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Electrophilic Addition and Substitution Reactions of Bis((trifluoromethyl)sulfonyl)amide and Its *N*-Chloro Derivative

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Lithium bis((trifluoromethyl)sulfonyl)amide (**1**) reacts with $S_2O_6F_2$ to form $FSO_2ON(SO_2CF_3)_2$ (**2**). Reaction of **2** with KF results in the cleavage of the S–N bond with the concomitant formation of CF_3SO_2F. The ease of electrophilic addition reactions of $HN(SO_2CF_3)_2$ (**3**) with $CH_2{=}CHF$, $CH_2{=}CF_2$, and $CHF{=}CF_2$ depends upon the hydrogen content of the olefin. Addition occurs in a unidirectional fashion according to Markovnikov's rule to form $CH_3CHFN(SO_2CF_3)_2$ (**4**), $CH_3CF_2N(SO_2CF_3)_2$ (**5**), and $CH_2FCF_2N(SO_2CF_3)_2$ (**6**), respectively. Cleavage of the CF_2–N bond in **5** by reaction with CsF leads to the formation of CH_3CF_3 in about 12% yield. The major product formed is CF_3SO_2F. The reactivity of fluorine atoms of the difluoromethylene group of **5** is shown by its reaction with $(CH_3)_3SiN(CH_3)_2$ in the presence of CsF under mild conditions where CF_3SO_2F, $(CH_3)_3SiF$, and $CH_3C[N(CH_3)_2]{=}NSO_2CF_3$ (**7**) are formed. $AgN(SO_2CF_3)_2$ is formed by the reaction of Ag_2CO_3 with an aqueous solution of **3** and undergoes metathetical reactions readily with compounds containing active halogen atoms to introduce the $N(SO_2CF_3)_2$ group. Strong Lewis acids such as $ZN(SO_2CF_3)_2$ [$Z = R_3Sn$, $R = CH_3$ (**8**), n-C_4H_9 (**9**), and C_6H_5 (**10**); $Z = (CH_3)_3Si$ (**11**)] can thus be conveniently prepared. The vinyltin(IV) compound $(CH_3)_3SnCF{=}CF_2$ (**12**) is synthesized by the reaction between $(CH_3)_3SnCl$ and $CF_2{=}CFBr$ in hexaethylphosphorus triamide and benzonitrile. Multinuclear NMR studies of the trialkylstannyl/silyl derivatives suggest a quasi-tetrahedral structure around the central silicon or tin atom as reflected by their very low ^{29}Si (55.9 ppm) and ^{119}Sn (~250 ppm) NMR chemical shifts and $^{1}J(^{119}Sn–^{13}C)$ and $^{2}J(^{119}Sn–^{1}H)$ coupling constants. Compounds **8**, **9**, and **11** can also be isolated by reaction of $ClN(SO_2CF_3)_2$ (**13**) with the respective alkylmetal chlorides in a noncoordinating solvent. However, **13** fails to add across the perfluorovinyl group in $CF_2{=}CFSn(CH_3)_3$ (**12**) and forms $CF_2{=}CFCl$ and **8** instead. Reactions of **13** with a variety of per/polyfluoroolefins, such as $CF_2{=}CFX$ [$X = H$, F, $\overline{CF_2CF_2CF_2CF_2N}$- and $\overline{CF_2CF_2OCF_2CF_2N}$-], $CH_2{=}CXY$ [$X = H$; $Y = F, CF_3$; $X = Y = F$] result in uni- or bidirectional addition to give **14**–**23**. Insertion of ClCN into the N–Cl bond of **13** results in the formation of an azaalkene, $CCl_2{=}NN(SO_2CF_3)_2$ (**24**). Reaction of $CFCl_2S(O)Cl$ with **13** forms $CFCl_2S(O)N(SO_2CF_3)_2$ (**25**) with concomitant evolution of chlorine.

Introduction

The chemistry of nitrogen acids, especially bis(fluoro/(perfluoroalkyl)sulfonyl)amides, has attracted considerable attention during the last decade. The interest in the chemistry of these compounds arises from the unusually high electronegativity of the (fluoro/(perfluoroalkyl)sulfonyl)amide group.[1-3] The increase in acidity of the residual proton bonded to the nitrogen atom bearing two fluoro/perfluoroalkylsulfonyl groups results in their high gas phase[4] and Brønsted solution acidities.[2,5-8] For example, the electronegativity of the -$N(SO_2X)_2$ group ($X = F$ or CF_3; $\chi \approx 3.6$) is comparable to that of $-SO_2CF_3$ but is slightly greater than that of chlorine.[2] Taking advantage of the high electronegativity of the $-SO_2CF_3$ group[9,10] leads to tremendous applications in organic synthesis.[11-13] As a consequence of the electronegativity effects, compounds containing the $N(SO_2X)_2$ ($X = F$ or CF_3) ligands show some very interesting properties with perhaps the most important being the formation of Xe–N bonds in some noble gas derivatives,[14-17] electrochemical applications,[18-20] and, in the case of $FN(SO_2CF_3)_2$, use as a novel selective fluorinating reagent.[21] A recent study shows that trimethylsilyl bis(fluorosulfonyl)amide is a better catalyst than trimethylsilyl triflate for allylation or aldol type reactions of acetals with trimethylsilyl nucleophiles.[22] Some novel graphite-like solid state structures of their metal salts are reported.[23] Recently, some new perhaloalkanesulfonyl halides which are precursors to some new nitrogen acids were synthesized.[8] Although the chemistry of bis(fluorosulfonyl)amide is developed considerably,[24]

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the chemistry of the corresponding ((perfluoroalkyl)sulfonyl)amides receives much less attention. Here, we describe the electrophilic addition and substitution reactions of bis((trifluoromethyl)sulfonyl)amide and its *N*-chloro derivative. The reactions and properties of some of these derivatives are explored.

Results and Discussion

Bis((perfluoroalkyl)sulfonyl)amides were prepared by employing a multistep synthetic route.[5-7] The availability of lithium bis((trifluoromethyl)sulfonyl)amide (1) as a gift from the 3M Co. provided an easy precursor for the preparation of $HN(SO_2CF_3)_2$. The inertness of $LiN(SO_2CF_3)_2$ is reflected by lack of reaction with active halogen-containing compounds such as $R_fN{=}CF_2$, CF_3COCl, CH_3COF, CH_3I, etc. where a variety of reaction conditions are used. On the other hand, the silver salt of one of the nitrogen acids, $CF_3SO_2N(Ag)SO_2C_4F_9$, reacts instantaneously with CH_3I and C_2H_5I.[7] However, $LiN(SO_2CF_3)_2$ is very reactive toward strong electrophiles. With $S_2O_6F_2$, **1** forms the bis((trifluoromethyl)sulfonyl)amide fluorosulfate **2** in good yield. The presence of two strong bands in the infrared spectrum at 1500 and 1473 cm^{-1} are assigned to $\nu_{as}(SO_2)$ of the $-SO_3F$ and $-N(SO_2CF_3)_2$ groups, respectively. Under vacuum $HN(SO_2CF_3)_2$ sublimes when **1** is heated with ~98% H_2SO_4.

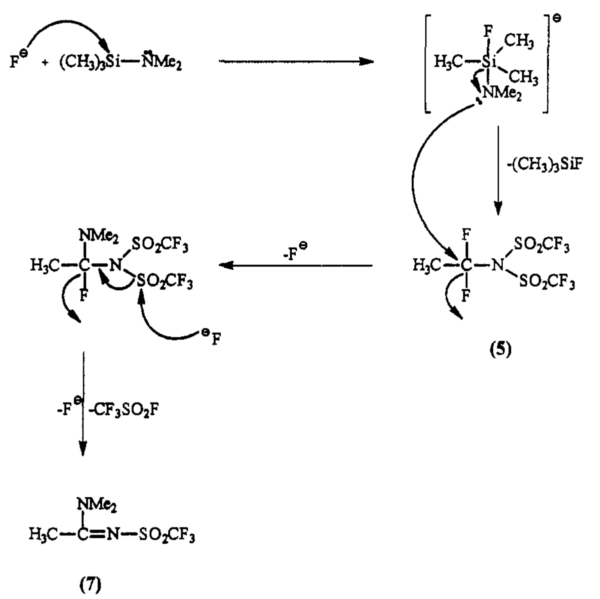
Electrophilic addition reactions of $HN(SO_2CF_3)_2$ are successfully accomplished using model polyfluoroolefins. These reactions obey Markovnikov's rule. This parallels some olefinic addition reactions of HX (X = F[25] or $N(SO_2F)_2$[26]). In the present study it is found that the temperature required to carry out the addition is a function of the fluorine content of the olefin. In the case of vinyl fluoride, the reaction requires initiation by warming to ~45 °C and then continuing at 25 °C for ~12 h. Heating the reaction for a longer time results in darkening of the reaction mixture and polymerization of the alkene. A higher reaction temperature and longer time are required in the case of $CH_2{=}CF_2$ (80 °C and 36 h) and $CHF{=}CF_2$ (~120 °C and 72 h) while tetrafluoroethylene does not react even at ~150 °C for 5 days. It is also observed that the stability of the products increases with increasing fluorine content.

The ^{19}F NMR spectrum of these adducts show long range (^5J) couplings between the fluorine atoms of the $-CF_2-N<$ and $N(SO_2CF_3)_2$ groups. The size of J increases with the increase in fluorine content of the adduct, i.e., 4.8, 6.8, and 12.3 Hz for $CH_3CHFN(SO_2CF_3)_2$ (**4**), $CH_3CF_2N(SO_2CF_3)_2$ (**5**), and $CH_2FCF_2N(SO_2CF_3)_2$ (**6**), respectively. The high-resolution ^{19}F NMR spectrum of **6** shows a 41-line (triplet–triplet–septet) pattern for the CH_2F fluorine atom arising from couplings to geminal protons, vicinal fluorine atoms, and long-range interactions with the $N(SO_2CF_3)_2$ fluorine atoms. This spectral pattern is also supported by theoretical simulation.

