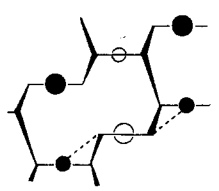
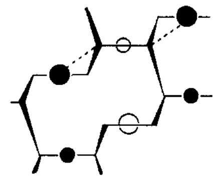
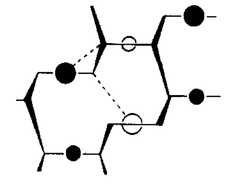
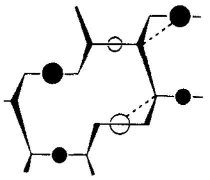
direction, metal atoms are linked by the P^0–P^0 and P^-–P^- linkages as shown in **13a** and **13b**, respectively. The P–P bonds around the P^0–P^0 and P^-–P^- linkages have gauche arrangements as indicated by the Newman projections **14b** and **14a**, respectively.

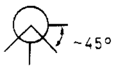

13a


13b

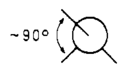

13c


13d

14a



14b



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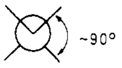
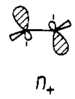


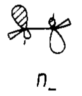
14d

Along the *b* and $(b - c/2)$ directions, metal atoms interact across the P_4^{2-} layers through the P^0–P^- and P^0–P^0 bridges as shown in **13c** and **13d**, respectively. The P–P bonds around the P^0–P^- linkage of **13c** have a gauche arrangement (**14c**), while those around the P^0–P^0 linkage of **13d** have a trans arrangement (**14d**).

In **14d** two n_σ orbitals on the P^0 centers are trans to each other, so the in-phase and out-of-phase combinations of these orbitals (n_+ and n_-, respectively, shown in **15**) effectively couple metal atoms across the P_4^{2-} layers. In **14a–c** the n_σ, n_p, or n'_σ orbitals of the two phosphorus centers do not have a trans arrangement. Nevertheless, the gauche arrangement allows the n_σ, n_p, or n'_σ orbitals to form n_+- and n_--like combinations. Since such orbitals contain π-like orbital components across the P–P linkages, they allow the metal t_{2g}-block levels to effectively interact through the P–P linkages.



15a



15b

Concluding Remarks

The present study shows that the t_{2g}-block bands of VP_4 are dispersive both along the chain direction and along the interchain and interlayer directions. This multidimensional character of the t_{2g}-block bands originates from the fact that the metal atom chains of VP_4 interact through the P–P bonds of the P_4^{2-} layers. Our Fermi surface calculations suggest that the electrical conductivity of VP_4 would be smaller along the chain than along the interchain or interlayer direction. Within a rigid band approximation, our study suggests that CrP_4 and MoP_4 are semimetals, in agreement with the available experimental data. Provided that TiP_4 is made to have the VP_4 structure, it would be metallic with a high density of states at the Fermi level.

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Infrared Spectra of Matrix-Isolated $CF_3S(O)F$ and Its Photolysis Product CF_3OSF

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By UV photolysis of matrix-isolated trifluoromethanesulfinyl fluoride, $CF_3S(O)F$, the isomer CF_3OSF is formed. Structural and bonding parameters of this first fluorosulfenyl ester are evaluated from the vibrational frequencies of the natural and the ^{13}C- and ^{18}O-enriched species. CF_3OSF is decomposed by prolonged UV irradiation to COF_2 and SF_2. Attempts to photoisomerize $CF_3S(O)F$ on a preparative scale lead to mixtures of COF_2, SOF_2, CF_3SSCF_3, and C_2F_6 in the gas phase as well as in solution.

Introduction

Sulfoxylic acid, H_2SO_2, and some of its derivatives are very unstable and therefore rarely characterized.[1] The following chart classifies the derivatives of sulfoxylic acid into stable and unstable species:

	SCl_2	$ClSOH$	$S(OH)_2$	$HOSF$	SF_2
stable		$ClSOR$	$S(OR)_2$	$ROSF$	unstable
		$ClSNR_2$	$S(NR_2)_2$	R_2NSF	

