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Contribution from the Department of Chemistry,
The University of Alabama, Tuscaloosa, Alabama 35487-9671

Bis[(pentafluorothio)(trifluoromethyl)amido]mercury, $Hg[N(CF_3)SF_5]_2$, and Bis[(pentafluorotelluro)(trifluoromethyl)amido]mercury, $Hg[N(CF_3)TeF_5]_2$

Joseph S. Thrasher,* Jon B. Nielsen, Simon G. Bott, Donna J. McClure, Sally A. Morris, and Jerry L. Atwood

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The mercurial compound $Hg[N(CF_3)SF_5]_2$ can be obtained in over 95% yield from the direct reaction of $SF_5N{=}CCl_2$ with excess HgF_2 at 150 °C. X-ray crystal structure analysis of the tellurium analogue $Hg[N(CF_3)TeF_5]_2$ reveals a linear N-Hg-N arrangement as well as a planar framework around each nitrogen [$\angle$TeNC = 119 (2)°]. $C_2F_{16}N_2HgTe_2$ crystallizes in the orthorhombic space group *Pbca*. Unit cell parameters: a = 10.746 (5) Å, b = 9.702 (6) Å, c = 12.718 (8) Å, Z = 4; R = 0.090, R_w = 0.101. Reactions of $Hg[N(CF_3)SF_5]_2$ with halogens or interhalogens give the series of tertiary amines $SF_5N(X)CF_3$, where X = F, Cl, Br, and I. Of these only the *N*-iodo compound is unstable at room temperature. The successful syntheses of $SF_5N(CH_3)CF_3$ and $TeF_5N(CH_3)CF_3$ from the respective mercurial compound and CH_3I allow the comparison of the relative group electronegativities of $SF_5N(CF_3)$- and $TeF_5N(CF_3)$- with $(CF_3)_2N$-, $(CF_3S)_2N$-, $(SF_5)_2N$-, $(CF_3SO_2)_2N$-, and $(FSO_2)_2N$-. The new perfluorinated tertiary amine $(SF_5)_2NCF_3$ is prepared in high yield from the gas-phase photolysis of $SF_5N(Cl)CF_3$. The bromoamine $SF_5N(Br)CF_3$ adds readily to the alkenes C_2H_4 and C_3F_6 to give $SF_5N(CF_3)CH_2CH_2Br$ and the mixture of isomers $SF_5N(CF_3)CF_2CF(Br)CF_3$ and $SF_5N(CF_3)CF(CF_3)CF_2Br$, respectively.

Introduction

A number of new Hg^{II} derivatives containing highly electron-withdrawing amino substituents have appeared lately. These mercurials, which include $Hg[N(CF_3)TeF_5]_2$,[1] $Hg[N(SF_5)_2]_2$,[2] $Hg[N(SO_2CF_3)_2]_2$,[3] and $Hg[N(SO_2F)_2]_2$,[3] are of interest because they serve as valuable precursors to a variety of derivatives containing these amino groups. For example, we recently reported a number of derivatives of the type $TeF_5N(CF_3)X$, where X = F, Cl, Br, I, SF_5, TeF_5, $C(O)CH_3$, CH_2CH_2Br, $CF_2CF(Br)CF_3$, and $CF(CF_3)CF_2Br$, starting from $Hg[N(CF_3)TeF_5]_2$.[1] As several of these derivatives have no known analogues in the chemistry of sulfur-nitrogen compounds,[4] it was of interest to attempt their preparation. We were also interested in comparing the relative group electronegativities of the $SF_5N(CF_3)$- and $TeF_5N(CF_3)$- groups, which could be most easily achieved by preparing the *N*-methyl derivatives $SF_5N(CH_3)CF_3$ and $TeF_5N(CH_3)CF_3$. Also reported herein are the results of our X-ray crystal structure analysis of $Hg[N(CF_3)TeF_5]_2$.

The mercurial $Hg[N(CF_3)SF_5]_2$ was first reported in 1964 by Tullock et al.[4] from the reaction of $SF_5N{=}CF_2$ with mercuric fluoride:

$$2SF_5N{=}CF_2 + HgF_2 \xrightarrow{100\text{-}125\ °C} Hg[N(CF_3)SF_5]_2 \quad 76\% \qquad (1)$$

The tellurium analogue $Hg[N(CF_3)TeF_5]_2$ can be prepared in a similar fashion;[1a] however, an improved synthesis was found in the direct reaction between $TeF_5N{=}CCl_2$ and HgF_2:[1b]

$$2TeF_5NHCF_3 \xrightarrow{HgF_2,\ 70\text{-}80\ °C} Hg[N(CF_3)TeF_5]_2 \quad 20\% \qquad (2)$$

$$2TeF_5N{=}CCl_2 + 3HgF_2 \xrightarrow{60\ °C} 2HgCl_2 + Hg[N(CF_3)TeF_5]_2 \quad 97\% \qquad (3)$$

It was obvious that our study would be easier if this same direct reaction were to work with the sulfur compound, thus eliminating two reaction steps in the preparation of $Hg[N(CF_3)SF_5]_2$.

Experimental Section

Spectra. Infrared spectra were recorded on either a Perkin-Elmer 283B or a Bio-Rad FTS-40 infrared spectrophotometer on gases at pressures between 1 and 10 Torr. Mass spectra were obtained on a Hewlett-Packard 5985A GC/MS system by using a controlled gas inlet probe. Only the most important ions are reported. The mass numbers are given for ^{202}Hg, ^{130}Te, ^{79}Br, or ^{35}Cl where applicable; the intensities include all isotopes. The ^{19}F and ^{1}H NMR spectra were recorded on either a Varian EM360L, a Nicolet NIC 200 FT, or a Bruker AM 500 nuclear magnetic resonance spectrometer. The ^{19}F and ^{1}H spectra were taken on dilute solutions in CCl_3F and referenced to CCl_3F and $Si(CH_3)_4$, respectively. Resonances appearing upfield from CCl_3F in the ^{19}F NMR spectra are designated negative. The ^{13}C NMR spectra were recorded on a Nicolet NIC 200 FT NMR spectrometer with TMS as the standard. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN.

Table I. Summary of Crystal Data and Data Collection Conditions for $Hg[N(CF_3)TeF_5]_2$

formula	$C_2N_2F_{16}HgTe_2$
space group	*Pbca*
a, Å	10.746 (5)
b, Å	9.702 (6)
c, Å	12.718 (8)
V, Å^3	1326
Z	4
d_{calcd}, g cm^{-3}	4.08
cryst dimens, mm	0.4 × 0.1 × 0.6
radiation	Mo Kα (graphite monochromated)
μ, cm^{-1}	161.73
scan width, deg	0.80 + 0.20 tan θ
std reflcns	400, 040, 004
variation of stds	<8%
2θ range, deg	2-50
no. of measd reflcns	1400
no. of abs reflcns	832
no. of variables	96
R	0.090
R_w	0.101
goodness of fit	1.52

Reagents. SF_5Cl,[4,5] $SF_5N{=}CCl_2$,[4] $Hg[N(CF_3)TeF_5]_2$,[1] HgF_2,[6] and ICl[7] were prepared by known literature methods. All other materials were taken from laboratory stock and purified, where necessary, before use. *Caution*! Mercury salts are poisonous, and thus suitable safety precautions should be kept in mind when working with the *volatile* mercurials describe herein.

