Synthesis, Isolation, and Chemistry of Perfluorinated Difluorocarbimides: Precursors to New Perfluorinated Tetrazanes

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N-Trifluoromethyl-*N*-perfluoroalkyldichlorocarbimides $CF_3(R_f)NN{=}CCl_2$ (R_f = CF_3, C_2F_5, C_3F_7 (**1**)) are chlorofluorinated with ClF to give stable chlorohydrazines $CF_3(R_f)NN(Cl)CF_2Cl$ (R_f = CF_3 (**2**), C_2F_5, C_3F_7 (**3**)). Trimethylsilylation of **2** with Me_3SiCl in a 1:1 molar ratio gives the silylhydrazine $(CF_3)_2NN(SiMe_3)CF_2Cl$ (**4**) with concomitant loss of chlorine. The hydrazines $CF_3(R_f)NN(Cl)CF_2Cl$ (R_f = CF_3 (**2**), C_2F_5, C_3F_7 (**3**)) are converted into the respective *N*-trifluoromethyl-*N*-(perfluoroalkyl)difluorocarbimides $CF_3(R_f)NN{=}CF_2$ (R_f = CF_3, C_2F_5 (**6**), C_3F_7 (**5**)) with catalytic amounts of Me_3SiCl. A chlorofluorocarbimide $CF_3(C_2F_5)NN{=}CFCl$ (**7**) is obtained when Me_3SnCl is used as a catalyst with $CF_3(C_2F_5)NN(Cl)CF_2Cl$. Chlorofluorination of **6** gives $CF_3(C_2F_5)NN(Cl)CF_3$ (**8**). Reaction of **5** with SF_5OCl forms the hydrazine $CF_3(C_3F_7)NN(Cl)CF_2OSF_5$ (**9**). With $(CF_3)_2NN{=}CF_2$, $(CF_3)_3COCl$ reacts to give the hydrazine $(CF_3)_2NN(Cl)CF_2OC(CF_3)_3$ (**10**). Photolysis of **2** and **3** results in formation of the tetrazanes $[CF_3(R_f)NNCF_2Cl]_2$ (R_f = CF_3 (**11**), C_3F_7 (**12**)), whereas the photolysis of **8** gives a perfluorinated tetrazane $[CF_3(C_2F_5)NNCF_3]_2$ (**13**). Photolysis of the ether hydrazines **9** and **10** yields the first SF_5-containing tetrazane $[CF_3(C_3F_7)NNCF_2OSF_5]_2$ (**14**) and $[(CF_3)_2NNCF_2OC(CF_3)_3]_2$ (**15**), respectively. Photolysis of **8** with cyanogen chloride allows the low yield preparation of a novel 3*N*-dichlorocarbimide $CF_3(C_2F_5)NN(CF_3)N{=}CCl_2$ (**16**).

Introduction

The reactivity of the nitrogen−chlorine bond in chlorobis(perfluoroalkyl)- or (polyfluoroalkyl)amines presents a myriad of opportunities for the generation of new families of compounds with high fluorine content. We and others[1,2] have taken advantage of this high reactivity to insert perfluoroalkenes and polyfluoroalkenes into the nitrogen−chlorine bond of $R_fR'_fNCl$ with mild heating to prepare tertiary (perfluoroalkyl)- or (polyfluoroalkyl)amines. On the basis of early work which demonstrated the ease of addition of SF_5Cl,[3] CF_3SF_4Cl,[4] or $(CF_3)_2NCl$[5] to nitriles, we utilized this methodology to prepare additional carbimides which are reactive precursors to a variety of new compounds.[1,2] For example, addition occurs to give the dichlorocarbimide

$$CF_3(R_f)NCl + ClCN \xrightarrow{h\nu} CF_3(R_f)NN{=}CCl_2$$

followed by chlorofluorination to form a stable hydrazine

$$CF_3(R_f)NN{=}CCl_2 + 2ClF \xrightarrow[-Cl_2]{25°C} CF_3(R_f)NN(Cl)CF_2Cl$$

that when photolyzed yields the hydrolytically and thermally stable tetrazane.

$$2CF_3(R_f)NN(Cl)CF_2Cl \xrightarrow[-Cl_2]{h\nu} CF_3(R_f)NN(CF_2Cl)N(CF_2Cl)N(R_f)CF_3$$

Attempts to prepare $(CF_3)_2NN{=}CF_2$ from $(CF_3)_2NN{=}CCl_2$ via fluorination with CsF result only in the formation of $(CF_3)_2NN(CF_3)CF{=}NN(CF_3)_2$.[5] Although suggested as an intermediate, the difluorocarbimide was never detected or isolated. However, it is possible to prepare and isolate a large family of azaalkenes, $R_fN{=}CF_2$, via the photolysis of *N*-chloroamines, e.g.

$$R_fN(Cl)CF_2CFCl_2 \xrightarrow[-CFCl_3]{h\nu} R_fN{=}CF_2$$ [1,2]

In our current report, we establish a high yield route to difluorocarbimides, $(R_f)_2NN{=}CF_2$. We also utilize the reactivity of the carbon-nitrogen double bond in these materials with hypochlorites and ClF to prepare precursors to new highly substituted tetrazanes.

Results and Discussion

Early work by the Emeléus school[5] demonstrated that under photolytic conditions $(CF_3)_2NCl$ adds to the triple bond of ClCN to form a dichlorocarbimide. This chemistry was extended to the preparation of the higher homologues $CF_3(C_2F_5)NN{=}CCl_2$[2] and $CF_3(C_3F_7)NN{=}CCl_2$ (**1**).

$$CF_3(R_f)NCl + ClCN \xrightarrow{h\nu} CF_3(R_f)NN{=}CCl_2$$

$R_f = CF_3$,[5] C_2F_5,[2] C_3F_7
1

Addition of chlorine fluoride to the dichlorocarbimides gives high yields of the respective *N*-chloro-*N*-(chlorodifluoromethyl)hydrazines.

$$CF_3(R_f)NN{=}CCl_2 + 2ClF \xrightarrow[-Cl_2]{} CF_3(R_f)NN(Cl)CF_2Cl$$

$R_f = CF_3$, C_2F_5,[2] C_3F_7
2 **3**

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(1) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28,* 2187, and references therein.

(2) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1989**, *28,* 3345, and references therein.

(3) Tullock, C. W.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86,* 357.

(4) Yu, S.-L.; Shreeve, J. M. *Inorg. Chem.* **1976**, *15,* 743.

(5) Dobbie, R. C.; Emeléus, H. J. *J. Chem. Soc. A* **1966**, 933.

