

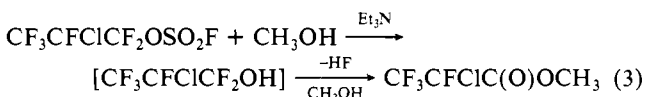
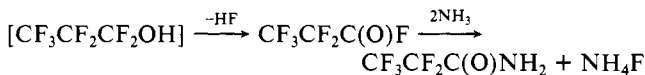
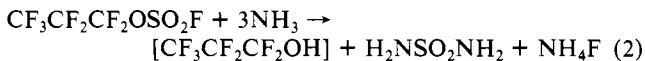
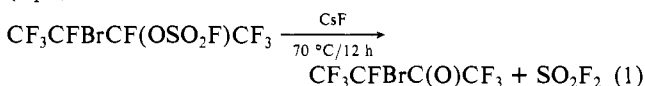
## Syntheses and Reactions of Polyfluoroalkyl Fluorosulfates

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Several polyfluoroalkyl fluorosulfates,  $R_f\text{OSO}_2\text{F}$  ( $R_f = \text{CF}_3\text{CH}(\text{CH}_3)$ ,  $\text{CF}_3\text{C}(\text{CH}_3)_2$ , and  $(\text{CF}_3)_2\text{CH}$ ), have been synthesized by the reaction of polyfluoro alcohols with sulfonyl fluoride or sulfonyl chloride fluoride. They reacted with nucleophilic reagents such as amines, polyfluoro alcohols, polyfluoroalkoxides and bromide ion to give sulfamates, dialkyl sulfates, and polyfluoroalkyl bromides, respectively. In the case of  $\text{CF}_3(\text{CH}_3)_2\text{COSO}_2\text{F}$  with bromide ion, the polyfluoroalkyl bromide loses hydrogen bromide to give 2-(trifluoromethyl)propene in high yield.

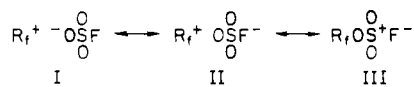
The presence of three electrophilic centers in polyfluoroalkyl fluorosulfates and chlorosulfates,<sup>1</sup> carbon, sulfur, and fluorine (chlorine), render the  $R_f\text{OSO}_2\text{X}$  ( $X = \text{Cl}, \text{F}$ ) substrates of considerable interest because nucleophiles may potentially react at one or several of these centers. It is well known that perfluoroalkyl and polyfluoroalkyl fluorosulfates undergo facile attack by nucleophiles such as fluoride ion, ammonia, or methanol to cleave the S-O bond to form ketones (eq 1),<sup>2</sup> amides (eq 2),<sup>3</sup> or esters (eq 3).<sup>4</sup>



We have reported a facile route to the syntheses of new sulfamates and dialkyl sulfate esters when 2,2,2-trifluoroethyl fluorosulfate and hexafluoroisopropyl fluorosulfate were reacted with amines and alcohols.<sup>5,6</sup> This reaction behavior was in sharp contrast with that of alkyl or perfluoroalkyl fluorosulfates with similar nucleophiles where attack does not occur at the sulfur-fluorine bond but rather at the carbon of the polyfluoroalkyl group or at the sulfur with concomitant scission of the sulfur-oxygen bond. Therefore, we were prompted to explore the reactions of nucleophiles with a range of substituted fluoroalkyl fluorosulfates in an attempt to understand and thus be able to predict the point in the molecule at which the nucleophile would attack and the products which would result. To this end we synthesized the polyfluoroalkyl fluorosulfates  $\text{CF}_3\text{CH}_2\text{OSO}_2\text{F}$ ,<sup>5</sup>  $(\text{CF}_3)_2\text{CHOSO}_2\text{F}$ ,<sup>5</sup>  $\text{CF}_3(\text{CH}_3)\text{CHOSO}_2\text{F}$ , and  $\text{CF}_3(\text{CH}_3)_2\text{COSO}_2\text{F}$  and studied their reactions with nucleophiles, such as amines, polyfluoroalkyl alcohols, polyfluoroalkoxides and bromide ion.

