Silylated Compounds as Transfer Reagents with Active Carbon–Chlorine, Carbon–Fluorine, or Sulfur–Fluorine Bonds

Nimesh R. Patel, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

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Photolytic insertion of $R_fC{\equiv}N$ or $ClC{\equiv}N$ into the nitrogen-chlorine bond of $(CF_3)_2NCl$ occurs readily to form $(CF_3)_2NN{=}C(R_f)Cl$ ($R_f = CF_3$ (**2**), C_2F_5 (**3**)) or $(CF_3)_2NN{=}CCl_2$ (**4**). Reactions of $CF_3N(C_2F_5)N{=}C(CF_3)Cl$, **2**, or **3** with $C_6F_5SiMe_3$ in the presence of CsF at 25 °C, result in $CF_3(R_f)NN{=}C(R_f')C_6F_5$ ($R_f = C_2F_5$, $R_f' = CF_3$, **8**; $R_f = CF_3$, $R_f' = CF_3$, **9**; $R_f = CF_3$, $R_f' = C_2F_5$, (**10**). Analogously, the silylated reagents $C_6F_5SiMe_3$, Me_2NSiMe_3, and CF_3SiMe_3 easily displace chlorine as Me_3SiCl from $SF_5N{=}C(C_2F_5)Cl$ to form $SF_5N{=}C(C_2F_5)X$ (X = C_6F_5 (**11**), NMe_2 (**12**), CF_3 (**13**)). The pentafluorophenyl moiety is also readily introduced into $(CF_3)_2NCF_2N{=}C(F)OC(CF_3)_2CH_3$ and $(CF_3)_2NN{=}C(Cl)F$ by metathesis with $C_6F_5SiMe_3$ to give $(CF_3)_2NCF_2N{=}C(C_6F_5)OC(CF_3)_2CH_3$ (**14**) and $(CF_3)_2NN{=}C(C_6F_5)N(CF_3)_2$ (**15**), respectively. Under similar mild conditions, $CF_3N{=}SF_2$ forms $CF_3N{=}S(R_f)_2$ ($R_f = CF_3$ (**17**), C_6F_5 (**18**)) with CF_3SiMe_3 and $C_6F_5SiMe_3$. With ClF, **17** is oxidatively fluorinated to *cis* and *trans*-$(CF_3)_2SF_4$. The nitriles $(CF_3)_2NCN$ and C_2F_5CN readily insert into the sulfur–chlorine bond of CF_3SCl to give $(CF_3)_2NC(Cl){=}NSCF_3$ and $C_2F_5C(Cl){=}NSCF_3$. With SF_5Cl, $(CF_3)_2NCN$ forms $(CF_3)_2NC(Cl){=}NSF_5$.

Introduction

Silylated perfluoroalkyl and perfluoroaryl compounds R_3SiR_f (R = alkyl; R_f = *F*-alkyl or *F*-aryl) are remarkably stable and easily prepared.[1-12] These compounds are powerful transfer reagents when reacted with active electrophiles in the presence of an alkali metal fluoride resulting in the concomitant substitution of the trialkylsilyl group. While these species have been known for many years, it is only recently that their roles as valuable precursors to highly fluorinated inorganic and organic compounds have been exploited. The methods for introduction of perfluorinated alkyl and aryl groups into other compounds are fraught with difficulty either because the precursors are unstable, viz., $LiCF_3 \rightarrow LiF + :CF_2$, or require special synthetic conditions, i.e., $CuCF_3$[2] or R_fMgX,[2] or are potential health hazards, e.g., $Hg(R_f)_2$. However, now given the ready accessibility of silylated perfluoroalkyl and aryl compounds, many difficult syntheses are readily accomplished in the presence of fluoride ion.

Applications involve reactions of trimethylsilyl per- or polyfluoroalkanes or arenes with electrophiles. While most effort has been directed toward the perfluoroalkylation or perfluorophenylation of a variety of organic compounds, e.g., olefins (external & internal), aryls, esters, ketones, aldehydes, etc., the methodology has been extended to perfluorinated internal azaalkenes[4,8] and to simple sulfinyl or sulfuryl compounds,[10] e.g.

$$(CH_3)_3SiR_f + R_f'S(O)_xF \xrightarrow[25\ °C]{KF} R_f'S(O)_xR_f$$

$R_f = CF_3$, C_6F_5; $R_f' = F$, $x = 1, 2$; *F*-alkyl, $x = 1,2$

in the latter case to provide an excellent high-yield route for the preparation of perfluoroalkyl or aryl sulfinyl fluorides, sulfonyl fluorides, sulfoxides, and sulfuranes.

Earlier we found that the products obtained when ClF was reacted with fluorinated sulfimides appear to be a function of the moieties bonded to the sulfur atom, e.g.

$$CF_3N{=}SF_2 + \text{excess ClF} \xrightarrow{-78\ °C} CF_3NCl_2 + SF_4$$ [13]

However, when the substituents on sulfur are less electronegative, oxidation to sulfur(VI) occurs.

$$CF_3N{=}S(OCH_2CF_3)_2 + \text{excess ClF} \xrightarrow{-78\ °C} CF_3NCl_2 + \textit{cis/trans}\text{-}SF_4(OCH_2CF_3)_2$$ [14]

In some cases the carbon–nitrogen bond in fluoroazenes is also severed in reactions with ClF, e.g.

$$2ClF + R_fN{=}C(OR_f')_2 \xrightarrow{-78\ °C} R_fNCl_2 + F_2C(OR_f')_2$$ [15]

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and

$$(CF_3)_2NC(OCH_2CF_3)=NCF_3 \xrightarrow[ClF]{-78\ ^\circ C} CF_3NCl_2 + (CF_3)_2NCF_2OCH_2CF_3$$[15]

but in other cases addition of ClF occurs to form stable compounds, e.g.

$$CF_3N=CFN(CF_3)_2 \xrightarrow[ClF]{-78\ ^\circ C} CF_3N(Cl)CF_2N(CF_3)_2$$[16,17]

$$(CF_3)_2NN=CF_2 \xrightarrow[ClF]{-78\ ^\circ C} (CF_3)_2NN(Cl)CF_3$$[18]

without concomitant breaking of the initial carbon-nitrogen bond.

