SF_6 as a Selective and Reactive Fluorinating Agent for Low-Valent Transition Metal Complexes[#]

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SF_6 has been found to react readily with vanadocene, yielding $V(C_5H_5)_2F$, while reactions with decamethylchromocene can lead to a number of products, depending on conditions. Among the products can be included $Cr(C_5Me_5)F_2(dmap)$ (dmap = *p*-dimethylaminopyridine), $Cr(C_5Me_5)_2{}^+[Cr_2(C_5Me_5)_2F_5]^-$, and $Cr_8(C_5Me_5)_6F_{18}$. Each of these reactions is likely to occur via the equivalent of an inner-sphere electron-transfer process. An even more rapid reaction was observed with the 19-electron $Fe(C_5H_5)[1,3,5\text{-}C_6H_3\text{-}(t\text{-}C_4H_9)_3]$ complex, leading to various salts of the expected 18-electron cation. In these cases, the reactions are likely to be analogous to an outer-sphere electron transfer, presumably leading initially to a "naked" fluoride ion. Structural characterization of each of these species has been obtained through X-ray diffraction studies.

Introduction

Organotransition metal halide complexes, perhaps especially (cyclopentadienyl)metal halides, have been found to be of great importance in both synthetic and catalytic applications.[1] Although the chlorides, bromides, and iodides have received more attention than fluoride complexes, it has been noted that in some cases the fluoride complexes may possess qualities superior to their heavier analogues, which has led to greater interest in developing new routes to organometallic fluoride compounds.[2] However, due to the toxicity and general sensitivity of fluorinating agents, it would be of some interest to develop synthetic approaches that were more convenient and less hazardous. In this regard, it was recently reported that the generally "extremely inert" SF_6, with an estimated lifetime of some 3200 years in the atmosphere, could actually be a more reactive fluorinating agent for low-valent organometallic compounds than XeF_2 or CoF_3.[3] Given the observation that significant sulfur or Me_3PS was formed as a byproduct of these reactions, this approach could also minimize the problems of dealing with the toxic byproducts often produced from fluorinating agents. We have therefore extended our initial studies to a variety of other metal complexes. As a result, SF_6 has indeed been found to react rapidly with both early (e.g., Ti) and late (e.g., Ni) low-valent organometallic and inorganic compounds, leading in some cases to species that might otherwise be difficult to prepare, and our observations are reported herein.

Experimental Section

All reactions were carried out under a nitrogen atmosphere in Schlenk apparatus. Hydrocarbon and aromatic solvents were dried by passage through activated alumina columns under a nitrogen atmosphere, while THF was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Gas volumes correspond to a pressure of ca. 640 mmHg. Elemental analyses were obtained from Desert Analytics. Solid-state magnetic susceptibilities were obtained on a Quantum Design $MPMS_2$ magnetometer (see Acknowledgment).

(Fluoro)bis(cyclopentadienyl)vanadium, $V(C_5H_5)_2F$, 1. Freshly sublimed vanadocene[4] (0.25 g, 1.4 mmol) was dissolved in 10 mL of toluene in a 100 mL Schlenk flask fitted with a rubber septum. Then 50 mL of SF_6 (1.7 mmol) was syringed into the flask through the septum and bubbled through the purple solution. The flask was left open to a mercury bubbler until the pressure equilibrated, at which time the stopcock was closed. The flask was stirred at ambient temperature overnight, and the solution gradually lightened to a pale purple. The solution was filtered through a Schlenk frit to remove some pale solid and was then concentrated to ca. 3 mL. Placement of the flask in a −60 °C freezer overnight yielded 160 mg (58% yield) of bright blue plates. Dissolution of these blue crystals in toluene led to a nearly colorless solution, which upon cooling yielded the same blue crystals. Complex **1** may also be prepared similarly by substituting stoichiometric AgF for the SF_6. Anal. Calcd for $VC_{10}H_{10}F$: C, 60.02; H, 5.04. Found: C, 59.64; H, 4.96. MS (EI, 70 eV) *m*/*z* (relative intensity): 200 (6), 135 (15), 91 (16), 66 (100), 65 (47), 40 (16), 39 (42), 32 (19), 28 (65). High-resolution MS: calcd 200.02063, found 200.02174.

(*p*-Dimethylaminopyridine)di(fluoro)(pentamethylcyclopentadienyl)chromium, $Cr(C_5Me_5)F_2(dmap)$, 2. Decamethyl-

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[#] Dedicated to the memory of Professor Robert W. Parry, a wonderful chemist, colleague, and human being.

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(4) (a) Vanadocene may be prepared from the reaction of VCl_3 or $VCl_3(THF)_3$ with 3 equiv of NaC_5H_5, or from 4 equiv of NaC_5H_5 and $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$,[4b,c] produced from the reduction of $VCl_3(THF)_3$ with zinc. (b) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913.

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chromocene (0.22 g, 0.68 mmol) was dissolved in 10 mL of toluene in a 250 mL Schlenk flask fitted with a rubber septum. Then 75 mg of powdered dmap was added as a solid and the flask swirled several times to dissolve the majority of the ligand. SF_6 (50 mL, 1.7 mmol) was then syringed into the flask and the pressure equilibrated through a bubbler. The stopcock was shut, and the flask was left to sit overnight. The solution color slowly changed from a red-orange to a brilliant blue, and small blue crystals slowly deposited on the sides of the flask. The solvent was removed via syringe, and the crystals were washed with 5 mL of toluene and two 5 mL aliquots of pentane and dried *in vacuo* to yield 135 mg (59%) of the product. Single crystals were grown by dissolving the compound in a minimum of warm (45−50 °C) THF, filtering the blue solution, and placing in a −30 °C freezer overnight. Anal. Calcd for $CrC_{17}H_{25}N_2F_2$: C, 58.78; H, 7.25; N, 8.06. Found: C, 58.50; H, 7.01; N, 8.12. Magnetic susceptibility: $\mu = 3.7\ \mu_B$.