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The positive character of the chlorine bonded to nitrogen in **2** gives rise to rapid reaction with Me_3SiCl in a polar solvent to form the trimethylsilylhydrazine **4**. The silylation reaction proceeds only in a polar solvent, such as benzonitrile. On standing in benzonitrile or in the gas phase, **4** decomposes rapidly to Me_3SiCl and the corresponding difluorocarbimide.

$$\mathbf{2} + Me_3SiCl \xrightarrow[-Cl_2]{PhCN} \underset{\mathbf{4}}{(CF_3)_2NN(SiMe_3)CF_2Cl}$$

$$\mathbf{4} \underset{<25\ ^\circ\text{C or nonpolar solvent}}{\overset{25\ ^\circ\text{C/gas phase or in polar solvent}}{\rightleftharpoons}} (CF_3)_2NN{=}CF_2 + Me_3SiCl$$

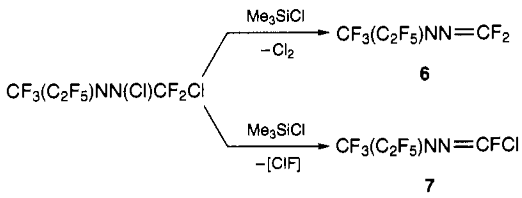
Below 25 °C or in nonpolar solvents such as $CDCl_3$, **4** is reformed. Although it is possible to detect the presence of $(CF_3)_2NN{=}CF_2$ (IR and ^{19}F NMR), it is impossible to isolate from a reaction mixture with 1:1 stoichiometry of Me_3SiCl and **2** because of the above equilibrium.

However, during the course of this investigation, it was found that *N*-chlorohydrazines such as **2** and **3**, are converted essentially quantitatively into the respective difluorocarbimides by using catalytic amounts of Me_3SiCl or Me_3SnCl. Under these conditions, these perfluorocarbimides, that are often claimed but not detected or separated, are easily isolable in high purity.[2,5−9]

$$\mathbf{2} \text{ or } \mathbf{3} \xrightarrow[-Cl_2]{Me_3SiCl} (CF_3)_2NN{=}CF_2,^{8}\ \underset{\mathbf{5}}{CF_3(C_3F_7)NN{=}CF_2}$$

While both compounds are also accessible by using trimethyltin chloride, the reaction to form **5** proceeds very slowly and in the process, products such as C_3F_7NCO, which may result from attack on the glass vessel, are also observed.

Interestingly, in contrast to the reactions of **2** and **3** with catalytic amounts of either Me_3SiCl or Me_3SnCl where chlorine is displaced to give the respective difluorocarbimides, $CF_3(C_2F_5)NN(Cl)CF_2Cl$[2] gives different products with the two reagents, *viz.*



With Me_3SiCl, loss of chlorine occurs to give the expected difluorocarbimide (**6**), with only minor amounts of **7** being produced. However, with Me_3SnCl equal amounts of chlorine and fluorine are lost to form the chlorofluorocarbimide (**7**) with essentially no trace of **6** being observed. Furthermore, trimethyltin chloride is still present at the end of the reaction. The mechanism for the formation of this product is currently under study in this laboratory.

The carbon−nitrogen bond in **6** is easily saturated with ClF to form the hydrazine (**8**), while reaction of **6** with chlorine to produce **7** occurs only in the presence of solvent.

$$\mathbf{6} + ClF \rightarrow \underset{\mathbf{8}}{CF_3(C_2F_5)NN(Cl)CF_3}$$

This requires addition of Cl_2 to the double bond with subsequent loss of [ClF], which because of its high reactivity cannot be identified in the reaction mixture.

$$\mathbf{6} + Cl_2 \xrightarrow[-[ClF]]{PhCN} \mathbf{7}$$

Chlorofluorination of **7** regenerates the parent hydrazine.

$$\mathbf{7} + ClF \rightarrow CF_3(C_2F_5)NN(Cl)CF_2Cl$$

At least two hypochlorites are sufficiently reactive to saturate the double bond in the difluorocarbimides to give highly substituted hydrazines at 25 °C, e.g.

$$\mathbf{5} + SF_5OCl \xrightarrow{20\ \text{min}} \underset{\mathbf{9}}{CF_3(C_3F_7)NN(Cl)CF_2OSF_5}$$

and considerably more slowly

$$(CF_3)_2NN{=}CF_2 + (CF_3)_3COCl \xrightarrow{1\ \text{d}} \underset{\mathbf{10}}{(CF_3)_2NN(Cl)CF_2OC(CF_3)_3}$$

The lower reactivity of $(CF_3)_3COCl$ is likely due to the bulky perfluoro-*tert*-butyl group as well as its lower thermal stability. The majority of the SF_5OCl behaves as a hypochlorite with little evidence for chlorofluorination occuring. The hydrazines **9** and **10** are similar to the hydrazines obtained when highly substituted carbimides such as $CF_3(C_2F_5)NN{=}C(OR_f)CF_3$ ($R_f = CH_2CF_3$, $CH(CF_3)_2$) are reacted with ClF.[10] Interestingly in the ^{19}F NMR spectrum of **9**, through space coupling between the four equatorial fluorines of the SF_5 moiety and the CF_3N group is apparently observed. This effect is a result of the relatively close approach of these two groups forced by the interaction of the lone pairs on the adjacent nitrogen atoms (the lone pairs in $[(CF_3)_2NNCF_3]_2$ are oriented at ~90° to each other).[8]

These new chlorohydrazines dimerize under photolysis at 3000 Å to form the corresponding tetrazanes in high yields, e.g.

$$2(\mathbf{2} \text{ or } \mathbf{3}) \xrightarrow[-Cl_2]{h\nu} CF_3(R_f)NN(CF_2Cl)N(CF_2Cl)N(R_f)CF_3$$

$$R_f = CF_3\ (\mathbf{11}),\ C_3F_7\ (\mathbf{12})$$

Perfluoroalkyl-substituted tetrazanes are easily accessible as well via the photolysis of the *N*-chlorotris(perfluoroalkyl)hydrazines derived from the respective difluorocarbimides.

$$2(CF_3)_2NN(Cl)CF_3{}^{8} \text{ or } \mathbf{8} \xrightarrow[-Cl_2]{h\nu} CF_3(R_f)NN(CF_3)N(CF_3)N(R_f)CF_3$$

$$R_f = CF_3,^{5,8,11}\ C_2F_5\ (\mathbf{13})$$

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(6) Krumm, B.; Kirchmeier, R. L.; Shreeve, J. M. Presented at the ACS 47th Northwest Regional Meeting, Missoula, MT, 1992; Abstr. No. 108.