## Results and Discussion

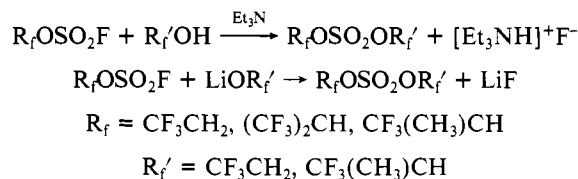
The polyfluoroalkyl fluorosulfate,  $R_f\text{OSO}_2\text{F}$ , is very similar structurally to its chlorosulfate analogue. The transition state for the reaction of fluorosulfates with nucleophiles may be represented by several resonance structures.<sup>1</sup> Contribution by structure III would reflect reactivity via sulfur-fluorine bond



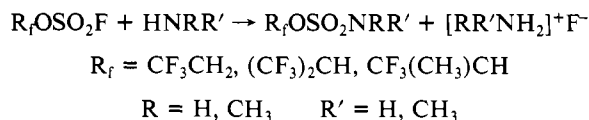
scission while contribution by structures I and II would account

for the carbonium ion type behavior of fluorosulfates.

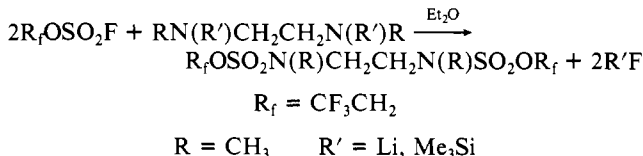
When polyfluoroalkyl fluorosulfates were reacted with polyfluoro alcohols in the presence of triethylamine or with lithium polyfluoroalkoxides, cleavage of the sulfur-fluorine bond occurred to give sulfates.



When amines were reacted with polyfluoroalkyl fluorosulfates, the products obtained were those also resulting from sulfur-fluorine bond scission



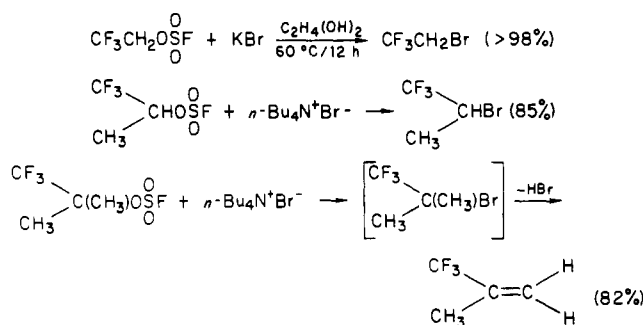
and with diamines a similar mode of behavior is observed:



In contrast, when perfluoroalkyl fluorosulfates were reacted with amines, the products that formed resulted from sulfur-oxygen bond cleavage, as has been reported.<sup>3</sup> We have confirmed this type of behavior.

It appears that the presence of fluorine atoms or three totally fluorinated groups on the  $\alpha$ -carbon of the fluorosulfate improves the leaving ability of the alkoxy group and allows this process to compete with the alternative process of fluorine as the leaving group in displacement at the sulfur atom.

Polyfluoroalkyl fluorosulfates are attacked at the  $\alpha$ -carbon by bromide ion to give polyfluoroalkyl bromides with  $-\text{OSO}_2\text{F}$  as the leaving group:



Primary and secondary polyfluoroalkyl fluorosulfates are remarkably stable thermally and to hydrolysis.<sup>6</sup> However, 2-(trifluoromethyl)isopropyl fluorosulfate is thermally unstable, decomposing spontaneously at room temperature. The sulfates and

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sulfamates are colorless, air- and water-stable liquids with low vapor pressures.

### Experimental Section

**Materials.**  $(CF_3)_2CHOSO_2F$ ,<sup>5</sup>  $SO_2ClF$ ,<sup>7</sup> and  $SO_2F_2$  were prepared according to literature procedures. The other materials,  $CF_3CH_2OH$ ,  $(CF_3)_2CHOH$  (Aldrich),  $CF_3CH(CH_3)OH$  (PCR),  $(CH_3)_2NH$  (Matheson), and  $CF_3C(CH_3)_2OH$  (PCR), were used as received without further purification. Triethylamine (Baker) was distilled from KOH before use.