Bis(pentamethylcyclopentadienyl)chromocinium (pentafluoro)bis(pentamethylcyclopentadienyl)dichromate(III), $[Cr(C_5Me_5)_2]^+\{(\mu_2\text{-}F)[Cr(C_5Me_5)F_2]_2\}^-$, 3. Decamethylchromocene[5] (0.20 g, 0.62 mmol) was dissolved in 5 mL of hexane in a 100 mL Schlenk flask fitted with a rubber septum. Then 50 mL of SF_6 (1.7 mmol) was syringed into the flask through the septum and the pressure equilibrated through a mercury bubbler. The stopcock was closed, and the flask was swirled several times and left to sit for 2 h. The initial orange-red solution rapidly turned green, and after several minutes, green microcrystals of the product deposited on the sides of the flask. When the reaction was completed, the supernatant was carefully removed via a glass syringe with a narrow bore needle and the bright green solid was washed with 5 mL of toluene and two 5 mL aliquots of pentane and dried *in vacuo* to yield 140 mg of product (85% yield). Single crystals were obtained by cooling a concentrated solution of the compound in a 50:50 mixture of toluene/THF to −30 °C. Anal. Calcd for $Cr_3C_{40}H_{60}F_5$: C, 60.67; H, 7.64. Found: C, 60.34; H, 7.81. Magnetic susceptibility: $\mu = 6.7\ \mu_B$.

Reaction of SF_6 with Decamethylchromocene in Toluene. Decamethylchromocene (0.20 g, 0.62 mmol) was dissolved in 20 mL of toluene in a 250 mL Schlenk flask fitted with a rubber septum. Then 50 mL of SF_6 (1.7 mmol) was syringed into the flask through the septum and the pressure equilibrated through a mercury bubbler. The stopcock was closed, and the flask was swirled several times and left to sit for 24 h. The color rapidly changed from orange-red to green and then slowly converted to a dark blue color. The solution was filtered through a coarse frit with Celite pad and placed in a −30 °C freezer. After 2−3 days, thin blue needles precipitated from the solution and were isolated by syringing off the supernatant and drying *in vacuo* (yield: 70 mg, 50%). The product can be recrystallized from blue toluene/pentane or THF/pentane solutions. Anal. Calcd for $\{(\mu_3\text{-}S)[Cr(C_5Me_5)(\mu_2\text{-}F)]_3\}^+[Cr(C_5Me_5)F_3]^-$: C, 53.68; H, 6.76. Found: C, 53.93; H, 6.88.

In a variation of the above, the initially prepared solution was left to sit in the presence of SF_6 for 5 days. Large hexagonal crystals separated from the supernatant along with some thin needles of the presumed $\{(\mu_3\text{-}S)[Cr(C_5Me_5)(\mu_2\text{-}F)]_3\}^+[Cr(C_5Me_5)F_3]^-$. The supernatant was removed via syringe and the solid dried *in vacuo*. In a glovebox, the two different types of crystals were separated mechanically, to yield 20 mg (16% yield) of the blue minor product, $Cr_8(C_5Me_5)_6F_{18}$, as a toluene solvate.

$\{Fe(C_5H_5)[1,3,5\text{-}C_6H_3(t\text{-}C_4H_9)_3]^+\}_2[HF_2]^-[H_2F_3]^-$. This reaction is best accomplished with the use of fluorinated greases such as Krytox. $\{Fe(C_5H_5)[1,3,5\text{-}C_6H_3(t\text{-}C_4H_9)_3]\}^+PF_6^-$ (0.45 g, 0.88 mmol) was dissolved in 20 mL of THF, and the flask was cooled to 0 °C in an ice bath. The yellow solution was transferred to a 250 mL Schlenk flask containing Na amalgam (40 mg of Na dissolved in ca. 3 mL of Hg) and was vigorously stirred at 0 °C for 1 h. The solution rapidly changed color to a bright green. The solution was then syringed away from the amalgam, and the solvent was removed *in vacuo* to leave a green residue. The residue was extracted with four 10 mL aliquots of pentane and filtered through a coarse frit covered by half of an inch of Celite. The solvent was then removed *in vacuo* to yield $Fe(C_5H_5)[1,3,5\text{-}C_6H_3(t\text{-}C_4H_9)_3]$[6] as a green solid. The solid was redissolved in 5 mL of THF and the flask fitted with a rubber septum. Then 50 mL of SF_6 (1.7 mmol) was introduced as mentioned above, and the solution was left to sit overnight. The color slowly converted from dark green to brown-yellow, and after a few hours, yellow crystals began to deposit on the sides of the flask. The supernatant was removed via syringe, and the crystals were washed with pentane and dried *in vacuo* (caution: it is possible that SF_4 and other toxic sulfur fluorides may have been formed). Further product could be isolated by concentrating a cool (0 °C) solution slowly *in vacuo* and isolating as above. Total yield: 170 mg (46%). Anal. Calcd for $Fe_2C_{46}H_{73}F_5$: C, 66.35; H, 8.84. Found: C, 66.31; H, 8.80.

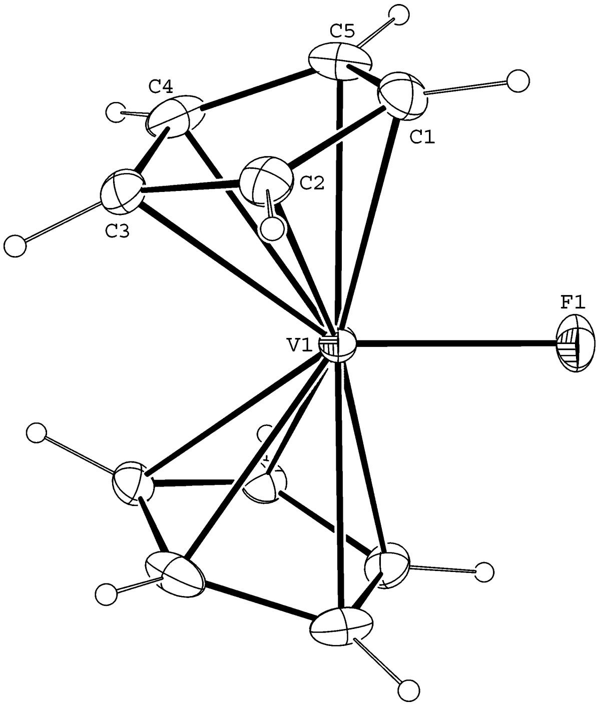

Figure 1. Structure of $V(C_5H_5)_2F$ with 30% probability ellipsoids.

