$(4bzpy)_2]^{2-}$ is obtained. The spectral transition from [*fac*-$ClRe(CO)_3(4bzpy)_2$] to [*fac*-$ClRe(CO)_3(4bzpy)_2]^{2-}$ is smooth. One-electron- and two-electron-reduced species exhibit nearly the same absorption maxima in the UV/vis region, but the intensity of the absorption band at 610 nm of the dianion is twice that of the monoanion. The UV/vis spectra of the reduced 4bzpy and Me-$4bzpy^+$ have been measured also. The $\pi$–$\pi^*$ absorptions ($\lambda_{max}$ at 258 nm for 4bzpy, $\lambda_{max}$ at 272 nm for Me-$4bzpy^+$) disappear upon reduction and two new bands appear ($\lambda_{max}$ at 324 and 696 nm for $4bzpy^-$, $\lambda_{max}$ at 330 and 508 nm for Me-$4bzpy^0$). The reduced forms of the complexed ligand, the free ligand, and the methylated ligand have the same absorption pattern in the UV/vis region.

The number, position, structure, and intensity of the observed UV/vis spectral features indicate that the electrons added to [*fac*-$ClRe(CO)_3(4bzpy)_2$] are localized on the 4bzpy ligands. The first electron added produces one $4bzpy^-$ anion, and the second electron added produces the second $4bzpy^-$ anion. Therefore, the one-electron- and the two-electron-reduced species have the same UV/vis absorptions, but for the two-electron-reduced product, the intensity of the absorption band at 610 nm, attributable to the absorption of the Re-bound $4bzpy^-$ ligand, is twice that of the one-electron-reduced product. The UV/vis spectra again support the view that the added electrons are localized on the 4bzpy.

**Reduction of Bound Ketone to Bound Alcohol.** In the presence of $CH_3COOH$ as a proton source, reduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] becomes chemically irreversible. [*fac*-$ClRe(CO)_3(4bzpy)_2$] can be electrochemically reduced to the bis(alcohol) complex in $CH_3CN$/0.1 M [*n*-$Bu_4N]PF_6$ with 0.1 M $CH_3COOH$ by using a mercury pool as the working electrode of which the potential is controlled at −1.4 V vs SCE (eq 3). The result is consistent with the mechanism proposed for the photoreduction of [*fac*-$ClRe(CO)_3(4bzpy)_2$] where the first step in the photoreduction is one-electron reduction of the Re complex.[10] It is well-known that ketones can be electrochemically reduced to alcohol,[14] and [*fac*-$ClRe(CO)_3(4bzpy)_2$] is unexceptional in this regard.

## Conclusions

The spectroelectrochemical studies of [*fac*-$ClRe(CO)_3(4bzpy)_2$], a complex having a lowest excited state corresponding to a Re to 4bzpy charge-transfer transition, allow comparison of IR and UV/vis spectra of the one-electron- and the two-electron-reduced products. The spectral and electrochemical data obtained are uniformly consistent with the conclusion that the reduced metal complex has the electron(s) localized on the 4bzpy ligand(s).

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## (Pentafluoro-$\lambda^6$-sulfanyl)(fluorosulfonyl)ketene

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In an attempt to find pathways to potentially useful compounds containing the unique pentafluorothio ($SF_5$) and fluorosulfonyl ($SO_2F$) groups, the new ketene $F_5SC(SO_2F){=}C{=}O$ (**1**) was synthesized. Recently, we found that $SF_5$-containing sultones were effective precursors to a number of derivatives potentially useful as acid electrolytes, surface-active agents, and ion-exchange resins.[1-3] It is anticipated that the new ketene and its derivatives will also serve in this role.

In order to obtain $F_5SC(SO_2F){=}C{=}O$ (**1**), it was necessary to prepare the new ester $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ (**2**) via reaction of the sultone $F_5S\overline{CHCF_2OS}O_2$ with 2-propanol in the presence of sodium fluoride:

$$F_5S\overline{CHCF_2OS}O_2 + (CH_3)_2CHOH + NaF \rightarrow \underset{\mathbf{2}}{F_5SCH(SO_2F)C(O)OCH(CH_3)_2} + NaHF_2 \quad (1)$$