X-ray Structure Analysis of $Hg[N(CF_3)TeF_5]_2$. Suitable crystals of $Hg[N(CF_3)TeF_5]_2$ obtained by vacuum sublimation were sealed under nitrogen in thin-walled glass capillaries. Final lattice parameters as determined by least-squares refinement of 24 reflections (2θ > 35°) accurately centered on the diffractometer are given in Table I. Data were collected on a Enraf-Nonius CAD-4 diffractometer by the θ-2θ scan

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Table II. Positional Parameters for $Hg[N(CF_3)TeF_5]_2$

atom	x	y	z	10^2U_{eq},[a] Å^2
Hg	0.5000	0.5000	0.0000	1.1 (3)
Te	0.4240 (2)	0.2744 (2)	0.1944 (2)	1.3 (2)
F(1)	0.568 (3)	0.367 (2)	0.191 (2)	3.8 (6)
F(2)	0.493 (3)	0.132 (3)	0.132 (3)	7.2 (50)
F(3)	0.281 (2)	0.174 (3)	0.199 (2)	3.6 (12)
F(4)	0.480 (2)	0.184 (3)	0.313 (2)	3.9 (6)
F(5)	0.365 (3)	0.401 (3)	0.283 (2)	5.1 (34)
F(6)	0.238 (3)	0.225 (3)	−0.009 (2)	4.5 (9)
F(7)	0.254 (2)	0.431 (3)	−0.062 (2)	3.6 (11)
F(8)	0.169 (3)	0.385 (3)	0.081 (2)	5.2 (7)
N	0.376	0.376 (3)	0.063 (2)	0.7 (6)
C	0.260 (4)	0.354 (4)	0.022 (3)	1.9 (8)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $Hg[N(CF_3)TeF_5]_2$

	Bond Lengths		
Hg–N	1.97 (3)	Te–N	2.01 (3)
Te–F(1)	1.79 (3)	Te–F(2)	1.76 (3)
Te–F(3)	1.82 (2)	Te–F(4)	1.85 (2)
Te–F(5)	1.79 (3)	C–N	1.37 (5)
C–F(6)	1.33 (5)	C–F(7)	1.30 (4)
C–F(8)	1.27 (5)		
	Bond Angles		
N–Hg–N′	180.000	N–Te–F(1)	88 (1)
F(1)–Te–F(2)	91 (2)	N–Te–F(2)	97 (2)
F(1)–Te–F(3)	178 (1)	F(2)–Te–F(3)	87 (1)
N–Te–F(3)	94 (1)	F(1)–Te–F(4)	88 (1)
F(2)–Te–F(4)	82 (2)	F(3)–Te–F(4)	90 (1)
N–Te–F(4)	176 (1)	F(1)–Te–F(5)	89 (1)
F(2)–Te–F(5)	168 (2)	F(3)–Te–F(5)	93 (1)
F(4)–Te–F(5)	86 (1)	N–Te–F(5)	95 (1)
N–C–F(6)	115 (3)	F(6)–C–F(7)	107 (3)
N–C–F(7)	106 (3)	F(6)–C–F(8)	105 (3)
F(7)–C–F(8)	109 (4)	N–C–F(8)	116 (3)
Hg–N–Te	118 (1)	Hg–N–C	124 (2)
Te–N–C	119 (2)		

technique.[8] Intensities were corrected for Lorentz and polarization effects. An absorption correction was also applied after the method of Churchill and Hollander.[9]

Calculations were carried out on an IBM-3081D computer with the SHELX system of computer programs.[10] Neutral-atom scattering for C, N, and F was taken from the compilation of Cromer and Waber;[11] scattering for Hg and Te was corrected for the real and imaginary components of anomalous dispersion by using the tabulations of Cromer and Liberman.[12] The structure was solved by Patterson methods, which revealed the positions of the Hg and Te atoms. All other atoms were located from a subsequent difference Fourier map. All atoms were refined with the use of anisotropic thermal parameters. The following reflections were deleted from the data set due to a large extinction problem (*hkl*): 111, 202, 222, 420, 122, 442, 313, 234, 054, 264, 515, 088, 2,6,10. Refinement using least-squares methods led to a final $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.090$, $R_w = \sum[w(F_o - F_c)^2/w(F_o)^2]^{1/2} = 0.101$. The weighting scheme was based on unit weights, and no systematic variation of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The largest peaks on the final difference map of 4.0 e Å^{-3} were located around the Hg atom. The final fractional coordinates are given in Table II, important distances and angles in Table III, and nonbonded intermolecular distances under 3.6 Å in Table IV.

Preparation of $Hg[N(CF_3)SF_5]_2$.[4] Mercuric fluoride (17.2 g, 72.1 mmol) was loaded into a 30-mL stainless steel cylinder in a drybox under nitrogen atmosphere. The cylinder was then evacuated, and $SF_5N{=}CCl_2$ (6.72 g, 30.0 mmol) was condensed in at −196 °C. The cylinder was then heated for 48 h at 150 °C. At that time the cylinder was cooled to −30 °C, and any materials volatile at that temperature were removed under vacuum. IR of the volatile materials (0.01 g) indicated the presence of SF_5NHCF_3, $SF_5N{=}C{=}O$, and $SF_5N{=}CF_2$.[4] The yield of 99+% was based on the volatiles removed and the weight gain (6.71 g) of the cylinder. The isolated salt contained 15.0 mmol of $Hg[N(CF_3)SF_5]_2$ along with 27.1 mmol of unreacted HgF_2 and 30.0 mmol of $HgCl_2$ or was 20.8 mol % in $Hg[N(CF_3)SF_5]_2$. Mass spectrum (70 eV): major *m/z* 622 (M^+, 1%), 431 ($M - SF_5NCF_2{}^+$, 2%), 412 ($M - SF_5NCF_3{}^+$, 3%), 202 (Hg^+, 19%), 191 ($SF_5NCF_2{}^+$, 3%), 172 ($SF_5NCF_2{}^+$, 15%), 127 ($SF_5{}^+$, 100%), 89 ($SF_3{}^+$, 31%), 70 ($SF_2{}^+$, 11%), 69 ($CF_3{}^+$, 70%).

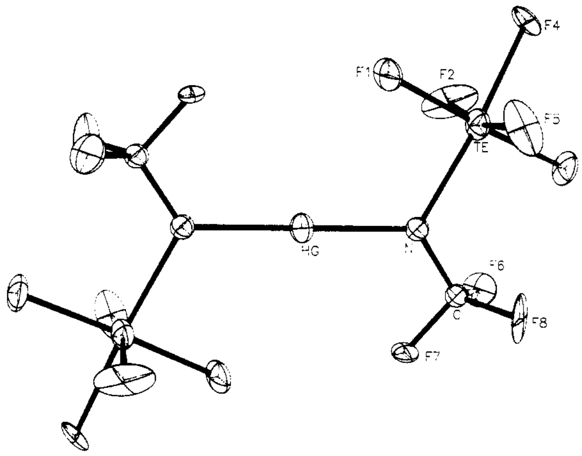

Figure 1. Molecular structure of $Hg[N(CF_3)TeF_5]_2$. The ellipsoids correspond to 50% probability.

