe(PF_3)(CO)_4$ molecule was first reported in 1964 by Clark.[52] However, it has not yet been characterized structurally by X-ray diffraction. Both DFT methods predict a trigonal bipyramid structure **Fe-1S** for $Fe(PF_3)(CO)_4$ (Figure 9 and Table 10). This structure is similar to $Fe(CO)_5$ except for the substitution of an equatorial CO group by a PF_3 group. Two $Fe(PF_2)(F)(CO)_4$ structures were optimized (Figure 9), but both have very high energies. These structures have distorted octahedral iron coordination. The first $Fe(PF_2)(F)(CO)_4$ structure **Fe-2S** has C_1 symmetry and lies 37.2 kcal/mol (B3LYP) or 39.9 kcal/mol (BP86) above **Fe-1S**. The second $Fe(PF_2)(F)(CO)_4$ structure **Fe-3S** lies 43.3 kcal/mol (B3LYP) or 48.8 kcal/mol (BP86) above **Fe-1S**. Structures **Fe-2S** and **Fe-3S** have *cis* and *trans* orientations of the PF_2 and F ligands, respectively.

3.3.3. $Ni(PF_3)(CO)_3$ and $Ni(PF_2)(F)(CO)_3$. The $Ni(PF_3)(CO)_3$complex was first synthesized by Clark and Brimm.[53] However, it apparently has not yet been structurally characterized by X-ray diffraction. Our optimized geometry of $Ni(PF_3)(CO)_3$ constrained to C_{3v} symmetry led to structure **Ni-1S** (Figure 10 and Table 11). Structure **Ni-1S** has a small imaginary vibrational frequency of 11*i* cm^{-1} (B3LYP) or 7*i* cm^{-1} (BP86), which is removed by using the finer (99, 590) integration grid. Therefore **Ni-1S** can be regarded as a genuine minimum. The nickel atom in **Ni-1S** has approximate tetrahedral coordination consistent with its formulation as a substitution product of $Ni(CO)_4$. The $Ni(PF_2)(F)(CO)_3$ isomer **Ni-2S** with separate PF_2 and F ligands is unknown experimentally. This is not surprising since this $Ni(PF_2)(F)(CO)_3$ structure is predicted to lie ~57 kcal/mol above $Ni(PF_3)(CO)_3$ in energy. The Ni atom in **Ni-2S** has trigonal bipyramidal coordination, with the PF_2 and F ligands in axial positions. The Ni atoms in both the **Ni-1S** and **Ni-2S** structures have the favored 18-electron configurations.

The harmonic vibrational frequencies predicted by the BP86 method for the $M(PF_3)(CO)_n$ and $M(PF_2)(F)(CO)_n$ structures are reported in Table 12. The terminal CO stretching frequencies fall in the range 1948 to 2115 cm^{-1}. The ν(PF) stretching

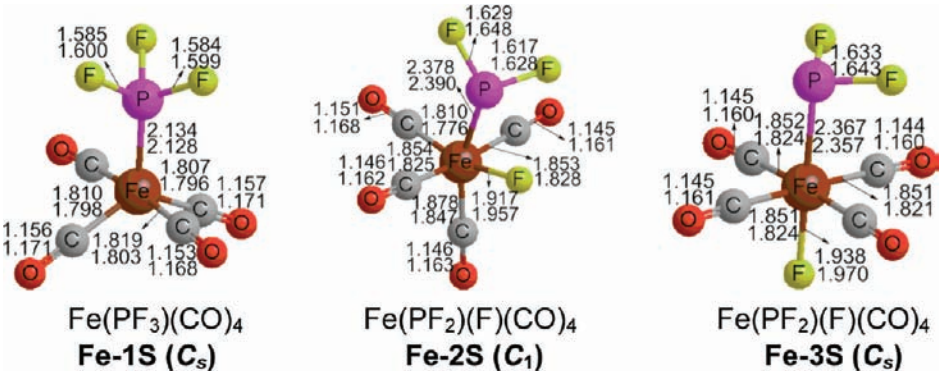

Figure 9. Optimized geometries for $Fe(PF_3)(CO)_4$ and $Fe(PF_2)(F)(CO)_4$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 10. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Fe(PF_3)(CO)_4$ and $Fe(PF_2)(F)(CO)_4$