If advantage is taken of silylated reagents, the syntheses of highly substituted fluorine-containing sulfimides and azenes are easier and can be broadened to a variety of new compounds. In this work, we introduce new substituents into the >C=N- and >S=N bonds and study the subsequent reactions of these new compounds with ClF.

Results and Discussion

A rather standard route to fluoroazenes is the insertion of a nitrile into the nitrogen–chlorine bond of R_fNCl or $(R_f)_2NCl$ based on the example of an earlier reaction between SF_5Cl and R_fCN.[19,20] This work has been greatly extended in our laboratory with insertions such as

$$CF_3N(C_2F_5)Cl + CF_3CN \xrightarrow{h\nu} CF_3N(C_2F_5)N=C(Cl)CF_3$$[16]
1

and in the present work in order to synthesize precursors for reactions with silylated reagents.

$$(CF_3)_2NCl + R_fCN \xrightarrow{h\nu} (CF_3)_2NN=C(R_f)Cl$$

$R_f = CF_3$ (2) C_2F_5 (3), Cl (4)[20]

$$R_fCl + (CF_3)_2NCN \xrightarrow{h\nu} (CF_3)_2NC(Cl)=NR_f$$

$R_f = SF_5$, CF_3S

$$CF_3SCl + C_2F_5CN \xrightarrow{h\nu} C_2F_5C(Cl)=NSCF_3$$

These azenes are subject to reaction with ClF where, for example, ClF plays a dual role in reaction with **4** of both saturation of the azene double bond and fluorination of one carbon-chlorine bond. Photolysis of **5** for 24 h

$$(CF_3)_2NN=CCl_2 + ClF \xrightarrow{25\ ^\circ C} (CF_3)_2NN(Cl)CF_2Cl$$
4 **5**

results in the loss of chlorine fluoride with concomitant formation of a new azene, $(CF_3)_2NN=C(Cl)F$ (**6**) which, in the presence of CsF, gives rise to the same dimer, $(CF_3)_2NN=CFN(CF_3)N(CF_3)_2$, that is also obtained when $(CF_3)_2NN=CCl_2$ is treated analogously.[20]

The azenes **1–3** and $SF_5N=C(C_2F_5)Cl$[21] (**7**) react with $C_6F_5SiMe_3$ in the presence of anhydrous CsF to give the new pentafluorophenyl-substituted azenes in essentially quantitative yields.

$$CF_3(R_f)NN=C(R_f')Cl + C_6F_5SiMe_3 \xrightarrow[CH_3CN,\ 25\ ^\circ C]{CsF} CF_3(R_f)NN=C(R_f')C_6F_5$$
8–10

	R_f	R_f'	
1	C_2F_5	CF_3	8
2	CF_3	CF_3	9
3	CF_3	C_2F_5	10

Also, other silylated reagents may be employed to give **12** and **13**.

$$SF_5N=C(C_2F_5)Cl + XSiMe_3 \xrightarrow[CH_3CN]{CsF} SF_5N=C(C_2F_5)X$$
7 **11–13**

X = C_6F_5 (**11**), NMe_2 (**12**), CF_3 (**13**)

The presence of a bulky substituent on the azene carbon apparently does not interfere with the transfer of the $C_6F_5^-$ moiety to the azene carbon in the presence of CsF, e.g.,

$$(CF_3)_2NCF_2N=C(F)OC(CF_3)_2CH_3 + C_6F_5SiMe_3 \xrightarrow[CH_3CN]{CsF} (CF_3)_2NCF_2N=C(C_6F_5)OC(CF_3)_2CH_3$$[22]
14

The reaction of azene **6** with $C_6F_5SiMe_3$ gives a product that is somewhat surprising at first glance, i.e., $(CF_3)_2NN=C(C_6F_5)N(CF_3)N(CF_3)_2$ (**15**). However, the reaction route is readily explained as follows:

$$(CF_3)_2NN=C(Cl)F \xrightarrow{F^-} (CF_3)_2NN=CF_2 \longrightarrow (CF_3)_2NN^-CF_3$$[18] (1)
6

$$(CF_3)_2NN=C(Cl)F + C_6F_5SiMe_3 \xrightarrow{F^-} [(CF_3)_2NN=C(C_6F_5)F]$$ (2)

$$(CF_3)_2NN^-CF_3 + [(CF_3)_2NN=C(C_6F_5)F] \longrightarrow (CF_3)_2NN=C(C_6F_5)N(CF_3)N(CF_3)_2$$
15 (3)

In our continuing effort to synthesize solid tetrazanes that would be suitable for X-ray crystal structure determination, **15** was reacted with ClF and the product photolyzed

$$(CF_3)_2NN=C(C_6F_5)N(CF_3)N(CF_3)_2 + ClF \rightarrow (CF_3)_2NN(Cl)CF(C_6F_5)N(CF_3)N(CF_3)_2$$
16

Unfortunately upon photolysis only decomposition occurs and no tetrazane was found.

Sulfimides can be reacted readily with both $C_6F_5SiMe_3$ and CF_3SiMe_3 under the same mild conditions as used for the azenes to give the highly substituted products in good yield, i.e.

$$CF_3N=SF_2 + R_fSiMe_3 \xrightarrow[CH_3CN,\ 25\ ^\circ C]{CsF} CF_3N=S(R_f)_2$$
17, 18

$R_f = CF_3$ (**17**), C_6F_5 (**18**)

When **17** is reacted with an excess of ClF, the major product is a mixture of *cis*- and *trans*-$(CF_3)_2SF_4$ in an isomeric ratio of 1:3.