**General Procedures.** A conventional vacuum line was used to free the products from unreacted starting materials and impurities, or the products were separated by gas chromatography.

**Preparation of 1,1,1-Trifluoroisopropyl Fluorosulfate,  $CF_3CH(CH_3)OSO_2F$ .** 1,1,1-Trifluoro-2-propanol (2 mmol) and triethylamine (2 mmol) were condensed into a 50-mL Pyrex round-bottomed flask fitted with a stopcock at  $-196^\circ C$ , and the mixture was warmed to room temperature for 20 min. Sulfuryl chloride fluoride (2 mmol) or sulfuryl fluoride (2 mmol) was condensed into the flask at  $-196^\circ C$ , which was warmed slowly to room temperature overnight. The reaction mixture was distilled through traps at  $-20$ ,  $-78$ , and  $-196^\circ C$ . The trap at  $-78^\circ C$  contained 1,1,1-trifluoroisopropyl fluorosulfate (54–58% yield).

The infrared spectrum of 1,1,1-trifluoroisopropyl fluorosulfate is as follows: 2980 w, br, 1470 s, 1410 m, br, 1290 s, 1240–1215 s, br, 1175 vs, 1110–1080 s, br, 1025 m, 970 s, 858 m, 810 w, 740 w, 678 w, 585–575  $m\text{ cm}^{-1}$ . The  $^1H$  NMR spectrum shows a multiplet at  $\delta$  5.12 (CH;  $J_{CH_3-CH} = 6.59$  Hz;  $J_{CF_3-CH} = 5.39$  Hz) and a doublet at  $\delta$  1.69 ( $CH_3$ ). In the  $^{19}F$  NMR spectrum, a quartet at  $\phi$  42.9 (SF;  $J_{CF_3-SF} = 3.30$  Hz) and a doublet of doublets at  $\phi$   $-77.1$  ( $CF_3$ ) are observed. The electron-impact mass spectrum shows fragments as follows ( $m/e$ , species, %): 181,  $M - CH_3^+$ , 4.1; 127,  $M - CF_3^+$ , 100; 113,  $CF_3(CH_3)CHO^+$ , 7.2; 97,  $CF_3(CH_3)CH^+$ , 23.9; 95,  $CF_3(CH_2)C^+$ , 12.8; 83,  $SO_2F^+$ , 20; 77,  $CF_2(CH_3)C^+$ , 53.6; 69,  $CF_3^+$ , 32.9.

Anal. Calcd for  $C_3H_4O_3S$ : C, 18.37; H, 2.04; F, 38.78. Found: C, 18.58; H, 2.15; F, 38.3.

**Preparation of 2-(Trifluoromethyl)isopropyl Fluorosulfate,  $CF_3C(CH_3)_2OSO_2F$ .** 2-Trifluoromethyl-2-propanol (2 mmol) was condensed into a flask charged with 2 mmol of *n*-butyllithium (1.5 M solution in hexane) and the mixture then stirred for 30 min at  $-20^\circ C$ . The solvent and butane were removed under vacuum. Sulfuryl fluoride (4 mmol) was condensed into the flask at  $-196^\circ C$ , and the mixture was warmed slowly to and held at room temperature for 1 week. The reaction mixture was separated by using trap-to-trap techniques. 2-(Trifluoromethyl)isopropyl fluorosulfate, which is a colorless liquid, was contained in a trap at  $-50^\circ C$ . The yield was 50%. When pure, it decomposes after 1 week at room temperature. This fact precluded submitting it for elemental analyses. The infrared spectrum has bands as follows: 2987 w, br, 1450 vs, 1385 w, 1215 w, 1230–1200–1150–1090 vs, br, 1025 m, 970 m, 830 m, 810 m, 730 vs, and 600 w,  $br\text{ cm}^{-1}$ . The  $^1H$  NMR spectrum consists of a quintet at  $\delta$  1.86 ( $J_{CH_3-CF_3} \cong J_{CH_3-SF} = 0.98$  Hz). The  $^{19}F$  NMR approximates a decet at  $\phi$  48.2 (SF;  $J_{SF-CF_3} \cong 1.1$  Hz) and an octet at  $\phi$   $-81.83$  ( $CF_3$ ). The chemical ionization mass spectrum is as follows ( $m/e$ , species, %): 195,  $M - CH_3^+$ , 4.4; 141,  $M - CF_3^+$ , 14.9; 111,  $M - OSO_2F^+$ , 55.4; 91,  $CF_2C(CH_3)CH_3^+$ , 100; and 69,  $CF_3^+$ , 10.8.