	B3LYP		BP86	
	$-E$	ΔE	$-E$	ΔE
Fe-1S (C_s)	2358.29866	0.0	2358.56697	0.0
Fe-2S (C_1)	2358.23945	37.2	2358.50339	39.9
Fe-3S (C_s)	2358.22970	43.3	2358.48923	48.8

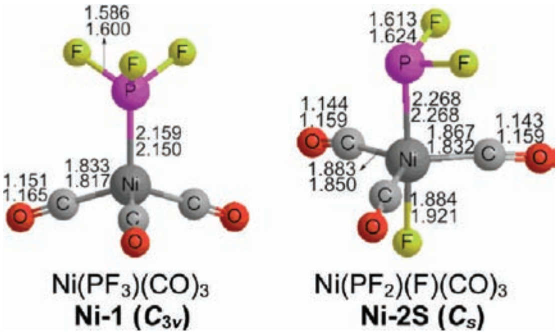

Figure 10. Optimized geometries for $Ni(CO)_3(PF_3)$ and $Ni(PF_2)(F)(CO)_3$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 11. Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Ni(CO)_3(PF_3$and $Ni(PF_2)(F)(CO)_3$

	B3LYP		BP86	
	$-E$	ΔE	$-E$	ΔE
Ni-1S (C_{3v})	2489.56389	0.0	2489.83670	0.0
Ni-2S (C_s)	2489.47295	57.1	2489.74706	56.2

frequencies for PF_2 group fall in the range 731 to 787 cm^{-1}, while those for the PF_3 group lie between 827 and 844 cm^{-1}. In contrast to the SF_3 and SF_2 complexes (Tables 4 and 8), the ν(PF) frequencies for PF_2 group are consistently lower than those for the PF_3 group by 60 to 100 cm^{-1}.

3.4. $(\eta^5\text{-}C_5H_5)M(PF_3)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(PF_2)(F)(CO)_n$. *3.4.1. $(\eta^5\text{-}C_5H_5)Mn(PF_3)(CO)_2$ and $(\eta^5\text{-}C_5H_5)Mn(PF_2)(F)(CO)_2$.* The very stable $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, commonly known as cymantrene, was first reported in 1954[54] and subsequently characterized structurally by X-ray diffraction.[55] This very stable compound has the favored 18-electron configuration for the Mn atom and is chemically stable. The trifluorophosphine derivative of cymantrene, namely, $(\eta^5\text{-}C_5H_5)Mn(PF_3)(CO)_2$, was prepared in 1972.[56] In the present study, only one structure **Mn-1S** was found for $(\eta^5\text{-}C_5H_5)Mn(PF_3)(CO)_2$, and one structure **Mn-2S** for its isomer $(\eta^5\text{-}C_5H_5)Mn(PF_2)(F)(CO)_2$, using either DFT method (Figure 11 and Table 13). The energy of **Mn-2S** is higher than **Mn-1S** by ~58 kcal/mol.

3.4.2. $(\eta^5\text{-}C_5H_5)Co(PF_3)(CO)$ and $(\eta^5\text{-}C_5H_5)Co(PF_2)(F)(CO)$. The radical anion $(\eta^5\text{-}C_5H_5)Co(CO)_2(PF_3)^{\bullet-}$ has been reported in the gas phase[57] but not the neutral counterpart. We have now optimized a stable structure **Co-1S** for neutral $(\eta^5\text{-}C_5H_5)Co(PF_3)(CO)$ (Figure 12 and Table 14). This structure has C_s symmetry with no imaginary vibrational frequencies. The Co atom in **Co-1S** has the favored 18-electron configuration. The $(\eta^5\text{-}C_5H_5)Co(PF_2)(F)(CO)$ isomer **Co-2S** is a high energy structure, lying ~31 kcal/mol above **Co-1S**.