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If the reaction

$$CF_3N{=}S(CF_3)_2 + \text{excess ClF} \xrightarrow{-78\ ^\circ C} \textit{cis} \text{ and } \textit{trans}\text{-}(CF_3)_2SF_4 + CF_3NCl_2$$

is carried out with less than the stoichiometric amount of ClF or is not allowed to go to completion, $(CF_3)_2SF_2$, as well as *cis* and *trans*-$(CF_3)_2SF_4$, is isolated. The likelihood of such an intermediate was suggested earlier but not proved.[14] Chlorine fluoride oxidatively fluorinates $(CF_3)_2SF_2$ to $(CF_3)_2SF_4$ although in lower yield than obtained when $(CF_3)_2S$ is the reactant with ClF.[23,24] This latter reaction gives a ratio of *cis* to *trans*-$(CF_3)_2SF_4$ isomers of 1:1.6 which on standing in CCl_3F for 2 years changes to a ratio of 1:1. This new route to $(CF_3)_2SF_4$ is more convenient than the oxidative fluorination of $(CF_3)_2S$ because the reaction precursors are more easily obtained.

It is possible to separate the isomeric mixture by reacting it with AsF_5 in CH_2Cl_2. The *cis* isomer combines with AsF_5 and the *trans* material may be removed under vacuum.[25] A study of the chemistry of this now readily available pure isomer (*cis*-$(CF_3)_2SF_4$) is underway.

Experimental Section

Materials. The reagents $(CF_3)_2NN{=}CCl_2$,[20] SF_5Cl,[26] $TMSC_6F_5$,[4,10] $SF_5N{=}C(C_2F_5)Cl$,[21] $(CF_3)_2NCN$,[27] and $CF_3N{=}SF_2$[28] were prepared by using literature methods. All other materials were purchased: chlorine fluoride (Ozark-Mahoning), cyanogen chloride (K & K Laboratories, Inc.), and CF_3CN and C_2F_5CN (PCR, Inc.).

General Procedure. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube and Televac thermocouple gauges. Products were purified by fractional condensation (trap-to-trap distillation). Volatile starting materials and products were measured by using standard *PVT* techniques. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared Fourier transform spectrometer by using a 10-cm gas cell equipped with KBr windows. ^{19}F and ^1H NMR spectra were recorded on a Bruker NR200 Fourier transform NMR spectrometer with CCl_3F and $(CH_3)_4Si$ as references, respectively. Mass spectra were obtained with a VG 7070 mass spectrometer operating at an ionization potential of 17 eV. Elemental analysis were performed by Beller Microanalytisches Laboratorium, Göttingen, Germany. Photolysis reactions were carried out in quartz reaction vessels irradiated in a Rayonet photochemical reactor at 3000 Å.

Reaction of Nitriles: (A) Reaction of R_fCN ($R_f = CF_3$, C_2F_5) with $(CF_3)_2NCl$. The *N*-chloro compound $(CF_3)_2NCl$ (5 mmol) and 20–25 mmol of nitrile (CF_3CN or C_2F_5CN) are condensed at −196 °C into an evacuated 2-L quartz vessel fitted with a Kontes Teflon stopcock. After the vessel warms to 25 °C it is irradiated at 3000 Å for 6–8 h. The products are separated and purified by trap-to-trap distillation.

Properties of $(CF_3)_2NN{=}C(Cl)CF_3$ (2). This compound is retained as a colorless liquid in ~60% yield in a trap at −78 °C having passed a trap at −45 °C. Spectral data are as follows. IR (gas): 1646 s, 1324 vs, 1309 vs, 1248 vs, 1205 vs, 1118 w, 1007 s, 980 s, 909 w, 849 w, 816 w, 759 m, 724 m, 656 s, 526 m cm^{-1}. ^{19}F NMR: δ −63.19 [$(CF_3)_2N$, s], −71.1 [CF_3C, s]. CIMS [*m/e* (species), intensity]: 284 ($M^+ + 2$), 11.6; 283 ($M^+ + 1$), 6.6; 282 (M^+), 34.3; 263 ($M^+ - F$), 37.6; 247 ($M^+ - Cl$), 20.4; 213 ($M^+ - CF_3$), 4.9; 194 ($M^+ - CF_4$), 5; 175 ($M^+ - CF_5$), 2.9; 159 ($M^+ - CClF_4$), 12.6; 125 ($M^+ - C_2F_7$), 8.9; 101 ($C_2F_4^+ + 1$), 7.5; 85 (CF_2Cl^+), 12.2; 69 (CF_3^+), 100.

Properties of $(CF_3)_2NN{=}C(Cl)C_2F_5$ (3). This compound is retained in a trap at −70 °C having passed a trap at −35 °C. It is formed in ~55% yield as a colorless liquid. Spectral data are as follows. IR (gas): 1633 s, 1323 s, 1253 s, 1211 s, 1188 m, 1118 m, 1097 m, 1085 m, 1049 m, 983 m, 907 s, 847 s, 817 sm 750 m, 726 m, 697 w, 652 w, 522 w cm^{-1}. ^{19}F NMR: δ −62.8 [$(CF_3)_2NN$, s], −81.8 [CCF_3, t, J = 1.5 Hz], −114.1 (CF_2, q, J = 1.5 Hz). CIMS [*m/e* (species), intensity]: 334 ($M^+ + 2$), 10.2; 333 ($M^+ + 1$), 28.4; 332 (M^+), 9.3; 209 ($M^+ - CF_3Cl$), 6; 167 ($(CF_3)_2NN^+ + 1$), 4.6; 153 ($(CF_3)_2N^+ + 1$), 19.9; 146 ($C_2F_5CN^+ + 1$), 6.1; 119 ($C_2F_5^+$), 22.0; 101 ($C_2F_4^+ + 1$), 21.7; 69 (CF_3^+), 100.

(B) Reactions of $(CF_3)_2NCN$ with R_fCl ($R_f = SF_5$, CF_3S). Five millimoles of $(CF_3)_2NCN$ and R_fCl ($R_f = SF_5$, CF_3S) each are condensed into an evacuated quartz vessel at −196 °C. After the vessel is warmed to 25 °C, the contents are photolyzed for 8 h at 3000 Å. The contents of the vessel are separated by trap-to-trap distillation.