**Reaction of 1,1,1,3,3,3-Hexafluoroisopropyl Fluorosulfate with Dimethylamine.** A 125-mL Pyrex flask fitted with a Kontes Teflon stopcock was charged with 2 mmol of 1,1,1,3,3,3-hexafluoroisopropyl fluorosulfate<sup>6</sup> and 4 mmol of dimethylamine at  $-196^\circ C$ . The mixture was then warmed slowly to room temperature over a period of 10 h. The mixture was distilled through traps at  $-20$  and  $-196^\circ C$ . The 1,1,1,3,3,3-hexafluoroisopropyl *N,N*-dimethylsulfamate,  $(CF_3)_2CHOSO_2N(CH_3)_2$ , was retained in a trap at  $-20^\circ C$  (50% yield). The infrared spectrum of the sulfamate is as follows: 2927 m, br, 1464 m, 1425 m, 1390–1368 s, 1290–1185 vs, br, 1070 s, 980 s, 907 m, 882 s, 798 vs, 752 m, 722 m, 695 s, 610 s, 573 m, 538 s, 460  $m\text{ cm}^{-1}$ . The  $^{19}F$  NMR spectrum shows a doublet at  $\phi$   $-71.64$  ( $J_{CF_3-H} = 5.61$  Hz). In the  $^1H$  NMR spectrum, a heptet is observed at  $\delta$  5.16 (1 H) assigned to CH and a singlet at  $\delta$  3.01 (6 H) due to  $N(CH_3)_2$ . The electron-impact mass spectrum contains a molecular ion at  $m/e$  275 (20.5% of base peak), in addition to the following peaks ( $m/e$ , species, %): 277,  $M + 2$ , 1.1; 276,  $M + 1$ , 2.5; 167,  $(CF_3)_2CHO^+$ , 100; 69,  $CF_3^+$ , 17.2; 44,  $(CH_3)_2N^+$ , 29.9.

Anal. Calcd for  $C_3H_7F_6NO_3S$ : C, 21.82; H, 2.55; F, 41.45. Found: C, 22.02; H, 2.61; F, 41.6.

**Reaction of 1,1,1-Trifluoroisopropyl Fluorosulfate with Dimethylamine.** A 50-mL Pyrex round-bottomed flask fitted with a Kontes Teflon stopcock was charged with 1,1,1-trifluoroisopropyl fluorosulfate (2 mmol) and  $(CH_3)_2NH$  (4 mmol) at  $-196^\circ C$ . It was warmed slowly to room temperature for 10 h. The volatile products were removed under vacuum at  $-15^\circ C$ . The  $CF_3CH(CH_3)OSO_2N(CH_3)_2$  remained in the trap at

$-15^\circ C$  (50–55% yield). The infrared spectrum is as follows: 2927 m, br, 1464 s, 1423 m, 1380 s, 1284 s, 1182 s; 1075 s, 1020 m, 980 s, 935 s, 800 s, 755 m, 730 m, 672 w, 570 s,  $br\text{ cm}^{-1}$ . The  $^{19}F$  NMR spectrum is comprised of a doublet at  $\phi$   $-77.8$  ( $J_{CH-CF_3} = 6.1$  Hz). The  $^1H$  NMR spectrum consists of a heptet at  $\delta$  4.82 (CH;  $J_{CH-CH_3} = 6.59$  Hz;  $J_{CH-CF_3} = 6.1$  Hz), a singlet at  $\delta$  2.90 ( $N(CH_3)_2$ ), and a pair of doublets centered at  $\delta$  1.534 and 1.526 ( $CH_3$ ). The latter arise from the presence of an asymmetric center. The EI mass spectrum contains a molecular ion and the following peaks ( $m/e$ , species, %): 223,  $M + 2^+$ , 1.2; 222,  $M + 1^+$ , 1.8; 221,  $M + 1$ , 24; 124,  $(CH_3)_2NSO_3^+$ , 77.1; 108,  $(CH_3)_2NSO_2^+$ , 74.2; 43,  $(C_2H_5N)^+$ , 100.