3.4.3. $(\eta^5\text{-}C_5H_5)Cu(PF_3)$ and $(\eta^5\text{-}C_5H_5)Cu(PF_2)(F)$. Although $CpCuPPh_3$ (ref 58) and $CpCuPEt_3$ (ref 59) are known experimentally, the analogous $CpCu(PF_3)$ has never been reported. Our theoretical study shows that the lowest energy structure **Cu-1S** for $(\eta^5\text{-}C_5H_5)Cu(PF_3)$ is a C_s structure with a pentahapto cyclopentadienyl ring (Figure 13 and Table 15), thereby giving the Cu atom in **Cu-1S** the favored 18-electron configuration. The $(\eta^5\text{-}C_5H_5)Cu(PF_2)(F)$ structure **Cu-2S** with distinct PF_2 and F ligands is a high energy structure, lying 39.6 kcal/mol (B3LYP) or 34.1 kcal/mol (BP86) in energy above **Cu-1S**.

The harmonic vibrational frequencies predicted by the BP86 method for the $CpM(PF_3)(CO)_n$ and $CpM(PF_2)(F)(CO)_n$ structures are listed in Table 16. The terminal ν(CO) stretching frequencies fall in the range 1939 to 2018 cm^{-1}. The ν(PF) stretching frequencies for PF_2 groups fall in the range 710 to 793 cm^{-1}, while those for the PF_3 groups lie between 800 and 845 cm^{-1}. The ν(PF) frequencies for the PF_3 groups are thus 50 to 100 cm^{-1} higher than those for the PF_2 groups, as is the case for the $M(PF_3)(CO)_n$ and $M(PF_2(F)(CO)_n$ derivatives discussed above.

4. DISCUSSION

This theoretical study predicts that the $[M]SF_3$ derivatives ($[M] = V(CO)_5$, $Mn(CO)_4$, $Co(CO)_3$, $(\eta^5\text{-}C_5H_5)Cr(CO)_2$, $(\eta^5\text{-}C_5H_5)Fe(CO)$, and $(\eta^5\text{-}C_5H_5)Ni$) are thermodynamically

Table 12. Harmonic Vibrational Frequencies (in cm^{-1}) for $M(PF_3)(CO)_n$ and $M(PF_2)(F)(CO)_n$ (with the BP86 Method)[a]

structures	ν(CO)	ν(PF)	ν(MF)
Ni-1S	2072(208),2022(847),2022(847)	835(141),835(141), 828(461)	
Ni-2S	2099(75), 2057(746),2052(752)	787(176),785(119)	507(74)
Fe-1S	2074(156),2006(141),2004(1232), 1992(1094)	843(142),833(159), 827(491)	
Fe-2S	2096(155),2038(506),2030(986), 2011(701)	780(158),731(209)	513(8)
Fe-3S	2115(60),2065(15),2039(1121), 2036(1128)	757(154),750(129)	474(23)
Cr-1S	2068(154),1997(9),1988(608), 1977(1560),1976(1546)	844(149),842(144), 827(453)	
Cr-2S	2083(206),2029(55),2013(1028), 2008(1317),1948(670)	780(109),774(169)	498(21)

[a] Infrared intensities are given in parentheses in km/mol.

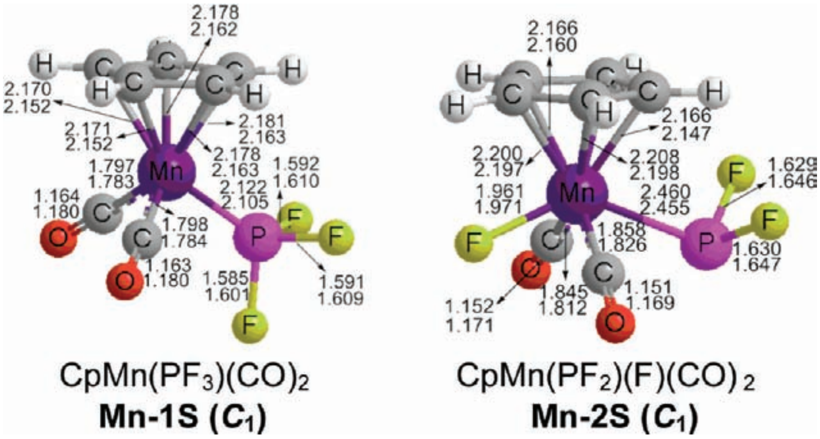

Figure 11. Optimized geometries for $(C_5H_5)Mn(PF_3)(CO)_2$ and $(C_5H_5)Mn(PF_2)(F)(CO)_2$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 13. Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $(\eta^5\text{-}C_5H_5)Mn(PF_3)(CO)_2$ and $(\eta^5\text{-}C_5H_5)Mn(PF_2)(F)(CO)_2$