Properties of $(CF_3)_2NC(Cl){=}NSF_5$. This compound is retained in a trap at −50 °C in 60% yield. Spectral data are as follows. IR (gas): 1662 s, 1356 vs, 1320 vs, 1290 vs, 1229 vs, 1182 m, 1029 w, 1004 s, 941 s, 912 vs, 892 vs, 852 s, 780 w, 736 s, 675 m, 627 w, 604 s, 572 w, 543 w, 482 w cm^{-1}. ^{19}F NMR: δ 71.4 (SF, p), 64.8 (SF_4, d, $J_{SF_4\text{-}SF}$ = 126.7 Hz), −54.6 ($(CF_3)_2N$, s). CIMS [*m/e* (species), intensity]: 341 ($M^+ + 1$), 1.7; 321 ($M^+ - F$), 18.4; 305 ($M^+ - Cl$), 16.9; 248 ($M^+ - Cl - 3F$), 1.7; 213 ($M^+ - SF_5$), 10.7; 188 ($M^+ - N(CF_3)_2$), 25.5; 127 (SF_5^+), 100; 101 ($C_2F_4^+ + 1$), 4.7; 89 (SF_3^+), 17.5; 69 (CF_3^+), 79.7. Anal. Calcd: C, 10.6; F, 61.5. Found: C, 10.8; F, 60.9.

Properties of $(CF_3)_2NC(Cl){=}NSCF_3$. This compound is retained in a trap at −60 °C in 10–15% yield. Spectral data are a follows. IR (gas): 1622 m, 1936 m, 1359 vs, 1286 s, 1256 s, 1246 s, 1196 vs, 1111 vs, 1030 w, 996 m, 936 w, 877 m, 796 s, 761 m, 730 m, 593 w, 490 w, 464 m, 457 m cm^{-1}. ^{19}F NMR: δ −56.1 ($(CF_3)_2N$, s), −49.2 (SCF_3, s), CIMS [*m/e* (species), intensity]: 316 ($M^+ + 2$), 1.1; 315 ($M^+ + 1$), 0.5; 314 (M^+), 1.9; 279 ($M^+ - Cl$), 4.5; 164 ($(CF_3)_2NC^+$), 1.9; 162 ($M^+ - N(CF_3)_2$), 5.4; 134 ($C_2F_5N^+ + 1$), 7.1; 133 ($C_2F_5N^+$), 3.7; 123 ($C_2F_2N_2S^+ + 1$), 3.5; 119 ($C_2F_5^+$), 26.5; 117 ($CF_3NS^+ + 2$), 15.6; 115 (CF_3NS^+), 6.5; 111 ($C_2F_2NCl^+$), 3.1; 109 ($C_2F_3N_2^+$), 2.0; 101 (CF_3S^+), 3.3; 95 ($C_2F_3N^+$), 4.6; 88 ($C_3F_2N^+$), 10.0; 84 ($CF_3N^+ + 1$), 100; 69 (CF_3^+), 100.

(C) Reaction of CF_3SCl with C_2F_5CN To Form $C_2F_5C(Cl){=}NSCF_3$. Five millimoles each of C_2F_5CN and CF_3SCl are condensed into a quartz vessel at −196 °C. After the vessel was warmed to 25 °C the contents are photolyzed for 8 h at 3000 Å. When the contents are separated by trap-to-trap distillation the product is isolated in ~30% yield in a trap held at −60 °C. Spectral data are as follows. IR (gas): 1630 m, 1341 m, 1223 s, 1190 vs, 1132 s, 1102 s, 906 m, 868 m, 796 w, 762 m, 735 s, 462 m cm^{-1}. ^{19}F NMR: δ −46.1 ($(CF_3)S$, s), −81.6 (CF_3CF_2, t, J = 1.8 Hz), −112 (CF_2, q, J = 1.76 Hz). CIMS [*m/e* (species), intensity]: 281 (M^+), 30.6; 262 ($M^+ - F$), 28.2; 246 ($M^+ - Cl$), 31.7; 162 ($M^+ - C_2F_5$), 13.5; 146 ($M^+ - CF_3SCl + 1$), 27.5; 119 ($C_2F_5^+$), 13.5; 101 (CF_3S^+), 22.7; 82 (CF_2S^+), 86; 69 (CF_3^+), 100.

Reaction of ClF with $(CF_3)_2NN{=}CCl_2$ To Give $(CF_3)_2NN(Cl)CF_2Cl$ (5). Five millimoles of $(CF_3)_2NN{=}CCl_2$ and 6 mmol of ClF are condensed at −196 °C into an evacuated 75-mL stainless steel vessel fitted with a Whitey stainless steel valve. The reactants are allowed to warm to and are held at 25 °C for 10–12 h. The contents of the vessel are separated by trap-to-trap distillation. The compound found in the trap at −85 °C is $(CF_3)_2NN(Cl)CF_2Cl$ in ~55% yield. Spectral data are as follows. IR (gas): 1336 s, 1295 s, 1242 vs, 1171 s, 1107 s, 1026 s, 986 m, 909 s, 847 w, 810 m, 796 m, 721 m, 655 w cm^{-1}. ^{19}F NMR: δ −61.01 [$(CF_3)_2$, s], −93.8 [CF_2Cl, S]. CIMS [*m/e* (species), intensity]: 286 (M^+), 2.0; 267 ($M^+ - F$), 1.8; 232 ($M^+ - ClF$), 25.6; 216 ($M^+ - 2Cl$), 22.6; 216 ($M^+ - CF_3 + 1$), 19.6; 198 ($M^+ - CF_4$), 29.6; 182 ($M^+ - CF_3Cl$), 19.5; 134 ($C_2F_5N^+ + 1$), 11.5; 114 ($M^+ - 2CF_3 - Cl + 1$), 40.7; 85 (CF_2Cl^+), 19.2; 69 (CF_3^+), 100.