Treatment of the ester with $P_4O_{10}$ and heat resulted in the formation of the new compound (pentafluoro-$\lambda^6$-sulfanyl)(fluorosulfonyl)ketene (**1**):

$$F_5SCH(SO_2F)C(O)OCH(CH_3)_2 + P_4O_{10} \xrightarrow{\Delta} \underset{\mathbf{1}}{F_5SC(SO_2F){=}C{=}O} \quad (2)$$

This procedure resulted in some contamination of **1** with $SF_5CH_2SO_2F$, and although the yields varied from 49 to 89%, it was found that they decreased upon attempts to prepare larger amounts (e.g. from 8.7 g of ester, only about 1 g of the ketene could be collected). Due to these problems, an alternate procedure was sought that involved dehydrofluorination of $F_5S\overline{CHCF_2OS}O_2$ or its rearranged isomer, $F_5SCH(SO_2F)COF$. Interestingly, with the comparatively weak base NaF, the sultone underwent rearrangement and partial dehydrofluorination to produce a mixture (14:86) of the ketene **1** and $F_5SCH(SO_2F)COF$, respectively. Sodium fluoride failed to give pure **1** even upon warming to 135 °C (15 h); under this condition some $COF_2$ and a 50:50 mixture of **1** and $F_5SCH(SO_2F)COF$ were produced. It was found, however, that treatment of the original mixture (14:86) with $BF_3{\cdot}N(C_2H_5)_3$ resulted in essentially quantitative conversion to pure ketene **1**. Overall, the reaction sequence is summarized as

$$F_5S\overline{CHCF_2OS}O_2 + NaF \rightarrow SF_5C(SO_2F){=}C{=}O/SF_5CH(SO_2F)COF \quad (3)$$

$$SF_5C(SO_2F){=}C{=}O/SF_5CH(SO_2F)COF + BF_3{\cdot}N(C_2H_5)_3 \rightarrow SF_5C(SO_2F){=}C{=}O \quad (4)$$

The ketene could not be directly prepared in pure form from the sultone and $BF_3{\cdot}N(C_2H_5)_3$. Ketene **1** fumes slightly in air and has a faintly pleasant odor. It reacts readily with alcohols and water according to the equations

$$F_5SC(SO_2F){=}C{=}O + ROH \rightarrow F_5SCH(SO_2F)C(O)OR \qquad R = CF_3CH_2,\ (CH_3)_2CH \quad (5)$$

$$F_5SC(SO_2F){=}C{=}O + H_2O \rightarrow F_5SCH_2SO_2F + CO_2 \quad (6)$$

The proposed acid intermediate $F_5SCH(SO_2F)C(O)OH$ is not stable and decarboxylates spontaneously.[2] With diethylamine the corresponding amide was produced:

$$F_5SC(SO_2F){=}C{=}O + (CH_3CH_2)_2NH \rightarrow F_5SCH(SO_2F)C(O)N(CH_2CH_3)_2 \quad (7)$$

(Pentafluoro-$\lambda^6$-sulfanyl)(fluorosulfonyl)ketene is thermally stable; it can be recovered (98%) after heating (4 h) to 220 °C.

Compounds containing $SF_5$ or $SO_2F$ groups show characteristic infrared bands; the pentafluorothio group shows very strong absorption bands in the region from 820 to above 900 $cm^{-1}$ (SF stretching modes) and absorption bands of medium strength in the region of 600 $cm^{-1}$ (SF deformation modes).[4] Likewise, compounds with an $SO_2$ group exhibit a strong asymmetric stretching band in the region 1400–1470 $cm^{-1}$ and a strong symmetric stretching band in the region 1200–1300 $cm^{-1}$. The S–F

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absorption band of the $SO_2F$ group is usually located near 790 cm$^{-1}$.[5] Ester **2** shows the corresponding bands (cm$^{-1}$) at 1443 (asym $SO_2$), 875 (str S–F), 801 (str SF), and 572 (def SF). No unambiguous assignment for the symmetric $SO_2$ stretching band can be made, as there are several bands in the region from 1200 to 1300 cm$^{-1}$ that are also characteristic of saturated carboxylic esters. The C(O) stretching frequency at 1761 cm$^{-1}$ is found in the same region as for other esters derived from the sultone, $F_5SCHCF_2OSO_2$.[2] For amide **3** the absorption band at 1661 cm$^{-1}$ is attributed to the carbonyl stretching frequency; other characteristic frequencies and assignments are 1432 cm$^{-1}$ (asym $SO_2$), 1222 cm$^{-1}$ (sym $SO_2$), 860 cm$^{-1}$ (str $SF_5$), 799 cm$^{-1}$ (str SF of $SO_2F$), and 562 cm$^{-1}$ (def SF).