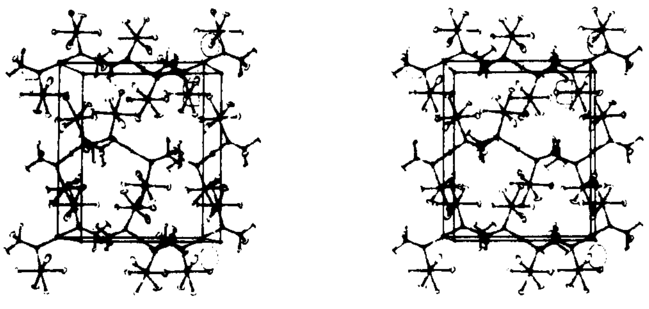

Figure 2. Stereoview of the unit cell packing of $Hg[N(CF_3)TeF_5]_2$.

Preparation of $SF_5N(F)CF_3$.[13,14] The mercurial $Hg[N(CF_3)SF_5]_2$ (4.14 g, 6.7 mmol) was distilled into a FEP reaction tube under dynamic vacuum. The reaction tube was then chilled to −196 °C, and fluorine (13.7 mmol) was condensed in. The reactor was placed in a −150 °C slush bath and allowed to warm slowly to room temperature overnight. The reactor was then cooled to −196 °C and pumped on in order to remove any residual fluorine. The condensable products were then distilled through a series of traps at −40, −115, and −196 °C with the product, $SF_5N(F)CF_3$ (1.66 g, 7.2 mmol; 54% yield), remaining in the trap held at −115 °C. The compound $SF_5N(F)CF_3$ was identified by IR, NMR, and mass spectroscopy.[13] Vapor pressure data treated by least-squares methods gave $\ln(P/P_0) = 17.86 - 3184.09T^{-1}$ (−55 to −20 °C), bp 10.3 °C, $\Delta H_v = 6.37$ kcal/mol, and $\Delta S_v = 22.32$ cal K^{-1} mol^{-1}.

Preparation of $SF_5N(Cl)CF_3$.[4] Chlorine (1.11 g, 15.8 mmol) was condensed into a stainless-steel cylinder containing $Hg[N(CF_3)SF_5]_2$ (4.44 g, 7.15 mmol; 11.3 mol %). The reaction mixture was then allowed to warm to room temperature and react overnight. The volatile materials were then removed from the cylinder and subjected to repeated trap-to-trap distillations (−40, −100, and −196 °C traps). The product $SF_5N(Cl)CF_3$ (3.42 g, 13.95 mmol; 98% yield) stopped in the trap held at −100 °C. The compound was identified by its IR, NMR, and mass spectra.[4]

Preparation of $SF_5N(Br)CF_3$. The preparation of the bromoamine was analogous to that of $SF_5N(Cl)CF_3$. A mixture of Br_2 (1.59 g, 10.0 mmol) and excess of $Hg[N(CF_3)SF_5]_2$ (5.90 g, 9.5 mmol; 15.5 mol %) was allowed to react overnight before the volatile portion was removed to the vacuum line and distilled through a series of traps at −40, −78, and −196 °C. A very pale yellow liquid, which stopped in the trap cooled to −78 °C, was subsequently identified as $SF_5N(Br)CF_3$ (1.30 g, 4.5 mmol; 80% yield). IR (gas): 1260 (vs), 1218 (vs), 1183 (vs), 962 (m), 915 (vs), 900 (vs), 735 (s), 700 (m), 603 (s) cm^{-1}. Chemical ionization mass spectrum (methane): major *m/z* 289 (M^+, 23%), 270 ($M - F^+$, 100%),

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Table IV. Nonbonded Intermolecular Distances (Å)[a] Less Than 3.6 Å

$Hg\cdots F(4)^{i}$	2.977	$F(5)\cdots F(6)^{ix}$	3.221
$Hg\cdots F(4)^{ii}$	2.977	$F(1)\cdots F(5)^{viii}$	3.222
$Hg\cdots F(6)^{iii}$	3.363	$F(3)\cdots F(8)^{vii}$	3.226
$Hg\cdots F(6)^{iv}$	3.363	$F(3)\cdots F(4)^{x}$	3.238
$F(5)\cdots F(7)^{v}$	2.856	$F(3)\cdots F(5)^{vii}$	3.256
$F(2)\cdots F(5)^{vi}$	2.916	$F(1)\cdots F(3)^{viii}$	3.266
$F(6)\cdots F(7)^{vii}$	2.940	$F(2)\cdots F(8)^{iv}$	3.309
$F(2)\cdots F(7)^{iv}$	3.000	$F(2)\cdots F(6)^{iv}$	3.357
$F(2)\cdots F(8)^{vii}$	3.034	$F(4)\cdots N^{ix}$	3.419
$F(1)\cdots F(6)^{iv}$	3.087	$F(4)\cdots F(5)^{vi}$	3.441
$F(1)\cdots F(8)^{viii}$	3.094	$F(2)\cdots C^{iv}$	3.468
$F(4)\cdots F(7)^{ix}$	3.104	$F(1)\cdots F(2)^{ii}$	3.478
$F(4)\cdots F(8)^{viii}$	3.118	$F(4)\cdots F(6)^{ix}$	3.562
$F(1)\cdots F(4)^{ii}$	3.122	$F(4)\cdots C^{ix}$	3.572
$F(3)\cdots F(7)^{ix}$	3.214		

[a] Symmetry transformations: (i) $x, {}^1/_2 - y, z - {}^1/_2$; (ii) $1 - x, y + {}^1/_2, {}^1/_2 - z$; (iii) ${}^1/_2 - x, y + {}^1/_2, z$; (iv) ${}^1/_2 + x, {}^1/_2 - y, -z$; (v) ${}^1/_2 - x, 1 - y, {}^1/_2 + z$; (vi) $1 - x, y - {}^1/_2, {}^1/_2 - z$; (vii) ${}^1/_2 - x, y - {}^1/_2, z$; (viii) $x + {}^1/_2, y, {}^1/_2 - z$; (ix) $x, {}^1/_2 - y, z + {}^1/_2$; (x) $x - {}^1/_2, y, {}^1/_2 - z$.

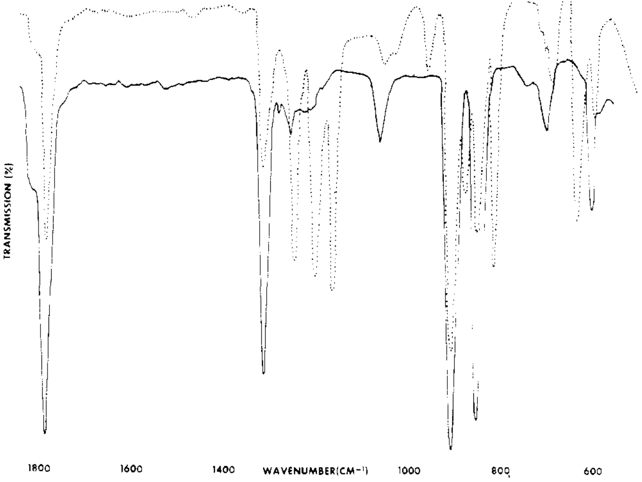

Figure 3. Gas-phase infrared spectra of $SF_5N{=}CF_2$ (—) and $SF_5N(I)CF_3/SF_5N{=}CF_2$ mixture (···) obtained from the reaction of $Hg[N(CF_3)TeF_5]_2$ with ICl, −196 and −55 °C trap contents, respectively.