Anal. Calcd for  $C_3H_{10}F_3NO_3S$ : C, 27.15; H, 4.52; F, 25.79. Found: C, 27.28; H, 4.55; F, 25.8.

**Reaction of 1,1,1-Trifluoroisopropyl Fluorosulfate with 2,2,2-Trifluoroethanol.** 2,2,2-Trifluoroethanol (2 mmol) and triethylamine (2 mmol) were condensed into a Pyrex flask at  $-196^\circ C$  and then warmed slowly to room temperature. After 20 min, 1,1,1-trifluoroisopropyl fluorosulfate (2 mmol) was condensed onto the mixture at  $-196^\circ C$ . The mixture was warmed slowly to  $70^\circ C$  and stirred for 3 h. The volatile products and unreacted starting materials were pumped off at  $-25^\circ C$ . The reaction product was distilled through traps. 1,1,1-Trifluoroisopropyl 2,2,2-trifluoroethyl sulfate was held in a trap at  $-10^\circ C$  (50% yield). The infrared spectrum is as follows: 2900–2942 w, br, 1448 m, 1380 w, 1288 s, 1182 vs, 1056 s, 952 s, 844  $m\text{ cm}^{-1}$ . The  $^{19}F$  NMR spectrum shows two doublets centered at  $\phi$   $-77.43$  and  $-77.61$  ( $J_{CF_3CH-CH} = 5.73$  Hz) and a triplet at  $\phi$   $-72.68$  ( $J_{CF_3-CH_2} = 7.56$  Hz). The  $^1H$  NMR spectrum consists of two doublets centered at  $\delta$  1.641 and 1.633 ( $CH_3$ ;  $J_{CH_3-CH} = 6.59$  Hz), a quartet of doublets centered at  $\delta$  4.555 and 4.536 ( $CH_2$ ;  $J_{CH_2-CF_3} = 7.57$  Hz), and two overlapping septets centered at  $\delta$  4.993 and 4.985 (CH). The CI mass spectrum shows the following peaks ( $m/e$ , species, %): 277,  $M + 1^+$ , 23.9 (quasi-molecular ion); 257,  $CF_3CH_2OSO_2CH(CH_3)CF_2^+$ , 8.0; 207,  $CH_3CHOSO_2CH_2CF_3^+$ , 15.6; 181,  $CF_3CH_2OSO_3H_2^+$ , 79; 161,  $CF_3(CH_3)CHOSO^+$ , 19.6; 77,  $CF_2C(CH_3)^+$ , 100; 69,  $CF_3^+$ , 7.2.

Anal. Calcd for  $C_5H_6F_6O_4S$ : C, 21.74; H, 2.17; F, 41.3. Found: C, 21.90; H, 2.31; F, 41.5.

**Reaction of 1,1,1-Trifluoroisopropyl Fluorosulfate with 1,1,1-Trifluoro-2-propanol.** 1,1,1-Trifluoro-2-propanol (3 mmol) was condensed into a Pyrex flask charged with 3.1 mmol of butyl lithium (1.6 M solution in hexane) at  $-196^\circ C$ , and the mixture was then warmed slowly to  $-30^\circ C$  for 5 min. The reaction mixture was warmed to room temperature, and the hexane was removed under vacuum. 1,1,1-Trifluoroisopropyl fluorosulfate (3 mmol) was condensed into the flask at  $-196^\circ C$  and warmed slowly to room temperature over a period of 20 h. The crude product was distilled through traps. Bis(1,1,1-trifluoroisopropyl) sulfate remained in the trap at  $0^\circ C$  (55% yield). The infrared spectrum is as follows: 3000–2860 w, br, 1462 m, 1422–1385 vs, br, 1335 w, 1280 vs, 1149 vs, br, 1120 w, 1068 m, 1018 m, 940 vs, 845 s, 690–675 w, br, and 593  $m\text{ cm}^{-1}$ . The  $^{19}F$  NMR and  $^1H$  NMR spectra are as follows: two doublets at  $\phi$   $-77.43$  and  $-77.61$  ( $CF_3$ ;  $J_{CF_3-H} = 5.74$ , 5.12 Hz) overlapping quartets at  $\delta$  5.00 and 4.99 (CH;  $J_{CH-CH_3} = 6.6$  and 6.59 Hz); doublets at  $\delta$  1.63 and 1.62 ( $CH_3$ ). The spectra are more complex because of the presence of two asymmetric centers. The EI mass spectrum contains the following peaks ( $m/e$ , species, %): 221,  $M^+ - CF_3$ , 27.5; 177,  $CF_3(CH_3)CHSO_3^+$ , 1.9; 141,  $CF_2=C(CH_3)SO_2^+$ , 1.8; 125,  $CF_2=C(CH_3)OS^+$ , 18.4; 97,  $CF_3CO^+$ , 16.8; 77,  $CF_2=CCH_3^+$ , 71.1; 69,  $CF_3^+$ , 26; 45,  $CF=CH_2^+$ , 100.