Attempted cleavage of the CF_2-N bond in $CH_3CF_2N(SO_2CF_3)_2$ (**5**) using CsF as a nucleophile results in the formation of only ~12% of the desired product, CH_3CF_3. The major product, CF_3SO_2F, results from attack at sulfur with concomitant N–S bond cleavage. In the presence of a polar solvent, e.g., CH_3CN, CF_3SO_2F is formed as the only volatile product. Reaction of **5** with $(CH_3)_3SiN(CH_3)_2$ in the presence of a catalytic amount of CsF, results in the formation of an azaalkene, $CH_3C(N(CH_3)_2){=}NSO_2CF_3$ (**7**), with accompanying formation of $(CH_3)_3SiF$ and CF_3SO_2F. The mechanism for the formation of **7** is shown in Scheme 1.

The reaction of silver carbonate with aqueous $HN(SO_2CF_3)_2$ results in the formation of $AgN(SO_2CF_3)_2$. This is a useful transfer reagent for the introduction of the $N(SO_2CF_3)_2$ group into various organometallic moieties.

Scheme 1



$$R_3MCl + AgN(SO_2CF_3)_2 \xrightarrow[\sim 10\,h]{CH_2Cl_2} \underset{\textbf{8–11}}{R_3MN(SO_2CF_3)_2} + AgCl\downarrow$$

$$M = Sn;\ R = CH_3\ (\textbf{8}),\ C_4H_9\ (\textbf{9}),\ C_6H_5\ (\textbf{10})$$

$$M = Si;\ R = CH_3\ (\textbf{11})$$

Recently it is reported that trialkylsilyl[22] and trialkylstannyl[27] bis(fluorosulfonyl)amides have unusually electron deficient metal centers. This observation is exploited for the trimethylsilyl derivative in organic synthesis,[22] and it is found that this reagent is more efficient than trimethylsilyl triflate. The ^1H and ^{19}F NMR spectral data of $(CH_3)_3SiN(SO_2CF_3)_2$, prepared by the methods in this study agree with those reported.[6] Additionally, the ^{29}Si NMR spectrum shows a peak at δ 55.9 which is among the lowest reported to date. This suggests that $(CH_3)_3SiN(SO_2CF_3)_2$ might be a better candidate as a reagent for organic synthesis in comparison to its $N(SO_2F)_2$ counterpart, especially where stability is concerned since the latter undergoes decomposition at 25 °C after a few days.

The trialkyltin(IV) derivatives also show highly deshielded tin nuclei as reflected by the low ^{119}Sn chemical shifts of ~250 ppm. Although a large quantity of triorganotin(IV) compounds appear in the literature, there is only one unambiguous report of the existence of the $(CH_3)_3Sn^+$ cation in highly acidic solution below −30 °C.[28] Two reports have appeared recently on stable cationic tricoordinate tin species in solution under ambient conditions.[29,30] The appearance of $\nu_{as}SO_2$ at ~1380 cm^{-1}, low ^{119}Sn chemical shift, and the position of the ^{19}F resonance ~−79 ppm in $R_3SnN(SO_2CF_3)_2$ are indicative of the ionic nature of these compounds. In order to demonstrate this highly polar property, their solvation behavior was studied by ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy (Tables 1 and 2). The series of solvents chosen for the trimethyl- and tri-*n*-butyltin bis((trifluoromethyl)sulfonyl)amides is based on increasing solvent donicities.

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Table 1. ^{1}H, ^{19}F, and ^{119}Sn NMR Spectral Data for R_3SnX ($R = CH_3, C_4H_9$; $X = N(SO_2CF_3)_2$)

			^2J(Sn–^{1}H), Hz					
compound	solvent[a]	δ(H)	^{117}Sn	^{119}Sn	θ(CH_3-Sn-CH_3)[b] (eq 1), deg	δ(^{19}F)	δ(^{119}Sn)	Δ(^{119}Sn)[c]
$(CH_3)_3SnN(SO_2CF_3)_2$ (**8**)	1	0.84	61.6	64.2	115	−78.5	240.2	10.8
	CH_2Cl_2	0.81	61.8	64.4	115.2	−78.8	251	
	CH_3CN	0.82	67.1	70.2	120.1	−78.9	44.6	206.4
	$(CD_3)_2SO$	0.48	67.4[d]	69.0[d]	119.0	−78.6	37.4	213.6
	Py	0.23	66.7[d]	68.5[d]	118.4	−78.6	−12.3	263.3
	HMPA	0.49	67.4	68.6	118.6	−78.8	−30.8	281.1
$(C_4H_9)_3SnN(SO_2CF_3)_2$ (**9**)	1	0.89 (t, 3H) 1.2–2.0 (m, 6H)				−78.5	242.3	9.4
	CH_2Cl_2	0.88 (t, 3H) 1.1–2.0 (m, 6H)				−78.7	251.7	
	CH_3CN	0.92 (t, 3H) 1.0–1.8 (m, 6H)				−79.5	46.4	205.3
	$(CD_3)_2SO$	0.89 (t, 3H) 1.0–1.8 (m, 6H)				−78.8	13.2	238.5
	Py	0.17 (t, 3H) 0.5–1.0 (m, 6H)				−78.8	−19.4	271.1
	HMPA	0.42 (t, 3H) 0.4–1.2 (m, 6H)				−78.9	−39.8	291.5

[a] 1 = Saturated solution ($R = CH_3$)/neat liquid; Py = pyridine; HMPA = hexamethylphosphoramide. [b] Reference 35. [c] δ(^{119}Sn) in DCM − δ(^{119}Sn) in other solvent. [d] Calculated from center of unresolved ^{119}Sn, ^{117}Sn satellites ($|J_{obsd}| \times 1.023$).[36]

Table 2. ^{13}C NMR Spectral Data for R_3SnX ($R = CH_3, C_4H_9$; $X = N(SO_2CF_3)_2$)

		δ(^{13}C)(R)				^nJ(^{119}Sn–^{13}C)						
						$n = 1$						
compound	solvent[a]	C1	C2	C3	C4	^{117}Sn	^{119}Sn	$n = 2$	$n = 3$	δ(CF_3)	$^1J_{CF}$, Hz	θ(CH_3–Sn–CH_3),[b] deg
$(CH_3)_3SnN(SO_2CF_3)_2$ (**8**)	1	2.1				394.1	412.6			118.7	320.4	113
	CH_2Cl_2	0.8				395.2	414.8			118.1	319.8	113
	CH_3CN	−1.7				467.6	489.5			119.4	320.7	119.7
	$(CD_3)_2SO$	0.7				499.0	512.2			120.0	321.7	121.6
	Py	−2.2				498.5	510.0			199.9	322.1	121.5
	HMPA	1.1				527.7	551.8			119.2	321.7	125.2
$(C_4H_9)SnN(SO_2CF_3)_2$ (**9**)	1	21.9	27.1	26.6	13.1	330.8	347.0	28.1	78.1	118.9	320.7	
	CH_2Cl_2	22.1	27.2	26.5	13.1	331.2	349.6	28.2	78.0	119.1	320.9	
	CH_3CN	18.1	27.0	25.8	12.3	405.2	423.7	29.5	73.6	119.4	321.1	
	$(CD_3)_2SO$	19.3	27.3	26.2	13.1	445.1	465.2	30.9	75.9	119.1	322.0	
	Py	17.3	27.2	25.9	12.3	440.3	461.6	28.7	82.5	119.8	322.1	
	HMPA	19.5	27.5	26.6	12.9	471.0	493.2	28.2	87.8	119.7	321.6	

[a] 1 = Saturated solution ($R = CH_3$)/neat liquid; Py = pyridine; HMPA = hexamethylphosphoramide. [b] Reference 35.

The ^{119}Sn NMR spectra of the parent compounds **8**–**11** (Table 1) show only a single broad peak due to quadrupolar broadening by nitrogen. Unlike the ^{119}Sn NMR data reported earlier for cationic trialkyltin(IV) compounds,[29] in no case is an additional peak observed due to hydrolysis. The position of the peaks in highly concentrated trimethyl and neat tri-*n*-butyltin derivatives (~240 ppm) shows a downfield shift of ~10 ppm upon dilution with dichloromethane which may be ascribed to the breakdown of intermolecular association upon solvation. These chemical shift values fall well below the range suggested for tetracoordinated organotin compounds,[31,32] i.e., +200 to −60 ppm measured with respect to tetramethyltin. The chemical shifts of compounds lying below 250 ppm, therefore, reflect the tricoordinate nature of these organotin species as observed previously.[27,29,30] In CH_2Cl_2, the ^{119}Sn chemical shift of $(CH_3)_3SnN(SO_2CF_3)_2$ is about 6 ppm lower than for $(CH_3)_3SnClO_4$,[29] but for the corresponding $(C_4H_9)_3Sn$ derivatives, this difference is ~30 ppm.[30] The ^{119}Sn chemical shift can, therefore, be used to estimate the relative coordinating ability of the anions to the trialkyltin(IV) moiety to be in the following order:[33]

$B(C_6F_5)_3H < N(SO_2F)_2 \approx N(SO_2CF_3)_2 < ClO_4 < SO_3CF_3 \approx BF_4 < Cl$. When δ(^{119}Sn) of $(CH_3)_3SnN(SO_2CF_3)_2$ is compared to δ(^{119}Sn) of $(CH_3)_3SnNEt_2$, the former resonates about 200 ppm lower than the latter.[34] This difference in chemical shift may be explained on the basis of the electronegativity difference of the two ligands and the low availability of the nitrogen lone pair for Sn–N pπ–dπ bonding in **8** (i.e. the electron pair is highly delocalized over the O_2–S–N–S–O_2 π-framework).