192 ($SF_5NHCF_2^+$, 25%), 172 (SF_5NCF^+, 24%), 127 (SF_5^+, 11%), 89 (SF_3^+, 7%). ^{19}F NMR (degenerate AB_4X_3 pattern): $\delta_A \simeq \delta_B = 68.3$, $\delta_X = -58.8$.

Preparation of $SF_5N(I)CF_3$. Iodine monochloride (1.30 g, 8.0 mmol) was condensed at −196 °C into a U-shaped FEP reaction vessel containing freshly distilled $Hg[N(CF_3)SF_5]_2$ (2.62 g, 4.22 mmol). The reaction mixture was then warmed and allowed to react at room temperature overnight. The volatile products were first distilled through −40 and −196 °C traps. The −40 °C trap stopped primarily I_2 and unreacted $Hg[N(CF_3)SF_5]_2$. The contents of the −196 °C trap were then redistilled through traps at −55, −80, and −196 °C. The −196 °C trap contained $SF_5N{=}CF_2$[4] (1.18 g, 6.18 mmol), while the −80 °C trap contained a mixture (0.44 g) of $SF_5N{=}CF_2$, I_2, and IF_5, the latter two resulting from the disproportionation of IF. The contents of the −55 °C trap, yellow needle-like crystals (0.40 g), were warmed to room temperature and quickly examined by both ^{19}F NMR and gas-phase infrared spectroscopy (see Figure 3). The spectra revealed the presence of $SF_5N{=}CF_2$ as well as a new $SF_5N(X)CF_3$ derivative, which was attributed to $SF_5N(I)CF_3$. IR (gas): 1249 (s), 1201 (s), 1165 (s), 875 (s) cm^{-1}. ^{19}F NMR (degenerate AB_4X_3 pattern): $\delta_A \simeq \delta_B = 65.8$, $\delta_X = -62.0$.

Preparation of $SF_5N(CH_3)CF_3$. The mercurial compound $Hg[N(CF_3)SF_5]_2$ (2.91 g, 4.6 mmol) was condensed into an FEP reaction tube held at −196 °C followed by methyl iodide (1.33 g, 9.3 mmol). The reaction mixture was allowed to warm slowly to room temperature. After 2 days the volatile products were removed to the vacuum line and repeatedly distilled through −90 and −196 °C traps. The contents of the −196 °C trap contained mainly $SF_5N{=}CF_2$[4] and CH_3F, which were identified by IR and NMR. The clear liquid that remained in the −90 °C trap was later identified as the product $SF_5N(CH_3)CF_3$ (0.69 g, 3.1 mmol; 33% yield). IR (gas): 2990 (w), 1300 (vs), 1275 (vs), 1172 (vs), 1150 (s), 1090 (m), 932 (s), 905 (vs), 830 (vs), 730 (w), 685 (m), 601 (m) cm^{-1}. Mass spectrum (70 eV): major *m*/*z* 225 (M^+, 6%), 224 ($M - H^+$, 2%), 206 ($M - F^+$, 6%), 127 (SF_5^+, 100%), 89 (SF_3^+, 44%), 69 (CF_3^+, 87%). Chemical ionization mass spectrum (methane): major *m*/*z* 226 ($M + H^+$, 10%), 225 (M^+, 9%), 206 ($M - F^+$, 100%), 127 (SF_5^+, 13%). ^{19}F NMR (AB_4X_3 pattern) $\delta_A = 76.8$, $\delta_B = 66.5$, $\delta_X = -60.0$ ($J_{AB} = 152.9$ Hz, $J_{BX} = 14.3$ Hz). ^1H NMR: δ 3.17 (bm, CH_3). $^{13}C\{^1H\}$ NMR (CCl_3F): δ 35.17 (CH_3), 121.8 (q, CF_3, $^1J_{CF} = 262.6$ Hz). Anal. Calcd for $C_2H_3NF_8S$: C, 10.67; H, 1.34; N, 6.22. Found: C, 10.43; H, 1.25; N, 6.24.

Preparation of $TeF_5N(CH_3)CF_3$. Under nitrogen atmosphere $Hg[N(CF_3)TeF_5]_2$ (3.00 g, 3.7 mmol) was loaded with a stirring bar into a 250-mL Pyrex glass reaction flask fitted with a Teflon stopcock. The flask was then degassed, and methyl iodide (1.21 g, 8.4 mmol) was condensed in at −196 °C. The reaction mixture was then allowed to warm to room temperature and was stirred overnight. Repeated fractionation through −78 and −196 °C traps yielded $TeF_5N(CH_3)CF_3$ (1.94 g, 6.1 mmol; 82% yield) stopping in the trap at −78 °C. Vapor pressure data treated by least-squares methods gave $\ln (P/P_0) = 19.08 - 4301.61T^{-1}$ (−34 to +22 °C), bp 72.4 °C, $\Delta H_v = 8.55$ kcal/mol, $\Delta S_v = 24.74$ cal K^{-1} mol^{-1}. IR (gas): 2999 (w), 1490 (w), 1453 (w), 1280 (s), 1172 (s), 1068 (w), 719 (s), 700 (m) cm^{-1}. Mass spectrum (70 eV): major *m*/*z* 323 (M^+, 15%), 304 ($M - F^+$, 14%), 225 (TeF_5^+, 7%), 187 (TeF_3^+, 46%), 97 ($CF_3NCH_2^+$, 9%), 96 (CF_3NCH^+, 34%), 69 (CF_3^+, 100%). ^{19}F NMR (AB_4C_3 pattern): $\delta_A = -40.7$, $\delta_B = -49.2$, $\delta_C = -57.6$ ($J_{AB} = 176.4$ Hz, $J_{BC} = 7.1$ Hz). ^1H NMR: δ 3.27 (bm, CH_3). $^{13}C\{^1H\}$ NMR (CCl_3F): δ 34.04 (CH_3), 122.5 (q, CF_3, $^1J_{CF} = 263.2$ Hz). Anal. Calcd for $C_2H_3NF_8Te$: C, 7.49; H, 0.94; N, 4.37. Found: C, 7.50; H, 1.12; N, 4.41.

Preparation of $(SF_5)_2NCF_3$. Method A. The chloroamine $SF_5N(Cl)CF_3$ (3.33 g, 13.6 mmol) was condensed into a 1-L photolysis vessel fitted with a quartz immersion well. The reactant was allowed to vaporize before being irradiated with a low-pressure mercury lamp for 3.5 h. The volatile contents were then moved to the vacuum line and distilled through −100 and −196 °C traps. The −196 °C trap contained Cl_2 (0.48 g) and $CF_3N{=}NCF_3$ (0.53 g).[15] The −100 °C trap contained 2.4 g of a clear liquid, later identified as a mixture of $(SF_5)_2NCF_3$ and $SF_5(CF_3)NN(CF_3)SF_5$.[4] The two compounds were separated by distillation using a Bantam organic distillation apparatus. $(SF_5)_2NCF_3$ was the first fraction collected, bp 72–74 °C (2.13 g, 6.3 mmol; 93% yield).

Method B. Irradiation of the bromoamine $SF_5N(Br)CF_3$ (5.62 g, 19.0 mmol) was carried out in the same fashion as above. Trap-to-trap distillation gave $CF_3N{=}NCF_3$[15] (IR) stopping in the −196 °C trap and a mixture of Br_2, unreacted $SF_5N(Br)CF_3$, $(SF_5)_2NCF_3$, and $SF_5(CF_3)N{-}N(CF_3)SF_5$[4] in the −90 °C trap ($^{19}F$ NMR: N–S–F compounds integrated 78:14:8, respectively). The desired product $(SF_5)_2NCF_3$ could not be separated from this mixture by trap-to-trap distillation.

