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Direct Fluorination of Carbon Disulfide. A Practical Synthesis for Difluoromethylenebis(sulfur trifluoride)

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The compound difluoromethylenebis(sulfur trifluoride) has been previously reported only as a very minor by-product in the electrochemical fluorination of carbon disulfide to CF_3SF_5[1] by Clifford, Haszeldine, El-Shamy, and Emeleus. The quantity produced was sufficient only to allow a boiling point and molecular weight determination to be carried out. Other fluorinations of CS_2 using AgF_2[2] or CoF_3[3] or direct fluorination in a diffusion-controlled fluorine flame[4] have yielded SF_5CF_3, $(SF_5)_2CF_2$, $SF_5CF_2SF_3$, and SF_3CF_3, but $(SF_3)_2CF_2$ was never detected in any of these cases.

Our technique of direct fluorination, using low temperatures and helium dilution, has been shown to be capable of very mild fluorination.[5,6] For this reason, reaction conditions providing a high yield of $(SF_3)_2CF_2$ were sought:

$$CS_2 \xrightarrow[-120\ ^\circ C]{F_2/He} SF_3CF_2SF_3$$

Experimental Section

^{19}F NMR spectra were taken on a Varian A56-60 spectrometer at 56.4 MHz and a Varian HA-100 spectrometer at 94.1 MHz equipped with a variable-temperature probe. $CFCl_3$ was used as an external standard for room-temperature spectra. At low temperatures $CFCl_3$ was used as an internal standard and solvent. Infrared spectra were taken on a Beckman IR20A spectrometer using a Pyrex gas cell equipped with KBr windows. Mass spectra were run on a Bell and Howell Model 21-491 instrument. The molecular weight determinations were carried out in a stainless steel and Kel-F vacuum line equipped with a Wallace and Tiernan metal gauge. The four-zone cold reactor fluorination system used has been described previously.[6]

In a typical reaction, 2 g of reagent grade CS_2 was injected into the reactor in which the second zone was held at −120 °C by means of a liquid nitrogen temperature controller system. The helium flow was set to 30 cm^3/min and the fluorine flow was set to 1.5 cm^3/min. These conditions were held for 3 days, after which the fluorine flow was terminated and the reactor warmed to room temperature. The products collected in the glass trap were transferred to a vacuum line and separated using a −78 °C trap. The materials which passed the trap were found to consist mainly of CF_4 and SF_4 with a trace of SF_6.[7] The material not passing the trap was pure $(SF_3)_2CF_2$. The yield based on the CS_2 injected was 60%, 3.6 g of $(SF_3)_2CF_2$.

$(SF_3)_2CF_2$. Calculated molecular weight, 228; found, 229. IR (cm^{-1}) 1255 (s), 1196 (s), 923 (m), 850 (s), 765 (w), 700 (vs), 578 (m), 527 (m). Mass spectral $(P - F)^+$ peak at *m/e* 209. ^{19}F NMR, room temperature (neat): broad peak at −6.6 ppm (assigned to SF_3 groups), sharp peak at 88.2 ppm (assigned to CF_2). Integral ratios were 3:1. At −80 °C (in $CFCl_3$) the SF_3 resonance had merged into the baseline and some splitting began to appear in the methylene resonance. The sample froze before the low-temperature exchange limit was reached. Similar temperature-dependent NMR behavior has been found for other SF_3 compounds.[2]

$(SF_5)_2CF_2$. The IR spectrum was in agreement with that reported by Clifford, El-Shamy, Emeleus, and Haszeldine.[1] The mass spectrum showed a parent peak at *m/e* 304. The ^{19}F NMR had three sets of peaks in the CF_2, axial S–F, and equatorial S–F regions. The spectrum was second order.

A second series of reactions was studied. The conditions were the same as the previous set for the first 3 days. Then the temperature was raised to −80 °C and the reaction allowed to continue for 3 more days. The product collection and separation were carried out in the same manner as the previous sample. The material passing the −78 °C trap was found to be mainly CF_4 and SF_4 with some SF_6 and possibly CF_3SF_3 and CF_3SF_5. The material not passing the −78 °C trap was found to be a mixture of $(SF_3)_2CF_2$ and $(SF_5)_2CF_2$ in the mole ratio of 23:27 (from integration of the CF_2 peaks in the ^{19}F NMR). Under these conditions the overall yield of $(SF_3)_2CF_2$ and $(SF_5)_2CF_2$ was found to be about 25% (0.7 g of $(SF_3)_2CF_2$ and 1.1 g of $(SF_5)_2CF_2$).

Results and Discussion

The major product of the −120 °C reaction was $(SF_3)_2CF_2$. The only other products, SF_4, CF_4, and SF_6, were much more volatile, and by collecting the reaction products with a −78 °C trap, essentially pure $(SF_3)_2CF_2$ can be obtained. This feature makes this a particularly convenient synthesis.