R = organic substituent

Of the unstable species, only SF_2 has been synthesized[2] and fully characterized.[3] The fluorosulfenyl esters CH_3OSF and C_2H_5OSF had been postulated[4] as products of the reaction of $(CH_3O)_2S$ with SSF_2. A reinvestigation by the same authors, however, showed that the ^{19}F NMR signals of CH_3F and C_2H_5F had been misassigned to the fluorosulfenyl esters.[5] Thus, no

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Table I. Vibrational Frequencies (cm^{-1}) for $CF_3S(O)F$ Isolated in an Argon Matrix[a]

$CF_3S(O)F$ [$CF_3{}^{34}S(O)F$]	$^{13}CF_3S(O)F$	$CF_3S(^{18}O)F$	assgnt[b]	
1260.0* vs	1256.6*	1215.8* vs	ν_1	$\nu(SO)$
[1252.0*]				
1238.3 s	1215.3	1238.8 s		
1227.5 vs	1196.1	1243.8 vs	ν_2	$\nu_{as}(CF_3)$
1203.0 vs	1169.9	1228.6 s	ν_3	$\nu_{as}(CF_3)$
		1198.0 s		
1169.0* w		1160.0* w		
1144.9* vs	1115.5*	1140.3 vs	ν_4	$\nu_s(CF_3)$
753.3 w	750.1	739.0* w	ν_5	$\delta(SO)$
744.0 vs	743.0*	746.0* vs	ν_6/ν_7	$\nu(SF)/\delta_s(CF_3)$
[735.0]				
586.6 s	584.4	583.7 s	ν_8	$\delta_{as}(CF_3)$
545.0 vw	542.0		ν_9	$\delta_s(CF_3)$
480.8 s	479.9	478.3 s	ν_{10}	$\nu(CS)/\delta(SO)$
[476.7]				
414.5* m	412.5*	407.4 m	ν_{11}	$\delta(SO)/\nu(CS)$
340.0 vw	340.0		ν_{12}	$\delta(SF)$
290.0 vw	286.0		ν_{13}	$\rho(CF_3)$

[a] Asterisks indicate bands that showed matrix splittings. [b] For comparison see ref 11.

example of the species ROSF is known.

We were able to show that UV photolysis of matrix-isolated sulfur compounds leads to intramolecular redox reactions:

$$SSF_2 \underset{h\nu/240\ nm}{\overset{h\nu/300\ nm}{\rightleftharpoons}} FSSF \quad \text{(ref 6)}$$

$$CF_3C{\equiv}SF_3 \xrightarrow{h\nu/200\ nm} C_2F_5SF \quad \text{(ref 7)}$$

Similar experiments with SOF_2 were not successful in forming the isomer FSOF. $CF_3S(O)F$, however, isomerizes to CF_3OSF under UV irradiation when isolated in an argon matrix. The evidence for this first fluorosulfenic ester is presented in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-A-10 MKS Baratron, Burlington) and valves with Teflon pistons (Young, London). The vacuum line was connected directly to an IR cell (l = 200 mm, Si windows) and by a glass tube. The IR spectra were recorded with a FTIR spectrometer MXS (Nicolet). Samples were purified by trap to trap condensation or by low-temperature distillation. A TQ 150 (Heraeus, FRG) medium-pressure mercury arc, which is focused by quartz lenses through a 2-cm water filter, was used for UV irradiation of $CF_3S(O)F$ in matrices, in the gas phase, or in CD_2Cl_2 solutions. The course of photolysis in an NMR tube (quartz glass, o.d. = 5 mm) at −80 °C was observed by ^{19}F NMR spectroscopy using a Bruker WP80 FTNMR spectrometer. Details of the apparatus for matrix isolation are given elsewhere.[8] Matrix spectra were recorded on the Bruker IFS-113v FTIR spectrometer in the range of 4200–200 cm^{-1} via a reflection accessory (resolution 1 cm^{-1}).

Synthesis of $CF_3S(O)F$. For the preparation of $CF_3S(O)F$ or $CF_3S(^{18}O)F$ according to ref 9, CF_3SF_3 and H_2O (molar ratio 1:1,3) or $H_2{}^{18}O$ (98%, Ventron) were successively condensed into a 25-mL stainless steel cylinder (filled with some KF). The cylinder was warmed from −196 to +20 °C and was kept at this temperature for 2 h. The volatile material was separated by fractional condensation under sustained vacuum through a series of traps at −50, −80, and −196 °C. The trap at −196 °C contained pure $CF_3S(O)F$. CF_3SF_3 was prepared by the reaction of CF_3SSCF_3 and AgF_2 according to ref 10 and purified by low-temperature distillation (−10 °C). The purity, checked by IR spectroscopy, was better than 99%.