(7) Krumm, B.; Kirchmeier, R. L.; Shreeve, J. M. Presented at the ACS Eleventh Winter Fluorine Conference, St. Petersburg, FL, 1993; Abstr. No. 37.

(8) Krumm, B.; Vij, A.; Kirchmeier, R. L.; Shreeve, J. M.; Oberhammer, H.; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 586.

(9) Kirchmeier, R. L.; Shreeve, J. M.; Verma, R. D. *Coord. Chem. Rev.* **1992**, *112*, 169.

(10) Sarwar, G.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1990**, *29*, 4255.

(11) Dacey, J. R.; Young, D. M. *J. Chem. Phys.* **1955**, *23*, 1302.

Photolysis of **9** and **10** gives rise to two new tetrazanes, **14** and **15**, containing the ether moiety. Compound **14** is the first example of an SF_5-containing tetrazane.

$$2(\mathbf{9}\text{ or }\mathbf{10}) \xrightarrow[-Cl_2]{h\nu} CF_3(R_f)NN(CF_2OR'_f)N(CF_2OR'_f)N(R_f)CF_3$$
$$R_f = C_3F_7 \text{ and } R'_f = SF_5\ (\mathbf{14})$$
$$R_f = CF_3 \text{ and } R'_f = C(CF_3)_3\ (\mathbf{15})$$

All of the new higher molecular weight tetrazanes we have prepared in this work are colorless, viscous liquids of low volatility that solidify as glasses. We have been unable to obtain crystalline materials suitable for X-ray structure determination in order to learn about the geometry of these thermally and hydrolytically highly stable compounds.[9] However, we have reported the gas phase electron diffraction structure of $[(CF_3)_2NNCF_3]_2$.[8]

The major product obtained when **8** is photolyzed, even in the presence of a large excess of cyanogen chloride, is **13**. The desired 3*N*-dichlorocarbimide (**16**) is only formed as a minor product in yields that range from 10–15%.

$$\mathbf{8} + ClCN \xrightarrow{h\nu} \underset{\mathbf{16}}{CF_3(C_2F_5)NN(CF_3)N{=}CCl_2} + \mathbf{13}$$

Subsequent attempts to chlorofluorinate the $N{=}CCl_2$ bond failed and resulted primarily in the fragmentation of **16**. We obtained only spectroscopic evidence (^{19}F NMR, MS) for the formation of the hoped-for *N*-chlorotriazane. Similar results were found previously in the reaction of ClF with $CF_3(C_2F_5)NN(C_2F_5)N{=}C(Cl)CF_3$.[10]

Increasing the fluorine content of the tetrazanes increases their immiscibility with ordinary solvents. For example, when measuring the ^{19}F NMR spectra of **13** and **14** two phases are invariably present which makes interpretation of the already broadened resonances more complex. Additionally, the two resonances assignable to the CF_3 groups bonded to the terminal nitrogen atoms are broad. Therefore, variable temperature ^{19}F NMR spectra were recorded for **11**, **13**, and hexakis(trifluoromethyl)tetrazane (Figure 1). Increasing the temperature at which the ^{19}F NMR spectra are recorded causes the two resonances to gradually broaden and finally coalesce into a single broad hump. The free energies of activation (ΔG) for these coalescences were calculated by using the Eyring equation.[12] Values obtained from the spectra are the temperatures of coalescence (T_c) and the shift differences between both signals ($\Delta\nu$). In Table 1 are found the measured values of T_c and the calculated free energies.

In general, the two dynamic processes to be considered for these compounds include restricted inversion at the nitrogen atoms and hindered rotation around the N–N bonds, either of which could give rise to magnetically nonequivalent CF_3 groups on the terminal nitrogen atoms. A definitive explanation for the process that occurs resulting in the coalescence of these resonances is difficult. In the case of $[(CF_3)_2NNCF_3]_2$,[13] we find that as the temperature is lowered the solubility of the tetrazane is reduced in the solvents $CDCl_3$ and $CFCl_3$[8] to give two phases that produce a double set of signals. This behavior is similar to that observed for the higher tetrazanes **13** and **14** at 25 °C. The fact that the resonances in the spectrum of **13** (where only one CF_3 group is attached to each terminal nitrogen atom) also coalesce is indicative of the same effect.

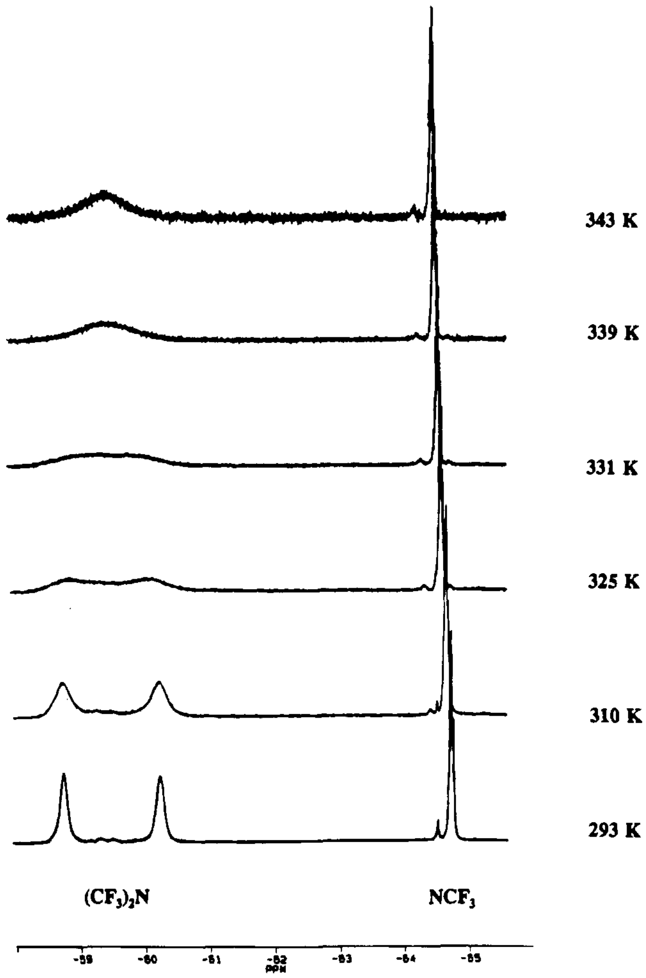

Figure 1. Variable temperature ^{19}F NMR spectrum of $(CF_3)_2NN(CF_3)N(CF_3)N(CF_3)_2$.