Despite the mild fluorination conditions, about 30% of the CS_2 starting material fragmented. No significant amounts of $\cdot SF_5$ compounds were found under these conditions. This would lead one to assume that higher temperature fluorination would lead to more fragmentation, rather than to the production of $\cdot SF_5$ compounds. Yet fluorination of CS_2 by Tyczkowski and Bigelow[4] in a controlled fluorine flame gave only about 35% CF_4, SF_4, and SF_6, and led to the formation of several $\cdot SF_5$ compounds.

The second series of reactions was carried out in an attempt to explain this discrepancy. These reactions were run for 3 days under conditions identical with the first set in order to produce $(SF_3)_2CF_2$ in the reactor. (The yield for this step was assumed to be about 50%. Running the reaction for less than 3 days leaves unreacted CS_2 in the reactor.) The temperature was then raised to −80 °C and the fluorination of the $\cdot SF_3$ compound was continued for 3 more days. The results showed that about 25% of the $(SF_3)_2CF_2$ was converted to $(SF_5)_2CF_2$, about 50% was converted to CF_4 and SF_4 (and possibly CF_3SF_3 and CF_3SF_5), and the rest was unchanged.

A possible explanation is that the fluorination first proceeds smoothly to $(SF_3)_2CF_2$; then further fluorination leads to $SF_3CF_2SF_4\cdot$ as an unstable intermediate. From there the intermediate can react further with fluorine to yield an $\cdot SF_5$ compound or decomposition products.

It is possible that at low temperatures the reactivity or reaction rate of the fluorine is reduced to the extent that SF_4 may be eliminated before the fluorination can be completed. It is also possible that as the temperature is raised, the fluorine becomes more reactive and forms $\cdot SF_5$ products more readily before the loss of SF_4 can occur.

Trifluorosulfur compounds in general are useful as reagents for the conversion of carbonyl and carboxyl groups to difluoroethylene and trifluoromethyl groups.[2] Difluoromethylenebis(sulfur trifluoride) would be expected to behave in a similar manner and should be investigated to discover the advantages it could offer for these reactions.

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Registry No. $(SF_3)_2CF_2$, 374-49-2; $(SF_5)_2CF_2$, 1512-21-6; CS_2, 75-15-0; F_2, 7782-41-4.

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(7) The IR spectra of these materials also showed peaks due to C–F compounds, which may have been CF_3SF_3 and CF_3SF_5. Positive identification was not possible because these materials were present in only small amounts, and the S–F IR region was dominated by SF_4 bands. Separation by GC was not possible since the mixture reacted with the column.

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Unusual Oxidation-State Stabilization of Iron Complexes by the Pyrrole-*N*-carbodithioate Ligand

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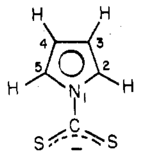
The tris(*N*,*N*-diorganodithiocarbamato)iron(III), [Fe(S_2CNR_2)$_3$], complexes have been studied extensively[1-8] because of the considerable interest in the electronic properties of complexes derived from sulfur ligands. The spectral and magnetic properties of a large number of these complexes are very dependent on the nitrogen substituent of the dithiocarbamate[9,10] and on temperature.[2,9] These properties have been attributed on the one hand to the R–N–R bond angle[9] and on the other to the inductive properties of the R substitutents.[10] One of the main problems is ascertaining the inductive influence that a substituent exerts. Most investigators have employed the basicity of the parent amine toward a proton as a criterion of electron donation toward the CS_2 group. In this study we report an iron(III) dithiocarbamate with unusual redox properties which is derived from the pyrrole-*N*-carbodithioate ligand (I).[11] An improved synthesis of this ligand is reported as well as the preparation of complexes with Cr(III), Fe(III), and Zn(II). Several of their physical properties related to the metal–ligand interactions have been studied.[12]



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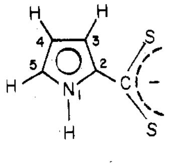

II

Experimental Section

(I) Syntheses. Sodium Pyrrole-*N*-carbodithioate. Approximately 1 M solutions of this ligand in Me_2SO were prepared as follows. Sodium hydride[13] (2.4 g) was reacted with an excess (100 mL) of dimethyl sulfoxide.[14] Freshly distilled pyrrole (7.0 mL) was then added. The resulting pale yellow solution was cooled to 20 °C in an ice bath, and carbon disulfide (6.2 mL) was slowly added. This step is exothermic and yields the deep orange-red solution of the ligand.

Bis(pyrrole-*N*-carbodithioato)zinc(II). Twenty milliliters of a 1 M solution of the ligand was slowly added to a stirred solution of zinc nitrate hexahydrate (3.0 g) in 100 mL of water. The yellow precipitate formed was filtered by suction, washed with water, and crystallized from methanol–water. Anal. Calcd for $C_{10}H_8N_2S_4Zn$: C, 34.33; H, 2.31; N, 8.0; Zn, 18.70. Found: C, 34.35; H, 2.37; N, 7.96; Zn, 18.51. The green tris(pyrrole-*N*-carbodithioato)chromium(III) was prepared in a similar fashion. It was crystallized from acetone–methanol. Anal. Calcd for $C_{15}H_{12}N_3S_6Cr$: C, 37.64; H, 2.53; N, 8.78; Cr, 10.86. Found: C, 37.54; H, 2.65; N, 9.06; Cr, 10.96.