When the ^{119}Sn NMR spectrum of **8** or **9** is recorded in donor solvents, there is a drastic upfield shift of the signal (Figure 1). The magnitude of this shift from the resonance value in dichloromethane, Δ(^{119}Sn), lies in the range 200 to 300 ppm (Table 1) and is a function of the donicity of the solvent, which is: hexamethylphosphoramide (HMPA) > pyridine (Py) > dimethyl sulfoxide (DMSO-d_6) > acetonitrile (AN) ≫ dichloromethane (DCM).

The ^{19}F NMR spectra of compounds **8**–**10** in a variety of solvents lie in the −78.5 to −79.5 ppm region which is characteristic of ionic $N(SO_2CF_3)_2$ derivatives.[6] The change in δ(^{19}F) upon solvolysis in donor solvents is much less than 1 ppm whereas, in the case of corresponding $N(SO_2F)_2$ derivatives, this change is about 3 ppm. This suggests that the fluorine atoms of CF_3 groups are less sensitive to the change in electron density around nitrogen when compared to that of the –SF group in $N(SO_2F)_2$.

The ^{1}H and ^{13}C NMR spectral data (Table 1 and 2) are also quite informative for the structural investigation of organotin compounds. The ^2J(^{119}Sn–^{1}H) values for **8** in concentrated (saturated solution in a 1:1 mixture of $CDCl_3$ and CH_2Cl_2) and

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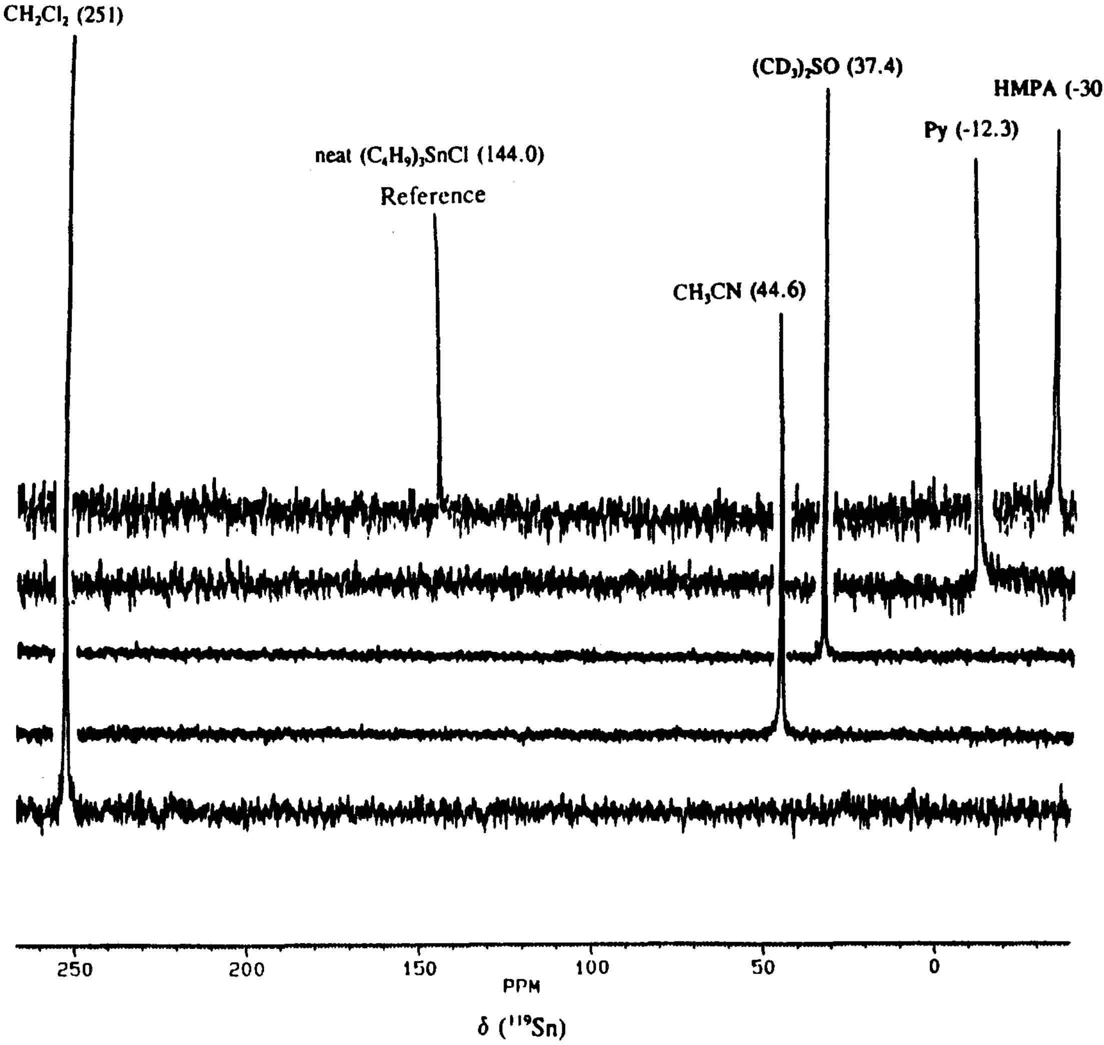

Figure 1. Effect of solvent nucleophilicity on the ^{119}Sn chemical shift of $(CH_3)_3SnN(SO_2CF_3)_2$. Py = pyridine, and HMPA = hexamethylphosphoramide.

CH_2Cl_2 solutions are 64.2 and 64.4 Hz, respectively. In donor solvents, this value increases to ~70 Hz due to an increase in the s-orbital contribution to the tin bonding orbitals. The geometry around the tin nucleus can be determined by estimating the average CH_3–Sn–CH_3 angles by employing Lockhart's equation,[35,36] i.e.,

$$\theta = 0.0161|^2J(^{119}\text{Sn}-^{1}\text{H})|^2 - 1.32|^2J(^{119}\text{Sn}-^{1}\text{H})| + 133.4 \quad (1)$$

The angles estimated by substituting the $^2J(^{119}\text{Sn}-^1\text{H})$ values into eq 1 are ~115° as the neat compounds or in solvents of low nucleophilicity which indicates a highly flattened tetrahedral geometry at tin possibly caused by elongation of the Sn–N bond. In donor solvents, these angles increase to ~120°, suggesting a planar $(CH_3)_3Sn$ arrangement due to orbital rehybridization to form a trigonal bipyramidal (TBP) structure with two donor molecules occupying the axial positions. The $^1J(^{119}\text{Sn}-^{13}\text{C})$ couplings obtained from ^{13}C NMR provide a better estimation of the environment around tin. If the Fermi contact term is regarded as a major contributor, the ^1J coupling constant is very sensitive to the s-electron character in the Sn–C bond. For compounds **8**–**10** the ^1J values are 414, 347, and 688 Hz, respectively, whereas an increase in these values by 100–150 Hz is observed in donor solvents. The CH_3–Sn–CH_3 angle can also be correlated to the $^1J(^{119}\text{Sn}-^{13}\text{C})$ values using[35]

$$|^1J(^{119}\text{Sn}-^{13}\text{C})| = 11.4\theta - 875 \quad (2)$$

The angles calculated for **8** are 113°, while in donor solvents these lie ~120° complementing the earlier results from eq 1. The proposed trans-TBP geometry (donor molecules situated along the axial positions) for solvated trialkyltin cations is supported from conductance and Mössbauer data.[27]

The mass spectral data for the organotin derivatives show a 10-line pattern for the $(M^+ - R)$ peaks as the highest fragment with the exception of $(CH_3)_3SnN(SO_2CF_3)_2$ for which a weak $M^+ + 1$ peak is observed. In the case of the butyl derivative, the appearance of a peak (^{120}Sn isotope) at *m/e* 233 is assigned to $C_4H_9Sn(H)CH_2CH_2CH{=}CH_2$ which is probably formed by the loss of butane *via* a hydride transfer mechanism.

Reaction of **1** with ClF results in the formation of $ClN(SO_2CF_3)_2$ (**13**) contaminated with traces of CF_3SO_2Cl. This method provides an alternate route for the preparation of the *N*-chloro derivative which was first prepared by the reaction of $HN(SO_2CF_3)_2$ with ClF and avoids manipulation of HF during the workup of the product.[6] Addition of **13** to fluoroolefins is not as straightforward as with **3**. Additions with **13** are accomplished either at room temperature or at 65–70 °C. With olefins such as $CHF{=}CH_2$, $CHF{=}CF_2$, $CH_2{=}CF_2$, and $CF_2{=}CF_2$ and ClCN, the addition reaction is regioselective. However, in the case of $CF_3CH{=}CH_2$, $\overline{CF_2CF_2CF_2CF_2N}CF{=}CF_2$, and $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$, the addition takes place bidirectionally as two isomers are easily identified by NMR. A recent study has shown that the addition of some electrophilic reagents to

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perfluorovinylamines takes place bidirectionally.[37,38] The addition reactions of **13** probably take place via a three-centered carbocationic intermediate controlled by electronic factors. A radical mechanism can be ruled out due to the instability of the $N(SO_2CF_3)_2$ radical.