The above reaction can also be carried out in toluene, although the product is then isolated as a powder. The use of silicone grease leads to the formation of a small amount of the expected complex iron cation, as a $Si(CH_3)_2F_3^-$ salt, which tends to crystallize as pale yellow-brown prisms, subsequent to the crystallization of the major product from the initial toluene reaction solutions.[7a]

X-ray Diffraction Studies. Single crystals of each compound were placed under Paratone oil for examination and thereafter were transferred to an Enraf-Nonius Kappa CCD diffractometer for unit cell determination and data collection. Subsequently, the structures were solved using direct methods routines in SIR 97 and refined using SHELX programs. In each case, the non-hydrogen atoms could be refined anisotropically. For the $Cr(C_5Me_5)F_2(dmap)$ structure, most of the hydrogen atoms could be refined isotropically, except those on C8, C9, and C17. Their hydrogen atoms were

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Table 1. Crystallographic Parameters for $V(C_5H_5)_2F$, $Cr(C_5Me_5)F_2(dmap)$, $Cr(C_5Me_5)_2{}^+[Cr_2(C_5Me_5)_2F_5]^-$, $Cr_8(C_5Me_5)_6F_{12}\cdot 4(toluene)$, and $\{Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]^+\}_2(HF_2^-)(H_2F_3^-)$

formula	$C_{10}H_{10}FV$	$C_{17}H_{25}CrF_2N_2$	$C_{40}H_{60}Cr_3F_5$	$C_{88}H_{122}Cr_8F_{18}$	$C_{46}H_{73}F_5Fe_2$
fw	200.12	347.39	791.88	1937.86	832.74
temperature (K)	150(1)	150(1)	150(1)	150(1)	150(1)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	triclinic
space group	$P2/a$	$P\bar{1}$	$P2_12_12$	$P\bar{1}$	$P\bar{1}$
unit cell dimens					
a (Å)	9.7874(2)	7.4526(2)	12.8139(2)	11.7587(7)	10.6504(2)
b (Å)	6.3569(2)	8.5308(4)	17.8524(4)	14.4911(12)	14.6996(3)
c (Å)	14.2795(3)	14.9544(8)	8.6190(2)	14.8362(13)	15.6216(3)
α (deg)	90	79.848(3)	90	97.213(4)	63.3130(11)
β (deg)	105.8677(17)	82.488(3)	90	111.974(5)	81.2757(11)
γ (deg)	90	65.649(3)	90	102.408(5)	81.5338(10)
volume (Å^3); Z	854.58(4); 4	850.82(6); 2	1971.67(7); 2	2229.6(3); 1	2151.17(7)
D_{calc}	1.555	1.356	1.334	1.443	1.286
absorp coeff (cm^{-1})	11.11	6.90	8.62	10.16	7.26
θ range (deg)	1.5−27.5	2.8−27.4	2.6−27.5	2.9−27.7	2.5−27.5
limiting indices	$-12 \leq h \leq 12$	$-9 \leq h \leq 9$	$-16 \leq h \leq 16$	$-15 \leq h \leq 14$	$-13 \leq h \leq 13$
	$-7 \leq k \leq 8$	$-11 \leq k \leq 10$	$-22 \leq k \leq 23$	$-18 \leq k \leq 18$	$-19 \leq k \leq 19$
	$-18 \leq l \leq 18$	$-17 \leq l \leq 19$	$-11 \leq l \leq 11$	$-19 \leq l \leq 19$	$-20 \leq l \leq 20$
no. of reflns collected	3246	5588	4514	17 089	18 704
no. of indep reflns; n: $I > n\sigma(I)$	1935; 2	3769; 2	4514; 2	9615	9828
$R(F)$	0.0278	0.0505	0.0361	0.0568	0.0456
$R_w(F^2)$	0.0707	0.1008	0.0850	0.1308	0.0980
max./min. diff Fourier peak (e Å^{-3})	0.28/−0.46	0.43/−0.47	0.71/−0.39	0.56/−0.80	0.59/−0.54

therefore placed in idealized positions and allowed to ride on their respective carbon atoms. For the other structures hydrogen atoms on metal-bound carbon atoms were refined isotropically, with the remaining hydrogen atoms being allowed to ride on their carbon atoms. The toluene molecules contained in the $Cr_8(C_5Me_5)_6F_{18}$ structure were highly disordered and modeled with atoms in partially occupied sites.

Results

SF_6 has long been regarded as an extremely inert molecule, whose few observed reactions generally occurred at high temperatures and pressures and in low yields.[8] Only recently has it become clear that SF_6 could engage in synthetically useful reactions, specifically ones involving low-valent Ti(II) and Zr(II) organometallic complexes.[3] As an extension of these results, we have now found that low-valent later metal complexes can also engage in these reactions. In the case of vanadocene's reaction with SF_6, straightforward characterization has revealed the product to be the previously unreported, paramagnetic 16-electron $V(C_5H_5)_2F$ (**1**), analogous to the known chlorine analogue.[9] The bright blue $V(C_5H_5)_2F$ crystallizes as two independent half-molecules, each with crystallographically imposed C_2 symmetry (Figure 1, Table 2). Overall, the structure is similar to that of $V(C_5H_5)_2Cl$,[10] although for that structure there was an imposed mirror plane, bisecting both C_5H_5 ligands, which were mutually staggered. The average V−C (2.291(5) vs 2.278(5) Å) and C−C (1.406(2) vs 1.395(5) Å) distances for the two compounds are similar, as are the tilts between the two C_5H_5 ligands, 143.4° vs 139.5°. There is a difference of 0.477 Å in the V−F and V−Cl bond lengths, which is dramatically larger than the difference of 0.35 Å in the halide covalent radii. This phenomenon has been observed previously, as for example in $Zr(C_5H_5)_2X_2$[11] and analogous 6,6-dimethylcyclohexadienyl[12] complexes, though not nearly to the same extent as found here. While one could invoke the ability of the fluoride ligand to serve as a π donor, resulting in an 18- rather than a 16-electron complex, the paramagnetism of $V(C_5H_5)_2F$ appears to argue against this.