	B3LYP		BP86	
	−*E*	Δ*E*	−*E*	Δ*E*
Mn-1S (C_1)	2212.42765	0.0	2212.66261	0.0
Mn-2S (C_1)	2212.33477	58.3	2212.56971	58.3

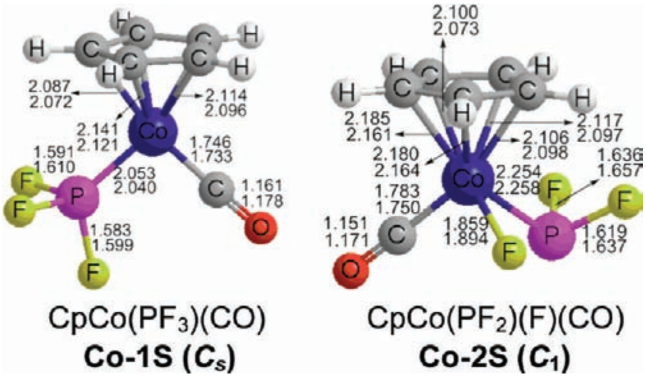

Figure 12. Optimized geometries for $(C_5H_5)Co(PF_3)(CO)$ and $(C_5H_5)Co(PF_2)(F)(CO)$. Bond distances are given in Å with the B3LYP values on top and the BP86 values on the bottom.

Table 14. Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $(\eta^5\text{-}C_5H_5)Co(PF_3)(CO)$ and $(\eta^5\text{-}C_5H_5)Co(PF_2)(F)(CO)$

	B3LYP		BP86	
	−*E*	Δ*E*	−*E*	Δ*E*
Co-1S (C_s)	2330.82838	0.0	2331.08558	0.0
Co-2S (C_1)	2330.77835	31.3	2331.03529	31.6

disfavored with respect to the corresponding $[M](F)(SF_2)$ derivatives. In other words, the sulfur-to-metal fluorine shift reactions converting $[M]SF_3$ derivatives to the corresponding $[M](F)(SF_2)$ derivatives are highly exothermic, with the heat of this reaction increasing in the sequence $Co(SF_3)(CO)_3 < (\eta^5\text{-}C_5H_5)Cr(SF_3)(CO)_2 < V(SF_3)(CO)_5 < (\eta^5\text{-}C_5H_5)Ni(SF_3) < (\eta^5\text{-}C_5H_5)Fe(SF_3)(CO) < Mn(SF_3)(CO)_4$. Thus the thermodynamically most favorable $[M]SF_3$ derivative of those investigated is $Co(SF_3)(CO)_3$, in which the conversion to $Co(F)(SF_2)(CO)_3$ involves transformation of a tetrahedral cobalt atom to a trigonal bipyramidal cobalt atom. Similarly, the thermodynamically least favored $[M]SF_3$ derivative is $Mn(SF_3)(CO)_4$ where the conversion to $Mn(F)(SF_2)(CO)_4$ involves rearrangement of a trigonal bipyramidal manganese atom to an octahedral manganese atom. This suggests that octahedral and tetrahedral structures are preferred over trigonal bipyramidal structures for these types of metal complexes.

A general conclusion from these results is that the prospects of synthesizing metal-SF_3 complexes analogous to metal nitrosyl derivatives are unpromising for the first row transition metals This is consistent with the absence of any stable known SF_3