Ketene **1** has a much simpler infrared spectrum. The characteristic ketene band (C=C=O) is found at 2193 cm$^{-1}$. This is in the region found for other fluorinated ketenes: $F_3CC(SO_2F)CO$ (2200 cm$^{-1}$),[6] $(CF_3)_2CCO$ (2203 cm$^{-1}$),[7] $F_5SCHCO$ (2177 cm$^{-1}$).[8] Interestingly, the strongly electron-withdrawing $SF_5$ and $SO_2F$ substituents do not produce any unusual shift in the ketene band. The other bands (cm$^{-1}$) are located at 1445 (asym $SO_2$), 1214 (sym $SO_2$), 875 (str SF), 801 (str SF), and 590 (def SF).

The $^{19}F$ NMR spectrum of ester **2** showed, for the $SF_5$ group, a collapsed $AB_4$ multiplet from which the coupling constants could not be determined; similarly, the sulfonyl fluoride resonance was a multiplet. In amide **3** a collapsed $AB_4$ pattern was observed; the $SO_2F$ spectrum was a multiplet. The $^1H$ NMR spectrum is more interesting, as two different methyl group resonances were observed along with a complex methylene spectrum. Tentatively, we are assuming a structure invoking hindered rotation about the C–N bond. Ketene **1** with an $AB_4X$ spectrum, had an inverted $AB_4$ pattern ($SF_5$) with the $F_A$ resonance appearing upfield from the $F_B$ doublet; the $SO_2F$ resonance appeared as a pentet; the $J_{AB}$ and $J_{BX}$ coupling constant values are 155 and 6.8 Hz, respectively.

It is worthwhile to point out that the $AB_4$ inversion has also been observed with $F_5SNCO$,[9] $F_5SCCH$,[10] $F_5SCHCO$,[8] and $F_5SOCN$.[11] The shielding imparted to $F_A$ seems to be related to the presence of a heteroallene or an alkyne system that is bonded to the $SF_5$ group. The $SO_2F$ fluorine in the ketene is also strongly deshielded; it resonates at $\phi$ 76.3 ppm, well below the range where it is usually found ($\phi$ 50–60 ppm).[6,2]

## Experimental Section

**Materials.** The following were obtained commercially: $SO_3$ (MCB), NaF (Baker), $CF_3CH_2OH$ (PCR), $(CH_3)_2CHOH$ and $(C_2H_5)_2NH$ (MCB), KOH (MCB), and $P_4O_{10}$ (Baker). $F_5SCH_2CF_2Br$,[12] $BF_3 \cdot N(C_2H_5)_3$,[13] and $F_5SCHCF_2OSO_2$[2] were prepared according to the literature; $F_5SCH{=}CF_2$ was obtained via a modified literature procedure.[14] Sodium fluoride was dried at 180 °C under vacuum for 5 h before use.

Gases were manipulated in a conventional Pyrex-glass vacuum line that was equipped with a mercury manometer and a Televac thermocouple gauge. Infrared spectra were obtained from the neat liquids or solids between KBr plates on a Nicolet 20 DX spectrometer. The $^{19}F$ and $^1H$ nuclear magnetic resonance spectra were recorded on a Varian Model EM-390 spectrometer operating at 90 MHz for proton and at 84.67 MHz for fluorine resonances or with a General Electric QE-300 FT NMR spectrometer. TMS and $CFCl_3$ were used as external standards. Mass spectra were obtained on a VG 7070 HS mass spectrometer at 70 eV. Gas chromatograms were run with a Varian Aerograph Model A-700 gas chromatograph, and elemental analyses were carried out by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