Table 1. Results of Variable Temperature ^{19}F NMR Studies of Selected Tetrazanes and Calculation of Free Energies

	T_c (K)	$\Delta\nu$ (Hz)	ΔG (kcal/mol)	solvent
$[(CF_3)_2NNCF_3]_2$	331	270	15.2	$CDCl_3$
$[(CF_3)_2NNCF_2Cl]_2$ (**11**)	363	242	16.8	$C_6D_5CD_3$
$[CF_3(C_2F_5)NNCF_3]_2$ (**13**)	359	486	16.1	$C_6D_5CD_3$

The ^{19}F NMR spectrum of $(CF_3)_2NN(CF_2OC(CF_3)_3)N(CF_2OC(CF_3)_3)N(CF_3)_2$ (**15**) exhibits an interesting resonance for the perfluoro-*tert*-butoxy group (Figure 2). The resonance is split into two signals with a relative ratio of 1:2. This arises because of nonequivalence of the CF_3 groups attached to the tertiary carbon as a result of hindered rotation of the bulky perfluoro-*tert*-butyl group around the C–O bond. Coupling of the CF_3 groups with the OCF_2 moiety is observed, and in addition, the triplet of the single CF_3 is split into septets from coupling to the adjacent two CF_3 groups. No change is found in the ^{19}F spectrum even when the sample is heated to 74 °C. Other reports[12] discuss restricted rotation observed with nonfluorinated *tert*-butyl groups, but no similar data for perfluorinated *tert*-butyl or *tert*-butoxy substituents were presented.

Conclusion

The behavior of Me_3SiCl and Me_3SnCl as catalysts to dechlorinate some *N*-chlorohydrazines is a new application for these ubiquitous compounds. While the preparation of silylated materials has provided a multitude of valuable transfer reagents, advantage has only rarely been taken where the silylated- (stannylated) group is introduced via a metathesis reaction with

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(12) Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry;* VCH Publishers Inc.: New York, 1985.
(13) Barlow, M. G.; Cheung K. W., *J. Fluorine Chem.* **1977**, *10*, 191.

Figure 2. ^{19}F NMR spectrum of the $(CF_3)_3CO$ resonances of $(CF_3)_2NN(CF_2OC(CF_3)_3)N(CF_2OC(CF_3)_3)N(CF_3)_2$ (**15**).

subsequent loss of Me_3XCl (X = Si, Sn) to give an azaalkene. It is likely that this chemistry will have broad synthetic application.

Experimental Section

Materials. The chemicals benzonitrile, trimethylsilyl chloride, and trimethyltin chloride (Aldrich Chemical Co. Inc.); ClCN (Solkatronic Chemicals Inc.); ClF and SF_4 (Atochem North America); and CF_3CN, C_2F_5CN, and $CF_2{=}CFCl$ (PCR) were purchased as indicated and used as received. The hexafluoroacetone is a gift from Daikin Industries, Japan. $(CF_3)_3COCl$ and SF_5OCl are prepared by the reaction of ClF with $(CF_3)_3COK$[14–16] and SOF_4,[17,18] respectively. The *N*-chloroamines $CF_3(R_f)NCl$ (R_f = CF_3,[1] C_2F_5,[1] and C_3F_7[19]) are also prepared by literature methods.

General Procedures. A conventional vacuum system, consisting of a Pyrex glass vacuum line fitted with Teflon needle stopcocks and equipped with Heise Bourdon tube and Televac thermocouple gauges, is used to handle gases and volatile liquids. Standard *PVT* techniques are used to quantitate starting materials or products. Fractional condensation (trap-to-trap distillation) is used for the purification of products. Infrared spectra are recorded on a Perkin-Elmer 1710 FT-IR spectrometer with a 10-cm glass cell equipped with KBr windows. ^{19}F and ^{1}H NMR spectra are obtained on a Bruker AC200 or AC300 FT-NMR instrument using $CDCl_3$ as solvent. Chemical shifts are reported with respect to $CFCl_3$ or $(CH_3)_4Si$. Mass spectra are obtained with a Varian VG 7070 HS mass spectrometer by using electron impact or chemical ionization techniques. Peak assignments of the chlorine-containing fragments are based on ^{35}Cl. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Photolysis reactions are carried out in quartz reaction vessels irradiated in a Rayonet photochemical reactor with 3000 Å UV lamps.

Reaction of $CF_3(C_3F_7)NCl$ with ClCN To Form $CF_3(C_3F_7)NN{=}CCl_2$ (1). A mixture consisting of 15 mmol $CF_3(C_3F_7)NCl$ and 50 mmol ClCN is photolyzed in a 2 L quartz vessel for 1 day at 3000 Å. Repeated distillations through traps at −50 and −60 °C gives **1** in ~50% yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1586 s ($\nu_{N=C}$), 1353 w, 1284 s, 1249 vs, 1171 s, 1146 w, 988 m, 911 w, 878 w, 854 w, 815 w, 738 m, 662 w. ^{19}F NMR ($CDCl_3$): δ −59.8 (CF_3N, tt), $^4J_{F,F}$ = 12.4 Hz, $^5J_{F,F}$ = 4.4 Hz; −81.0 (CF_3C, t), $^4J_{F,F}$ = 10.5 Hz; −100.0 (CF_2N, mult); −125.9 (CCF_2C, mult) ppm. MS EI [*m/e* (species) intensity]: 348 (M^+) 6; 329 ($M^+ - F$) 2; 313 ($M^+ - Cl$) 8; 229 ($M^+ - C_2F_5$) 34; 179 ($M^+ - C_3F_7$) 4; 169 ($C_3F_7^+$) 19; 125 (CF_2NNCCl^+) 16; 119 ($C_2F_5^+$) 16; 114 ($C_2F_4N^+$) 15; 100 ($C_2F_4^+$) 8; 96 ($NCCl_2^+$) 14; 82 (CCl_2^+) 11; 69 (CF_3^+) 100.

Chlorofluorination of $(CF_3)_2NN{=}CCl_2$ To Form $(CF_3)_2NN(Cl)CF_2Cl$ (2). A 5 mmol sample of $(CF_3)_2NN{=}CCl_2$ and 11 mmol ClF are condensed at −196 °C into an evacuated 150 mL stainless steel vessel fitted with a stainless steel valve. The reactants are allowed to warm to and remain at 25 °C for 12 h. Distillation of the contents of the vessel gives **2** which stops in a trap at −80 °C, in quantitative yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1337 s, 1285 s, 1263 m, 1240 m, 1212 s, 1168 m, 1112 m, 1061 m, 985 m, 909 w, 846 w, 811 w, 792 w, 724 m, 635 w. ^{19}F NMR ($CDCl_3$): δ −42.5 (CF_2Cl, sept), $^5J_{F,F}$ = 6.1 Hz; −61.2 ($(CF_3)_2N$, t) ppm. MS CI [*m/e* (species) intensity]: 267 ($M^+ - F$) 2; 251 ($M^+ - Cl$) 2; 232 ($M^+ - ClF$) 4; 216 ($M^+ - Cl_2$) 47; 197 ($(CF_3)_2NNCF^+$) 90; 128 (CF_3NNCF^+) 17; 109 (CF_3NNC^+) 3; 85 (CF_2Cl^+) 9; 69 (CF_3^+) 100.