IR (gas) for $(SF_5)_2NCF_3$: 1369 (m), 1300 (m), 1258 (w), 935 (s), 905 (s), 850 (s), 820 (m), 795 (m), 715 (w), 600 (w), 585 (w), 550 (w) cm^{-1}. Chemical ionization mass spectrum (methane): major *m*/*z* 192 ($SF_5NCF_2 + H^+$, 89%), 172 (SF_5NCF^+, 100%), 127 (SF_5^+, 33%), 89 (SF_3^+, 3%). ^{19}F NMR ($AA'B_4B_4'X_3$ pattern): $\delta_A \simeq \delta_{A'} = 67.6$, $\delta_B \simeq \delta_{B'} = 82.8$, $\delta_X = -48.1$ ($J_{AB} \simeq J_{A'B'} = 155$ Hz, $J_{BX} \simeq J_{B'X} = 20.3$ Hz). Anal. Calcd for $CNF_{13}S_2$: C, 3.56; N, 4.15; S, 19.02. Found: C, 3.49; N, 5.04; S, 19.91.

Preparation of $SF_5N(CF_3)CH_2CH_2Br$. A mixture of $SF_5N(Br)CF_3$ (4.5 mmol, 1.30 g) and C_2H_4 (8.0 mmol) were condensed into a 100-mL glass reaction vessel at −196 °C and allowed to warm to room temperature. Within a period of 15 min the reaction mixture had become completely colorless. After the reaction was allowed to proceed overnight, the volatiles were moved to the vacuum line for distillation. Repeated distillations gave $SF_5N(CF_3)CH_2CH_2Br$ (1.25 g, 3.9 mmol; 87% yield) stopping in a trap at −60 °C; mp −65 to −68 °C. IR (gas): 1375 (s), 1350 (m), 1270 (m), 1255 (m), 921 (w), 900 (s), 890 (s), 829 (s), 668 (w) cm^{-1}. Mass spectrum (70 eV): *m*/*e* 317 (M^+, <1%), 224 ($SF_5N(CF_3)CH_2^+$, 26%), 127 (SF_5^+, 100%), 107 ($BrCH_2CH_2^+$, 13%), 89 (SF_3^+, 45%), 69 (CF_3^+, 82%). Chemical ionization mass spectrum (methane): major *m*/*z* 318 ($M + H^+$, 7%), 298 ($M - F^+$, 16%), 238 ($SF_5N(CF_3)CH_2CH_2^+$, 40%), 224 ($SF_5N(CF_3)CH_2^+$, 100%), 192 ($SF_5NCF_2H^+$, 77%), 127 (SF_5^+, 9%), 107 ($BrCH_2CH_2^+$, 54%). ^{19}F NMR (AB_4X_3 pattern): $\delta_A = 77.1$, $\delta_B = 68.7$, $\delta_X = -57.3$ ($J_{AB} = 151.6$ Hz, $J_{BX} = 11.3$ Hz). ^1H NMR (A_2M_2 pattern): δ 3.84 (t, NCH_2, $J_{HH} = 8.24$ Hz), 3.41 (t, $BrCH_2$, $J_{HH} = 8.24$ Hz). Anal. Calcd for $C_3H_4NBrF_8S$: C, 11.33; H, 1.27; N, 4.40. Found: C, 11.26; H, 1.19; N, 4.46.

Reaction of $SF_5N(Br)CF_3$ with C_3F_6. The bromoamine (3.18 g, 11.0 mmol) was reacted with an excess of C_3F_6 (15.0 mmol) in a glass reaction vessel. Because little or no reaction was found to take place at room temperature to 150 °C, the reaction mixture was heated at 170 °C for

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3 days. At this time the contents of the reactor were moved to the vacuum line for separation by trap-to-trap distillation (−45 and −196 °C traps). The trap at −45 °C was found to contain $SF_5N(CF_3)C_3F_6Br$ (2.58 g, 5.9 mmol) as a colorless liquid in 53% yield. The product was found to be a mixture of the isomers $SF_5N(CF_3)CF_2CF(CF_3)Br$ and $SF_5N(CF_3)CF(CF_3)CF_2Br$ in an approximate ratio of 99.5:0.5 as determined by NMR spectroscopy. The latter isomer was observed only with the enhanced sensitivity and signal averaging of the 500 MHz (470.6 MHz for ^{19}F) NMR spectrometer. The following characterization data was obtained on the isomer mixture. IR (gas): 1309 (s), 1279 (s), 1259 (s), 1247 (s), 1230 (s), 1214 (s), 1178 (m), 1122 (m), 934 (s), 919 (sh), 855 (s), 806 (s), 713 (m), 603 (m) cm^{-1}. Chemical ionization mass spectrum (methane): major m/z 420 ($M - F^+$, 3%), 401 ($M - 2F^+$, 7%), 192 ($SF_5NCF_2H^+$, 100%), 172 (SF_5NCF^+, 15%), 127 ($SF_5{}^+$, 33%), 69 ($CF_3{}^+$, 7%). ^{19}F NMR ($F^ASF^B{}_4N(CF_3{}^V)C(F^W)F^XCF^Y(CF_3{}^Z)Br$): $\delta_A = 67.6$, $\delta_B = 80.4$, $\delta_V = -50.8$, $\delta_W = -78$, $\delta_X = -81$, $\delta_Y = -129.8$, $\delta_Z = -76.4$ ($J_{AB} = 153$ Hz, $J_{WX} = 232$ Hz, $J_{BV} = 14$ Hz). ^{19}F NMR ($F^ASF^B{}_4N(CF_3{}^V)CF^W(CF_3{}^X)CF^Y(F^Z)Br$): δ_A unresolved, $\delta_B = 83.1$, $\delta_V = -50.0$, $\delta_W = -139.3$, $\delta_X = -72.0$, δ_Y unresolved, δ_Z unresolved. Anal. Calcd for $C_4NBrF_{14}S$: C, 10.92; N, 3.18; Br, 18.16. Found: C, 10.83; N, 3.33; Br, 17.69.

Reaction of $SF_5N(Br)CF_3$ with CO. The bromoamine $SF_5N(Br)CF_3$ (2.31 g, 7.9 mol) was reacted at room temperature with an excess of CO (10.6 mmol) in a 500-mL glass reaction vessel. After a reaction period of 5 days, the reaction vessel was chilled to −196 °C and the unreacted CO was pumped away. Fractional distillation of the condensable products gave unreacted $SF_5N(Br)CF_3$ and Br_2 (0.85 g) stopping in the trap at −75 °C and a mixture of SF_5Br[16] and $CF_3N{=}C{=}O$[17] (1.15 g) in the −196 °C trap.

Attempted Preparation of SF_5I. Iodine monochloride (2.27 g, 14.0 mmol) and $Hg[N(CF_3)SF_5]_2$ (4.47 g, 7.2 mmol) were condensed into a 500-mL glass reaction vessel and allowed to react in the presence of excess CO (20 mmol) for 3 h at room temperature. The reaction vessel was then chilled to −196 °C, unreacted CO was removed under vacuum, and the condensable products were distilled through traps at −75, −115, and −196 °C. The −75 °C trap contained I_2 and unreacted $Hg[N(CF_3)SF_5]_2$ (0.31 g), the −115 °C trap of a mixture of $SF_5N{=}CF_2$[4] and $FC(O)I$[18] (3.41 g), and the −196 °C trap primarily COF_2 with traces of $SF_5N{=}CF_2$ and FC(O)I (0.22 g). No spectroscopic evidence was obtained for SF_5I.