The partial positive nature of chlorine in **13** is revealed by the electrophilic substitution of the chlorine atom in trialkylsilyl/stannyl chlorides. The products obtained from these reactions, after removing the solvent (CCl_4 or $CFCl_3$) and Cl_2, are identified as **8**, **9**, and **11** which are also obtained by the silver salt metathesis discussed above. These reactions are analogous to the previously reported reaction between $ClN(SO_2F)_2$ and $(CH_3)_3SnCl$.[39] However, reaction of **13** with $(C_6H_5)_3SnCl$ gives a complicated mixture of products probably due to attack of the chloronium ion on the aromatic ring. The addition of **13** to a slight excess of $(CH_3)_3SnCF{=}CF_2$ results in electrophilic substitution rather than addition to yield compound **8** and $CF_2{=}CFCl$ quantitatively. Similarly, the S–Cl bond in $CFCl_2S(O)Cl$ is substituted by the $N(SO_2CF_3)_2$ group with concomitant evolution of chlorine. The ^{19}F NMR spectrum of $CFCl_2S(O)N(SO_2CF_3)_2$ contains a doublet assigned to the fluorine atoms in $N(SO_2CF_3)_2$ while a septet is seen for the $CFCl_2$ fluorine atom arising from long range coupling ($^6J_{FF}$ = 7.5 Hz).

Conclusion

This paper describes the electrophilic addition and substitution reactions of $HN(SO_2CF_3)_2$ and its *N*-chloro derivative. Multinuclear NMR studies reveal that the organosilyl/stannyl bis((trifluoromethyl)sulfonyl)amides constitute a class of compounds with a highly electron deficient metal center which makes these derivatives strong candidates as reagents for organic synthesis. The chemical shifts of the organotin derivatives are among the lowest observed to date and are found at ~251 ppm in CH_2Cl_2. Due to the weak nucleophilicity of the $N(SO_2CF_3)_2$ group, the fluoroalkyl bis((trifluoromethyl)sulfonyl)amide derivatives obtained by electrophilic addition of $HN(SO_2CF_3)_2$ or $ClN(SO_2CF_3)_2$ to fluoroalkenes have good potential for transfer of the fluoroalkyl group, an area of study that is currently being persued in our laboratories.

Experimental Section

Lithium bis((trifluoromethyl)sulfonyl)amide, $\overline{CF_2CF_2CF_2CF_2N}$-$CF{=}CF_2$, $\overline{CF_2CF_2OCF_2CF_2N}CF{=}CF_2$, and $S_2O_6F_2$ were received as gifts from Dr. Fred Behr (3M Co.), Dr. T. Abe (Government Industrial Research Institute, Nagoya, Japan), and Prof. F. Aubke (UBC, Canada), respectively, and used as received. ClF (Ozark Mahoning Atochem North America), $CH_2{=}CHF$ and $CH_2{=}CF_2$ (Japan Halon), $CF_2{=}CHF$ (PCR Inc.), H_2SO_4 (J. T. Baker Inc.), R_3SnCl (R = CH_3, C_4H_9, and C_6H_5), and $(CH_3)_3SiCl$ (Aldrich) were purchased and used as received. $CFCl_2SOCl$ is prepared as reported in the literature.[40] Volatile reactants and products are handled in a conventional Pyrex vacuum line equipped with a Heise Bourdon tube and Televac thermocouple guages. Standard *PVT* techniques or direct weighing are used to quantitate reactants and products. Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR spectrometer with a 10-cm glass cell equipped with AgCl windows (volatile products) or as a neat film between AgCl disks (nonvolatile liquids/solids). ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{119}Sn NMR spectra are obtained on a Bruker AC300 FT-NMR spectrometer operating at 300.31 (^1H), 75.469 (^{13}C), 282.41 (^{19}F), and 111.92 (^{119}Sn) MHz, respectively, using a ~1-mm sealed capillary filled with DMSO-d_6 for locking in the case of nondeuterated solvents. After the ^1H, ^{13}C and ^{19}F NMR spectra of a compound are recorded, another sealed capillary filled with neat tributyltin chloride is inserted into the 5 mm NMR tube and the ^{119}Sn NMR recorded. Chemical shifts are referenced to $(CH_3)_4Si$ (^1H, ^{29}Si), $CFCl_3$ (^{19}F) and neat $(C_4H_9)_3SnCl$ (^{119}Sn, 144 ppm[31]). The ^{13}C NMR chemical shifts are determined relative to the solvent signal, i.e. dimethyl-d_6 sulfoxide (39.6 ppm), $CDCl_3$ (77.0 ppm), HMPA (36.0 ppm). Chemical shifts for the tributyltin(IV) derivatives are assigned on the basis of the known relation $^1J(^{119}Sn–^{13}C) \gg {}^3J(^{119}Sn–^{13}C) > {}^2J(^{119}Sn–^{13}C)$.[41] Mass spectra are obtained on a Varian VG 7070 HS mass spectrometer. Peaks reported correspond to ^{35}Cl and ^{120}Sn isotopes. Elemental analyses are performed by Beller Microanalytisches Laboratorium, Göttingen, Germany. Since the reactants and products are highly moisture sensitive, all reactions and sample preparation are performed with the strict exclusion of moisture.

Reaction of $LiN(SO_2CF_3)_2$ with $S_2O_6F_2$. $LiN(SO_2CF_3)_2$ **1** (2.3 mmol) is placed in a 100-mL Pyrex reactor fitted with a Teflon stem valve and evacuated at –196 °C for several hours. $S_2O_6F_2$ (3 mmol) is then transferred under vacuum. The reaction mixture is slowly warmed to 25 °C and stirred for about 2 h. The products are separated by trap-to-trap distillation.

Properties of $FSO_2ON(SO_2CF_3)_2$ (2). Compound **2** is isolated as a colorless liquid in 87% yield in a trap cooled to –30 °C having passed through a trap at –10 °C. Spectral data are as follows. IR (gas) (cm^{-1}): 1500 vs, 1473 s, 1248 vs, 1132 s, 1029 m, 879 s, 851 vs, 797 m, 755 vs. ^{19}F NMR [$F^ASO_2ON(SO_2CF_3{}^B)_2$]: δ 47.8 (A, s), –68.9 (B, s). MS CI [*m/e* (species) intensity]: 310 ($M^+ - CF_3$) 1.7; 296 ($ON(SO_2CF_3)_2{}^+$) 2.7; 282 ($HN(SO_2CF_3)_2{}^+ + 1$) 53.1; 212 ($CF_3SO_2NSO_2H^+$) 2.6; 150 ($CF_3SO_2NH_2{}^+ + 1$) 10; 133 ($CF_3SO_2{}^+$) 28.1; 69 ($CF_3{}^+$) 100.

Preparation of $HN(SO_2CF_3)_2$. Into a 50-mL vacuum sublimator is added ~5 g of anhydrous **1** followed by 25 mL of H_2SO_4 (~98%). The solution is heated with stirring in an oil bath at 70 °C and $HN(SO_2CF_3)_2$ collects in the cooler parts of the sublimator (80–93% yield) as a white crystalline solid. It is resublimed twice under dynamic vacuum at 60–65 °C and characterized by its melting point and spectral data.[6]

Insertion reactions of 3 with fluoroolefins. Preparation of $CH_3CHFN(SO_2CF_3)_2$ (4), $CH_3CF_2N(SO_2CF_3)_2$ (5), and $CH_2FCF_2N(SO_2CF_3)_2$ (6). In a drybox, $HN(SO_2CF_3)_2$ (4.8–6 mmol) is loaded into a 75-mL Pyrex reaction vessel fitted with a Kontes Teflon needle valve. The reaction vessel is then evacuated at –196 °C, and ~10% excess of the required fluoroolefin [$CH_2{=}CHF$ (A), $CH_2{=}CF_2$ (B), or $CHF{=}CF_2$ (C)] is introduced. The reaction mixture is warmed to 25 °C , heated to 45–50 °C for about 1 h, and allowed to remain at 25 °C overnight (A), heated at ~80 °C for about 36 h (B), or heated at ~120 °C for 72 h (C).

Properties of $CH_3CHFN(SO_2CF_3)_2$ (4). Compound **4** is isolated as a colorless liquid in 34% yield in a trap cooled to –20 °C following trap-to-trap distillation of the viscous brownish reaction mixture which leaves behind a brownish-black unidentified polymeric residue. Spectral data obtained for **4** are as follows. IR (neat liquid/AgCl) (cm^{-1}): 1446 vs, 1426 s, 1387 ms, 1348 ms, 1230 vs, br, 1156 s, 1127 vs, br, 1079 vs, 956 s, 904 ms, 875 s, 797 w, 776 w, 745 w, 687 ms, 618 vs, 594 s, 584 s, 530 m, 506 ms, 486 m, 463 m. NMR [$CH_3{}^ACH^BF^CN(SO_2CF_3{}^D)_2$]: ^1H, δ 6.33 (B, dq), 1.92 (A, dd); ^{19}F, δ –72.9 (D, d), –129.9 (C, br s). J_{AB} = 6.2 Hz, J_{AC} = 13.8 Hz, J_{BC} = 44.4 Hz, J_{CD} = 4.8 Hz. MS CI [*m/e* (species) intensity]: 328 ($M^+ + 1$) 1.0; 308 ($M^+ - F$) 4.1; 296 ($CH_3N(SO_2CF_3)_2{}^+ + 1$) 7.1; 282 ($HN(SO_2CF_3)_2{}^+ + 1$) 89.7; 244 ($M^+ - CH_2CF_3$) 16.5; 212 ($N(SO_2)SO_2CF_3{}^+ + 1$) 2.9; 173 ($FCN(SO_2)_2{}^+$) 16.8; 133 ($CF_3SO_2{}^+$) 10.9; 69 ($CF_3{}^+$) 100.