Photolysis of $(CF_3)_2NN(Cl)CF_2Cl$ To Form $(CF_3)_2NN{=}C(Cl)F$ (6). Six millimoles of 5 is condensed at −196 °C into an evacuated 2-L quartz vessel. After the vessel is warmed to 25 °C, the contents are photolyzed for 3 h (3000 Å). When the contents of the vessel are distilled, **6** is found in ~57% yield in a trap at −90 °C after passing a trap at −50 °C. Spectral data are as follows. IR (gas): 1664 s, 1324 vs, 1259 vs, 1216 vs, 1118 m, 1083 m, 1042 m, 981 s, 910 s, 845 m, 816 m, 796 w, 752 s, 736 m, 724 m cm^{-1}. ^{19}F NMR: δ −64.5 [$(CF_3)_2$, s], −21.7 [CF, s]. CIMS (*m/e* (species), intensity]: 232 (M^+), 14.5; 213 ($M^+ - F$), 4.8; 197 ($M^+ - Cl$), 1.0; 181 ($M^+ + 15 - CClF$), 4.3; 169 ($M^+ + 15 - NCClF + 2$), 3.8; 153 ($(CF_3)_2N^+ + 1$), 1.1; 84 ($CF_3N^+ + 1$), 100%; 83 (CF_3N^+), 5; 69 (CF_3^+), 37.

Dimerization of $(CF_3)_2NN{=}C(Cl)F$ to $(CF_3)_2NN{=}CFN(CF_3)N(CF_3)_2$. Four millimoles of 1 is condensed at −196 °C into a Pyrex glass reaction vessel equipped with a Teflon stopcock that contains 4 mmol of anhydrous CsF. The mixture is warmed to 25 °C and stirred for 5–6 h. When the contents of the flask are distilled, the dimer is obtained in a

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trap at −85 °C as a colorless liquid. Spectral data are as follows. IR (gas): 1729 s, 1431 w, 1410 w, 1358 s, 1320 s, 1301 s, 1262 s, 1218 s, 1189 m, 1116 m, 1009 w, 997 m, 980 w, 910 w, 748 w, 731 m, 690 w cm^{-1}. ^{19}F NMR: δ −61.0 [$(CF_3)_2NNCF_3$, 9 F, m], −65.7 [$(CF_3)_2NN$, 6 F, d, J = 4.61 Hz], −49.1 [CF_3, 3 F, m].

Preparation of 8, 9, 10, 11, and 15. Six millimoles of $(CH_3)_3SiC_6F_5$ and $CF_3(C_2F_5)NN{=}C(Cl)CF_3$, $(CF_3)_2NN{=}C(Cl)CF_3$, $(CF_3)_2NN{=}C(Cl)C_2F_5$, $SF_5N{=}C(Cl)C_2F_5$, or $(CF_3)_2NN{=}C(Cl)F$ (6 mmol) are condensed into a Pyrex glass vessel equipped with a Teflon stopcock and containing 7 mmol of anhydrous CsF. To that, 8 mmol of CH_3CN is condensed at −196 °C. The flask is warmed slowly to 25 °C and the contents stirred for 8–10 h. The resulting mixtures are separated by trap-to-trap distillation to give the respective compounds.

Properties of $CF_3(C_2F_5)NN{=}C(CF_3)C_6F_5$ (8). Compound **8** is isolated in a trap at −50 °C in 65% yield. Spectral data obtained are as follows. IR (gas): 1660 s, 1526, s, 1508 vs, 1440 w, 1377 w, 1285 s, 1220 vs, 1180 s, 1153 s, 1091 s, 1048 w, 1034 w, 998 s, 911 s, 868 m, 808 w, 786 w, 757 m, 739 s, 710 w, 699 w, 520 m cm^{-1}. ^{19}F NMR: δ −58.2 [CF_3N, mult], −69.8 [CF_3C, t, $J_{CF_3-CF(ortho)}$ = 6.2 Hz], −81.6 [CF_3CF_2, mult], −99.5 [CF_2, mult], −135.5 [ortho, 2 F, br mult], −145.2 [para, 1 F, mult], −158.8 [meta, 2 F, mult]. CIMS [m/e (species), intensity]: 465 (M^+ + 1), 20.3; 464 (M^+), 44.4; 445 (M^+ − F), 28.3; 395 (M^+ − CF_3), 36.2; 345 (M^+ − C_2F_5), 2.6; 307 (M^+ − C_2F_5 − 2F), 1.5; 262 (M^+ − CF_3-$(C_2F_5)N^+$), 24.8; 248 ($C(CF_3)C_6F_5^+$), 16.8; 229 (M^+ − C_6F_5 − CF_3 + 1), 5; 193 ($NCC_6F_5^+$), 25.1; 179 ($CF_3NNCCF_3^+$ + 1), 14.9; 167 ($C_6F_5^+$), 2.8; 148 ($C_6F_4^+$), 2.7; 119 ($C_2F_5^+$), 10; 69 (CF_3^+), 100. Anal. Calcd: C, 28.4; F, 65.5; N, 6.03. Found: C, 28.57; F, 65.6; N, 6.11.

Properties of $(CF_3)_2NN{=}C(CF_3)C_6F_5$ (9). Compound **9** is isolated as a colorless liquid in 68% yield in a trap at −60 °C. Spectral data obtained are as follows. IR (gas): 1661 s, 1526 s, 1508 s, 1312 s, 1249 s, 1198 s, 1145 m, 1092 m, 1072 m, 997 s, 976 s, 872 s, 836 s, 759 m, 735 w, 719 m, 705 w, 687 m, 624 w, 549 m cm^{-1}. ^{19}F NMR: δ −62.2 [$(CF_3)_2N$, tr, $J_{CF_3-ortho\ F}$ = 4.8 Hz], −69.6 [CF_3C, tr, $J_{CF_3C-ortho\ F}$ = 6.4 Hz], −135.2 [ortho, 2 F, mult], −145.0 [para, 1 F, m], −158.2 [meta, 2 F, m]. CIMS [m/e (species), intensity]: 415 (M^+ + 1), 27.0; 414 (M^+), 22.2; 395 (M^+ − F), 26.8; 345 (M^+ − CF_3), 13.5; 262 (M^+ − $N(CF_3)_2^+$), 9.5; 248 (M^+ − C_6F_5 + 1), 12.3; 202 (M^+ − CF_3 − C_4F_5), 9.1; 194 (M^+ − $N(CF_3)_2$ − CF_3 + 1), 21.9; 179 (M − C_6F_5 − CF_3 + 1), 5; 168 ($C_6F_5^+$ + 1), 21.9; 134 ($C_2F_5N^+$ + 1), 8.5; 98 (CF_3NN^+ + 1), 5.3; 69 (CF_3^+), 50.5. Anal. Calcd: C, 28.9; F, 64.2. Found: C, 28.2; F, 63.7.