**$F_5SCH{=}CF_2$.** To an aqueous potassium hydroxide solution (81.5 g, 42.5% by weight) in a 100-mL Pyrex-glass round-bottomed flask, equipped with a magnetic stirring bar, was added $F_5SCH_2CF_2Br$ (33.70 g, 124.4 mmol) at room temperature. A 20-cm reflux condenser that was connected to a cold trap (−78 °C) was also attached to the reaction vessel. The mixture was slowly heated with vigorous stirring to a temperature of 100 °C, and warm water (40 °C) was passed through the condenser; after the disappearance of the bottom layer in the reaction flask (30 min), heating was maintained for another 3 h. The product was collected in the cold trap (22.90 g, 120.5 mmol, 96.9% yield). A gas chromatogram (Carbowax, 20% on Chromosorb W, 100 °C) showed only one product to be present; the IR spectrum agreed with the literature values.[14]

**$F_5SCH(SO_2F)C(O)OCH(CH_3)_2$.** To a 100-mL Pyrex-glass reaction vessel, equipped with a Teflon stirring bar and a Kontes Teflon valve and containing dry sodium fluoride (30.08 g, 716.2 mmol), was added 2-propanol (10.13 g, 168.8 mmol) by vacuum condensation. The sultone $F_5SCHCF_2OSO_2$ was then added in three portions (12.37 g, 45.8 mmol; 8.70 g, 32.2 mmol; 15.91 g, 58.9 mmol) at −196 °C, with the vessel being warmed to room temperature after each addition and the mixture stirred for a few minutes. For each addition slight warming was noticed when room temperature was reached. After addition was complete, the mixture was stirred at 52 °C for 15 h and at 68 °C for 0.5 h. The crude product was condensed (41.29 g), and distillation gave 100.5 mmol (31.12 g) of a colorless oily liquid with an unpleasant odor: yield 73.3%; bp 92–94 °C (26–28 Torr).

Infrared spectrum (cm$^{-1}$): 2995 (m), 2952 (sh), 1761 (s), 1443 (s), 1395 (vw), 1382 (w), 1352 (vw), 1296 (m), 1276 (m), 1221 (m), 1168 (w), 1102 (ms), 981 (vw), 875 (vs, sh 900), 837 (wm), 819 (wm), 801 (wm), 781 (w), 769 (w), 733 (vw), 688 (vw), 650 (vw), 612 (w), 572 (s), 491 (vw), 458 (vw).

$^{19}F$ NMR spectrum (neat sample): multiplet, centered at $\phi$ 70.9 ppm, area 5.0 ($SF_5$); multiplet, $\phi$ 58.8 ppm, area 1.0 ($SO_2F$).

$^1H$ NMR spectrum (neat sample): multiplet, $\delta$ 6.4 ppm, area 1.0 ($F_5SC\text{-}H$); septet, $\delta$ 5.4 ppm, area 1.1 ($O{-}C\underline{H}(CH_3)_2$); doublet, $\delta$ 1.5 ppm, area 6.2 ($O{-}CH(C\underline{H_3})_2$), $J_{H-H}$ = 6.22 Hz.

Mass spectrum (chemical ionization) (*m/e*, species, relative abundance): 311, $MH^+$, 0.32; 269, $M - H_3F_2^+$, 4; 205, $MH - (CH_3)_2CHCO_2 - F^+$, 7.5; 143, $S_2C_2OF_2H^+$, 14.8; 127, $SF_5^+$, $CFO_2S_2^+$, 20.5; 125, $C_2H_2FO_3S^+$, 8.4; 99, $C_4H_3SO^+$, 9.2; 91, $C_2FSO^+$, 4.2; 89, $SF_3^+$, 100; 79, $FSCO^+$, 4.1; 70, $SF_2^+$, 10.8; 67, $FSO^+$, 24.6; 65, $CH_2FS^+$, 19; 59, $C_3H_7O^+$, 55.8; 58, $C_3H_6O^+$, 5.5; 55, $C_3H_2O^+$, 4.8.

Anal. Calcd for $C_5H_8F_6O_4S_2$: C, 19.36; H, 2.60; F, 36.8; S, 20.67. Found: C, 19.27; H, 2.55; F, 37.1; S, 20.82.