Attempted Preparation of TeF_5I. A mixture of $Hg[N(CF_3)TeF_5]_2$ (3.25 g, 4.0 mmol), ICl (1.2 g, 7.4 mmol), and CO (8 mmol) was allowed to react as in the preceding reaction. Fractional distillation gave primarily I_2 stopping in the −55 °C trap, $TeF_5N{=}CF_2$[1] (4.4 mmol) in the −90 °C trap, FC(O)I[18] (4.2 mmol) in the −125 °C trap, and COF_2 (1.6 mmol) in the −196 °C trap. Again no evidence was obtained for the existence of a pentafluorochalcogen iodide.

Results and Discussion

The direct reaction between $SF_5N{=}CCl_2$ and HgF_2 gives $Hg[N(CF_3)SF_5]_2$ in close to quantitative yield, but the required reaction temperature is almost 100 °C more than what is necessary in the analogous reaction with $TeF_5N{=}CCl_2$:[1b]

$$2SF_5N{=}CCl_2 \xrightarrow[150\ °C]{HgF_2\ (excess)} 2HgCl_2 + Hg[N(CF_3)SF_5]_2 \quad 99\% \qquad (4)$$

Other mercurials, namely $[(CF_3)_2N]_2Hg$ and $[(CF_3)_2NNCF_3]_2Hg$, have also been formed in a like manner from $N{\equiv}CCl$[19] and $(CF_3)_2NN{=}CCl_2$,[20] respectively. $Hg[N(CF_3)SF_5]_2$ was not always isolated as a pure substance due to its extreme sensitivity to moisture[4] and near-room-temperature melting point (10–12 °C). Instead, on occasion, we used the mixture of mercury salts obtained in eq 4 with the concentration of $Hg[N(CF_3)SF_5]_2$ ranging from 10 to 20 mol %.

Structure of $Hg[N(CF_3)TeF_5]_2$. The tellurium compound, unlike the sulfur derivative, has a melting point (67–68 °C) sufficiently above room temperature for an X-ray crystal structure determination to be successful without the use of a low-temperature accessory. The structure of this compound represents the third structure determination of a $TeF_5N<$ compound, the other two being of $TeF_5N{=}WCl_4$ (X-ray)[21] and $TeF_5N{=}C{=}O$ (electron diffraction).[22] The two most interesting features of the molecular structure of $Hg[N(CF_3)TeF_5]_2$ (Figure 1) are the linear N–Hg–N arrangement and the planar geometry around each nitrogen [∠TeNC = 119 (2)°]. The N–Hg–N bond angle of 180° compares closely to that observed in $Hg[N{=}SF_2)_2$ of 178 (1)°.[23] The planar geometry around the nitrogen atoms is not surprising, especially when one considers the structural effect of fluorine incorporation in tertiary amines.[24] For example, the following compounds all have planar frameworks around nitrogen: $(SF_5)_2NH$,[25] $(SF_5)_2NF$,[25] and $(CF_3SO_2)_2NH$.[26] Other important bond distances and angles are given in Table III.

The observed Te–N distance of 2.01 (3) Å in $Hg[N(CF_3)TeF_5]_2$ compares with those of 1.98 (3) Å in $TeF_5N{=}WCl_4$,[21] 1.859 (21) Å in $TeF_5N{=}C{=}O$,[22] and 1.980 (3) Å in $Ar_2Te{=}NTos$.[27] This comparison clearly indicates that the latter compound should in no way be viewed as having a discreet Te–N double bond. Both the low melting point and the Hg–N distance of 1.97 (3) Å suggest a covalent bonding for $Hg[N(CF_3)TeF_5]_2$. Other Hg^{II}–N compounds that have been structurally characterized have Hg–N distances greater than 2.03 Å[23,28-30] and hence are more ionic.

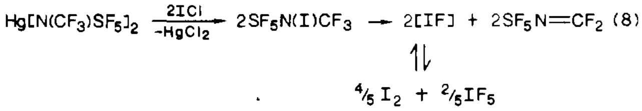
As shown in Figure 2, the normal, distorted octahedral coordination for Hg^{II} compounds[30] is also seen in $Hg[N(CF_3)TeF_5]_2$. Although there are several close intramolecular contacts between the mercury and fluorine atoms [four at 2.84 Å, Hg–F(1) and Hg–F(7)], these interactions are virtually coplanar with the N–Hg–N skeleton. It is four nonbonded fluorine atoms (two at 2.98 Å and two at 3.36 Å) of different molecules that complete the coordination around each mercury atom. Other nonbonded intermolecular distances less than 3.6 Å are also shown in Table IV.

$SF_5N(CF_3)$– Derivatives. Reactions of $Hg[N(CF_3)SF_5]_2$ with halogens or interhalogens have led to the series of trisubstituted amines $SF_5N(X)CF_3$, where X = F, Cl, Br, I:

$$Hg[N(CF_3)SF_5]_2 \xrightarrow[-HgF_2]{2F_2} 2SF_5N(F)CF_3 \quad 54\% \qquad (5)$$

$$Hg[N(CF_3)SF_5]_2 \xrightarrow[-HgCl_2]{2Cl_2} 2SF_5N(Cl)CF_3 \quad 98\% \qquad (6)$$

$$Hg[N(CF_3)SF_5]_2 \xrightarrow[-HgBr_2]{2Br_2} 2SF_5N(Br)CF_3 \quad 80\% \qquad (7)$$



$$\begin{array}{l} Hg[N(CF_3)SF_5]_2 \xrightarrow[-HgCl_2]{2ICl} 2SF_5N(I)CF_3 \rightarrow 2[IF] + 2SF_5N{=}CF_2 \quad (8) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad {}^4/_5\, I_2 + {}^2/_5 IF_5 \end{array}$$

The *N*-fluoro derivative had previously been prepared from the direct fluorination of both $CF_3N{=}SF_2$[13] and $SF_5N{=}CF_2$,[14] while

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the *N*-chloro compound had been obtained by heating a mixture of SF_5NHCF_3, AgF_2, and Cl_2.[4] The current syntheses represent an improvement over the original methods. Like its tellurium analogue,[1] $SF_5N(I)CF_3$ is unstable with respect to elimination of iodine monofluoride. The best evidence for the existence of this derivative was obtained from the infrared spectra shown in Figure 3. The infrared spectrum of each $SF_5N(X)CF_3$ derivative generally exhibits three strong stretching frequencies in the CF region of 1300–1150 cm^{-1}. As in the related $(CF_3)_2NX$[31] and $TeF_5N(X)CF_3$ derivatives,[1] one can readily observe progressive shifts in these stretching frequencies with respect to the mass and electron-withdrawing power of X.