Properties of $CH_3CF_2N(SO_2CF_3)_2$ (5). Compound **5** is isolated as a highly moisture sensitive, colorless liquid in 82% yield in a trap cooled to –20 °C, having passed a trap at 0 °C. Spectral data obtained for **5** are as follows. IR (neat liquid/AgCl) (cm^{-1}): 1456 vs, 1430 vs, 1400 s, 1333 m, 1225 vs, vbr, 1180 sh, 1124 vs, br, 1065 w, 975 s, 960 s, 914 ms, 884 s, 836 m, 771 w, 746 vw, 686 m, 619 vs, 600 s, 573 vs, 515 vs. NMR [$CH_3{}^ACF_2{}^BN(SO_2CF_3{}^C)_2$]: ^1H, δ 2.23 (A, t); ^{19}F, δ –59.6 (B, br s), –71.1 (C, t). J_{AB} = 16.7 Hz, J_{BC} = 6.8 Hz. MS CI [*m/e* (species) intensity]: 346 ($M^+ + 1$) 1.2; 311 ($M^+ - F - CH_3$) 2.9; 296 ($CH_3N(SO_2CF_3)_2{}^+ + 1$) 6.5; 282 ($HN(SO_2CF_3)_2{}^+ + 1$) 95.3; 262 ($M^+ - CH_3CF_3 + 1$) 2.6; 213 ($M^+ - CF_3SO_2 + 1$) 1.3; 194 ($M^+ - F - CF_3SO_2 + 1$) 9.1; 150 ($H_2NSO_2CF_3{}^+ + 1$) 7.9; 147 ($NSO_2CF_3{}^+$) 4.7; 133 ($CF_3SO_2{}^+$) 8.8; 69 ($CF_3{}^+$) 63.1; 65 ($CH_3CF_2{}^+$) 100. Anal. Calcd for $C_4H_3F_8NO_4S_2$: C, 13.9; H, 0.90; N, 4.06; F, 44.1. Found: C, 13.79; H, 0.87; N, 4.06; F, 43.2.

Properties of $CH_2FCF_2N(SO_2CF_3)_2$ (6). Compound **6** is isolated as a colorless liquid in 68% yield in a trap cooled to –20 °C after trap-to-trap distillation of the reaction mixture. Spectral data obtained for **6** are as follows. IR (neat liquid/AgCl) (cm^{-1}): 1456 vs, 1436 s, 1410 sh, 1332 w, 1296 sh, 1284 ms, 1233 vs, vbr, 1177 m, 1122 vs, br, 1051 m, 975 ms,

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876 s, 787 w, 771 w, 684 m, 645 s, 611 s, 585 s, 574 s, 514 s. NMR [$CH_2{}^AF^BCF_2{}^CN(SO_2CF_3{}^D)_2$]: ^{1}H, δ 4.89 (A, dt); ^{19}F, δ −70.4 (D, dt), −77.6 (C, br s), −231.3 (B, 41 lines, ttsept). J_{AB} = 45.4 Hz, J_{AC} = 11.3 Hz, J_{BC} = 18.6 Hz, J_{BD} = 3.8 Hz, J_{CD} = 12.3 Hz. MS CI [*m/e* (species) intensity]: 364 (M^+ + 1) 12.8; 296 ($M^+ - CF_3$ + 2) 3.1; 282 ($HN(SO_2CF_3)_2{}^+$ + 1) 75.1; 226 ($M^+ - C_2F_6$ + 1) 2.6; 212 ($M^+ - F - CF_3SO_2$ + 1) 15.9; 150 ($H_2NSO_2CF_3{}^+$ + 1) 9.4; 133 ($CF_3SO_2{}^+$) 15.8; 83 ($CH_2FCF_2{}^+$) 35.1; 69 ($CF_3{}^+$) 100. Anal. Calcd for $C_4H_2F_9NO_4S_2$: C, 13.2; H, 0.55; F, 47.1. Found: C, 12.67; H, 0.71; F, 45.9.

Reaction of 5 with CsF. Dry CsF (1.5 mmol) is loaded into a modified reaction vessel fitted with a Kontes Teflon stopcock and a B-10 joint side arm fitted with a rubber septum and evacuated for several hours, first at 25 °C and then at −196 °C. Compound **5** (1.2 mmol) is injected into the reaction vessel under a positive dry nitrogen atmosphere. After evacuating the vessel, the mixture is allowed to warm slowly to 25 °C. Following trap-to-trap distillation, a mixture of CF_3SO_2F and CF_3CH_3 in a 6.5:1 ratio is isolated in a trap held at −196 °C. When acetonitrile is used as a solvent in the above reaction, CF_3SO_2F is formed exclusively. The spectral data for CF_3SO_2F[42] and CF_3CH_3[43] are consistent with those reported.

Reaction of 5 with $(CH_3)_3SiN(CH_3)_2$. A catalytic amount of CsF (~0.05 mmol) is loaded into the modified reaction vessel described above and evacuated at −196 °C. Compound **5** (1.5 mmol) is syringed into the reaction vessel *via* the septum. The solution is degassed for about 30 min followed by introduction of $(CH_3)_3SiN(CH_3)_2$ (1.5 mmol) under vacuum. The reaction mixture is stirred and slowly warmed to 25 °C overnight. Upon trap-to-trap distillation, a mixture of CF_3SO_2F and $(CH_3)_3SiF$ is obtained in traps at −80 and −110 °C, leaving behind a yellowish solid. This solid is extracted into diethyl ether and identified as $CH_3C(N(CH_3)_2){=}NSO_2CF_3$ (**7**).

Properties of $CH_3C(N(CH_3)_2){=}NSO_2CF_3$ (7). The spectral data obtained for **7** are as follows. IR (neat solid/KBr) (cm^{-1}): 2952 mw, br, 1592 vs ($\nu_{C=N}$), 1489 vs, 1425 vs, 1403 vs, 1316 vs, 1268 vs, br, 1191 vs, br, 1130 vs, 1019 s, 981 ms, 855 vs, 790 w, 760 ms, 727 s, 642 vs, 592 s, 580 s, 531 ms, 482 m, 428 w. NMR [$CF_3{}^ASO_2N{=}C(CH_3{}^B)N(CH_3{}^C)CH_3{}^D$]: ^{1}H, δ 3.11 (C, s), 3.07 (D, s), 2.4 (B, s); ^{19}F, δ −79.7 (A, s). MS CI [*m/e* (species) intensity]: 219 (M^+ + 1) 100; 149 ($H_2NSO_2CF_3{}^+$) 22.9; 133 ($CF_3SO_2{}^+$) 17.7; 85 ($M^+ - CF_3SO_2$) 12.1; 69 ($CF_3{}^+$) 7.2.

Preparation of $AgN(SO_2CF_3)_2$. A slight excess of Ag_2CO_3 (~12 mmol) is added, with stirring, to a solution of $HN(SO_2CF_3)_2$ (20 mmol) in 40 mL of distilled water in a 100-mL beaker wrapped with aluminum foil. The reaction mixture is heated to ~65 °C, filtered, and concentrated to about 10 mL. A white solid is isolated upon removing excess water under vacuum and is dried at ~80 °C for 6 h. This compound is dissolved in about 50 mL of dry diethyl ether, stirred for ~2 h, and filtered to remove solid impurities, if any. Removal of the solvent under vacuum gives $AgN(SO_2CF_3)_2$ as a fine white powder in 79% yield. Spectral data of $AgN(SO_2CF_3)_2$ are as follows. IR (neat solid/AgCl) (cm^{-1}): 1338 vs, 1213 vs, 1140 vs, 1058 s, 972 s, 798 s, 771 m, 742 s, 647 vs, 587 s, 579 vs, 567 s, 516 vs. NMR [$AgN(SO_2CF_3)_2$]: ^{19}F, δ −78.7 (s). Anal. Calcd for $C_2F_6S_2O_4Ag$: Ag, 27.97. Found: Ag, 28.21.

Reaction of $AgN(SO_2CF_3)_2$ with R_3MCl (M = Sn, R = CH_3, *n*-C_4H_9, and C_6H_5; M = Si, R = CH_3). In a typical preparation, a solution of R_3MCl (~4 mmol) in CH_2Cl_2 is transferred using standard techniques into a Schlenk flask protected with Al foil and containing a slight excess (~4.2 mmol) of $AgN(SO_2CF_3)_2$ in the same solvent. The mixture is stirred for 10 h. Filtration under a positive nitrogen atmosphere followed by solvent removal under vacuum gives the desired trialkylsilyl/stannyl bis((trifluoromethyl)sulfonyl)amides in essentially quantitative yields.

Properties of $(CH_3)_3SnN(SO_2CF_3)_2$ (8). This compound is isolated as a highly moisture sensitive, low melting (37–38 °C), off-white solid. The spectral data obtained for compound **8** are as follows. IR (neat/AgCl) (cm^{-1}): 1378 vs br, 1337 sh, 1225 sh, 1202 vs, 1137 vs, 1061 vs, 876 ms, 797 ms, 781 sh, 745 m, 646 ms, 608 vs, 575 s, 515 s. MS CI [*m/e* (species) intensity] (tin-containing fragments assigned to ^{120}Sn isotope): 446 (M^+ + 1) 0.4; 430 ($M^+ - (CH_3)$) 7.0; 296 ($CH_3N(SO_2CF_3)_2{}^+$ + 1) 3.9; 282 ($HN(SO_2CF_3)_2{}^+$ + 1) 25.6; 185 ($(CH_3)_2SnOF^+$) 10.33; 169 ($(CH_3)_2SnF^+$) 38.4; 165 ($(CH_3)_3Sn^+$) 100; 139 (SnF^+) 2.9; 135 (CH_3Sn^+) 9.8; 133 ($CF_3SO_2{}^+$) 8.9; 120 (Sn^+) 2.4; 69 ($CF_3{}^+$) 64.1.