Table I. Abbreviations for $RR'NCS_2^-$

R	R'	Abbrev	R	R'	Abbrev
CH_3	CH_3	ME	C_2H_5	C_2H_5	ET
n-C_4H_9	*n*-C_4H_9	NBU	*n*-C_6H_{13}	*n*-C_6H_{13}	NHX
i-C_4H_9	*i*-C_4H_9	IBU	C_6H_{11}	C_6H_{11}	CHX
CH_3	C_6H_5	MPH	C_2H_5	C_6H_5	EPH
$-CH_2CH_2CH_2CH_2-$		SPYR	–CH=CHCH=CH–		APYR

Tris(pyrrole-*N*-carbodithioato)iron(III). Anhydrous ferric chloride (1.6 g) was dissolved in 100 mL of methanol and the solution was filtered. Thirty milliliters of a 1 M solution of the ligand was diluted with 10 mL of water and added dropwise to the stirred ferric solution. The almost-black precipitate that formed was filtered by suction, washed with methanol, and air-dried. It was dissolved in the minimum amount of dichloromethane, filtered, and reprecipitated with methanol. Anal. Calcd for $C_{15}H_{12}N_3S_6Fe$: C, 37.34; H, 2.71; N, 8.71; Fe, 11.57. Found: C, 37.48; H, 2.74; N, 8.74; Fe, 11.53.

(II) Physical Methods. Visible spectra were obtained in $CHCl_3$ solution on a Cary-14 instrument. Infrared spectra were recorded as KBr pellets and Nujol mulls on a Beckman IR-12 spectrophotometer. NMR spectra in $CHCl_3$ solution were obtained on a Varian Model EM 390B instrument. All chemical shifts were measured relative to internal Me_4Si. Magnetic susceptibilities at ~35 °C in $CHCl_3$ solution were obtained by the Evans[15] method using Me_4Si as a reference on a Varian T-60 instrument. A concentric NMR tube was used. Solid-state magnetic susceptibilities were obtained at 25 °C using a Gouy balance. $[Ni(en)_3]S_2O_3$ was used[16] as the calibrant. Electrochemical work was done in acetone (0.1 M in *n*-Bu_4NClO_4 and 10^{-4} M in the complex). Potentials were obtained vs. a saturated calomel reference electrode. Mössbauer spectra of powdered samples were obtained at room temperature using a constant acceleration Doppler-shifted ^{57}Co source and a 1024 channel analyzer (512 channels were used). Iron foil was recorded for calibration. Spectra were computer-fit using the program PARLORS.[17]

Results and Discussion

The ^1H NMR spectrum of $Zn(APYR)_2$ (see abbreviations in Table I) in $CHCl_3$ shows two multiplets of equal intensities centered at τ 2.3 and 3.6 ppm. This AA′BB′ system is consistent with a structure for the ligand in which the CS_2 is bonded to the nitrogen as shown in structure I. Further evidence for this structure is obtained from the infrared spectrum of the zinc adduct in Nujol which shows the absence of the strong N–H bending and stretching modes which are found at 1146 and 3400 cm^{-1}, respectively, in pyrrole.[18] The infrared spectrum of $Fe(APYR)_3$ is similar to that of $Zn(APYR)_2$ in those two regions, suggesting the same ligand structure. A strong absorption at 1330 cm^{-1} in the infrared spectra of the zinc and iron adducts is assigned to the coupled C–N stretch of the $N\text{–}CS_2^-$ residue.[11] We were unable to detect by NMR or infrared spectroscopy the isomeric 2-pyrroledithiocarboxylate moiety (II) reported in the synthesis of Kellner et al.[11]

Table II contains the results from Mössbauer spectroscopy, cyclic voltammetry, and magnetism of $Fe(APYR)_3$ displayed simultaneously with those of other tris(*N*,*N*-diorganodithiocarbamato)iron(III) compounds for comparison. The solid-state and solution magnetic moment of $Fe(APYR)_3$ (~2.2 μ_B) indicates that it is a low-spin species. Ewald et al.[9] have argued that the trend influencing the magnetic behavior of the ferric dithiocarbamates arises from the differences in the R–N–R bond angle in the coordinated $RRNCS_2^-$. The larger this angle is, the lower is the magnetic moment of that particular ferric dithiocarbamate. This interpretation breaks down since $Fe(APYR)_3$ has a lower magnetic moment than $Fe(CHX)_3$ even though the expected CHX–N–CHX bond angle is larger (steric repulsions between the bulky cyclohexyl groups) than the C_2–N–C_5 bond angle of pyrrole[19] (~109°). The isomer shift (δ) of $Fe(APYR)_3$ is essentially indistinguishable from most of the other iron(III) dithiocarbamates