**$F_5SC(SO_2F){=}C{=}O$. Method I.** In a representative experiment, $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ (2.65 g, 8.55 mmol) was mixed with powdered $P_4O_{10}$ (8.85 g, 31.1 mmol) in a 100-mL Pyrex-glass round-bottomed flask. The flask was connected to a short vacuum-transfer line equipped with a 10-mL receiving flask that was cooled to −196 °C. The pressure was lowered to 500 Torr, and the mixture was heated to 100 °C (10 min). The reaction flask was cooled to −196 °C, evacuated, and reheated (100 °C). In 30 min, 1.60 g (6.4 mmol) of crude ketene was collected. Prolonged heating led to transfer of unreacted ester (0.34 g, 1.1 mmol): yield 85.9% (with respect to recovered ester). In similar experiments, the yields varied from 49 to 89%. In this fashion, 4.92 g of crude ketene was obtained from 9.35 g (30.16 mmol) of ester. Distillation gave 4.09 g (16.36 mmol) of pure ketene in 54.2% overall yield; bp 55 ± 1 °C (125–128 Torr).

Infrared spectrum (cm$^{-1}$): 2193 (vs), 1445 (vs), 1305 (m), 1214 (vs), 1025 (vs), 875 (vs), 845 (s, sh), 801 (s), 689 (m), 635 (m), 618 (m), 590 (m), 520 (w), 470 (w), 432 (vw).

$^{19}F$ NMR spectrum ($CDCl_3$, $AB_4X$ spectrum): $\phi_A$ 73.1 ppm, area 1.0; $\phi_B$ 86.7 ppm, area 3.9; $\phi_X$ 76.3 ppm ($SO_2F$), pentet, area 1.0; $J_{AB}$ = 155 Hz, $J_{BX}$ = 6.8 Hz.

Mass spectrum (electron impact) (*m/e*, species, relative abundance): 250, $M^+$, 16.4; 231, $M - F^+$, 3.2; 129, $M{-}SO_2F_3^+$, 5.3; 127, $SF_5^+$, $CFO_2S_2^+$, 94.7; 91, $C_2FOS^+$, 6.4; 89, $SF_3^+$, 100; 72, $SC_2O^+$, 1.9; 70, $SF_2^+$, 11.6; 67, $FSO^+$, 25.2; 63, $CFS^+$, 7.1.

Anal. Calcd for $C_2F_6O_3S_2$: C, 9.60; F, 45.6; S, 25.63. Found: C, 9.86; F, 45.4; S, 25.82.

**NaF-Catalyzed Rearrangement of $F_5SCHCF_2OSO_2$.** In a dry-100-mL Pyrex-glass flask, equipped with a Kontes Teflon valve and a stirring bar, NaF (5.30 g, 126.2 mmol) was dried, and the sultone $F_5SCHCF_2OSO_2$ (14.99 g, 44.4 mmol) was then added. The mixture was stirred at 83–85 °C for 4 days. Vacuum transfer afforded 14.15 of a product that consisted ($^{19}F$ NMR spectrum) solely of a 14:86 mixture of the ketene $F_5SC(SO_2F)CO$ and the acyl fluoride $F_5SCH(SO_2F)COF$.

**$F_5SC(SO_2F){=}C{=}O$. Method II.** To 5.00 g of the 14:86 mixture of ketene and acyl fluoride, as obtained from the NaF-catalyzed rear-

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rangement of the sultone $F_5S\overline{CHCF_2OS}O_2$, in a 25-mL Pyrex-glass round-bottomed flask, equipped with a stirring bar, was added the base $BF_3 \cdot N(C_2H_5)_3$ (3.17 g, 18.8 mmol). The flask was attached to a vacuum-transfer line equipped with a 10-mL receiving flask that was cooled to −196 °C. The pressure in the system was lowered to 500 Torr, and the mixture was heated to 100 °C over a 25-min period. At ~85 °C a crystalline precipitate was observed in the homogeneous melt, which disappeared at ~90 °C, leaving an upper brown and a lower colorless liquid layer. Heating was continued at 100 °C (25 min). The product (4.45 g) was transferred under vacuum (30 min) to the 10-mL receiving flask cooled to −196 °C. The $^{19}F$ NMR and IR spectra showed that only the ketene was present; yield (based on the 14:86 mixture) 95%.

**$F_5SC(SO_2F){=}C{=}O$ in a Sealed Tube.** The ketene (0.49 g, 1.96 mmol) was heated in an evacuated dry 50-mL Carius tube to 220 °C for 4 h. The liquid inside was slightly discolored, but 0.48 g of unchanged ketene was recovered.