complexes in which the SF_3 ligand functions as a formal three-electron donor like the linear nitrosyl ligand. However, in the one known SF_3 metal complex, namely, the iridium complex[12] $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, the SF_3 ligand clearly must function as a one-electron donor rather than a three-electron donor to give the central iridium atom the favored 18-electron configuration. Our theoretical studies led to two stereoisomers of this $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, namely, **P2Ir-1S** with the phosphine ligands in *trans* positions and **P2Ir-2S** with the phosphine ligands in *cis* positions (Figure 4). The *trans* isomer was found to lie significantly lower in energy than the corresponding *cis* isomer by ~17 kcal/mol, possibly owing to steric hindrance between the phosphine ligands in the *cis* isomer. Most significantly our theoretical study predicts $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ to be stable relative to the seven-coordinate $(Et_3P)_2Ir(CO)(Cl)(F)_2(SF_2)$ isomer in which the SF_3 ligand has converted to $SF_2 + F$. In fact, we were not even able to optimize a seven-coordinate $(Et_3P)_2Ir(CO)(Cl)(F)_2(SF_2)$ structure. Attempted optimizations of $(Et_3P)_2Ir(CO)(Cl)(F)_2(SF_2)$ led to loss of the chlorine atom. However, the simpler four-coordinate $Ir(SF_3)(CO)_3$ was found to lie 25.8 kcal/mol (B3LYP) or 18.3 kcal/mol (BP86) above the five-coordinate $Ir(SF_2)(F)(CO)_3$ structure, an even larger energy difference than for the analogous cobalt pair $Co(SF_3)(CO)_3/Co(SF_2)(F)(CO)_3$. This indicates that the stability of $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ arises not from the third row transition metal iridium relative to the first row transition metal cobalt but to the favorable coordination number of six for the iridium atom and the SF_3 group functioning as a one-electron donor rather than a three-electron donor. The vanadium derivative $V(SF_3)(CO)_5$ also has a favorable metal coordination number of six but, unlike $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$, its SF_3 group is a three-electron donor rather than a one-electron donor.

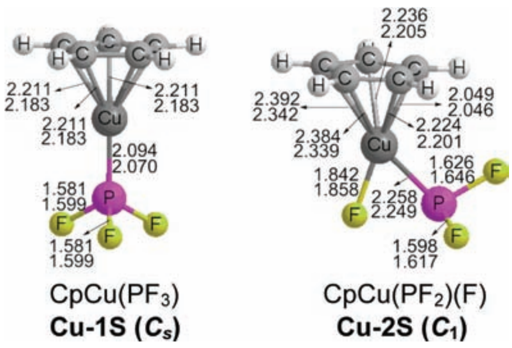

Figure 13. Optimized geometries for $(C_5H_5)Cu(PF_3)$ and $(C_5H_5)Cu(PF_2)(F)$. Bond distances are given in Å with the B3LYP values on the top and the BP86 values on the bottom.

Table 15. Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $(\eta^5\text{-}C_5H_5)Cu(PF_3)$ and $(\eta^5\text{-}C_5H_5)Cu(PF_2)(F)$

	B3LYP		BP86	
	−*E*	Δ*E*	−*E*	Δ*E*
Cu-1S (C_s)	2475.19324	0.0	2475.43331	0.0
Cu-2S (C_1)	2475.13011	39.6	2475.37884	34.1

Our theoretical work suggests that the nature of the SF_3 ligand, that is, whether the SF_3 ligand functions as a three-electron or a one-electron donor, is indicated by the coordination geometry of the sulfur atom. This is analogous to the dichotomy in metal nitrosyl chemistry[8,9] where linear nitrosyl groups function as formal three-electron donor ligands, but bent nitrosyl groups function as formal one-electron donor ligands (Figure 14). Thus the bent nitrosyl groups have pseudotricoordinate nitrogen in which one of the coordination positions consists of a stereochemically active lone pair so that only a single electron from the NO group is available for donation to the central metal atom.

A situation analogous to the dichotomy between linear and bent nitrosyl groups occurs with the predicted structures for SF_3 metal complexes. Thus the lowest energy structures of $V(SF_3)(CO)_5$, $Mn(SF_3)(CO)_4$, $Co(SF_3)(CO)_3$, $(C_5H_5)Cr(SF_3)(CO)_2$, and $(C_5H_5)Cu(SF_3)$ are all singlet states in which the neutral SF_3 ligand is a three-electron donor with tetrahedral sulfur coordination (Figure 15). However, the lowest energy $(C_5H_5)Fe(SF_3)(CO)$ structure **Fe-4T** (Figure 6) is a triplet state in which the neutral SF_3 ligand is only a one electron donor, with a stereochemically active lone pair in one of the basal positions of a

Figure 14. Comparison of a linear 3-electron donor NO group with a bent 1-electron donor NO group.