Chlorofluorination of 1 To Form $CF_3(C_3F_7)NN(Cl)CF_2Cl$ (3). A 20 mmol sample of **1** and 50 mmol ClF are condensed at −196 °C into an evacuated 150 mL stainless steel vessel fitted with a stainless steel valve. The reactants are allowed to warm to and remain at 25 °C for 3 days. Distillation of the contents of the vessel gives **3** which stops in a trap at −40 °C, in quantitative yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1353 m, 1310 s, 1247 s, 1164 s, 1138 s, 1110 s, 907 w, 875 w, 809 w, 780 w, 739 s, 712 m, 651 m, 534 w. ^{19}F NMR ($CDCl_3$): δ −39.9/−42.2 (CF_2Cl, AB mult), $^2J_{F,F}$ = 118.5 Hz; −57.0 (CF_3N, mult); −81.0 (CF_3C, t), $^4J_{F,F}$ = 10.8 Hz; −98.0 (CF_2N, mult); −126.1 (CCF_2C, mult) ppm. MS CI [*m/e* (species) intensity]: 367 ($M^+ - F$) 4; 317 ($M^+ - CF_3$) 19; 297 ($CF_3(C_3F_7)NNCF^+$) 38; 247 ($CF_3(C_2F_5)NNCF^+$) 4; 197 ($C_2F_5NNCF_2^+$) 29; 169 ($C_3F_7^+$) 9; 119 ($C_2F_5^+$) 4; 114 ($C_2F_4N^+$) 9; 100 ($C_2F_4^+$) 4; 85 (CF_2Cl^+) 5; 69 (CF_3^+) 100.

Trimethylsilylation of 2 To Form $(CF_3)_2NN(SiMe_3)CF_2Cl$ (4). A 2 mmol sample of **2** and one of trimethylsilyl chloride are condensed into a round-bottomed flask equipped with a stirrer and containing 5 mL of benzonitrile. When warmed to 25 °C, the mixture turns green due to the formation of chlorine. After 1 h the contents are distilled through a trap at −80 °C, where **4** is retained (yield ~80%). Spectral data are as follows. IR (gas) (cm^{-1}): 2980 w, 1490 m, 1481 m, 1341 s, 1281 s, 1221 s, 1155 s, 1120 m, 1069 m, 1040 s, 977 s, 855 m, 828 m, 719 m, 655 w, 579 w. ^{19}F NMR ($CDCl_3$): δ −41.3 (CF_2Cl, sept), $^5J_{F,F}$ = 5.2 Hz; −63.8 ($(CF_3)_2N$, t) ppm. ^{1}H NMR ($CDCl_3$): δ 0.40 ($SiMe_3$, s) ppm. MS EI [*m/e* (species) intensity]: 232 ($M^+ - Me_3SiF$) 1; 216 ($M^+ - Me_3SiCl$) 22; 197 ($(CF_3)_2NNCF^+$) 13; 147 ($CF_3NNCF_2^+$) 3; 128 (CF_3NNCF^+) 20; 109 (CF_3NNC^+) 3; 93 (Me_2SiCl^+) 69; 85 (CF_2Cl^+) 4; 77 (Me_2SiF^+) 35; 73 (Me_3Si^+) 17; 69 (CF_3^+) 100. Anal. Calcd for $C_6H_9ClF_8N_2Si$: C, 22.19; H, 2.80; F, 46.81. Found: C, 21.91; H, 2.63; F, 46.4.

Conversion of 3 into $CF_3(C_3F_7)NN{=}CF_2$ (5). A 5 mmol sample of **3** is condensed into a round-bottomed flask with a stirrer that contains a catalytic amount of trimethylsilyl chloride dissolved in 5 mL of benzonitrile. After being warmed to 25 °C, the mixture is stirred for 24 h and turns green. This reaction is slow because of the immiscibility of **3** with the solvent. Distillation through a trap at −70 °C where **5** is retained, separates the product from Cl_2 (yield = 75%). Spectral data are as follows. IR (gas) (cm^{-1}): 1748 s ($\nu_{N=C}$), 1360 s, 1290 s, 1250 vs, 1213 m, 1175 m, 1133 m, 961 w, 881 w, 852 w, 717 w. ^{19}F NMR ($CDCl_3$): δ −38.4/−62.8 ($N{=}CF_2$, AB), $^2J_{F,F}$ = 93.9 Hz; −61.8 (CF_3N, mult); −81.3 (CF_3C, td), $^4J_{F,F}$ = 9.5 Hz, 2.9 Hz (through space to N=CF), −101.3 (CF_2N, mult); −126.2 (CCF_2C, mult) ppm. MS EI [*m/e* (species) intensity]: 316 (M^+) 6; 297 ($M^+ - F$) 7; 247 (M^+ −

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(14) Kotun, S. P.; Anderson, J. D. O.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 1124.

(15) Patel, N. R.; Kirchmeier, R. L. *Inorg. Chem.* **1992**, *31*, 2537.

(16) Young, D. E.; Anderson, L. R.; Gould, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 2313.

(17) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310.

(18) Schack, C. J.; Wilson, R. D.; Muirhead, J. S.; Cohz, S. N. *J. Am. Chem. Soc.* **1969**, *91*, 2907.

(19) Chen, Y.; Patel N. R.; Kirchmeier R. L.; Shreeve J. M. *Inorg. Chem.* **1992**, *31*, 4917.

CF_3) 3; 209 ($C_2F_5(CF_2)NNC^+$) 5; 197 ($C_2F_5NNCF_2^+$) 46; 169 ($C_3F_7^+$) 37; 119 ($C_2F_5^+$) 19; 114 ($C_2F_4N^+$) 17; 109 (CF_3NNC^+) 6; 100 ($C_2F_4^+$) 15; 69 (CF_3^+) 100.