It is interesting to contrast the reactivity of the mercurials $Hg[N(CF_3)EF_5]_2$, where E = S and Te, with other bis(amido)mercury compounds. For example, halogens do not react with either $Hg[N(SF_5)]_2$[2] or $Hg[N(SO_2CF_3)_2]_2$[3] to give the respective *N*-haloamines:

$$Hg[N(SF_5)]_2 + 2X_2\ (X = Cl, Br) \rightarrow \text{no reaction} \quad (9)$$

$$Hg[N(SO_2CF_3)_2]_2 + 2Br_2 \rightarrow \text{no reaction} \quad (10)$$

Instead these derivatives must be formed either by alternate methods[25,32] or by reaction with polar halogenides such as $BrOSO_2F$.[3]

$$Cs^+N(SF_5)_2^- + XF\ (X = F, Cl) \rightarrow (SF_5)_2NX + CsF \quad (11)$$

$$Hg[N(SO_2CF_3)_2]_2 + 2BrOSO_2F \rightarrow 2(CF_3SO_2)_2NBr + Hg(SO_3F)_2 \quad (12)$$

On the other hand, all of the *N*-halobis(trifluoromethyl)amines have been prepared from reactions of $Hg[N(CF_3)_2]_2$ with halogens with the exception of the *N*-fluoro derivative:[24]

$$Hg[N(CF_3)_2]_2 + 2X_2\ (X = Cl, Br, I) \rightarrow 2(CF_3)_2NX + HgX_2 \quad (13)$$

Mews has attributed the lack of reactivity of $Hg[N(SF_5)]_2$ with halogens to the greater N–X bond polarity in the expected *N*-haloamines (Pearson principle[33]), which would result from the greater group electronegativity of $(SF_5)_2N–$ versus $(CF_3)_2N–$. It is also conceivable that the greater steric bulk of the SF_5 groups lowers the reactivity of this mercurial compound with respect to $Hg[N(CF_3)_2]_2$. The group electronegativities (Pauling scale) of $(SF_5)_2N–$ (3.2–3.45) and $(CF_3)_2N–$ (2.85–3.0)[2] were determined from a correlation of ^1H chemical shifts of a series of methyl derivatives CH_3X with the electronegativity of X.[34] We were able to use this same correlation to compare the group electronegativities of $SF_5N(CF_3)–$ and $TeF_5N(CF_3)–$ upon the successful syntheses of the *N*-methyl derivatives as shown in eq 14. A competing reaction was observed in the case of $Hg[N(CF_3)SF_5]_2$ (eq 15, cf. ref 2).

$$Hg[N(CF_3)EF_5]_2\ (E = S, Te) + 2CH_3I \rightarrow 2EF_5N(CH_3)CF_3 + HgI_2 \quad (14)$$

$$Hg[N(CF_3)SF_5]_2 + 2CH_3I \rightarrow 2CH_3F + 2SF_5N{=}CF_2 + HgI_2 \quad (15)$$

In Figure 4 the ^1H chemical shifts of the *N*-methylamines $CH_3N(SO_2F)_2$,[35] $CH_3N(SO_2CF_3)_2$,[36] $CH_3N(SF_5)_2$,[2] $CH_3N(SCF_3)_2$,[37] $CH_3N(CF_3)TeF_5$, $CH_3N(CF_3)SF_5$, and $CH_3N(CF_3)_2$[2] are correlated with those of the methyl halides. Although the chemical shifts of the *N*-methylamines were not obtained at infinite dilution in CCl_4[34] (some were obtained as 10–20% solutions in CCl_3F), the relative order of electronegativities of the amino substituents is consistent with the reactivities displayed by their parent mercurials. A comparison of electronegativity with ^{13}C chemical shifts,[34] for those which are known, gave a similar trend with the exception that $(CF_3S)_2N–$ was found to be the most electronegative (3.7) among the amino substituents.[37] Haas and co-workers have previously reported a group electronegativity of 3.7 for $(CF_3S)_2N–$ from ^{13}C NMR data on a series of $(CF_3S)_2NCH_2X$ derivatives.[37] We cannot account for the large difference that is projected for the $(CF_3S)_2N–$ group electronegativity between the ^1H and ^{13}C NMR data at this time. To our knowledge no report has appeared describing reactions between $Hg[N(SCF_3)]_2$[38] and the halogens; however, it is known that the respective *N*-haloamines are unstable with respect to a 1,3 halogen atom shift:[39]

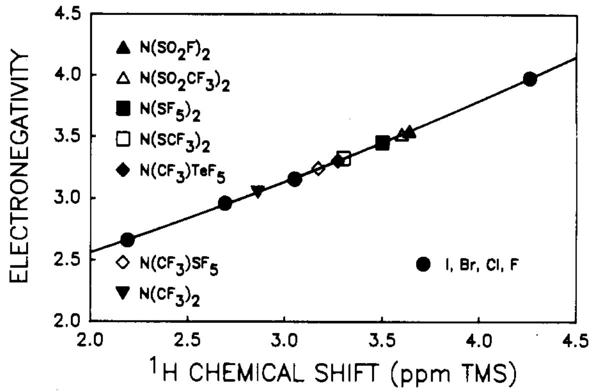

Figure 4. Plot of the electronegativity of substituents (Pauling scale) versus ^1H chemical shifts of the methyl derivatives CH_3X, where X = F, Cl, Br, and I.[34] Interpolation of the ^1H chemical shifts of the *N*-methylamines $CH_3N(SO_2F)_2$,[35] $CH_3N(SO_2CF_3)_2$,[36] $CH_3N(SF_5)_2$,[2] $CH_3N(SCF_3)_2$,[37] $CH_3N(CF_3)TeF_5$, $CH_3N(CF_3)SF_5$, and $CH_3N(CF_3)_2$[2] yields approximate electronegativities for these amino groups.

$$(CF_3S)_2NH + X_2 \xrightarrow[-HX]{} [(CF_3S)_2NX] \rightarrow CF_3SN{=}S(X)CF_3 \quad (16)$$

We had hoped that the above correlations would provide evidence for either the SF_5 or TeF_5 group being more electronegative than the other. This was not the case as both the ^1H and ^{13}C chemical shifts of the methyl derivatives $SF_5N(CH_3)CF_3$ and $TeF_5N(CH_3)CF_3$ were found to be in close proximity of one another; in fact the relative order of chemical shifts between the two switched upon going from one correlation to the other. An earlier comparison between SF_5NH_2 and TeF_5NH_2, which showed TeF_5NH_2 to be more stable against HF elimination and less basic, indicated that the TeF_5 group was probably more electron withdrawing than SF_5.[21,40] However, these observations may be due instead to the inability of tellurium(VI) to form four- or five-coordinated species, while this is obviously not the case with sulfur(VI) as SF_5NH_2 is known to exist in equilibrium with $N{\equiv}SF_3$, for example.

A variety of other $SF_5N(CF_3)–$ derivatives were prepared through reactions of the *N*-haloamines $SF_5N(Cl)CF_3$ and $SF_5N(Br)CF_3$. The new perfluorinated tertiary amine $(SF_5)_2NCF_3$ was formed in over 90% yield from the gas-phase UV photolysis of $SF_5N(Cl)CF_3$:

$$2SF_5N(Cl)CF_3 \xrightarrow{h\nu} (SF_5)_2NCF_3 + Cl_2 + {}^1/_2CF_3N{=}NCF_3 \quad (17)$$

A small amount (<5%) of the hydrazine $SF_5N(CF_3)NN(CF_3)SF_5$[4] was also produced in this reaction. In contrast, the photolysis of $(SF_5)_2NCl$ gives exclusively the hydrazine $(SF_5)_2NN(SF_5)_2$.[41] Photolysis of the bromoamine $SF_5N(Br)CF_3$ was not nearly as

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efficient and gave a mixture of $(SF_5)_2NCF_3$ and $SF_5N(CF_3)N(CF_3)SF_5$, which could not be separated from the unreacted starting material.