Anal. Calcd for  $C_6H_8F_6$ : C, 24.83; H, 2.76; F, 39.31. Found: C, 24.89; H, 2.69; F, 39.50.

**Reaction of 2-(Trifluoromethyl)isopropyl Fluorosulfate with *n*-Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>.** 2-(Trifluoromethyl)isopropyl fluorosulfate (2 mmol) was condensed into a Pyrex flask charged with *n*-Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup> (4–5 mmol) at  $-196^\circ C$ , and the mixture was warmed slowly to room temperature for 4 h. The reaction mixture was distilled through traps at  $-20$ ,  $-60$ , and  $-196^\circ C$ . The product, 2-(trifluoromethyl)propene, was retained in the trap at  $-196^\circ C$  (82.5% yield). The infrared spectrum is as follows: 2900 m, 1455 m, 1403 w, 1452 s, 1148 vs, br, 1012 w, 932  $m\text{ cm}^{-1}$ . The  $^{19}F$  NMR and  $^1H$  NMR spectra are multiplets at  $\phi$   $-69.79$  ( $CF_3$ ) and at  $\delta$  5.58 (CH; 1 H), 5.30 (CH; 1 H), and  $\delta$  1.90 ( $CH_3$ ; 3 H). The EI mass spectrum shows peaks as follows ( $m/e$ , species, %): 110,  $M^+$ , 70.9; 95,  $CF_3-C=CH_2^+$ , 42.1; 77,  $CF_2=C-CH_3^+$ , 13.4; 69,  $CF_3^+$ , 17.3; 64,  $CF_2=CH_2^+$ , 21.6; 41,  $CH_2=C-CH_3^+$ , 100.

**Reaction of 2,2,2-Trifluoroethyl Fluorosulfate with LiN(CH<sub>3</sub>)CH<sub>2</sub>C-H<sub>2</sub>N(CH<sub>3</sub>)Li.** *N,N'*-Dimethylethylenediamine,  $CH_3NHCH_2CH_2NHC-H_3$  (2 mmol), was condensed into a Pyrex flask charged with 4 mmol of *n*-BuLi at  $-196^\circ C$ . The mixture was warmed slowly to  $-30$  to  $-40^\circ C$  over a period of 20 min. Then, 6 mmol of 2,2,2-trifluoroethyl fluorosulfate was condensed onto the reaction mixture at  $-196^\circ C$ , and the flask was allowed to warm to room temperature slowly. The mixture was stirred overnight. The sulfamate,  $CF_3CH_2OSO_2N(CH_3)CH_2CH_2N(C-$

$\text{H}_3\text{SO}_2\text{OCH}_2\text{CF}_3$ , which was distilled bulb-to-bulb at  $\sim 75^\circ\text{C}$  was found in  $\sim 25\%$  yield. 2,2,2-Trifluoroethyl fluorosulfate was reacted with  $\text{Me}_3\text{SiN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SiMe}_3$  under similar conditions to give the sulfamate in approximately 30% yield.