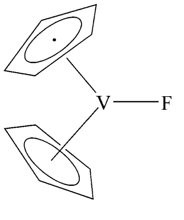

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Table 2. Pertinent Bonding Distances for $V(C_5H_5)_2F$

V1−F	1.9128(14)	V2−F2	1.9131(14)
V1−C1	2.3149(16)	V2−C6	2.2887(17)
V1−C2	2.3086(15)	V2−C7	2.2714(17)
V1−C3	2.2763(17)	V2−C8	2.2751(17)
V1−C4	2.2725(17)	V2−C9	2.3065(16)
V1−C5	2.2927(17)	V2−C10	2.3065(16)
C1−C2	1.403(2)	C6−C7	1.400(3)
C1−C5	1.407(3)	C6−C10	1.409(3)
C2−C3	1.413(2)	C7−C8	1.407(3)
C3−C4	1.405(3)	C8−C9	1.410(3)
C4−C5	1.405(3)	C9−C10	1.396(2)

Although chromocene was also found to react with SF_6, the insolubilities of some of the products suggested that the use of a more soluble derivative such as decamethylchromocene might be more profitable. Indeed, depending on solvent and reaction conditions, any one of several species can be obtained (Scheme 1). Interestingly, in contrast to the results for titanium, vanadium, and zirconium, all of the chromium complexes underwent loss of at least one C_5Me_5 ligand. The simplest product, $Cr(C_5Me_5)$-

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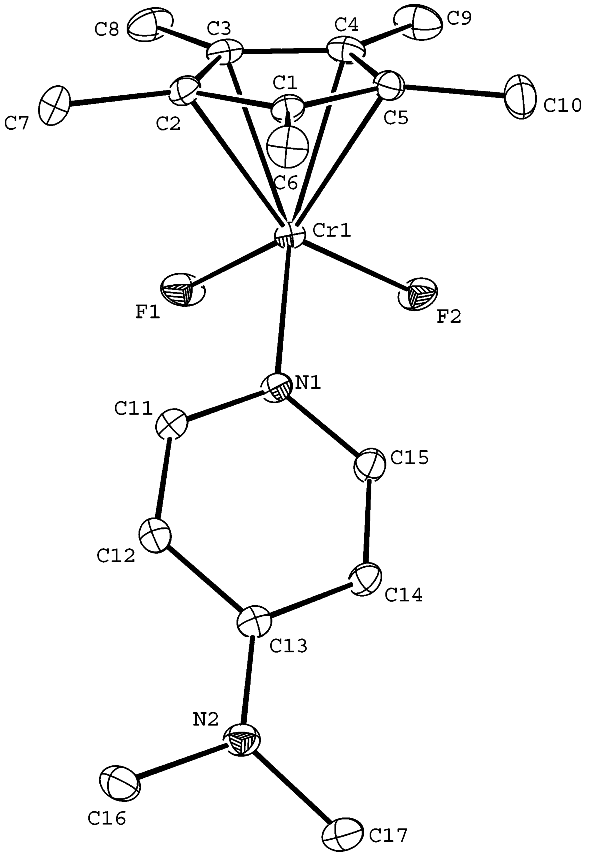
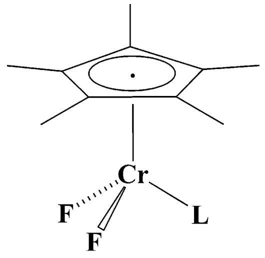


Figure 2. Structure of Cr(C$_5$Me$_5$)F$_2$(dmap) with 30% probability ellipsoids.

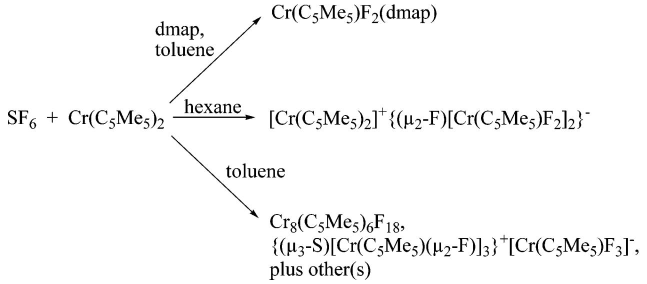
F$_2$(dmap) (**2**, L = dmap), was isolated from reactions carried out in the presence of dmap (*p*-dimethylaminopyridine). The product exhibited a room-temperature magnetic moment of 3.7 μ_B in the solid state, consistent with the presence of three unpaired electrons in the 15-electron complex, thereby ruling out any significant π donation by fluoride.



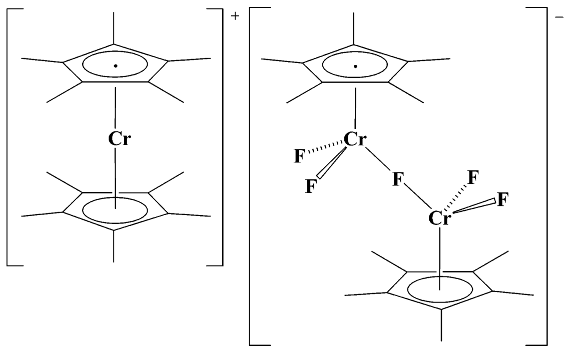
2 (L = dmap)

The structure of Cr(C$_5$Me$_5$)F$_2$(dmap) is presented in Figure 2, with bonding parameters summarized in Table 3. The complex adopts the expected piano stool structure, with average Cr−C, Cr−N, and Cr−F distances of 2.241(6), 2.063(2), and 1.868(2) Å. The shortening by ca. 0.05 Å of the Cr−F and Cr−C bonds relative to the V−F and V−C bonds in V(C$_5$H$_5$)$_2$F slightly exceeds the difference of 0.025 Å in the ionic radii of Cr(III) and V(III),[13] possibly as a result of the greater number of interactions in V(C$_5$H$_5$)$_2$F. The F−Cr−N and F−Cr−F angles, ranging from 91.96(9)° to 97.18(9)°, are more in accord with an octahedral arrangement than a tetrahedral one. The tilts of the Cr−F and Cr−N vectors relative to the Cr−C$_5$Me$_5$ centroid vector are 121.7° and 124.0°, respectively.