Properties of $(CF_3)_2NN{=}C(C_2F_5)C_6F_5$ (10). Compound **10** is found in ∼60% yield in a trap at −50 °C. Spectral data obtained are as follows. IR (gas): 1657 s, 1525 s, 1507 vs, 1438 w, 1315 vs, 1197 vs, 1148 s, 1093 m, 1046 w, 1003 s, 980 s, 963 m, 860 m, 755 m, 719 m, 524 w cm^{-1}. ^{19}F NMR: δ −62.8 [$(CF_3)_2N$, tr, $J_{(CF_3)_2N-ortho\ F}$ = 4.5 Hz], −82.6; [CF_3, mult], −114.8 [CF_2, mult], −135.4 [ortho, 2 F, br], −145.4 [para, 1 F, mult], −158.8 [meta, 2 F, mult]. CIMS [m/e (species), intensity]: 466 (M^+ + 2), 1.1; 465 (M^+ + 1), 18.3; 464 (M^+), 13.5; 445 (M^+ − F), 20.4; 345 (M^+ − C_2F_5), 11.9; 297 (M^+ − C_6F_5), 42.6; 257 (M^+ − 3CF_3), 1.4; 248 (M^+ − $(CF_3)_2NN$ − CF_2), 8.3; 228 (M^+ − C_6F_5 − CF_3), 2.3; 194 ($C_6F_5CN^+$ + 1), 10.2; 193 ($C_6F_5CN^+$), 9.6; 179 ($C_6F_5C^+$), 2.2; 168 ($C_6F_5^+$ + 1), 18.7; 167 ($C_6F_5^+$), 1.1; 153 ($(CF_3)_2N^+$ + 1), 7.0; 119 ($C_2F_5^+$), 12.6; 101 ($C_2F_4^+$ + 1), 6.1; 69 (CF_3^+), 100. Anal. Calcd: C, 28.4, F, 65.5. Found: C, 28.5, F, 65.0.

Properties of $SF_5N{=}C(C_2F_5)C_6F_5$ (11). Compound **11** is found in ∼55% yield in a trap at −70 °C. Spectral data obtained are as follows. IR (gas): 1685 s, 1655 m, 1524 s, 1509 vs, 1475 w, 1449 w, 1356 m, 1326 m, 1214 s, 1183 m, 1140 s, 1092 s, 1075 m, 999 s, 982 m, 961 m, 894 vs, 868 s, 837 s, 754 m, 735 m, 718 w, 688 m, 602 s, 549 m, 522 m cm^{-1}. ^{19}F NMR: δ 68.5 (SF, p), 62.05 (SF_4, d), −80.9 (CF_3CF_2, tr, $J_{CF_3-CF_2}$ = 1.64), −114.7 (CF_3CF_2, q), −136.3 (ortho, 2 F, br), −145.6 (para, 1 F, mult). CIMS [m/e (species), intensity]: 441 (M^+ + 2), 1.1; 440 (M^+ + 1), 9.4; 439 (M^+), 10.4; 420 (M^+ − F), 9.4; 346 (M^+ − C_3F_3), 1.2; 320 (M^+ − C_2F_5), 22.3; 312 (M^+ − SF_5), 37.3; 274 (M^+ − SF_5 − 2F), 1.9; 248 (M^+ − NSF_5 − CF_2), 10.3; 208 (M^+ − C_2F_5 − C_3F_4), 3.3; 194 (M^+ − SF_5 − C_2F_5 + 1), 13.7; 193 (M^+ − SF_5 − C_2F_5), 14.6; 182 (M^+ − SF_5 − C_3F_5 + 1), 3.0; 168 ($C_6F_5^+$ + 1), 12.8; 167 ($C_6F_5^+$), 5.2; 148 ($C_6F_4^+$), 2.7; 127 (SF_5^+), 100; 119 ($C_2F_5^+$), 15.5; 104 (SF_3N^+ + 1), 76.8; 103 (SF_3N^+), 63.2; 89 (SF_3^+), 15.2; 76 ($C_3F_2H_2^+$), 17.1; 69 (CF_3^+), 100. Anal. Calcd: C, 24.6; F, 64.9. Found: C, 23.9; F, 64.1.

Properites of $SF_5N{=}C(C_2F_5)NMe_2$ (12). Compound **12** is isolated in 70% yield in a trap at −50 °C. Spectral data are as follows. IR (gas): 2960 s, 2836 m, 1646 vs, 1599 s, 1490 s, 1479 s, 1470 s, 1445 m, 1426 m, 1397 m, 1338, 1245 s, 1187 s, 1137 s, 1064 m, 1035 s, 898 s, 848 s, 769 s, 742 m, 669 m, 605 w, 586 s, 519 w cm^{-1}. ^{1}H NMR: δ 3.20 (NMe_2, mult). ^{19}F NMR: δ 87.3 (SF_4, d), 88.5 (SF, p, J_{SF_4-SF} = 159.4 Hz), −79.3 (CF_3, mult), −109.1 (CF_2, mult). CIMS [m/e (species), intensity]: 318 (M^+ + 2), 1.3; 317 (M^+ + 1), 21.1; 316 (M^+), 1.5; 297 (M^+ − F), 100; 273 (M^+ − NMe_2 + 1), 2.9; 253 (M^+ − NMe_2 − F), 1.2; 197 (M^+ − C_2F_5), 5.5; 190 (M^+ − SF_5 + 1), 10.1; 189 (M^+ − SF_5), 83.1; 182 (M^+ − C_2F_5 − CH_3), 1.0; 175 (M^+ − SF_5N), 3.9; 170 (M^+ − SF_6^+), 1.8; 160 (M^+ − C_2F_5 − 2F + 1), 27.1; 146 ($C_2F_5NC^+$ + 1), 50.9; 131 ($C_2F_5C^+$), 3.6; 127 (SF_5^+), 31.5; 126 ($C_2F_4CN^+$), 10.3; 119 ($C_2F_5^+$), 22.6; 104 (SF_3N^+ + 1), 2.6; 100 ($C_2F_4^+$), 2.8; 89 (SF_3^+), 25.9; 81 ($C_2F_3^+$), 5.2; 76 (CF_2CN^+), 15.9; 70 (SF_2^+), 28.6; 69 (CF_3^+), 61.3. Anal. Calcd: C, 18.9; F, 60.1. Found: C, 19.1; F, 60.3.