The compound $SF_5N(Br)CF_3$ reacted readily with ethylene upon warming to room temperature to give $SF_5N(CF_3)CH_2CH_2Br$ in over 85% yield:

$$SF_5N(Br)CF_3 + C_2H_4 \rightarrow SF_5N(CF_3)CH_2CH_2Br \quad (18)$$

On the other hand, a temperature of 170 °C was required for its reaction with hexafluoropropylene. The addition product, which was isolated in 53% yield, was found to be largely one of two possible isomers:

$$SF_5N(Br)CF_3 + CF_3CF{=}CF_2 \rightarrow SF_5N(CF_3)CF_2CF(CF_3)Br + SF_5N(CF_3)CF(CF_3)CF_2Br \quad 99.5{:}0.5 \quad (19)$$

In fact, the second isomer was observed only with the enhanced sensitivity and signal averaging obtained from an NMR spectrometer operating at 470.6 MHz. The distribution of isomers is as expected based on the results of other addition reactions of hexafluoropropylene.[1,42] Generally attack is favored at the CF_2 position not only because it is sterically advantageous but also because a more stable anionic or radical intermediate (depending on the mechanism) is formed.[42a] The results outlined above point to a rather surprising thermal and photolytic stability for the bromoamine $SF_5N(Br)CF_3$.

As with the tellurium chemistry,[1] the reaction of $SF_5N(Br)CF_3$ with carbon monoxide failed to give the carbamoyl bromide $SF_5N(CF_3)C(O)Br$ but gave SF_5Br and $CF_3N{=}C{=}O$ instead:

$$SF_5N(Br)CF_3 + CO \rightarrow [SF_5N(CF_3)C(O)Br] \rightarrow SF_5Br + CF_3N{=}C{=}O \quad (20)$$

Attempts failed to prepare the first pentafluorochalcogen iodides by this reaction pathway, and a different route was observed when the reaction was repeated with the *N*-iodoamines (prepared in situ):

$$Hg[N(CF_3)EF_5]_2 \ (E = S, Te) + 2ICl + 2CO \rightarrow 2[EF_5N(CF_3)C(O)I] + HgCl_2 \rightarrow 2EF_5N{=}CF_2 + 2IC(O)F \quad (21)$$

It is quite possible that the carbamoyl iodide was never formed and that the IC(O)F resulted from the reaction of IF (IF_5) with CO.[18] Nevertheless, we saw no evidence for the formation of a pentafluorochalcogen iodide under these conditions.

Conclusion. This investigation has demonstrated the utility of the mercurials $Hg[N(CF_3)SF_5]_2$ and $Hg[N(CF_3)TeF_5]_2$ for incorporating the $SF_5N(CF_3)$– and $TeF_5N(CF_3)$– groups into a variety of materials. The group electronegativities of $SF_5N(CF_3)$– and $TeF_5N(CF_3)$–, although not discernible from one another, clearly lie between the values for $(CF_3)_2N$– and $(SF_5)_2N$–. The structural investigation of $Hg[N(CF_3)TeF_5]_2$ provides yet another example of the ability of highly electron-withdrawing, bulky substituents to flatten the geometry about an otherwise pyramidal amine.

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Registry No. $Hg[N(CF_3)TeF_5]_2$, 98720-67-3; $Hg[N(CF_3)SF_5]_2$, 2375-55-5; HgF_2, 7783-39-3; $SF_5N{=}CCl_2$, 1801-00-9; $SF_5N(F)CF_3$, 4101-60-4; $SF_5N(Cl)CF_3$, 2194-08-3; $SF_5N(Br)CF_3$, 112043-76-2; $SF_5N(I)CF_3$, 112043-77-3; $SF_5N(CH_3)CF_3$, 112043-78-4; CH_3I, 74-88-4; $TeF_5N(CH_3)CF_3$, 112043-79-5; $(SF_5)_2NCF_3$, 112043-80-8; $SF_5(CF_3)NN(CF_3)SF_5$, 2375-56-6; $SF_5N(CF_3)CH_2CH_2Br$, 112043-81-9; C_2H_4, 74-85-1; C_3F_6, 116-15-4; $SF_5N(CF_3)CF_2CF(CF_3)Br$, 112043-82-0; $SF_5N(CF_3)CF(CF_3)CF_2Br$, 112043-83-1; SF_5Br, 15607-89-3; $CF_3N{=}C{=}O$, 460-49-1; $SF_5N{=}CF_2$, 2375-32-8; FC(O)I, 1495-48-3; COF_2, 353-50-4; $TeF_5N{=}CF_2$, 98720-68-4; F_2, 7782-41-4; Cl_2, 7782-50-5; Br_2, 7726-95-6; ICl, 7790-99-0; CO, 630-08-0.

Supplementary Material Available: Anisotropic thermal parameters (Table S-I) (1 page); structure factors (Table S-II) (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of California, Irvine, California 92717, and University of Alabama, University, Alabama 35486

Synthesis and X-ray Crystal Structure of the Divalent [Bis(trimethylsilyl)amido]samarium Complexes $[(Me_3Si)_2N]_2Sm(THF)_2$ and $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$

William J. Evans,*[1a] Donald K. Drummond,[1a] Hongming Zhang,[1b] and Jerry L. Atwood*[1b]

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$SmI_2(THF)_2$ reacts with 2 equiv of $NaN(SiMe_3)_2$ in THF to form $[(Me_3Si)_2N]_2Sm(THF)_2$, which crystallizes from hexane in space group $P2_1/c$ with unit cell dimensions a = 8.690 (5) Å, b = 19.721 (5) Å, c = 19.870 (5) Å, β = 97.78 (5)°, and Z = 4 for D_{calcd} = 1.21 g cm^{-3}. Least-squares refinement on the basis of 2041 unique observed reflections converged to a final R = 0.040. The THF oxygen atoms and the $N(SiMe_3)_2$ nitrogen atoms form a distorted tetrahedron around the Sm atom with average Sm–O and Sm–N distances of 2.59 (1) and 2.43 (1) Å, respectively. $[(Me_3Si)_2N]_2Sm(THF)_2$ reacts with 1 equiv of $SmI_2(THF)_2$ in a THF/DME mixture to form $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$, which crystallizes from a THF/DME mixture in space group $C2/c$ with unit cell dimensions a = 28.580 (4) Å, b = 8.7679 (14) Å, c = 20.247 (3) Å, β = 90.224 (11)°, and Z = 4 (dimers) for D_{calcd} = 1.57 g cm^{-3}. Least-squares refinement on the basis of 2617 unique observed reflections converged to a final R = 0.042. The THF oxygen atom, the silylamide nitrogen atom, the two bridging iodide ligands, and the two DME oxygen atoms describe an irregular six-coordinate geometry around samarium. The Sm–N distance is 2.455 (7) Å; the Sm–I distances are 3.3414 (9) and 3.3553 (9) Å.

Introduction

As part of our study of the remarkable organometallic chemistry of Sm(II), we have used the pentamethylcyclopentadienyl ligand extensively.[2-8] Traditionally, cyclopentadienyl ligands have been important in organolanthanide chemistry because they meet the electrostatic and steric requirements necessary to form thermally

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