Scheme 1



In the absence of a coordinating ligand such as dmap, and using hexane as solvent, a trimetallic salt, Cr(C$_5$Me$_5$)$_2$$^+$[Cr$_2$(C$_5Me_5$)$_2F_5$]$^-$ (**3**), could be isolated from the reaction of Cr(C$_5$Me$_5$)$_2$ with SF$_6$. As in the previous reaction, all of the chromium centers are trivalent, and the overall room-temperature magnetic moment of 6.7 μ_B is consistent with each metal center having three unpaired electrons. This would be expected on the basis of previous data for [Cr(C$_5$Me$_5$)$_2$$^+$][5] and Cr(C$_5Me_5$)F$_2$(dmap).



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The structure of Cr(C$_5$Me$_5$)$_2$$^+$[Cr$_2$(C$_5Me_5$)$_2F_5$]$^-$ is presented in Figure 3, with pertinent bonding parameters being contained in Table 4. Not only does the given formulation lead to all of the chromium centers being trivalent, it also is consistent with other structural data. Thus, the average Cr−C distance for the Cr(C$_5$Me$_5$)$_2$ unit is 2.198(1) Å, very close to the values observed in other Cr(C$_5$Me$_5$)$_2$$^+$ salts.[14] Additionally, the Cr−C and Cr−F(terminal) distances of 2.237(4) and 1.867(1) Å in the Cr$_2$(C$_5$Me$_5$)$_2$F$_5$ unit are quite similar to those of Cr(C$_5$Me$_5$)F$_2$(dmap) (*vide supra*). The Cr−F(bridging) distance of 1.9655(5) Å is, as expected, longer than the terminal analogues. The F−Cr−F angles average 95.3(4)°, while the average tilt between the Cr−F and Cr−C$_5$Me$_5$ centroid vectors is 122.7° for F2 and F3, vs 118.7° for F1.

Use of toluene as the solvent instead of hexane for the Cr(C$_5$Me$_5$)$_2$ reaction with SF$_6$ allowed for the initially formed

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Table 3. Pertinent Bonding Parameters for $Cr(C_5Me_5)F_2(dmap)$

Bond Distances (Å)			
Cr−F1	1.8638(17)	Cr−C2	2.232(3)
Cr−F2	1.8730(18)	Cr−C3	2.245(3)
Cr−N1	2.063(2)	Cr−C4	2.232(3)
Cr−C1	2.261(3)	Cr−C5	2.235(3)
Bond Angles (deg)			
N1−Cr−F1	92.57(9)	F1−Cr−F2	97.18(9)
N1−Cr−F2	91.96(9)		

Table 4. Pertinent Bonding Parameters for $Cr(C_5Me_5)_2{}^+[Cr_2(C_5Me_5)_2F_5]^-$

Bond Distances (Å)			
Cr1−C1	2.247(2)	Cr2−C11	2.198(2)
Cr1−C2	2.233(3)	Cr2−C12	2.198(3)
Cr1−C3	2.226(2)	Cr2−C13	2.202(2)
Cr1−C4	2.247(2)	Cr2−C14	2.197(2)
Cr1−C5	2.230(2)	Cr2−C15	2.197(2)
Cr1−F1	1.9655(5)	Cr1−F3	1.8638(17)
Cr1−F2	1.8696(17)		
Bond Angles (deg)			
F1−Cr1−F2	95.98(8)	F2−Cr1−F3	95.29(9)
F1−Cr1−F3	94.74(8)	Cr1−F1−Cr1′	165.10(15)

Table 5. Pertinent Bonding Parameters for $Cr_8(C_5Me_5)_6F_{12}$

Bond Distances (Å)			
Cr1−C1	2.185(4)	Cr1−F1	1.859(2)
Cr1−C2	2.217(4)	Cr1−F2	1.957(2)
Cr1−C3	2.220(4)	Cr1−F3	1.947(2)
Cr1−C4	2.222(4)	Cr2−F2	1.932(2)
Cr1−C5	2.204(4)	Cr2−F4	1.955(2)
Cr2−C11	2.201(4)	Cr2−F5	1.951(2)
Cr2−C12	2.187(4)	Cr3−F3	1.952(2)
Cr2−C13	2.203(4)	Cr3−F6	1.968(2)
Cr2−C14	2.209(4)	Cr3−F7	1.857(2)
Cr2−C15	2.232(4)	Cr4−F4′	1.911(2)
Cr3−C21	2.215(5)	Cr4−F5	1.926(2)
Cr3−C22	2.181(4)	Cr4−F6′	1.900(2)
Cr3−C23	2.206(4)	Cr4−F8	1.821(2)
Cr3−C24	2.212(4)	Cr4−F9	1.930(2)
Cr3−C25	2.221(4)	Cr4−F9′	1.969(2)
Bond Angles (deg)			
F1−Cr1−F2	91.36(10)	F4′−Cr4−F5	175.24(11)
F1−Cr1−F3	95.44(11)	F4′−Cr4−F6′	91.09(9)
F2−Cr1−F3	93.13(10)	F4′−Cr4−F8	92.11(10)
F2−Cr2−F4	92.19(10)	F4′−Cr4−F9	88.18(9)
F2−Cr2−F5	90.61(10)	F4′−Cr4−F9′	87.85(10)
F4−Cr2−F5	94.69(9)	F5−Cr4−F6′	89.89(9)
F3−Cr3−F6	94.21(10)	F5−Cr4−F8	92.47(11)
F3−Cr3−F7	94.66(11)	F5−Cr4−F9	90.13(9)
F6−Cr3−F7	92.71(10)	F5−Cr4−F9′	87.46(10)
Cr1−F2−Cr2	151.68(13)	F6′−Cr4−F8	94.16(11)
Cr1−F3−Cr3	166.17(13)	F6′−Cr4−F9	171.09(11)
Cr2−F4−Cr4′	134.02(12)	F6′−Cr4−F9′	92.16(10)
Cr2−F5−Cr4	132.98(13)	F8−Cr4−F9	94.74(10)
Cr3−F6−Cr4′	144.38(13)	F8−Cr4−F9′	173.69(10)
Cr4−F9−Cr4′	101.05(10)	F9−Cr4−F9′	78.94(10)