$^{13}CF_3S(O)F$ was obtained in the following way, starting with ^{13}C (90%, Sharp & Dohme):

$$^{13}C \xrightarrow{S\ vapor/1000\ ^\circ C} {}^{13}CS_2 \xrightarrow{HgF_2} Hg(S^{13}CF_3)_2 \xrightarrow{I_2}$$
$$^{13}CF_3SS^{13}CF_3 \xrightarrow{AgF_2} {}^{13}CF_3SF_3 \xrightarrow{H_2O/KF} {}^{13}CF_3S(O)F$$

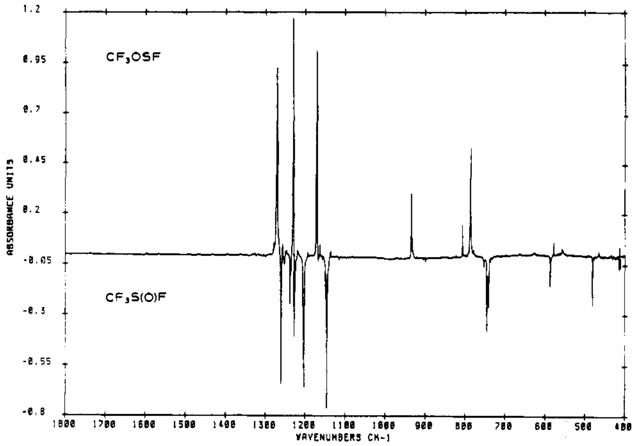

Figure 1. Difference IR spectrum of $CF_3S(O)F$ and its photolysis product: $CF_3S(O)F:Ar$ = 1:1000 (0.833-mmol matrix); resolution 1 cm^{-1}; DTGS detector; 64 scans.

Table II. Vibrational Frequencies (cm^{-1}) for CF_3OSF Isolated in an Argon Matrix[a]

CF_3OSF ($CF_3O^{34}SF$)	$^{13}CF_3OSF$	$CF_3{}^{18}OSF$	approx descrpn of mode	
2096.5* w	2060.0	2060.9	$\nu_3 + \nu_4$	
1596.6* vw	1594.0	1554.0	$\nu_4 + \nu_7$	
1327.5* w	1328.0	1302.7	$2\nu_7$	
1272.3* vs	1234.0	1271.1	ν_1	$\nu_{as}(CF_3)$
1230.7 vs	1193.3	1229.9	ν_2	$\nu_{as}(CF_3)$
1171.6* vs	1136.4	1166.4	ν_3	$\nu_s(CF_3)$
934.1 s	933.6	903.8	ν_4	$\nu_{as}(CF_3{-}O{-}SF)$
806.9 m	806.0	795.5	ν_5	$\nu_s(CF_3{-}O{-}SF)$
786.4 s	786.3	780.7	ν_6	$\nu(SF)$
(778.4)				
663.7 vw	663.0	651.1	ν_7	$\delta_s(CF_3)$
626.2* w	625.0	618.5	ν_8	$\delta_{as}(CF_3)$
557.3 m	556.0	551.5	ν_9	$\delta_{as}(CF_3)$
464.9 m	464.5	456.3	ν_{10}	$\delta(OSF)$
413.3* m	413.0	407.4	ν_{11}	$\delta(CF_3OS)$
295.0 vw			ν_{12}	$\rho(CF_3)$

[a] Asterisks indicate bands that showed matrix splittings.