Conversion of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ into $CF_3(C_2F_5)NN{=}CF_2$ (6). A 30 mmol sample of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ is condensed into a round-bottomed flask equipped with a stirrer that contains a catalytic amount of trimethylsilyl chloride dissolved in 30 mL benzonitrile. After being warmed to 25 °C, the mixture is stirred for 12 h and turns green. The Cl_2 that is formed is removed by exposing all volatile materials to Hg for 2 h. Traces of **7** are detected by IR. Distillation through traps at −80 °C where **7** is retained and at −95 °C gives pure **6** in 85% yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1747 s ($\nu_{N=C}$), 1361 s, 1298 s, 1245 vs, 1215 s, 1186 s, 1097 m, 962 m, 899 m, 735 m, 719 m. ^{19}F NMR ($CDCl_3$): δ −39.1/−62.9 ($N{=}CF_2$, AB), $^2J_{F,F}$ = 94.5 Hz; −62.6 (CF_3N, mult); −82.7 (CF_3C, mult); −104.2 (CF_2, q), $^4J_{F,F}$ = 12.4 Hz; ppm. MS EI [*m/e* (species) intensity]: 266 (M^+) 2; 247 ($M^+ - F$) 18; 197 ($M^+ - CF_3$) 19; 119 ($C_2F_5^+$) 80; 114 ($C_2F_4N^+$) 28; 100 ($C_2F_4^+$) 16; 69 (CF_3^+) 100.

Conversion of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ into $CF_3(C_2F_5)NN{=}CFCl$ (7). A 5 mmol sample of $CF_3(C_2F_5)NN(Cl)CF_2Cl$ is condensed into a round-bottomed flask equipped with a stirrer that contains a catalytic amount of trimethyltin chloride dissolved in 5 mL of benzonitrile. After being warmed to 25 °C, the mixture is stirred for 12 h and turns green. The Cl_2 is removed by exposing all volatile materials to Hg. Distillation through a trap at −80 °C gives pure **7** in 90% yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1663 s ($\nu_{N=C}$), 1380 w, 1295 s, 1242 vs, 1214 s, 1182 s, 1098 m, 1034 w, 990 w, 902 m, 847 w, 765 s, 750 s, 709 w. ^{19}F NMR ($CDCl_3$): δ −20.3 ($N{=}CF$, br); −61.5 (CF_3N, tq), $^4J_{F,F}$ = 12.1 Hz, $^5J_{F,F}$ = 3.2 Hz; −82.3 (CF_3C, q); −103.5 (CF_2, dq), $^5J_{F,F}$ = 1.5 Hz; ppm. MS EI [*m/e* (species) intensity]: 282 (M^+) 3; 263 ($M^+ - F$) 2; 247 ($M^+ - Cl$) 2; 213 ($M^+ - CF_3$) 17; 144 ($CF_2NNCFCl^+$) 2; 125 (CF_2NNCCl^+) 5; 119 ($C_2F_5^+$) 27; 109 (CF_3NNC^+) 4; 100 ($C_2F_4^+$) 2; 69 (CF_3^+) 100. Anal. Calcd for $C_4ClF_9N_2$: C, 17.00; F, 60.53. Found: C, 16.63; F, 56.9. (This low value may be the result of decomposition which occurs by maintaining **7** for longer periods at 25 °C.)

Reaction of 6 with Chlorine. A 2 mmol sample of **6** and 3 mmol chlorine are condensed into a round-bottomed flask equipped with a stirrer and containing 5 mL of benzonitrile. After being warmed to 25 °C, the mixture is stirred for 24 h. Distillation through a trap at −80 °C gives **7** in 75% yield.

Chlorofluorination of 6 To Form $CF_3(C_2F_5)NN(Cl)CF_3$ (8). A 10 mmol sample of **6** and 12 mmol ClF are condensed at −196 °C into an evacuated 150 mL stainless steel vessel fitted with a stainless steel valve. The reactants are allowed to warm to and remain at 25 °C for 12 h. Distillation of the contents of the vessel gives **8** that stops in a trap at −85 °C, in quantitative yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1380 w, 1319 s, 1281 s, 1246 vs, 1215 s, 1169 m, 1100 m, 1035 w, 902 w, 822 w, 759 m, 734 m. ^{19}F NMR ($CDCl_3$): δ −57.0 (CF_3N, mult); −67.1 (CF_3NCl, mult); −83.3 (CF_3C, mult); −102.9 (CF_2, qq), $^4J_{F,F}$ = 12.1 Hz, $^5J_{F,F}$ = 1.9 Hz; ppm. MS CI [*m/e* (species) intensity]: 301 ($M^+ - F$) 1; 285 ($M^+ - Cl$) 2; 266 ($M^+ - ClF$) 13; 247 ($CF_3(C_2F_5)NNCF^+$) 49; 197 ($C_2F_5NNCF_2^+$) 27; 119 ($C_2F_5^+$) 100; 109 (CF_2NNCF^+) 2; 69 (CF_3^+) 52.

Reaction of 5 with SF_5OCl To Form $CF_3(C_3F_7)NN(Cl)CF_2OSF_5$ (9). A 3 mmol sample of **5** and 4 mmol of freshly distilled SF_5OCl are cocondensed into a glass vessel, allowed to warm to and remain at 25 °C for 20 min. Repeated distillation through a trap at −40 °C separates **9** (yield ~75%) from $CF_3(C_3F_7)NN(Cl)CF_3$ (identified by its ^{19}F NMR spectrum) that stops in a trap at −70 °C. Spectral data are as follows. IR (gas) (cm^{-1}): 1353 m, 1315 s, 1249 vs, 1164 s, 1136 s, 1115 m, 964 m, 941 s, 928 s, 862 s, 833 w, 781 m, 739 m, 642 w, 602 s. ^{19}F NMR ($CDCl_3$): δ 70.3 (SF_4, dtq), $^2J_{F,F}$ = 156.8 Hz, $^4J_{F,F}$ = 12.7 Hz, 4.7 Hz (through space to CF_3N); 62.2 (SF, second order of t), $^4J_{F,F}$ = 2.0 Hz; −57.3 (CF_3N, mult); −66.3 (CF_2O, br); −81.3 (CF_3C, t), $^4J_{F,F}$ = 10.4 Hz; −97.8/−99.0 (CF_2N, AB mult), $^2J_{F,F}$ = 220 Hz; −126.8 (CCF_2C, mult) ppm. MS CI [*m/e* (species) intensity]: 475 ($M^+ - F$) 2; 459 ($M^+ - Cl$) 1; 351 ($M^+ - OSF_5$) 36; 316 ($CF_3(C_3F_7)NNCF_2^+$) 75; 298 ($CF_3(C_3F_7)NNCFH^+$) 94; 279 ($CF_3(C_3F_7)NNCH^+$) 10; 247 ($CF_3(C_2F_5)NNCF^+$) 65; 243 ($C_2F_4OSF_5^+$) 85; 234 ($C_3F_7NCF_2H^+$) 36; 229 ($CF_3(C_2F_5)NNCH^+$) 93; 214 ($C_3F_7NCF^+$) 52; 209 ($C_2F_5(CF_2)NNC^+$) 88; 198 ($C_2F_5NNCF_2H^+$) 72; 193 ($CF_2OSF_5^+$) 15; 169 ($C_3F_7^+$) 20; 159 ($C_2F_5NNC^+$) 54; 143 (OSF_5^+) 56; 127 (SF_5^+) 100; 119 ($C_2F_5^+$) 58; 86 (SOF_2^+) 67; 70 (HCF_3^+) 83.