product(s) to remain in solution and undergo further reaction, yielding at least two further isolable products. The major new product also appeared to be composed exclusively of Cr(III), again as a salt, $\{[Cr(C_5Me_5)(\mu_2\text{-}F)]_3(\mu_3\text{-}S)\}^+[Cr(C_5Me_5)F_3]^-$, providing an interesting example in which the sulfur of the SF_6 becomes incorporated in the metal-containing product. Notably, in an earlier reaction that yielded a Ti(III) complex, the presence of PMe_3 seemed to have played a crucial role in its formation by serving as a scavenger for the sulfur. Although satisfactory analytical data were obtained for this formulation of the chromium salt, a structural study revealed a complication. While the expected atoms were present, the observation of significant electron density near the sulfur and two metal centers suggested the partial presence of an additional atom, presumably oxygen.

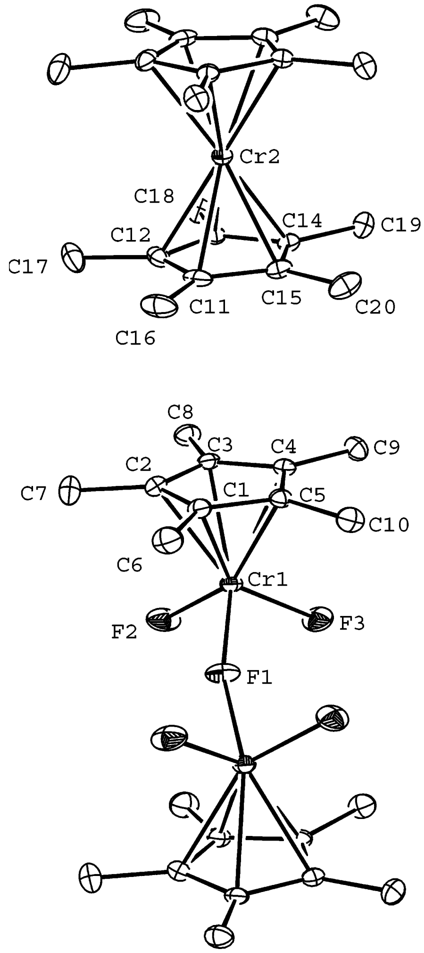

Figure 3. Structure of $Cr(C_5Me_5)_2{}^+[Cr_2(C_5Me_5)_2F_5]^-$ with 30% probability ellipsoids.

Although the nature of the above species is not entirely understood, a minor byproduct could also be isolated upon prolonged exposure to SF_6. This species was found to have the stoichiometry $Cr_8(C_5Me_5)_6F_{18}$. The structure of $Cr_8(C_5Me_5)_6F_{18}$ is presented in Figure 4, with pertinent bonding parameters being given in Table 5. Again, all chromium centers are trivalent, and the complex may be regarded as being derived from six $Cr(C_5Me_5)F_2$ and two CrF_3 units. The complex lies on a crystallographic inversion center, leading to four independent chromium ion sites. The unique site lacking a C_5Me_5 ligand, Cr4, achieves pseudooctahedral coordination by six fluoride ions, only one of which, F8, is not shared with another chromium center. Two fluorides, F9 and F9′, are shared with Cr4′, while the other three (F4′, F5, and F6′) are shared with Cr2′, Cr2, and Cr3′, respectively. The Cr4−F8 distance of 1.821(2) Å is significantly shorter than the Cr4−F(bridging) distances, which range from 1.900(2) to 1.969(2) Å, those involving Cr4 and Cr4′ being the longest for this grouping. Of the three independent C_5Me_5-bound chromium sites, only Cr2 has no terminally bound fluoride ligands. Its Cr−F distances average 1.953(1) Å for those shared with Cr4 and Cr4′ and 1.932(2) Å for F2, shared with Cr1. Both Cr1 and Cr3 have a single terminal fluoride each, with the average Cr−F distance being 1.858(1) Å, significantly longer than the Cr4−F8 bond (1.821(2) Å). These two chromium centers are also coordinated by two bridging