Results and Discussion

1. UV Photolysis of Matrix-Isolated $CF_3S(O)F$. Mixtures of argon and trifluoromethanesulfinyl fluoride ($Ar:CF_3S(O)F$ = 1000:1; 0.8–1.8 mmol) were deposited at 16 K for 15 min. The infrared spectra recorded immediately after deposition showed absorptions of the precursor exclusively. As the vibrational spectra of $CF_3S(O)F$ are incompletely known,[11] the measured data are listed in Table I. After 3 min of photolysis with unfiltered light of the medium-pressure mercury arc, approximately 80% of the precursor was decomposed and new absorptions appeared. A difference spectrum of $CF_3S(O)F$ and its photolysis product is shown in Figure 1. The peak locations and intensities of the new absorptions are listed in Table II. On further photolysis, the intensities of all new bands decreased and absorptions centered at 1937/1906/1254/969/774/625 cm^{-1} and 823/792 cm^{-1} increased. By comparison with literature data, the first group of bands must be assigned to COF_2[12] (1942.0/1914.2/1243.0/965.6/767.4/620.1 cm^{-1}) and the second group of bands to SF_2[13] (831.9/804.1 cm^{-1}). The differences in frequencies arise from the fact that the complete photodecomposition of $CF_3S(O)F$ leads to the molecular complex [$COF_2{\cdot}SF_2$] and not to isolated COF_2 and SF_2 molecules. The other possible compounds CF_4 and SO are not formed. The intermediate photoproduct is an isomer of $CF_3S(O)F$, and the composition of this isomer can be deduced by the characteristic frequencies and the observed isotopic shifts in Table II. There are characteristic frequencies for a CF_3– and

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Table III. Calculated Structural Parameters[a] for CF_3OSF

C–F^5	135.4	C–F^6	135.7	C–F^7	135.5
C–O	139.1	O–S	157.4	S–F	159.3
F^{5}CF^6	108.0	F^{5}CF^7	108.2	F^{6}CF^7	107.4
F^{5}CO	108.3	F^{6}CO	112.0	F^{7}CO	112.8
COS	119.1	OSF	104.5	τ	81.9

[a] Bond lengths in pm; angles in deg.

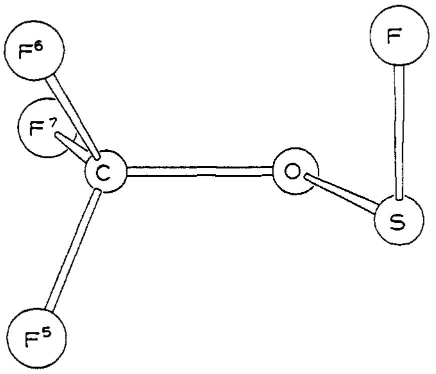

Figure 2. Theoretical structure of CF_3OSF.

Table IV. Fundamental Frequencies and Isotopic Shifts (Corrected for Anharmonicity; Relative to CF_3OSF, cm^{-1}) for the Normal-Coordinate Analysis

CF_3SOF	$\Delta\nu$ ($^{13}CF_3OSF$)	$\Delta\nu$ ($CF_3{}^{18}OSF$)	PED[b]
1272.3 (1274.0)[a]	38.7 (38.6)	1.2 (6.5)	76(CF)
1230.7 (1231.4)	37.8 (36.9)	0.8 (3.7)	50(CF) + 48(CO)
1171.6 (1170.0)	35.6 (36.2)	5.3 (0.3)	92(CF)
934.1 (934.4)	0.5 (0.4)	30.1 (31.7)	12(CF) + 34(CO) + 39(SO)
806.9 (807.5)	0.9 (2.1)	11.5 (12.2)	32(CF) + 10(CO) + 26(SO)
786.4 (786.7)	0.1 (0.4)	5.8 (6.2)	92(SF)
663.7 (663.8)	0.7 (1.8)	12.7 (11.7)	36(FCF) + 13(CF)
626.2 (623.8)	1.2 (0.9)	7.8 (1.0)	64(FCF)
557.3 (556.8)	1.3 (1.1)	5.9 (5.3)	69(FCF)
464.9 (467.2)	0.4 (0.1)	8.7 (15.9)	29(FCO) + 26(OSF)
413.3 (411.6)	0.3 (0.3)	6.0 (0.6)	25(SO) + 39(FCO)
295.0 (295.1)	- (0.4)	- (0.1)	29(FCO) + 38(OSF)
- (231.0)	- (0.2)	- (1.1)	79(COS)
- (130.6)	- (0.1)	- (-)	70(FSCO, torsion)
- (64.0)	- (-)	- (-)	86(FCOS, torsion)

[a] Values in parentheses are calculated from the best force field. [b] Potential energy distribution (%).

a SF- group at about 1200 and 800 cm^{-1}, respectively. The characteristic CF_3–O vibration at about 900 cm^{-1} shows the expected $^{16/18}O$ isotopic shift. The SF- bond must be connected with an oxygen atom because the SF vibration has an strong $^{16/18}O$ isotopic shift. These characteristics and the following more detailed analysis of the spectral data lead to the unique assignment of the photoproduct to CF_3OSF.