Properties of $SF_5N{=}C(C_2F_5)CF_3$ (13). Compound **13** is isolated in 55% yield in a trap at −78 °C. Spectral data obtained are as follows. IR (gas): 1715 m, 1497 w, 1482 w, 1464 m, 1338 m, 1268 s, 1246 vs, 1146 m, 1079 s, 1018 m, 973 w, 918 m, 885 m, 852 s, 800 w, 754 m, 619 w cm^{-1}. ^{19}F NMR: δ 70.1 (SF_4, d), 66.3 (SF, p, J_{SF_4-SF} = 158.1 Hz), −67.9 (CCF_3, mult), −81.0 (CF_2CF_3, mult), −119.0 (CF_2CF_3, mult). CIMS [m/e (species), intensity]: 343 (M^+ + 2), 0.7; 341 (M^+), 1.1; 322 (M^+ − F), 42.4; 272 (M^+ − CF_3), 17.1; 222 (M^+ − C_2F_5), 1.1; 181 (M^+ − SF_6N), 4.6; 147 ($SF_4NC_2^+$ + 1), 18.2; 146 ($SF_4NC_2^+$), 6.7; 145 (C_2F_5-CN^+), 1.6; 131 ($C_2F_5C^+$), 1.6; 127 (SF_5^+), 100; 119 ($C_2F_5^+$), 50.1; 108 ($CF_3C_2N^+$ + 1), 1.1; 96 (SF_2NC^+), 13.5; 89 (SF_3^+), 30.5; 77 ($SFNC^+$), 13.7; 69 (CF_3^+), 66.1. Anal. Calcd: C, 14.1; F, 72.4. Found: C, 13.7; F, 71.9.

Properties of $(CF_3)_2NCF_2N{=}C(C_6F_5)OC(CF_3)_2CH_3$ (14). Spectral data are as follows. IR (gas): 2966 m, 1651 m, 1537 s, 1515 s, 1409 w, 1360 m, 1262 s, 1228 s, 1183 s, 1141 m, 1075 s, 1001 w, 957 s, 912 m, 852 s, 757 w, 716 w cm^{-1}. ^{1}H NMR: δ 2.12 (CCH_3, sept). ^{19}F NMR: δ −56.29 (CF_3N, tr, $J_{CF_3N-CF_2}$ = 3.95 Hz), −59.8 (CF_3N, tr, $J_{CF_3N-CF_2}$ = 4.89 Hz), −75.27 [$(CF_3)_2C$, q, $J_{(CF_3)_2C-CH_3}$ = 21.0 Hz), −76.35 (NCF_2N, mult), −138.7 (ortho, 2 F, mult), −154.4 (para, 1 F, mult), −162.2 (meta, 2 F, mult). CIMS [m/e (species), intensity]: 557 (M^+ − F), 0.5; 458 (M^+ − C_2F_5 + 1), 1.2; 445 (M^+ − C_3F_5), 4.4; 444 (M^+ − C_3F_5H), 2.9; 438 (M^+ − 2 CF_3), 1.1; 430 (M^+ − $C_4H_3F_5$), 8.1; 424 (M^+ − $N(CF_3)_2$), 24.6; 410 (M^+ − C_6F_5 + 1), 2.3; 360 (M^+ − $(CF_3)_2NCF_2N$), 5.2; 347 (M^+ − $(CF_3)_2N$ − CH_3 − 2CF), 4.0; 310 (M^+ − $(CF_3)_2NCF_2N$ − CF_2), 1.7; 279 ($C_6F_5OC(CH_3)(CF_3)^+$), 14.0; 274 (M^+ − $(CF_3)_2NCF_2$ − C_2F_4), 6.7; 262 (M^+ − $(CF_3)_2N$ − CF_3 − 3CF), 17.9; 217 ($(CF_3)_2NCF_2N^+$ + 1), 2.0; 202 ($(CF_3)_2NCF_2^+$), 2.7; 195 ($OC_7F_5^+$), 37.8; 181 ($OC(CF_3)_2CH_3^+$), 2.2; 168 ($C_6F_5^+$ + 1), 96.2; 167 ($C_6F_5^+$), 18.0; 148 ($C_6F_4^+$), 4.1; 147 ($C_2F_5N_2^+$), 9.7; 145 ($C_2F_5NC^+$), 4.7; 133 ($CF_3NCF_2^+$), 4.2; 119 ($C_2F_5^+$), 5.0; 114 ($C_2F_4N^+$), 2.3; 104 ($C_4H_2F_2O^+$), 100; 95 (CF_3NC^+), 6.9; 85 (CF_3O^+), 1.2; 69 (CF_3^+), 46.7.

Properties of $(CF_3)_2NN{=}C(C_6F_5)N(CF_3)N(CF_3)_2$ (15). Compound **15** was found in 52% yield as a colorless liquid in a trap at −45 °C. Spectral data are as follows. IR (gas): 1719 s, 1515 vs, 1356 s, 1323 s, 1297 vs, 1260 m, 1221 s, 1110 w, 1076 w, 1008 m, 992 m, 736 s. ^{19}F NMR: δ −60.5 [$(CF_3)_2NNCF_3$, 9 F, mult], −65.2 [$(CF_3)_2N$, 6 F, mult], −140.4 [ortho, 2 F, mult], −155.8 [para, 1 F, mult], −160.4 (meta, 2 F, mult). CIMS [m/e (species), intensity]: 581 (M^+ + 1), 4.2; 580 (M^+), 5; 561 (M^+ − F), 9.7; 413 (M^+ − C_6F_5), 15.2; 345 (M^+ − C_6F_5 − CF_3 + 1), 7.1; 248 ($CN_2(CF_3)_3^+$ + 1), 74.0; 168 ($C_6F_5^+$ + 1), 92.0; 167 ($C_6F_5^+$), 80.0; 133 ($C_2F_5N^+$), 46.5; 117 ($C_5F_3^+$), 84.0; 97 (CF_3NN^+), 48.0; 93 ($C_3F_3^+$), 51.2; 81 ($C_2F_3^+$), 53.7; 69 (CF_3^+), 100.