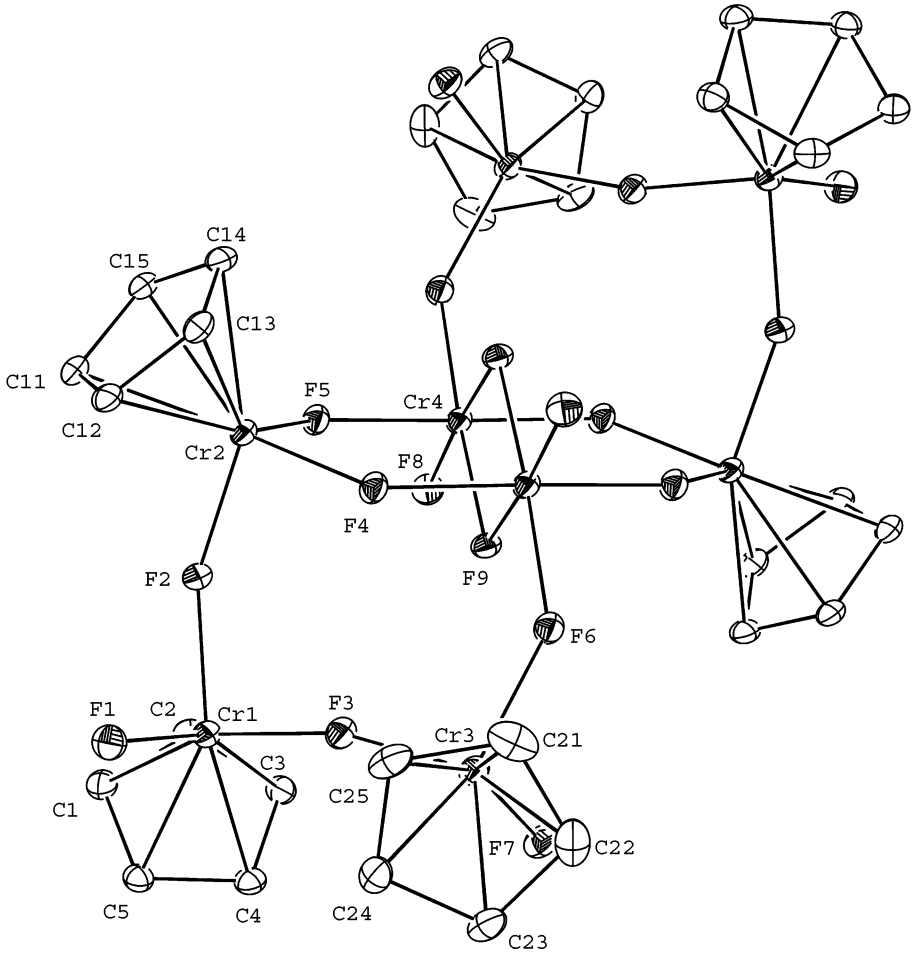

Figure 4. Structure of $Cr_8(C_5Me_5)_6F_{18}$ with 30% probability ellipsoids. Methyl groups are not shown for clarity.

fluoride ions each, with the Cr−F distances ranging from 1.947(2) to 1.968(2) Å. The longest, to F6, is the only one of these that is also coordinated to either Cr4 or Cr4′. The average Cr−C distances for the three chromium sites are all essentially equivalent, at 2.210(7), 2.206(7), and 2.207(7) Å, respectively, for Cr1−Cr3. The average Cr−C distance is 2.208(4) Å. Notably, the Cr−F−Cr and F−Cr−F angles display significant variations throughout the structure. For example, the Cr4−F9−Cr4′ angle is only 101.05(10)°, while the Cr1−F3−C3 angle is 166.17(13)°. The cis F−Cr−F angles can be as small as 78.94(10)° for F9−C4−F9′ and as large as 95.44(11)° for F1−Cr1−F3.

SF_6 was also observed to react with the 19-electron $Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]$, even much more rapidly than for the electron-deficient species. The use of *t*-butyl rather than methyl or other alkyl substituents with α-hydrogen atoms was made in order to avoid the possibility of proton abstraction by a fluoride ion. As expected, the product contained the 18-electron $Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]^+$ ion. When silicone grease was used to seal the reaction vessel, a product with the accompanying counterion being $Si(CH_3)_2F_3^-$ was isolated, whereas the use of fluorinated grease led to a 1:1 mix of HF_2^- and $H_2F_3^-$ counterions.[7a] The rapidity of these reactions can be ascribed to the strong reducing ability of the 19-electron complex. SF_6 is known to react rapidly with other electron-transfer agents such as ketyls.[15] As opposed to the other reactions reported herein, for which something akin to an inner-sphere electron-transfer mechanism can be proposed, the iron reaction would clearly have to proceed via an outer-sphere process.[16] In fact, $Cr(C_6H_6)_2$ has also been observed to react readily with SF_6.[17]

The structure of one of the two independent $Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]^+$ ions is presented in Figure 5, with pertinent bonding parameters being given in Table 6. The two independent cations do not differ significantly from each other in general structure, although there may be a slight difference in the average Fe−C distances for the C_5H_5 ligands, 2.066(2) vs 2.057(4) Å. As the carbon atoms for the second C_5H_5 ligand have *U* values ca. 50% larger than those of the first ligand, 2.066(2) Å can be taken as the best value for the Fe−C(C_5H_5) distance. The Fe−C (arene) distances fall in two sets. The Fe−C(H) distances average 2.090(3) Å, while the Fe−C(t-C_4H_9) distances average 2.119(3) Å. This small but real difference arises from a contraction of the arene rings' CH−C(R)−CH angles relative to the RC−C(H)−CR angles (R = t-C_4H_9), 117.6(1)° vs 122.4(1)°. Related contractions have been commonly found in pentadienyl[18] and other[19] ligand complexes.

Two different counterions are present in the lattice, one being HF_2^-, the other $H_2F_3^-$. The H−F distances are similar for the

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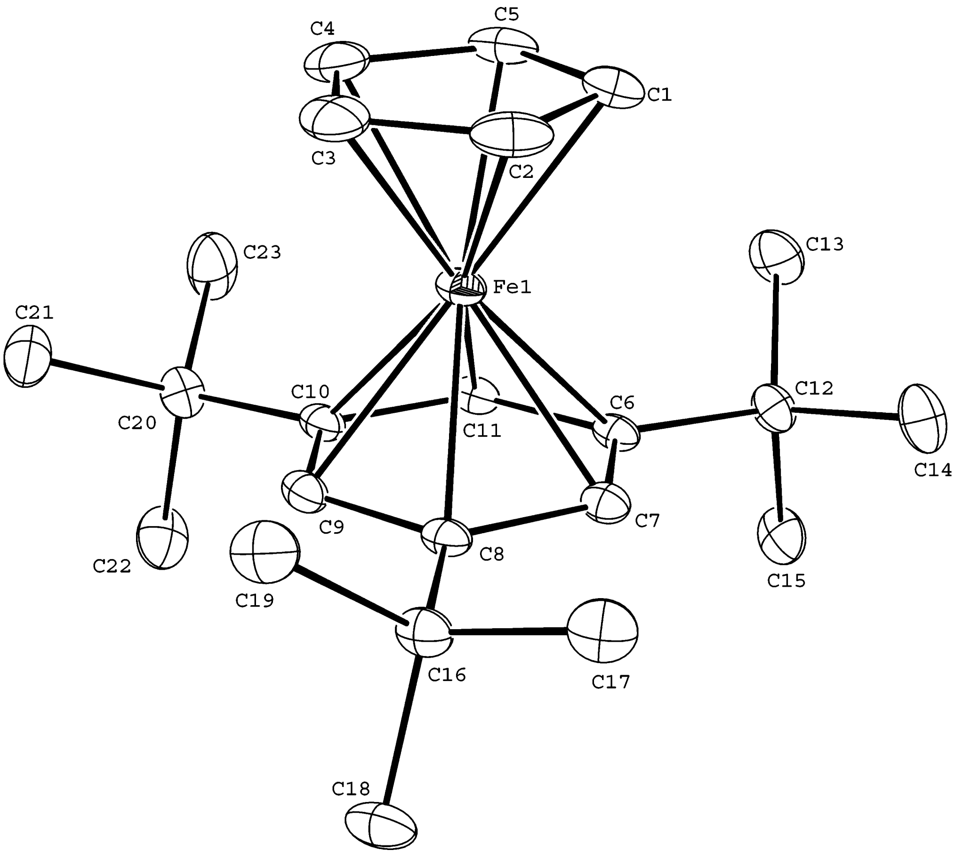