**$F_5SC(SO_2F){=}C{=}O$ and 2-Propanol.** To 118 mg of 2-propanol (1.94 mmol) in a 1-mL dry reaction vessel was added dropwise ketene **1** (497 mg, 1.92 mmol). Initially, the reaction was vigorous, but it subsided after addition of approximately half of the ketene. After addition was complete, the reaction vessel was kept at room temperature (0.5 h) and 568 mg of product was collected. The infrared and $^{19}F$ NMR spectra agreed with those found for ester **2**. Gas chromatography (Carbowax 20% on Chromosorb W, 110 °C) showed the product to be essentially pure (>95%).

**$F_5SC(SO_2F){=}C{=}O$ and 2,2,2-Trifluoroethanol.** Into 0.50 g (2.0 mmol) of the ketene in a dry 30-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve, was condensed $CF_3CH_2OH$ (0.24 g, 2.4 mmol) at −196 °C. The mixture was allowed to attain room temperature slowly and was heated to 83 °C for 1 h. The liquid product was transferred out and washed with water (2 × 0.5 mL); the lower layer was taken up with a pipet, transferred to a 5-mL flask, and dried ($Na_2SO_4$). The infrared spectrum of the product (0.59 g) was essentially identical with the published spectrum of $F_5SCH(SO_2F)C(O)OCH_2CF_3$.[2] The $^{19}F$ NMR spectrum revealed that the product was essentially trifluoroethyl ester with some $F_5SCH_2SO_2F$ as a minor impurity; yield 82% (NMR spectrum).

**$F_5SC(SO_2F){=}C{=}O$ and $H_2O$.** Into a 100-mL reaction vessel, equipped with a Kontes Teflon valve and containing water (40.5 mg, 2.25 mmol), was condensed ketene **1** (485.3 mg, 1.94 mmol). The mixture was warmed to room temperature and remained there for 2 h. It was then cooled to −78 °C, and the infrared spectrum of the volatile material showed $CO_2$ to be present; 85.4 mg (1.94 mmol) of $CO_2$ with trace impurities was formed in 100% yield. The residue was transferred at elevated temperature and dried ($Na_2SO_4$). A total of 369.0 mg product was collected. A gas chromatogram (Carbowax, 20%, 6 ft, on Chromosorb W, 100 °C) showed only one product; its infrared and $^{19}F$ NMR spectra were identical with the published spectra of $F_5SCH_2SO_2F$;[2] yield 84.9%.

**$F_5SC(SO_2F){=}C{=}O$ and $(C_2H_5)_2NH$.** The ketene (0.49 g, 1.96 mmol) was condensed into a 50-mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve and containing 2 mL of dry $CH_2Cl_2$ at −196 °C. The vessel was warmed above the melting point of the solution, shaken, and cooled again to −196 °C, and diethylamine (0.142 g, 1.94 mmol) was added. Upon being warmed to the melting temperature, the solution was shaken, frozen (−196 °C), and allowed to slowly attain room temperature. During warming to room temperature, the solution turned brownish. At room temperature it was decanted, concentrated, and recrystallized from $CH_2Cl_2$, leaving 302 mg (0.93 mmol) of product $F_5SCH(SO_2F)C(O)N(CH_2CH_3)_2$: mp 108–110 °C; yield 47.7%.

$^{19}F$ NMR spectrum ($CDCl_3$): multiplet, $\phi$ 72.2 ppm, area 4.8 ($SF_5$); multiplet, $\phi$ 62.3 ppm, area 1.0 ($SO_2F$).

$^1H$ NMR spectrum: triplet, $\delta$ 1.19 ppm, $J_{H-H} = 7.1$ Hz, area 3.0 ($CH_3$); triplet $\delta$ 1.32, $J_{H-H} = 7.1$ Hz, area 3.0 ($CH_3$); multiplet, centered at 3.5 ppm, area 4.3 ($CH_2$); pentet, $\delta$ 6.00 ppm, $J_{H-F} = 4.0$ Hz, area 0.9 (CH).

Infrared spectrum: 2990 (w), 1661 (vs), 1460 (vw), 1432 (s), 1390 (w), 1363 (w), 1320 (w), 1278 (w), 1222 (m), 1212 (m), 1129 (w), 1096 (w), 1083 (vw), 953 (w), 899 (m), 860 (vs), 820 (m), 799 (m), 740 (w), 647 (w), 562 (m), 488 (w), 458 (w).