Properties of $(C_4H_9)_3SnN(SO_2CF_3)_2$ (9). This compound is isolated as a highly moisture sensitive, evil smelling, colorless viscous liquid which is not distillable under vacuum. The spectral data obtained are as follows. IR (neat/AgCl) (cm^{-1}): 2959 s, 2935 s, 2863 ms, 1467 m, 1418 w, 1380 m, 1347 vs br, 1323 sh, 1267 ms, 1232 sh, 1206 vs, 1129 vs, 1116 vs, 1079 sh, 1060 vs, 963 w, 881 m, 850 vw, 799 m, 768 mw, 744 vs, 706 ms, 680 ms, 652 ms, 615 vs, 571 ms, 509 ms, 456 vw. MS EI [*m/e* (species) intensity] (tin-containing fragments assigned to ^{120}Sn isotope): 514 ($M^+ - C_4H_9$) 100; 400 ($SnN(SO_2CF_3)_2{}^+$) 17.3; 291 ($(C_4H_9)_3Sn^+$) 12.8; 269 ($(C_4H_9)_2SnOF^+$) 3.61; 253 ($(C_4H_9)_2SnF^+$) 37.3; 233 ($C_4H_9Sn(H)CH_2CH_2CH{=}CH_2{}^+$) 4.6; 177 ($C_4H_9Sn^+$) 56.47; 139 ($SnF^+$) 29.3; 133 ($CF_3SO_2{}^+$) 6.1; 121 ($SnH^+$) 24.5; 69 ($CF_3{}^+$) 90.

Properties of $(C_6H_5)_3SnN(SO_2CF_3)_2$ (10). This compound is isolated as a highly moisture sensitive, grayish-white solid. The spectral data obtained for compound **10** are as follows. IR (AgCl/Nujol bands deleted) (cm^{-1}): 1377 s, 1348 sh, 1224 sh, 1203 vs, 1133 s, 1060 s, 998 mw, 796 w, 732 m, 697 mw, 608 mw, 575 mw, 515 w. NMR [$(C_6H_5)_3{}^ASnN(SO_2CF_3{}^B)$]: ^{1}H, δ 7.65, 7.35 (A, m in ratio 2:3); ^{13}C, δ 137.7 (ipso, C_i), 136.1 (ortho, C_o), 130.6 (para, C_p), 128.8 (meta, C_m), 118.5 (B, quart), $^1J(^{119}Sn{-}^{13}C_i)$ = 688 Hz, $^1J(^{117}Sn{-}^{13}C_i)$ = 659.1 Hz, $^2J(^{119}Sn{-}C_o)$ = 51.4; $^3J(^{119}Sn{-}^{13}C_m)$ = 72.3 Hz, $^4J(^{119}Sn{-}^{13}C_p)$ = 15.3 Hz, $J(^{19}F{-}^{13}C)$ = 321.4 Hz; ^{19}F, δ −78.02; ^{119}Sn, δ −79.23. MS CI [*m/e* (species) intensity] (tin containing fragments assigned to ^{120}Sn isotope): 554 ($M^+ - C_6H_5$) 54.6; 400 ($SnN(SO_2CF_3)_2{}^+$) 1.4; 351 ($(C_6H_5)_3Sn^+$) 100; 309 ($(C_6H_5)_2SnOF^+$) 12.5; 293 ($(C_6H_5)_2SnF^+$) 23.9; 282 ($HN(SO_2CF_3)_2{}^+$ + 1) 6.4; 274 ($(C_6H_5)_2Sn^+$) 2.7; 197 ($C_6H_5Sn^+$) 14.7; 154 ($(C_6H_5)_2{}^+$) 35.7; 139 (SnF^+) 6.3; 133 ($CF_3SO_2{}^+$) 3.9; 120 (Sn^+) 11.2; 69 ($CF_3{}^+$) 58.7. Anal. Calcd for $C_{20}H_{15}F_9NO_4S_2Sn$: C, 38.12; H, 2.4; F, 18.1. Found: C, 38.52; H, 2.68; F, 17.8.

Properties of $(CH_3)_3SiN(SO_2CF_3)_2$ (11). Spectral data of $(CH_3)_3SiN(SO_2CF_3)_2$ agree with the literature.[6] The ^{13}C and ^{29}Si NMR data are not reported and are as follows. ^{13}C NMR: δ −0.08 (CH_3, s), 118.7 (CF_3, q). J_{CF} = 320.5 Hz. ^{29}Si NMR: δ 55.9.

Preparation of $CF_2{=}CFSn(CH_3)_3$ (12). The preparation of perfluorovinyltin(IV) compounds by employing Grignard synthesis is reported[44] but a different synthetic approach is described here. Trimethyltin(IV) chloride (5 mmol) is loaded in a 50-mL reaction flask fitted with a Kontes Teflon stopcock followed by injection of hexaethylphosphorus triamide (5.1 mmol) and ~15 mL of benzonitrile. The reaction mixture is degassed at −196 °C, and $CF_2{=}CFBr$ (~6.5 mmol) is then condensed *via* vacuum. After the mixture is warmed to 25 °C, the reactants are stirred for ~12 h followed by trap-to-trap distillation. $CF_2{=}CFSn(CH_3)_3$ is obtained as a colorless liquid in 89% yield in a trap held at -100 °C, having passed a trap at −40 °C. Spectral data obtained are as follows: IR (cm^{-1}) (gas): 3058 vw, 2997 mw, 2931 m, 1719 vs ($\nu_{C=C}$), 1280 s, 1210 mw, 1121 ms, 1008 ms, 782 m, 725 mw, 540 m, 513 sh. NMR [$C(F)^AF^B{=}CF^CSn^D(CH_3{}^E)_3$]: ^{1}H, δ 0.23 (E, s). $^2J(^{117}Sn{-}^1H)$ = 57.1 Hz, $^2J(^{119}Sn{-}^1H)$ = 59.6 Hz; ^{119}Sn, δ − 30.5 (D, d); ^{19}F, δ −88.2 (B, dd), −122.9 (A, dd), −194.4 (C, dd). $^3J_{BC}$ = 116 Hz, $^3J_{AC}$ = 25.9 Hz, $^2J_{AB}$ = 75 Hz, $^2J(^{117}Sn{-}^{19}F_C)$ = 159.7 Hz, $^2J(^{119}Sn{-}^{19}F_C)$ = 167.9 Hz, $^3J(^{119}Sn{-}^{19}F_D)$ = 11.4 Hz, $^3J(^{119}Sn{-}^{19}F_A)$ = 23.9 Hz.

Reaction of $LiN(SO_2CF_3)_2$ with ClF. The preparation of $ClN(SO_2CF_3)_2$ by reacting $HN(SO_2CF_3)_2$ with ClF is described earlier.[6] An alternative preparation of $ClN(SO_2CF_3)_2$ (**13**) from $LiN(SO_2CF_3)_2$ is described here. $LiN(SO_2CF_3)_2$ (2.3 mmol) is loaded into a passivated 25-mL stainless steel vessel and evacuated at −196 °C for several hours. ClF (6.3 mmol) is transferred into the reaction bomb *via* vacuum. The vessel is then allowed to warm slowly to 25 °C in an empty liquid nitrogen dewar over a period of 17 h. The reaction mixture is then fractionated by trap-to-trap distillation. Compound **13** is isolated as a pale yellowish liquid along with traces of CF_3SO_2Cl in a trap held at -40 °C having passed the trap at −10 °C. Repeated trap-to-trap distillations gives $ClN(SO_2CF_3)_2$ as a colorless liquid in 61% yield. The spectral data are in agreement to that reported earlier.[6]

Reaction of 13 with $CF_2{=}CFSn(CH_3)_3$. In a reaction vessel equipped with a Kontes Teflon stopcock, 2.1 mmol of **13** was transferred followed by 2.12 mmol of $CF_2{=}CFSn(CH_3)_3$ at −196 °C under vacuum. The reaction mixture is allowed to warm to 25 °C over a period of ~12 h with stirring. Separation of the reaction products by trap-to-trap distillation results in the isolation of $CF_2{=}CFCl$ essentially quantitatively in a trap at −196 °C, having passed a trap at −100 °C. A quantitative yield of

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(42) The ^{19}F NMR chemical shifts of an authentic sample of CF_3SO_2F supplied by the 3M Co. are at δ 38.3 (SF, q) and −72.4 (CF_3, d), J_{FF} = 18.15 Hz.

(43) *Proton and Fluorine Nuclear Magnetic Resonance Spectral Data*; Japan Halon Company Ltd.: Tokyo, 1988; spectra 12 and 13.

(44) Kaesz, H. D.; Stafford, S. L.; Stone, F. G. *J. Am. Chem. Soc.* **1960**, *82*, 6232.

8 is obtained in the reaction flask as a nonvolatile gellike solid. The ^{119}Sn NMR of the product shows a peak at 238 ppm which supports the formation of **8**. The other spectral properties are similar to those listed earlier.

Insertion Reactions of 13 with Fluoroolefins. In a typical reaction, a slight excess of the fluoroolefin (~4.5 mmol) is added to pure $\mathrm{ClN(SO_2CF_3)_2}$ (~4 mmol) contained in a 40-mL Pyrex reaction tube fitted with a ChemGlass Teflon needle valve at −196 °C. The reaction mixture is slowly allowed to warm to 25 °C and then heated to 65–70 °C for 12–21 h. The products are separated by trap-to-trap distillation.