Structure of CF_3OSF. For the molecule CF_3OSF either C_1 or C_s symmetry is possible in principle. Some sensible bond lengths and bond angles can be estimated from the structural parameters of CF_3OCl[14] and SF_2.[15] This starting structure was optimized by the SINDO1 program,[16] a semiempirical SCF–MO method. The resulting structure (Figure 2, Table III) shows that the CF_3OSF molecule belongs to C_1 symmetry, with a structure analogous to that of H_2O_2. A confirmation of these structural parameters is possible with the Teller–Redlich product rule.[17] For this purpose the vibrational frequencies of natural and ^{13}C- and ^{18}O-isotope-enriched molecules were used. It is necessary to know all fundamental frequencies of an isotopic pair, or at least those vibrations in which the movement of the isotope shows a significant contribution. In the case of the CF_3OSF molecule, we were able to measure and assign all vibrations in which the carbon or oxgyen atom is strongly involved. The products $\prod(\nu/\nu_i)$

$$\prod(\nu[CF_3OSF]/\nu[^{13}CF_3OSF]) = 1.10584 \text{ and } 1.10808$$

$$\prod(\nu[CF_3OSF]/\nu[CF_3{}^{18}OSF]) = 1.14519 \text{ and } 1.14784$$

were calculated from Table II and, after correction for the isotopic shifts for anharmonicity (all with $x_e = 0.005$), from Table IV, respectively. These numbers are in good agreement with the products calculated with the structural parameters $\prod(\nu/\nu_i)_{calcd}$

$$\prod(\nu[CF_3OSF/\nu[^{13}CF_3OSF])_{calcd} = 1.11024$$

$$\prod(\nu[CF_3OSF/\nu[CF_3{}^{18}OSF])_{calcd} = 1.14347$$

Variations in bond length of 3 pm and bond angles of 5° result in variations of the $\prod(\nu/\nu_i)_{calcd}$ values in the range of one part in 10^{-3}. This tells us that the calculated structural parameters are reliable.

IR Spectra of CF_3OSF and Assignment. Fifteen IR fundamental modes are expected for the CF_3OSF molecule with C_1 symmetry: six stretchings, seven bending modes, and 2 torsions. Apart from the CF_3–O and O–SF torsional modes, which are expected below 100 cm^{-1}, all possible vibrations could be detected. The measured frequencies and approximate descriptions of modes are listed in Table II.

The CF_3 Stretching Vibrations ν_1, ν_2, and ν_3. The three CF_3 stretching vibrations of the natural species are located at 1272.3, 1230.7, and 1171.6 cm^{-1}. Similar modes in CF_3OCl[18] are found at 1268.1, 1219.1, and 1200.2 cm^{-1}. The absorption at 1171.6 cm^{-1} shows the largest $^{16/18}O$ isotopic shift (5.2 cm^{-1}). In this vibration, therefore, the oscillating dipole moment has a large component in the direction of the CO bond. Hence, it follows that this mode can be described as "$\nu_s(CF_3)$". In CF_3 groups with local C_{3v} symmetry the remaining two stretching vibrations are degenerate, but in this case they are split by 42 cm^{-1}. In CF_3SCl[19] and CF_3OCl[18] the corresponding splittings are 7 and 49 cm^{-1}, respectively. This shows that in CF_3OCl and CF_3OSF the CF_3 group is strongly distorted.

The CF_3–O–SF Vibrations ν_4 and ν_5. The absorptions at 934.1 and 806.9 cm^{-1} should correspond to oxygen stretching modes, because the frequencies are similar in CF_3OCl[18] (ν(CO) = 917.9 cm^{-1}, ν(OCl) = 781.0 cm^{-1}) and in $(CF_3)_2O$[20] ($\nu_s(C_2O)$ = 852, $\nu_{as}(C_2O)$ = 971 cm^{-1}). The $^{16/18}O$ isotopic shifts (30.3 and 11.4 cm^{-1}) show that the vibrations at 934.1 and 806.9 cm^{-1} can be described as an antisymmetric and a symmetric O atom stretching mode between the CF_3 and the SF group.