Reaction of $(CF_3)_2NN{=}CF_2$ with $(CF_3)_3COCl$ To Form $(CF_3)_2NN(Cl)CF_2OC(CF_3)_3$ (10). A 1 mmol sample of $(CF_3)_2NN{=}CF_2$ and 2 mmol of $(CF_3)_3COCl$ are cocondensed into a glass vessel and kept at 25 °C for 1 day. Distillation through a trap at −60 °C gives pure **10** in 70% yield. An excess of hypochlorite is recommended because it decomposes into $(CF_3)_2CO$ and CF_3Cl at 25 °C. In addition, some $(CF_3)_3COH$ is found arising from slow hydrolysis of $(CF_3)_3COCl$. Spectral data are as follows. IR (gas) (cm^{-1}): 1338 s, 1286 vs, 1214 s, 1167 s, 1134 s, 984 s, 843 w, 733 m, 724 m. ^{19}F NMR ($CDCl_3$): δ −61.3 ($(CF_3)_2N$, t), $^5J_{F,F}$ = 5.0 Hz; −63.8 (CF_2, mult); −70.3 ($C(CF_3)_3$, t), $^5J_{F,F}$ = 9.3 Hz; ppm. MS CI [*m/e* (species) intensity]: 467 ($M^+ - F$) <1; 433 ($MH^+ - ClF$) 2; 413 ($M^+ - ClF_2$) 1; 217 ($(CF_3)_2NNCF_2H^+$) 88; 197 ($(CF_3)_2NNCF^+$) 47; 167 ($(CF_3)_2COH^+$) 7; 147 ($CF_3NNCF_2^+$) 9; 128 (CF_3NNCF^+) 11; 109 (CF_3NNC^+) 19; 97 (CF_3CO^+) 27; 81 ($C_2F_3^+$) 11; 69 (CF_3^+) 100.

Photolysis of 2 To Form $[(CF_3)_2NNCF_2Cl]_2$ (11). A 4 mmol sample of **2** is condensed into a 100 mL quartz vessel and photolyzed for 12 h at 3000 Å. Distillation of the contents gives the tetrazane (**11**) which is retained in a trap at −60 °C in ~90% yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1343 s, 1294 s, 1234 s, 1180 s, 1128 m, 1092 m, 1059 m, 1029 m, 987 s, 862 m, 824 m, 724 s, 686 w, 665 w, 481 w. ^{19}F NMR ($CDCl_3$): δ −37.8/−40.9 (CF_2Cl, AB) ppm, $^2J_{F,F}$ = 130.0 Hz, coalescence at 101 °C (toluene-d_8), ΔG = 16.4 kcal/mol; −58.3/−59.1 ($(CF_3)_2N$, br) ppm, coalescence at 90 °C (toluene-d_8), ΔG = 16.8 kcal/mol. MS CI [*m/e* (species) intensity]: 417 ($M^+ - CF_2Cl$) <1; 350 ($M^+ - (CF_3)_2N$) <1; 251 ($(CF_3)_2NNCF_2Cl^+$) 16; 216 ($(CF_3)_2NNCF_2^+$) 4; 197 ($(CF_3)_2NNCF^+$) 3; 163 ($CF_3NNCFCl^+$) 12; 147 ($CF_3NNCF_2^+$) 17; 128 (CF_3NNCF^+) 12; 85 (CF_2Cl^+) 100; 83 (CF_3N^+) 48; 69 (CF_3^+) 98. Anal. Calcd for $C_6Cl_2F_{16}N_4$: C, 14.33; F, 60.44. Found: C, 14.19; F, 60.8.

Photolysis of 3 To Form $[CF_3(C_3F_7)NNCF_2Cl]_2$ (12). A 4 mmol sample of **3** is photolyzed in a 100 mL quartz vessel for 12 h at 3000 Å. Removing all volatile materials under vacuum leaves **12** as a nonvolatile liquid in nearly quantitative yield. Spectral data are as follows. IR (liquid) (cm^{-1}): 1347 m, 1317 s, 1208 vs, 1130 s, 1088 m, 1040 m, 1013 m, 973 w, 924 w, 905 m, 848 w, 814 m, 792 w, 736 s, 710 m, 643 w, 540 w. ^{19}F NMR ($CDCl_3$): δ −37 (CF_2Cl); −57 (CF_3N); −82 (CF_3C); −91 (CF_2N); −124 (CCF_2C) ppm. All signals are broad and very complex. Therefore, only average values for chemical shifts are given. MS CI [*m/e* (species) intensity]: 618 ($MH^+ - CF_2Cl$) <1. MS EI [*m/e* (species) intensity]: 351 ($CF_3(C_3F_7)NNCF_2Cl^+$) 2; 316 ($CF_3(C_3F_7)NNCF_2^+$) 2; 297 ($CF_3(C_3F_7)NNCF^+$) 3; 247 ($CF_3(C_2F_5)NNCF^+$) 8; 197 ($C_2F_5NNCF_2^+$) 30; 169 ($C_3F_7^+$) 54; 147 ($CF_3NNCF_2^+$) 6; 119 ($C_2F_5^+$) 24; 100 ($C_2F_4^+$) 14; 85 (CF_2Cl^+) 100; 69 (CF_3^+) 100. Anal. Calcd for $C_{10}Cl_2F_{24}N_4$: C, 17.08; F, 64.86. Found: C, 16.94; F, 65.1.

Photolysis of 8 To Form $[CF_3(C_2F_5)NNCF_3]_2$ (13). A 2 mmol sample of **8** is condensed into a 100 mL quartz vessel and photolyzed for 12 h at 3000 Å. Distillation of the contents gives the tetrazane (**13**) which is retained in a trap at −50 °C (yield = 90%). Spectral data are as follows. IR (gas) (cm^{-1}): 1299 s, 1283 s, 1247 s, 1177 w, 1119 w, 1079 m, 956 w, 918 w, 738 m. ^{19}F NMR ($CDCl_3$): δ −56.9/−58.6 ($CF_3N(1)$, br), coalescence at 86 °C (toluene-d_8), ΔG = 16.1 kcal/mol; −63.6 ($CF_3N(2)$, br); −83.0 (CF_3C, br); −97.9 (CF_2, br) ppm. MS EI [*m/e* (species) intensity]: 368 ($M^+ - CF_3(C_2F_5)N$) <1; 285 ($CF_3(C_2F_5)NNCF_3^+$) 5; 266 ($CF_3(C_2F_5)NNCF_2^+$) 2; 247 ($CF_3(C_2F_5)NNCF^+$) 3; 197 ($C_2F_5NNCF_2^+$) 11; 147 ($CF_3NNCF_2^+$) 3; 119 ($C_2F_5^+$) 72; 100 ($C_2F_4^+$) 1; 69 (CF_3^+) 100. Anal. Calcd for $C_8F_{22}N_4$: C, 16.85; F, 73.32. Found: C, 16.94; F, 72.9.