Properties of $\mathrm{CH_2ClCHFN(SO_2CF_3)_2}$ (14). This compound is isolated as a colorless liquid in 73% yield in a trap held at −20 °C when $\mathrm{CH_2{=}CHF}$ is used as the olefin. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 3029 w, 2986 vw, 1451 s, 1421 s, 1391 ms, 1341 ms, 1298 mw, 1225 vs br, 1152 s, 1123 vs br, 1080 vs, 972 m, 953 s, 891 s, 794 w, 767 w, 725 w, 685 ms, 620 vs, 597 s, 582 m, 483 mw. NMR [$\mathrm{CH_2{}^AClCH^BF^CN(SO_2CF_3{}^D)_2}$]: ^{1}H, δ 6.23 (B, dt), 4.1 (A, m); ^{19}F, δ −71.7 (D, d), −137.6 (C, br s). J_{AB} = 6.4 Hz, J_{AC} = 43.6 Hz, J_{CD} = 5.2 Hz. MS CI [*m/e* (species) intensity]: 362 ($\mathrm{M^+}$ + 1) 0.8; 342 ($\mathrm{M^+ - F}$) 1.6; 296 ($\mathrm{M^+ - CH_2ClO}$) 8.7; 282 ($\mathrm{H_2N(SO_2CF_3)_2{}^+}$) 53.0; 272 ($\mathrm{M^+ - CF_4 - H}$) 15.0; 149 ($\mathrm{H_2NSO_2CF_3{}^+}$) 6.1; 133 ($\mathrm{CF_3SO_2{}^+}$) 32.6; 81 ($\mathrm{CH_2ClCHF^+}$) 29.4; 69 ($\mathrm{CF_3{}^+}$) 100.

Properties of $\mathrm{CHFClCF_2N(SO_2CF_3)_2}$ (15). This compound is isolated as a colorless liquid in 66% yield in a trap held at −20 °C using $\mathrm{CHF{=}CF_2}$ as the olefin. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1457 s, 1437 m, 1406 vs, 1370 vs, 1327 s, 1232 vs, 1132 vs, 1082 vs, 901 vs, 856 s, 822 m, 802 m, 788 s, 770 w, 732 s, 704 s, 646 s, 600 vs, 572 vs, 485 s. NMR [$\mathrm{CH^AF^BClCF_2{}^CN(SO_2CF_3{}^D)_2}$]: ^{1}H, δ 6.31 (A, dm); ^{19}F, δ −69.6 (C, br), −72.9 (D, s), −154.5 (B, dm). J_{AB} = 47.1 Hz. MS CI [*m/e* (species) intensity]: 398 ($\mathrm{M^+}$ + 1) 28.1; 328 ($\mathrm{M^+ - CF_3}$) 2.9; 282 ($\mathrm{H_2N(SO_2CF_3)_2{}^+}$) 13.9; 264 ($\mathrm{M^+ - CF_3SO_2}$) 0.8; 246 ($\mathrm{CF_3SO_2NCF_2CHCl^+}$ + 1) 1.2; 150 ($\mathrm{H_2NSO_2CF_3{}^+}$ + 1) 5.9; 133 ($\mathrm{CF_3SO_2{}^+}$) 11.7; 119 ($\mathrm{C_2F_5{}^+}$) 23.0; 117 ($\mathrm{CF_2CHFCl^+}$) 82.4; 69 ($\mathrm{CF_3{}^+}$) 100.

Properties of $\mathrm{CH_2ClCF_2N(SO_2CF_3)_2}$ (16). This compound is isolated as a colorless liquid in 64% yield in a trap held at −20 °C using $\mathrm{CH_2{=}CF_2}$ as the olefin. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1456 s, 1429 s, 1401 m, 1368 m, 1338 m, 1325 m, 1225 s, 1127 s, 1048 m, 975 w, 955 m, 881 m, 843 w, 813 w, 790 w, 771 w, 732 s, 744 w, 688 w, 671 w, 643 m, 628 s, 601 s, 572 s, 505 vs, 487 vs, 474 vs, 465 vs. NMR [$\mathrm{CH_2{}^AClCF_2{}^BN(SO_2CF_3{}^C)_2}$]: ^{1}H, δ 4.21 (A, t); ^{19}F, δ −69.6 (B, br), −71.8 (C, t). J_{AB} = 11.29 Hz, J_{BC} = 7.5 Hz. MS CI [*m/e* (species) intensity]: 380 ($\mathrm{M^+}$ + 1) 1.8; 296 ($\mathrm{CH_3N(SO_2CF_3)_2{}^+}$ + 1) 12.9; 282 ($\mathrm{H_2N(SO_2CF_3)_2{}^+}$) 100; 266 ($\mathrm{H_2N(SO_2CF_3)SOCF_3{}^+}$) 2.7; 228 ($\mathrm{M^+ - F - SO_2CF_3}$ + 1) 22.9; 212 ($\mathrm{M^+ - Cl - SO_2CF_3}$ + 1) 4.1; 192 ($\mathrm{M^+ - Cl - F - SO_2CF_3}$) 5.3; 174 ($\mathrm{M^+ - Cl - 2F - SO_2CF_3}$ + 1) 14.6; 150 ($\mathrm{H_2NSO_2CF_3{}^+}$ + 1) 61.9; 133 ($\mathrm{CF_3SO_2{}^+}$) 54.2; 112 ($\mathrm{CHClCF_2N^+}$) 29.8; 99 ($\mathrm{CH_2ClCF_2{}^+}$) 42.6; 69 ($\mathrm{CF_3{}^+}$) 100.

Properties of $\mathrm{CF_2ClCF_2N(SO_2CF_3)_2}$ (17). This compound is isolated as a colorless liquid in 70% yield in a trap held at −20 °C having passed a trap at −5 °C when $\mathrm{CF_2{=}CF_2}$ is the olefin. Spectral data obtained are as follows. IR (gas) (cm^{-1}): 1427 s, 1386 s, 1279 vs, 1242 vs, 1194 m, 1143 s, 1126 s, 1088 vs, 946 s, 800 w, 786 w, 771 w, 730 w, 652 w, 603 m, 574 w, 565 w, 540 vw, 498 w. NMR [$\mathrm{CF_2{}^AClCF_2{}^BN(SO_2CF_3{}^C)_2}$]: ^{19}F, δ −51.1 (B, m), −72.6 (C, m), −77.9 (A, m). MS CI [*m/e* (species) intensity]: 416 ($\mathrm{M^+}$ + 1) 9.3; 350 ($\mathrm{CF_3N(SO_2CF_3)_2{}^+}$ + 1) 49.2; 330 ($\mathrm{CF_2N(SO_2CF_3)_2{}^+}$) 1.1; 280 ($\mathrm{N(SO_2CF_3)_2{}^+}$) 10.3; 150 ($\mathrm{H_2NSO_2CF_3{}^+}$ + 1) 5.0; 133 ($\mathrm{CF_3SO_2{}^+}$) 19.7; 119 ($\mathrm{C_2F_5{}^+}$) 17.31; 69 ($\mathrm{CF_3{}^+}$) 100. Anal. Calcd for $\mathrm{C_4ClF_{10}NO_4S_2}$: C, 11.54; F, 45.8. Found: C, 11.17; F, 47.2.

Properties of $\mathrm{CF_3CHN(SO_2CF_3)_2CH_2Cl}$ (18) and $\mathrm{CF_3CHClCH_2N(SO_2CF_3)_2}$ (19). An inseparable mixture of compounds **18** and **19** in the ratio of 1.2:1 is isolated as a nonvolatile colorless liquid in 84% yield when $\mathrm{CF_3CH{=}CH_2}$ is the olefin. Spectral data obtained for the isomeric mixture are as follows. IR (gas) (cm^{-1}): 3027 vw, 2861 vw, 1457 vs, 1430 s, 1398 s, 1337 s, 1232 vs br, 1196 sh, 1133 vs, 1090 s, 1038 m, 989 m, 952 ms, 887 m, 877 m, 824 s, 791 mw, 769 w, 726 m, 685 vw, 647 mw, 610 vs, 587 m, 572 ms, 507 ms, 450 vw, 402 w. NMR [$\mathrm{CF_3{}^ACH^BN(SO_2CF_3{}^C)_2CH_2{}^DCl}$ and $\mathrm{CF_3{}^ECH^FClCH_2{}^GN(SO_2CF_3{}^H)_2}$] : ^{1}H, 4.93 (B, F, m, 1H), 4.38 (D, G, m, 2H); ^{19}F, two sets of peaks in the ratio of 2:1 are observed at δ −71.6 and −73.4 and δ −74.4 and −78.0, assigned as H and C and as E and A, respectively. MS CI [*m/e* (species) intensity]: 412 ($\mathrm{M^+}$ + 1) 2.3; 341 ($\mathrm{M^+ - CF_3H}$) 0.4; 294 ($\mathrm{M^+ - CF_3CHCl}$) 12.1; 230 ($\mathrm{M^+ - CF_3SO_2CH_2Cl}$ + 1) 29.6; 194 ($\mathrm{CF_3CClNSO_2{}^+}$) 14.1; 131 ($\mathrm{M^+ - N(SO_2CF_3)_2}$) 76.9; 69 ($\mathrm{CF_3{}^+}$) 100. Anal. Calcd for $\mathrm{C_5H_3ClF_9NO_4S_2}$: C, 14.60; H, 0.73; F, 41.6; N, 3.4. Found: C, 14.56; H, 0.79; F, 41.2; N, 3.5.

Properties of $\mathrm{CF_2CF_2CF_2CF_2NCFClCF_2N(SO_2CF_3)_2}$ (20) and $\mathrm{CF_2CF_2CF_2CF_2NCF[N(SO_2CF_3)_2]CF_2Cl}$ (21). A colorless mixture of nonvolatile isomers **20** and **21** in the ratio of 1:1.5 is obtained in 72% yield upon removal of all volatile materials from the reaction of $\mathrm{CF_2CF_2CF_2CF_2NCF{=}CF_2}$ and **13**. The spectral data obtained for the mixture are as follows. IR (neat liquid) (cm^{-1}): 1455 s, 1414 m, 1399 m, 1380 sh, 1342 s, 1227 vs br, 1185 vs, 1131 vs, 1095 ms, 1045 ms, 1015 mw, 974 vs, 947 m, 929 m, 870 ms, 845 m, 786 mw, 778 mw, 769 w, 711 w, 687 vw, 642 m, 611 s, 574 ms, 501 ms.