The infrared spectrum is as follows: 2960 w, br, 1450 w, 1375 vs, br, 1290 vs, br, 1240 m, 1175 vs, br, 1100 w, 1050 vs, 1010 m, 970 vs, 900 vs, 865 m, 810 m, br, 720 w, 660 w, 605 w, 505 vs, 525 w  $\text{cm}^{-1}$ . The  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR spectra are as follows: a triplet at  $\delta -74.13$  ( $\text{CF}_3$ ;  $J_{\text{CF}_3-\text{CH}_2} = 8.1$  Hz); a quartet at  $\delta 4.43$  ( $\text{CH}_2\text{CF}_3$ ) and two singlets at  $\delta 3.05$  ( $\text{NCH}_3$ ) and 2.99 ( $\text{CH}_3$ ). The EI mass spectrum contains the following peaks ( $m/e$ , species, %): 412,  $\text{M}^+$ , 0.06; 392,  $\text{M}^+ - \text{HF}$ , 0.2; 313,  $\text{M}^+ - \text{CF}_3\text{CH}_2\text{O}$ , 0.3; 312,  $\text{M}^+ - \text{CF}_3\text{CH}_2\text{O}$ , 4.2; 249,  $\text{M}^+ - \text{CF}_3\text{C}-\text{H}_2\text{OSO}_2$ , 0.5; 248,  $\text{M}^+ - \text{CF}_3\text{CH}_2\text{OSO}_2$ , 6.0; 206,  $\text{CF}_3\text{CH}_2\text{OSO}_2\text{N}(\text{CH}_3)\text{CH}_2^+$ , 5.2; 205,  $\text{CF}_3\text{CH}_2\text{OSO}_2\text{N}(\text{CH}_3)\text{CH}_2^+$ , 100; 69,  $\text{CF}_3^+$ , 0.9; 64,  $\text{SO}_2$ , 2.8; 43,  $\text{CH}_3\text{NCH}_2^+$ , 16.8.

Anal. Calcd for  $\text{C}_8\text{H}_{14}\text{F}_6\text{N}_2\text{O}_6\text{S}_2$ : C, 23.30; H, 3.40; F, 27.67. Found: C, 23.22; H, 3.38; F, 27.5.

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**Registry No.**  $\text{CF}_3\text{CH}(\text{CH}_3)\text{OSO}_2\text{F}$ , 99809-93-5;  $\text{CF}_3\text{C}(\text{CH}_3)_2\text{OSO}_2\text{F}$ , 99809-94-6;  $(\text{CF}_3)_2\text{CHOSO}_2\text{N}(\text{CH}_3)_2$ , 78162-70-6;  $\text{CF}_3\text{CH}(\text{CH}_3)\text{OS}-\text{O}_2\text{N}(\text{CH}_3)_2$ , 99809-95-7;  $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_3$ , 110-70-3;  $\text{CF}_3\text{C}-\text{H}_2\text{OSO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SO}_2\text{OCH}_2\text{CF}_3$ , 99809-96-8;  $\text{Me}_3\text{SiN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{SiMe}_3$ , 1821-97-2; 1,1,1-trifluoro-2-propanol, 374-01-6; 2-(trifluoromethyl)-2-propanol, 507-52-8; 1,1,1,3,3,3-hexafluoroisopropyl fluorosulfate, 38252-04-9; 2,2,2-trifluoroethanol, 75-89-8; 1,1,1-trifluoroisopropyl 2,2,2-trifluoroethyl sulfate, 99809-97-9; bis-(1,1,1-trifluoroisopropyl) sulfate, 99809-98-0; 2-(trifluoromethyl)propene, 374-00-5; 2,2,2-trifluoroethyl fluorosulfate, 66950-71-8.