Reaction of Chlorine Fluoride with $(CF_3)_2NN{=}C(C_6F_5)N(CF_3)_2$ To Form Compound 16. Three millimoles of $(CF_3)_2NN{=}C(C_6F_5)N(CF_3)$-$(CF_3)_2$ and 3 mmol of ClF are condensed at −196 °C into a 75-mL stainless steel vessel fitted with a Whitey stainless steel valve. The reactants are allowed to warm to and were held at 25 °C for 7–8 h. The contents of the vessel were separated by trap-to-trap distillation. Compound **16** was found in the trap at −40 °C. Spectral data are as follows. IR (gas): 1518 s, 1502 m, 1359 s, 1320 s, 1290 s, 1255 m, 1219 s, 1115 w, 1080 w, 998 m, 978 m, 839 w, 740 m cm^{-1}. ^{19}F NMR: δ −59.7 ($(CF_3)_2$-$NNCF_3$, 9 F, mult), −61.1 ($(CF_3)_2$, 6 F, mult), −74.58 (CF, 1 F, mult), −140.3 (ortho, 2 F, mult), −155.5 (para, 1 F, mult), −160.8 (meta, 2 F, mult), CIMS [m/e (species), intensity]: 433 (M^+ − Cl − C_6F_5 + 1), 1.0; 432 (M^+ − Cl − C_6F_5), 1.5; 413 (M^+ − C_6F_5 − ClF), 2.4; 237 ($N_2(CF_3)_3^+$ + 2), 1.1; 228 ($(CF_3)_2NNC_2F_2^+$), 1.2; 202 ($(CF_3)_2N_2Cl^+$ + 1), 3.1; 181 ($C_6F_5C^+$ + 1), 0.8; 166 ($(CF_3)_2N_2^+$), 0.5; 119 ($C_2F_5^+$), 10.1; 88 (CF_4^+), 100; 84 (CF_3N^+ + 1), 100; 83 (CF_3N^+), 9.9; 69 (CF_3^+), 7.6.

Reactions of $CF_3N{=}SF_2$ with CF_3TMS or C_6F_5TMS. Four millimoles of $CF_3N{=}SF_2$ and 8 mmol of CF_3TMS or of C_6F_5TMS are condensed at −196 °C into an evacuated Pyrex glass vessel equipped with a Teflon stopcock which contains 8 mmol of CsF. Then 9 mmol of acetonitrile or benzonitrile is added, the flask is warmed to 25 °C, and the contents are stirred at this temperature for 8–10 h. The resulting mixtures were separated by trap-to-trap distillation.

Properties of $CF_3N{=}S(CF_3)_2$ (17). Compound **17** is obtained in ~68% yield in a trap at −80 °C having passed a trap at −30 °C. Spectral data obtained are as follows. IR (gas): 1288 vs, 1262 s, 1204 s, 1136 s, 1081 s, 813 w, 752 m, 568 w, 468 m cm^{-1}. ^{19}F NMR: δ −46.4 (CF_3N, 3 F, sept, $J_{CF_3N-(CF_3)_2S}$ = 2.9 Hz), −61.2 ($CF_{32}S$, 6 F, q, J = 2.9 Hz). CIMS [*m/e* (species), intensity]: 254 ($M^+ + 1$), 2.5; 253 (M^+), 3.7; 234 ($M^+ - F$), 62.0; 184 ($M^+ - CF_3$), 8.6; 165 ($M^+ - CF_3 - F$), 31.2; 146 ($M^+ - CF_3 - 2\ F$), 27.5; 114 ($C_2F_3S^+ + 1$), 4.3; 101 (CF_3S^+), 3.1; 96 (CF_2NS^+), 7.5; 83 (CF_3N^+), 1.8; 82 (CF_2S^+), 5.6; 69 (CF_3^+), 100. Anal. Calcd: C, 14.2; F, 67.5. Found: C, 14.0; F, 67.2.

Properties of $CF_3N{=}S(C_6F_5)_2$ (18). Compound **18** is obtained in ~52% yield in a trap at −35 °C. Spectral properties are as follows. IR (gas): 1510 s, 1505 s, 1481 s, 1395 m, 1298 m, 1250 s, 1163 s, 1100 s, 993 s, 909 s, 861 w, 808 m, 735 s, 688 m, 651 s, 627 w, 588 w, 564 w, 549 w cm^{-1}. ^{19}F NMR: δ −45.4 (CF_3N, tr, $J_{CF_2N-ortho\ F}$ = 1.6 Hz), −136.6 (ortho, 2 F, mult), −142.4 (para, 1 F, mult), −156.4 (meta, 2 F, mult). CIMS [*m/e* (species), intensity]: 451 ($M^+ + 2$), 1.0; 450 ($M^+ + 1$), 8.1; 449 (M^+), 5.2; 430 ($M^+ - F$), 24.7; 366 ($M^+ - NCF_3$), 36.1; 347 ($M^+ - NCF_3 - F$), 4.7; 316 ($M^+ - NCF_3 - CF_2$), 4.7; 282 ($M^+ - C_6F_5$), 2.6; 251 ($M^+ - C_6F_5 - CF$), 11.4; 199 ($SC_6F_5^+$), 38.8; 181 ($C_6F_4S^+ + 1$), 11.7; 168 ($C_6F_5^+ + 1$), 18.43; 104 (C_6S^+), 100; 69 (CF_3^+), 100.

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