NMR [$\mathrm{CF_2{}^ACF_2{}^{BC}CF_2{}^{BC}CF_2{}^ANCF^DClCF_2{}^EN(SO_2CF_3{}^F)_2}$ and $\mathrm{CF_2{}^ACF_2{}^{GH}CF_2{}^{GH}CF_2{}^ANCF^I[N(SO_2CF_3{}^J)_2]CF_2{}^KCl}$]: ^{19}F, δ −70.2 to −78.0 (E, F, J, K complex m, 8 F), −83.1 to −97.9 (A, $\mathrm{A_2B_2}$ m, 4 F), −104.3 and −105.7 (D, I, m, 1 F), −128.9 to −138 (BC, GH, AB m, 4 F). J_{BC} = 245 ± 3 Hz. MS CI [*m/e* (species) intensity]: 459 ($\mathrm{M^+ - F - SO_2CF_3}$ + 1) 0.5; 405 ($\mathrm{M^+ - 2F - Cl - SO_2CF_3}$ + 1) 0.9; 330 ($\mathrm{M^+ - N(SO_2CF_3)_2}$) 74.3; 295 ($\mathrm{M^+ - Cl - N(SO_2CF_3)_2}$) 22.6; 282 ($\mathrm{HN(SO_2CF_3)_2{}^+}$ + 1) 9.3; 276 ($\mathrm{C_6F_{10}N^+}$) 34.0; 242 ($\mathrm{C_4F_8NCO^+}$) 26.4; 196 ($\mathrm{C_4F_7N^+}$ + 1) 23.3; 195 ($\mathrm{C_4F_7N^+}$) 12.8; 176 ($\mathrm{C_4F_6N^+}$) 30.4; 150 ($\mathrm{H_2NSO_2CF_3{}^+}$ + 1) 23.6; 135 ($\mathrm{C_2F_4Cl^+}$) 24.4; 133 ($\mathrm{CF_3SO_2{}^+}$) 11.9; 119 ($\mathrm{C_2F_5{}^+}$) 9.6; 114 ($\mathrm{C_2F_4N^+}$) 7.3; 100 ($\mathrm{C_2F_4{}^+}$) 29.4; 85 ($\mathrm{CF_2Cl^+}$) 63.6; 69 ($\mathrm{CF_3{}^+}$) 100. Anal. Calcd for $\mathrm{C_8ClF_{17}NO_4S_2}$: C, 15.74; F, 52.9; N, 4.60. Found: C, 15.44; F, 52.0; N, 4.71.

Properties of $\mathrm{CF_2CF_2OCF_2CF_2NCFClCF_2N(SO_2CF_3)_2}$ (22) and $\mathrm{CF_2CF_2OCF_2CF_2NCF[N(SO_2CF_3)_2]CF_2Cl}$ (23). Compounds **22** and **23** are obtained as a colorless mixture of nonvolatile isomers in 80% yield in the ratio 1:1.3 upon removal of all volatile materials from the reaction product of $\mathrm{CF_2CF_2OCF_2CF_2NCF{=}CF_2}$ and **13**. The spectral data obtained for the mixture are as follows. IR (neat liquid) (cm^{-1}): 1460 mw, 1439 sh, 1416 vs, 1376 s, 1333 ms, 1305 s, 1284 s, 1228 vs, br, 1187 vs, 1138 vs, 1088 vs, 1028 ms, 926 s, 833 m, 786 mw, 767 m, 734 mw, 691 m, 677 m, 666 m, 622 ms, 570 m, 489 ms. NMR [$\mathrm{CF_2{}^ACF_2{}^BOCF_2{}^BCF_2{}^ANCF^CClCF_2{}^DN(SO_2CF_3{}^E)_2}$ and $\mathrm{CF_2{}^FCF_2{}^GOCF_2{}^GCF_2{}^FNCF^H[N(SO_2CF_3{}^I)_2]CF_2{}^JCl}$]: ^{19}F, δ −70.5 to −78.2 (D, E, I, J, complex m, 8 F), −83.3 to −94.4 (A, B,F,G, complex m, 4 F), −100.8 and −102.4 (C, H, m, 1 F). MS CI [*m/e* (species) intensity]: 346 ($\mathrm{M^+ - N(SO_2CF_3)_2}$) 12.7; 311 ($\mathrm{M^+ - Cl - N(SO_2CF_3)_2}$) 41.7; 292 ($\mathrm{M^+ - Cl - F - N(SO_2CF_3)_2}$) 61.4; 280 ($\mathrm{N(SO_2CF_3)_2{}^+}$) 2.0; 258 ($\mathrm{C_4F_8ONCO^+}$) 4.0; 242 ($\mathrm{C_4F_8NCO^+}$) 3.7; 192 ($\mathrm{C_4F_6NO^+}$) 26.1; 176 ($\mathrm{C_4F_6N^+}$) 7.7; 164 ($\mathrm{C_3F_6N^+}$) 15.5; 145 ($\mathrm{C_3F_5N^+}$) 60.3; 133 ($\mathrm{CF_3SO_2{}^+}$) 3.0; 119 ($\mathrm{C_2F_5{}^+}$) 78.1; 114 ($\mathrm{C_2F_4N^+}$) 14.4; 100 ($\mathrm{C_2F_4{}^+}$) 41.6; 85 ($\mathrm{CF_2Cl^+}$) 36.8; 69 ($\mathrm{CF_3{}^+}$) 100. Anal. Calcd for $\mathrm{C_8ClF_{17}NO_5S_2}$: C, 15.33; F, 51.5. Found: C, 15.10; F, 50.9.

Insertions of ClCN into the N–Cl bond of 13. Into a 40-mL thick-walled Pyrex glass tube fitted with a ChemGlass Teflon needle valve are condensed **13** (~3 mmol) and ClCN (~5 mmol) at −196 °C. The reaction mixture is allowed to warm slowly to 25 °C and then heated at 65–70 °C for 14–25 h. The products are then separated by trap-to-trap distillation.

Properties of $\mathrm{Cl_2C{=}NN(SO_2CF_3)_2}$ (24). This compound is isolated as a colorless liquid in 75% yield in a trap cooled to −20 °C. The spectral data obtained for this compound are as follows. IR (neat liquid) (cm^{-1}): 1572 m, 1456 s, 1436 m, 1335 w, 1225 vs, 1121 vs, 896 m, 776 vw, 732 w, 634 m, 607 s, 577 s, 569 m. NMR [$\mathrm{CCl_2{=}NN(SO_2CF_3{}^A)_2}$]: ^{19}F, δ −69.4 (A, s). MS CI [*m/e* (species) intensity]: 341 ($\mathrm{M^+ - Cl}$) 0.4; 313 ($\mathrm{M^+ - SO_2}$ + 1) 9.8; 277 ($\mathrm{M^+ - Cl - SO_2}$ + 1) 18.1; 243 ($\mathrm{CF_3SO_2NN{=}CCl_2{}^+}$) 0.6; 227 ($\mathrm{CF_3SONN{=}CCl_2{}^+}$) 4.69; 175 ($\mathrm{H_2NCNSOCF_3{}^+}$) 58.8; 150 ($\mathrm{H_2NSO_2CF_3{}^+}$ + 1) 73; 96 ($\mathrm{N{=}CCl_2{}^+}$) 40.1; 69 ($\mathrm{CF_3{}^+}$) 100. Anal. Calcd for $\mathrm{C_3Cl_2F_6NO_4S_2}$: Cl, 18.62; F, 30.2; S, 17.02. Found: Cl, 18.09; F, 29.7; S, 17.42.

Reaction of 13 with $\mathrm{R_3SnCl}$ (R = $\mathrm{CH_3}$, $\mathrm{C_4H_9}$) or $\mathrm{(CH_3)_3SiCl}$. In a typical reaction, **13** (~1.5 mmol) is transferred at −196 °C, via vacuum, to an equimolar amount of trialkylsilyl/stannyl chloride in 15 mL of trichlorofluoromethane taken up into a round-bottomed flask fitted with a ChemGlass Teflon stopcock *via* a B-14 ground joint. The reaction mixture is allowed to warm slowly to 25 °C over a period of ~2 h., with stirring, during which the reaction mixture turns pale yellow. Removal of volatile materials leaves behind **8**, **9**, or **11** in essentially quantitative yield. Spectral properties are similar to those reported earlier. Attempts to react triphenyltin(IV) chloride results in the formation of a mixture of products.

Reaction of 13 with $CFCl_2S(O)Cl$. This reaction is carried out by a similar procedure. The separation of products by trap-to-trap distillation gave $CFCl_2S(O)N(SO_2CF_3)_2$ (**25**) as a pale yellowish liquid in 47% yield in a trap at −10 °C. Spectral properties of **25** are as follows. IR (neat liquid) (cm^{-1}): 1457 vs, 1437 s, 1341 mw, 1225 vs, 1134 vs, 1058 w, 995 s, 875 sh, 859 ms, 795 mw, 770 vw, 760 mw, 602 vs, 581 ms, 572 ms, 533 sh, 511 s, 446 mw. NMR [$CF^ACl_2S(O)N(SO_2CF_3^B)_2$]: ^{19}F, δ −29.1 (A, sept), −69.1 (B, d). J_{AB} = 7.5 Hz. MS CI [*m*/*e* (species) intensity]: 282 ($HN(SO_2CF_3)_2^+ + 1$) 2.2; 176 ($CF_2SO_2NSO^+$) 8.2; 150 ($H_2NSO_2CF_3^+ + 1$) 4.7; 133 ($CF_3SO_2^+$) 23.5; 128 ($CFClNSO^+$) 35.2; 114 ($CF_2SO_2^+$) 16.9; 101 ($CFCl_2^+$) 54.2; 69 (CF_3) 100.

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