Figure 5. Structure of one of the two independent $Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]^+$ ions with 30% probability ellipsoids.

Table 6. Pertinent Bonding Parameters for $\{Fe(C_5H_5)[C_6H_3(t\text{-}C_4H_9)_3]^+\}_2(HF_2^-)(H_2F_3^-)$

Bond Distances (Å)			
Fe1−C1	2.068(3)	Fe2−C1A	2.043(3)
Fe1−C2	2.065(3)	Fe2−C2A	2.057(3)
Fe1−C3	2.062(3)	Fe2−C3A	2.063(3)
Fe1−C4	2.075(3)	Fe2−C4A	2.061(3)
Fe1−C5	2.062(3)	Fe2−C5A	2.061(3)
Fe1−C6	2.122(2)	Fe2−C6A	2.111(2)
Fe1−C7	2.098(2)	Fe2−C7A	2.087(2)
Fe1−C8	2.121(2)	Fe2−C8A	2.131(2)
Fe1−C9	2.086(2)	Fe2−C9A	2.080(2)
Fe1−C10	2.118(2)	Fe2−C10A	2.112(2)
Fe1−C11	2.097(2)	Fe2−C11A	2.095(3)
H1F−F1	1.03(5)	H1F−F2	1.30(5)
H2F−F2	1.15(4)	H2F−F3	1.21(4)
H4F−F4	1.18(5)	H4F−F5	1.22(4)
Bond Angles (deg)			
F1−H1F−F2	164(4)	H1F−F2−H2F	108(3)
F2−H2F−F3	166(4)	F4−H4F−F5	141(4)

two species, averaging 1.18(4) Å. A single H−F−H angle is present for the H_2F_3 anion and has a nearly tetrahedral value, 108(3)°. The F−H−F angle for HF_2^- is 141(4)°, appearing to be smaller than the average value of 165(3)° for $H_2F_3^-$. While other reported $H_2F_3^-$ structures[20] provide some suggestion that the ion may be looked upon as having a central F^- coordinated to two HF units, the large thermal motions of some of the fluorine atoms likely result in some systematic error in the atomic positions, and together with the uncertainties in the bonding parameters for this structure, a clear assessment cannot be made.

Discussion

While the greenhouse gas SF_6 has long been believed to be extremely inert,[21] the fact that the S−F bond is significantly weaker than the C−F bond (68 vs 116 kcal/mol) or many M−F bonds (e.g., Zr−F, ca. 155 kcal/mol),[22] suggested that appropriate lower valent metal centers should be able to abstract one or more fluorine atoms, via the equivalent of an inner-sphere electron-transfer process. Although such a term is generally applied to metallic complexes, one could readily envision a number of similar reactions for WF_6, or other metal hexafluorides, for which there would be no hesitation in applying inner-sphere designations. A potential synthetic advantage of the SF_6 reactions is that as it is converted to more reactive lower fluorides, they can then react preferentially, thereby more efficiently utilizing the fluorine atoms and leading to sulfur or a trapped sulfur species such as Me_3PS as the predominant byproduct,[3] rather than highly toxic lower sulfur fluorides. While most fluorinating agents and their byproducts are toxic and hazardous, the SF_6/sulfur combination is by comparison fairly innocuous and may lead to products not obtained readily through

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other routes. Of course, as noted herein, in some situations the sulfur byproduct can become incorporated into the metal-containing product. Generally, the presence of a sulfur scavenger such as Me_3P can be used when desired to inhibit this.[3]

As noted above, the fluorine atom transfers (abstractions) may be looked upon as analogues to an inner-sphere electron-transfer process, although minor variations on this are possible. In particular, one or two fluorine atoms may initially coordinate and be transferred to the metal center. In the latter case, SF_4 would be produced, which could subsequently react with a second metal center. In the former situation, a transfer of one fluorine atom could lead to SF_5, which could also undergo further reaction, through additional fluorine atom abstractions, whether directly ("inner-sphere" reactions) or indirectly via M−S bond formation[23] and subsequent α-elimination. In either case, the second transfer would not need to involve the same metal center.

A second type of reaction occurs with metal complexes that are very susceptible to one-electron oxidations, such as 19-electron species. In such cases, an outer-sphere process can take place, perhaps through a fluoride/π contact. A reaction of the readily oxidized 18-electron $Cr(C_6H_6)_2$ with SF_6 has, in fact, also been observed recently, by Richmond and Scheffler.[17] With very powerful reducing agents such as 19-electron complexes, the fluorine abstractions are likely to be less selective, so that unless a stoichiometric quantity of SF_6 is used, significant quantities of the toxic lower sulfur fluorides could be produced, including SF_4 and the weakly bound dimer S_2F_{10}.

It is worth noting that low-valent, electron-rich late metal complexes such as $Ni(PMe_3)_4$ also react readily with SF_6.[7] Given the potential of SF_6 to serve as a nontoxic and relatively safe fluorinating agent, and its ability to react with both early and late low-valent transition metal complexes, it can be expected that many further useful synthetic applications for both organometallic and coordination compounds will be forthcoming.

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Supporting Information Available: Structural data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The M−S bond formation may or may not involve the metal atom that originally abstracted the first fluorine atom. In cases in which it was the same metal center, this would lead to the product of a formal S−F oxidative addition.