The SF Stretching Mode ν_s. The absorption at 786.4 cm^{-1} can be assigned to this mode because it shows an expected ^{34}S satellite at 778.4 cm^{-1}. The $^{16/18}O$ isotopic shift of 5.7 cm^{-1} indicates some SO stretching character.

The CF_3 Bending Modes ν_7, ν_8, ν_9, ν_{12}, and ν_{13}. The assignment is not always clear, because the bending modes are strongly coupled to one another. By comparison with those of other CF_3 compounds, the absorption at 663.7 cm^{-1} is assigned to the CF_3 umbrella mode and those at 626.2 and 557.3 cm^{-1} are assigned to $\delta_{as}(CF_3)$. The CF_3 rocking modes are expected as weak absorptions in the range of 400–200 cm^{-1}. The peak at 295 cm^{-1} is likely to correspond to this mode.

The OSF and CF_3OS Bending Modes ν_{10} and ν_{11}. The remaining peaks at 464.9 and 413.3 cm^{-1} are assigned to these modes. As the absorption at 464.9 cm^{-1} shows the larger $^{16/18}O$ isotopic shift, it is assigned to the OSF bending mode.

Normal-Coordinate Analysis. A normal-coordinate analysis was undertaken to confirm the suggested assignment and obtain a better description of the bonding in CF_3OSF. For the computation of the general valence force field, the structural parameters from

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Table V. Force Field of CF_3OSF[a]

CF^5	6.15	CF^5/CF^6	1.55	CF^6/F^5CF^7	−0.62
CF^6	5.49	CF^5/CF^7	1.36	CF^7/F^6CF^7	0.65
CF^7	5.75	CF^6/CF^7	1.15	CF^7/F^5CF^7	0.39
CO	5.36	CF^5/CO	0.69	CF^7/F^5CF^6	−0.44
OS	4.19	CF^6/CO	0.86	CO/COS	0.68
SF	4.48	CF^7/CO	0.75	CO/OS	0.60
F^5CF^6	2.30	CO/F^5CF^6	−0.81	OS/SF	0.50
F^5CF^7	2.20	CO/F^5CF^7	−0.56	OS/OSF	0.31
F^8CF^7	1.79	CO/F^6CF^7	−0.41	SF/OSF	0.24
F^5CO	1.77	CF^5/F^5CF^6	0.61	COS/OSF	0.72
F^6CO	1.09	CF^5/F^5CF^7	0.59	OS/COS	0.35
F^7CO	0.81	CF^5/F^6CF^7	−0.23		
COS	1.79	CF^6/F^5CF^6	0.47		
OSF	1.27	CF^6/F^6CF^7	0.14		
FCOS (torsion)	0.10				
FSCO (torsion)	0.21				

[a] Force constants in 10^2 N/m; bending force constants and bending–stretching constants normalized on 10^{-10} m.

Table III, vibrational frequencies and isotopic shifts from Table IV, and the program NCA[21] were used. The final result is shown in Table V, and the calculated frequencies and isotopic shifts are listed in Table IV. Because the vibrational couplings are very strong in this molecule, it was not possible to get a satisfying agreement between observed and calculated frequencies. Nevertheless, the results are reasonable for the proposed CF_3OSF structure.

2. UV Photolysis of $CF_3S(O)F$ in the Gas Phase and in CD_2Cl_2 Solution. Photolysis of $CF_3S(O)F$ in a quartz glass bulb at 10–100 mbar and 20 °C, or diluted in CD_2Cl_2 at −80 °C in an NMR tube, does not generate CF_3OSF. The molecules COF_2, SOF_2, CF_3SSCF_3, and C_2F_6 in various ratios could be detected by IR and ^{19}F NMR spectroscopy.

Conclusion

The compound CF_3OSF is formed by UV photolysis of matrix-isolated trifluoromethanesulfinyl fluoride, $CF_3S(O)F$. In contrast to the photoisomerization of S_2F_2[6] or Se_2F_2,[22] there is no stationary equilibrium between the isomers of $CF_3S(O)F$. By prolonged UV irradiation, it decomposed to COF_2 and SF_2.