Photolysis of 9 To Form $[CF_3(C_3F_7)NNCF_2OSF_5]_2$ (14). A 6 mmol sample of **9** is condensed into a 100 mL quartz vessel and photolyzed for 12 h at 3000 Å. Removing all volatile materials under vacuum leaves **14** as a nonvolatile liquid (yield ~95%). Spectral data are as follows. IR (liquid) (cm^{-1}): 1384 w, 1322 s, 1229 vs, 1131 s, 1015 m, 965 m, 918 s, 893 m, 877 m, 854 s, 788 m, 770 w, 737 m, 685 w, 621 w, 595 s, 567 w, 540 w. ^{19}F NMR ($CDCl_3$): δ 70.7 (SF_4, br d), $^2J_{F,F}$ = 152 Hz; 61.8 (SF, second order); −57 (CF_3N); −63 (CF_2O); −82 (CF_3C); −92 (CF_2N); −125 (CCF_2C) ppm. Signals with negative chemical shifts are broad and very complex. Therefore, only average values are given. MS CI [*m/e* (species) intensity]: 459 ($CF_3(C_3F_7)$-

$NNCF_2OSF_5^+$) 5; 297 ($CF_3(C_3F_7)NNCF^+$) 1; 214 ($C_3F_7NCF^+$) 11; 197 ($C_2F_5NNCF_2^+$) 5; 193 ($CF_2OSF_5^+$) 8; 169 ($C_3F_7^+$) 28; 127 (SF_5^+) 100; 119 ($C_2F_5^+$) 8; 114 ($C_2F_4N^+$) 44; 100 ($C_2F_4^+$) 6; 89 (SF_3^+) 12. Anal. Calcd for $C_{10}F_{34}N_4O_2S_2$: C, 13.08; F, 70.35. Found: C, 13.25; F, 70.1.

Photolysis of 10 To Form $[(CF_3)_2NNCF_2OC(CF_3)_3]_2$ (15). A 1 mmol sample of **10** is photolyzed in a 100 mL quartz vessel for 12 h at 3000 Å. Distillation gives **15** which is retained in a trap at −50 °C, in 80% yield. Spectral data are as follows. IR (gas) (cm^{-1}): 1348 m, 1289 s, 1263 s, 1233 s, 1220 s, 1158 m, 986 m, 859 w, 735 m. ^{19}F NMR ($CDCl_3$): δ −58.1/−58.7 ($(CF_3)_2N$, mult); −60.0 (CF_2, mult); −69.4 (CF_3CO, tsept), $^4J_{F,F} = 1.3$ Hz, $^5J_{F,F} = 9.6$ Hz; −69.8 ($(CF_3)_2CO$, t(br)) ppm. Recording variable temperature ^{19}F NMR up to 74 °C in $CDCl_3$ did not cause any change of the line appearance of the inequivalent *tert*-butyl CF_3 groups nor for the $(CF_3)_2N$ moiety. MS CI [*m/e* (species) intensity]: 297 ($(CF_3)_2NN(CF_2OH)NCF_2^+$) 46; 247 ($(CF_3)_2NN(CF_2OH)N^+$) 3; 217 ($(CF_3)_2NNCF_2H^+$) 1; 197 ($(CF_3)_2NNCF^+$) 47; 167 ($(CF_3)_2COH^+$) 1; 128 ($CF_3NNCF^+$) 2; 109 ($CF_3NNC^+$) 5; 97 ($CF_3CO^+$) 4; 69 ($CF_3^+$) 100. The azaalkene $(CF_3)_2NN{=}CFOC(CF_3)_3$ is found as a minor product that stops in a trap at −70 °C and is identified by IR ($\nu_{N=C}$ 1664 cm^{-1}) and ^{19}F NMR ($CDCl_3$): δ −41.4 (N=CF, sept), $^5J_{F,F} = 5.2$ Hz; −64.9 ($(CF_3)_2N$, d); −70.0 ($C(CF_3)_3$, s) ppm.

Reaction of 8 with ClCN To Form $CF_3(C_2F_5)NN(CF_3)N{=}CCl_2$ (16). A mixture consisting of 8 mmol **8** and 60 mmol ClCN is placed into a 2 L quartz vessel and photolyzed for 12 h at 3000 Å. Distillation through a −60 °C trap removes most of the excess ClCN. The fraction retained at −60 °C is distilled several times (10−15) through traps cooled to −20, −30 and −196 °C. **16** is more volatile than tetrazane **13** and passes through the trap at −30 °C. Most of **13** stops in the trap at −20 °C. **16** is enriched in this manner up to a purity of ~95%. The overall yield does not exceed 10−15%. Spectral data are as follows. IR (gas) (cm^{-1}): 1583 m ($\nu_{N=C}$), 1379 w, 1319 s, 1283 s, 1242 s, 1205 s, 1167 m, 1094 m, 1029 w, 986 m, 957 w, 903 w, 872 w, 739 m, 674 w. ^{19}F NMR ($CDCl_3$): δ −55.7 ($CF_3N(1)$, mult); −65.6 ($CF_3N(2)$, mult); −83.0 (CF_3C, mult); −99.6(AB)/−103.9(ABqq) (CF_2), $^2J_{F,F} = 220$ Hz, $^4J_{F,F} = 17.2$ Hz, $^5J_{F,F} = 2.5$ Hz; ppm. MS EI [*m/e* (species) intensity]: 381 (M^+) 3; 312 ($M^+ - CF_3$) 6; 285 ($CF_3(C_2F_5)NNCF_3^+$) 16; 280 ($CF_3(C_2F_5)NN(CF_2)N^+$) 5; 266 ($CF_3(C_2F_5)NNCF_2^+$) 2; 247 ($CF_3(C_2F_5)NNCF^+$) 1; 197 ($C_2F_5NNCF_2^+$) 9; 147 ($CF_3NNCF_2^+$) 4; 119 ($C_2F_5^+$) 82; 69 (CF_3^+) 100.

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