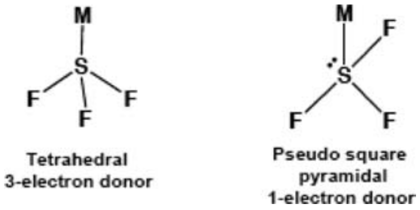

Figure 15. Comparison of a tetrahedral 3-electron donor SF_3 group with a pseudo square pyramidal 1-electron donor SF_3 group.

Table 16. Harmonic Vibrational Frequencies (in cm^{-1}) for $(\eta^5\text{-}C_5H_5)M(PF_3)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(PF_2)(F)(CO)_n$ (with the BP86 Method)[a]

	ν(CH)	ν(CO)	ν(PF)	ν(MF)
Cu-1S	3188(3),3176(3),3176(3), 3161(0), 3161(0)		845(581),835(139),835(138)	
Cu-2S	3191(2),3182(0),3176(0), 3167(1),3162(0)		793(191),732(205)	546(25)
Co-1S	3196(1),3190(0),3179(1), 3170(0),3164(0)	1986(705)	844(283),823(338), 800(130)	
Co-2S	3202(1),3191(1), 3190(1), 3178(0),3172(0)	2011(645)	758(145),710(178)	507(28)
Mn-1S	3196(0),3189(0),3184(0), 3174(0),3169(0)	1982(668), 1939(796)	838(154),819(129),808(135)	
Mn-2S	3204(0),3196(2),3192(1), 3183(0),3181(0)	2018(413), 1974(860)	742(149),727(102)	514(16)

[a] Infrared intensities are given in parentheses in km/mol.

pseudo square pyramidal sulfur atom (Figure 15). A similar one electron donor SF_3 group with pseudo square pyramidal sulfur atom having a stereochemically active lone pair is also found in a higher energy triplet $Co(SF_3)(CO)_3$ structure, namely **Co-5T** (Figure 3). Such pseudo square pyramidal geometry is also predicted for the sulfur atom in the known,[12] but not yet structurally characterized iridium complex $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$ in which simple electron counting suggests that the neutral SF_3 ligand is a formal one-electron donor.

This research also suggests the possibility of synthesizing transition metal complexes with a two-electron donor SF_2 ligand. However, sulfur difluoride itself appears too unstable to be used effectively as a synthetic reagent.[60,61] Furthermore, the observation of $[M](F)(SF_2)$ derivatives as lower energy isomers of $[M](SF_3)$ derivatives does not exclude the possibility that such SF_2 derivatives might be unstable with respect to further fluorine shift reactions from sulfur to the central metal atom, thereby leading to metal SF or metal-sulfido complexes.

ASSOCIATED CONTENT

Supporting Information. Tables S1 to S10. Coordinates of $(SF_2)(F)M(CO)_n$ and $(SF_3)M(CO)_n$; Tables S11 to S18. Coordinates of $(\eta^5\text{-}C_5H_5)M(SF_2)(F)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(SF_3)(CO)_n$; Tables S19 to S25. Coordinates of $(PF_3)M(CO)_n$ and $(PF_2)(F)M(CO)_n$; Tables S26 to S31. Coordinates of $(\eta^5\text{-}C_5H_5)M(PF_3)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(PF_2)(F)(CO)_n$; Tables S32 to S41 Harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $(SF_2)(F)M(CO)_n$ and $(SF_3)M(CO)_n$; Tables S42 to S49 Harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $(\eta^5\text{-}C_5H_5)M(SF_2)(F)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(SF_3)(CO)_n$; Tables S50 to S56 Harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $(PF_3)M(CO)_n$ and $(PF_2)(F)M(CO)_n$; Tables S57 to S62 Harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $(\eta^5\text{-}C_5H_5)M(PF_3)(CO)_n$ and $(\eta^5\text{-}C_5H_5)M(PF_2)(F)(CO)_n$; Tables S63 to S66. Optiimized coordinates of $(SF_2)(F)Ir(CO)_3$, $(SF_3)Ir(CO)_3$, and. $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$; Tables S67 to S70 Harmonic vibrational frequencies (cm^{-1}) and IR intensities (km/mol) of $(SF_2)(F)Ir(CO)_3$, $(SF_3)Ir(CO)_3$, and $(Et_3P)_2Ir(CO)(Cl)(F)(SF_3)$; complete Gaussian 03 reference (Ref 42). This material is available free of charge via the Internet at http://pubs.acs.org.

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