CF_3OSF is the first known fluorosulfenyl ester. It was not possible to synthesize it on a preparative scale by gas-phase or solution photolysis. Likely primary photolysis products are CF_3 and OSF radicals, which may recombine in the matrix cage to CF_3OSF, but in the gas phase or in solution they can diffuse and form other more stable products.

For the fluorosulfenyl trifluoromethyl ester 13 of 15 possible fundamental vibrations were measured and assigned. Data were also obtained for the ^{13}C- and ^{18}O-enriched species, enabling us to deduce a reliable structure and force field for this unusual molecule.

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Registry No. $CF_3S(O)F$, 812-12-4; CF_3OSF, 115095-67-5; CF_3SF_3, 374-10-7; $^{13}CF_3S(O)F$, 115095-68-6; $CF_3S(^{18}O)F$, 115095-69-7; $CF_3{}^{34}S(O)F$, 115095-70-0; $^{13}CF_3OSF$, 115095-71-1; $CF_3{}^{18}OSF$, 115095-72-2; $CF_3O^{34}SF$, 115095-73-3.

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Anionic Perphosphido and Perarsenido Complexes of Gallium and Indium

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Reaction of 4 equiv of $LiEPh_2$ with MCl_3 in THF at −78 °C yields the anionic perphosphido and perarsenido complexes $[Li(THF)_4][M(EPh_2)_4]$ (**1**, M = Ga, E = P; **2**, M = In, E = P; **3**, M = Ga, E = As) in 70–80% yields. The air-sensitive complexes are yellow and crystalline and can be recrystallized from THF/toluene mixtures. The X-ray structures of **1**–**3** have been determined. The anionic moieties of **1**–**3** are very similar. The M–E bond lengths, EPh_2 geometries, and $M(EC_2)_4$ conformations are indicative of M–E single bonding in each case. Crystal data for **1**: $C_{64}H_{72}GaLiO_4P_4$, $M_r = 1105.84$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 13.945$ (7) Å, $b = 18.332$ (5) Å, $c = 23.671$ (4) Å, $V = 6051.7$ (3) Å^3, $D_{calcd} = 1.214$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 5.99 cm^{-1}. Refinement of 4127 reflections ($I > 3\sigma(I)$) out of 4155 unique observed reflections ($3° \leq 2\theta \leq 44°$) gave R and R_w values of 0.0688 and 0.0747, respectively. Crystal data for **2**: $C_{64}H_{72}InLiO_4P_4$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 14.017$ (4) Å, $b = 18.402$ (9) Å, $c = 23.696$ (5) Å, $V = 6112.6$ (9) Å^3, $D_{calcd} = 1.251$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 5.25 cm^{-1}. Refinement of 4163 reflections ($I > 3\sigma(I)$) out of 4189 unique observed reflections ($3° \leq 2\theta \leq 44°$) gave R and R_w values of 0.0558 and 0.0644, respectively. Crystal data for **3**: $C_{68}H_{80}As_4GaLiO_5$, triclinic, $P\bar{1}$ (No. 2), $a = 13.392$ (7) Å, $b = 13.521$ (5) Å, $c = 19.025$ (7) Å, $\alpha = 87.92$ (3)°, $\beta = 76.19$ (4)°, $\gamma = 83.16$ (3)°, $V = 3321.1$ (7) Å^3, $D_{calcd} = 1.354$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 24.30 cm^{-1}. Refinement of 8132 reflections ($3° \leq 2\theta \leq 44°$) gave R and R_w values of 0.0626 and 0.0707, respectively. There is a disordered THF molecule not bound to Li in the structure of **3**.

Over 20 years ago, Coates, Beachley, and co-workers pioneered the synthesis of compounds featuring bonding between the heavier group 13 and 15 elements.[1] Such compounds have attracted recent attention[2,3] because of their potential utility as percursors to compound semiconductor materials such as gallium arsenide and indium phosphide. Gallium–arsenic and indium–phosphorus compounds have now been characterized in which two or three phosphorus- or arsenic-containing groups are directly bonded to the group 13 element.[2,3] However, to the best of our knowledge, no compounds are known in which the gallium or indium to

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(1) See, for example: Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233. Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241.

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