Mass spectrum (electron impact) (*m*/*e*, species, relative abundance): 323, $M^+$, 1.6; 308, $(M-CH_3)^+$, 12.1; 280, $C_6H_4F_6NO_3S_2^+$, 2.0; 231, $C_2F_5O_3S_2^+$, 4.6; 196, $M - SF_5^+$, 14.9; 176, $M - HF - SF_5^+$, 5.8; 127, $(SF_5, CFO_2S_2)^+$, 7.4; 125, $C_2H_2FO_3S^+$, 2.9; 112, $(CH_3CH_2)_2NCOC^+$, 2.9; 105, $C_2HO_3S^+$, 2.7; 100, $C_5H_{10}NO^+$, 5.8; 89, $SF_3^+$, 14.8; 73, $C_2HOS^+$, 2.0; 72, $NC_4H_{10}^+$, $C_2OS^+$, 42.4; 71, $NC_4H_9^+$, 3.4; 70, $NC_4H_8^+$, $SF_2^+$, 4.4; 67, $FSO^+$, 5.5; 58, $C_2H_4NO^+$, 100; 56, $NC_3H_6^+$, $C_2H_2NO^+$, 21.5; 54, $C_2ON^+$, 2.0.

Anal. Calcd for $C_6H_{11}F_6NO_2S_2$: C, 22.29; H, 3.43; F, 35.3; N, 4.33; S, 19.83. Found: C, 22.37; H, 3.54; F, 35.2; N, 4.26; S, 19.91.

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# Stability of Synthetic Zeolite ZSM-5 to Dealumination with Chromium(III) Salt Solutions

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We have previously reported dealumination of dense zeolites such as erionite[1] and also the larger pore faujasites[2] by reaction of the zeolite with hot aqueous solutions of chromium(III) salts. The dealuminated dense zeolite residues are left with very little chromium, usually less than 1 wt %, while the dealuminated faujasite Y contains much more chromium, up to 7 wt %, with evidence that the chromium is "healing" to some extent the rupture in the silica alumina lattice created by hydrolysis and removal of the aluminum atoms.

We now find that the synthetic zeolite ZSM-5 undergoes less than 10% dealumination with $CrCl_3$ solutions under conditions giving greater than 40% dealumination of the dense zeolites and faujasite. In addition, the chromium content of the treated ZSM-5 is <0.1 wt %, demonstrating the intrinsic stability of this high silica zeolite in an acid environment.

## Experimental Section

Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell.

Synthetic ZSM-5 was prepared by the method of Argauer and Landolt.[3] Analysis by weight: 97.0% $SiO_2$, 2.10% $Al_2O_3$, 2.7% Na; calculated $SiO_2/Al_2O_3$ molar ratio 77/1. In the first experiment 8.7 g of the powdered zeolite was added to 300 mL of refluxing (~101 °C) aqueous 2.0 N $CrCl_3$, pH 1.5, and the mixture was stirred for 2 h. The flask contents were then filtered through paper by suction, and the residue was treated twice more with 300 mL of $CrCl_3$ solution (total of 102 mL of solution/g of zeolite). In all cases, the filtrate remained clear. The final filter cake was water washed until chloride ion free and then dried overnight at 110 °C. Analysis by weight: 98.0% $SiO_2$, 1.98% $Al_2O_3$, <0.01% Na, 0.02% Cr; calculated $SiO_2/Al_2O_3$ ratio 84/1; alumina removal 8 wt %.

In a second experiment using more severe treatment conditions, 6.0 g of the zeolite was added to 600 mL of refluxing 4.0 N $CrCl_3$, pH 1.4, and the mixture was stirred for 48 h (100 mL of solution/g of zeolite). The flask contents were filtered as in the first experiment; the filter cake was water washed until chloride ion free and then dried overnight at 110 °C. Analysis by weight: 95.2% $SiO_2$, 2.00% $Al_2O_3$, <0.01% Na, 0.04% Cr; calculated $SiO_2/Al_2O_3$ ratio 8.1; alumina removal 5 wt %.

## Discussion

In the earlier work dealuminating erionite with $CrCl_3$, it was found that treatment of the zeolite with HCl solutions of the same pH as the $CrCl_3$ solutions removed only about one-fourth as much alumina.[1] Further evidence was given of a complex of the chromium with the hydrolyzed alumina, accounting for its greater removal from the framework. Further, in the earlier work it was

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