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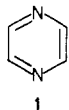
## Charge-Transfer and Electron-Transfer Properties of $d^6$ Metal Complexes with $\mu$ -Pyrazine. Mononuclear and Binuclear Manganese(I) Compounds

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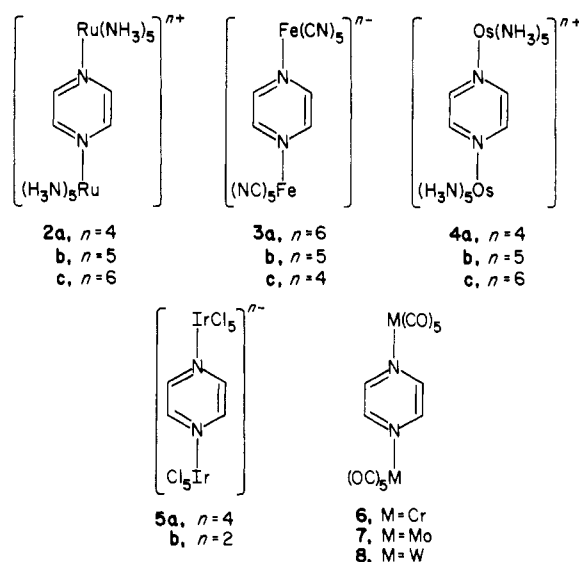
The electronic structures and the electron-transfer behavior of decacarbonyl( $\mu$ -pyrazine)dichromium(0) (**6**) and of tetracarbonyl( $\mu$ -pyrazine)dimanganese(I) (**10**) ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$ ,  $\eta^5\text{-C}_5(\text{CH}_3)_3$ ) have been studied by electron spectroscopy, cyclic voltammetry, and high-resolution electron spin resonance (ESR) of the corresponding anion radicals. This combination of techniques allowed us to characterize the lowest unoccupied complex orbital as ligand-centered ( $\pi^*$ ) and the first electronic transition as a metal-to-ligand charge-transfer (MLCT) process. However, in agreement with their pronounced light sensitivity, another close and apparently photoreactive excited state is indicated by the unexpectedly small  $g$  values of the anion radicals  $\mathbf{10}^{\cdot-}$  of the binuclear Mn(I) complexes. While the persistence of these anion radical complexes increases with the number of methyl substituents at the cyclopentadienyl rings due to less facile cleavage of  $\text{Cp}^-$ , the reverse stability sequence has been observed for the photochemically induced ligand dissociation. A comparison of the binuclear organometallic complexes with related Fe(II), Ru(II), Os(II), and Ir(III) species suggests some similarity between the Mn(I) and Ru(II) systems according to a diagonal relationship and indicates a rather small splitting of  $d$  levels in the organometallic Mn(I) systems. Inclusion of mononuclear Mn(I) compounds **9** in the electrochemical and ESR studies reveals facile exchange processes such as the rapid formation of the more stable binuclear anion radicals  $\mathbf{10}^{\cdot-}$  upon reduction. On the other side, the oxidation of all Mn(I)-pyrazine complexes was found to be irreversible in dimethylformamide (DMF) due to an ECE mechanism yielding solvent complexes of  $\text{CpMn}(\text{CO})_2$ .

Pyrazine **1** is a small ligand with two special features: The presence of a low-lying molecular  $\pi^*$  orbital allows for back-bonding with suitable metal fragments and for facile one-electron reduction, and despite its low basicity toward non-back-bonding electrophiles, pyrazine may act as a linear bridge ( $\mu$ -pyrazine) between two metals.<sup>1</sup>



Both features of ligand **1** have been recognized and exploited by Creutz and Taube in their preparation of a series of Ru(II)/Ru(III) pentaammine complex **2**, including the first deliberately synthesized mixed-valence complex **2b**, the Creutz-Taube ion.<sup>2</sup> The unusual and still unresolved nature<sup>3</sup> of this complex has stimulated the synthesis of related binuclear pyrazine complexes with other metals in  $d^6$  or  $d^5$  configurations, among these being pentacyanoiron **3**<sup>4</sup> and osmium ammine complexes such as **4**<sup>5</sup> (group 8d),<sup>4b</sup> pentachloroiridate complexes **5**<sup>6</sup> (group 9d), and pentacarbonylchromium, -molybdenum, and -tungsten complexes **6-8**<sup>7-11</sup> (group 6d).

Whereas mixed-valence oxidation states of the latter organometallic species were not reported, these compounds may undergo reversible one-electron reduction in nonaqueous media,<sup>10</sup> and in



the cases of molybdenum and tungsten those ligand-centered anion radical complexes  $\mathbf{7}^{\cdot-}$  and  $\mathbf{8}^{\cdot-}$  and their P-donor substitution

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