

## Tellurium-Nitrogen Compounds. Reactions of ((Dichloromethylene)amino)pentafluorotellurium, $\text{TeF}_5\text{N}=\text{CCl}_2$ , and Its Derivatives<sup>1</sup>

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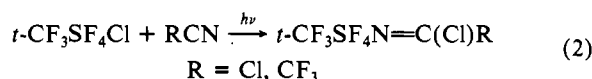
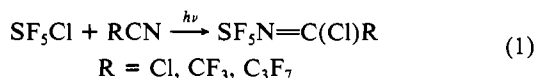
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The amine  $\text{TeF}_5\text{NHC}_3\text{F}_7$  was produced in high yield as a colorless, stable liquid from the reaction of  $\text{TeF}_5\text{N}=\text{CCl}_2$  with HF. Further reactions of this amine with various alkali-metal fluorides have led to the following compounds:  $\text{TeF}_5\text{N}=\text{CF}_2$ ,  $\text{TeF}_5\text{N}=\text{C}(\text{F})\text{N}(\text{CF}_3)\text{TeF}_5$ ,  $\text{TeF}_5\text{NHC}(\text{F})=\text{NCF}_3$ ,  $\text{TeF}_5\text{N}=\text{C}=\text{NCF}_3$ , and  $\text{K}^+[\text{TeF}_5\text{NC}(\text{F})\text{NCF}_3]^-$ . The mercury derivative  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  has also been obtained by the reaction of  $\text{TeF}_5\text{N}=\text{CCl}_2$  with excess  $\text{HgF}_2$ . Reactions of this colorless, sublammable mercurial with halogens or interhalogens have led to the trisubstituted amines  $\text{TeF}_5\text{N}(\text{X})\text{CF}_3$ , where X = F, Cl, Br, and I. Of these only the *N*-iodo compound is unstable at room temperature. The first material with two  $\text{TeF}_5$  groups bonded to the same nitrogen,  $(\text{TeF}_5)_2\text{NCF}_3$ , was prepared from the photolysis of  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$ . The *N*-bromo compound added readily to the alkenes  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{F}_6$  to give  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Br}$  and the mixture of isomers  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}_2\text{CF}(\text{Br})\text{CF}_3$  and  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}(\text{CF}_3)\text{CF}_2\text{Br}$ , respectively. Nucleophilic reagents also reacted with  $\text{TeF}_5\text{N}=\text{CCl}_2$  to give mono- and disubstituted derivatives, e.g.  $\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{OCH}_3$ ,  $\text{TeF}_5\text{N}=\text{C}(\text{OCH}_3)_2$ .

### Introduction

We recently reported the synthesis of a large number of tellurium-nitrogen compounds starting with either  $\text{TeF}_5\text{NHSi}(\text{CH}_3)_3$  or  $\text{TeF}_5\text{NH}_2$ .<sup>3</sup> As several of these derivatives, including  $\text{TeF}_5\text{N}=\text{PCl}_3$  and  $\text{TeF}_5\text{N}=\text{SeCl}_2$ , had no known analogues in the chemistry of sulfur-nitrogen compounds, it was of interest to attempt their preparation. Both  $\text{SF}_5\text{N}=\text{PCl}_3$  and  $\text{SF}_5\text{N}=\text{SeCl}_2$  were prepared by starting from  $\text{SF}_5\text{NCl}_2$ ; however, they were found to be unstable at room temperature in sharp contrast to the above-mentioned pentafluorotellurium derivatives.<sup>4</sup> Along with this research it was our aim to further expand the field of tellurium-nitrogen chemistry.

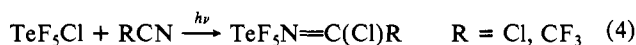
A vast array of chemistry has resulted from the imine derivatives formed in the photolytic reactions of either  $\text{SF}_5\text{Cl}$  or *t*- $\text{CF}_3\text{SF}_4\text{Cl}$  with select nitriles:<sup>5-8</sup>



On the other hand, previous attempts to add  $\text{TeF}_5\text{Cl}$  photolytically to unsaturated systems have failed:<sup>9</sup>



We have now found that  $\text{TeF}_5\text{Cl}$  can be added photolytically to nitriles under retention of the  $\text{TeF}_5$  group.<sup>10</sup>



In this paper, we give improved syntheses and further data for many of the compounds reported in our preliminary account as well as the results leading to many new pentafluorotellurium-nitrogen derivatives.

### Experimental Section

**Spectra.** Infrared spectra were obtained on a Beckman Acculab 10 infrared spectrophotometer, either on gases, pressure 1–10 torr, or on mulls in either halocarbon or mineral oil; the window material most commonly used was KCl. Raman spectra were taken on a Cary 82 instrument using an Ar laser for excitation (Spectra-Physics). Mass spectra were obtained on either a Varian 711 or MAT 112S high-resolution mass spectrometer using either a solid inlet probe or a controlled gas flow inlet. Only the most important ions are reported. The mass numbers are given for <sup>130</sup>Te as well as <sup>202</sup>Hg, <sup>79</sup>Br, or <sup>35</sup>Cl where applicable; the intensities include all isotopes. The <sup>19</sup>F and <sup>1</sup>H NMR spectra were recorded on either a Varian EM 360 or a JEOL FX 90Q nuclear magnetic resonance spectrometer using  $\text{CCl}_3\text{F}$  and  $(\text{CH}_3)_4\text{Si}$ , respectively, as external standards. Resonances appearing upfield from  $\text{CCl}_3\text{F}$  in the <sup>19</sup>F NMR spectra are designated negative. The <sup>13</sup>C NMR spectra were recorded on a JEOL FX 90Q NMR spectrometer using acetone-*d*<sub>6</sub> as a standard. Elemental analyses were obtained from Beller Microanalytical Laboratory in Göttingen, West Germany.

**Reagents.** The compounds  $\text{TeF}_4$ ,<sup>11</sup>  $\text{ClF}$ ,<sup>12</sup>  $\text{ClCN}$ ,<sup>13</sup>  $\text{CF}_3\text{CN}$ ,<sup>14</sup>  $\text{BrF}_3$ ,<sup>15</sup> and  $\text{ICl}$ <sup>16</sup> were prepared according to literature methods. The reaction between  $\text{TeF}_4$  and  $\text{ClF}$ <sup>17</sup> was scaled up to produce  $\text{TeF}_5\text{Cl}$  in 100-mmol quantities; the yield was generally 90%. All other reagents were taken from laboratory stock and were purified, where necessary, before use.

**Preparation of  $\text{TeF}_5\text{N}=\text{CCl}_2$ .** Approximately equimolar quantities of  $\text{TeF}_5\text{Cl}$  and  $\text{ClCN}$  were loaded into a 6-L Pyrex flask to give a pressure of about 1 atm at room temperature. This mixture was then irradiated for 4<sup>1/2</sup>–5 h with an internal low-pressure mercury lamp. The volatile products were distilled under vacuum through a series of traps at –70, –110, and –196 °C. The trap at –70 °C contained the crude product mixture, the –110 °C trap unreacted  $\text{TeF}_5\text{Cl}$  and  $\text{ClCN}$ —which could be rephotolyzed, and the –196 °C trap mostly  $\text{TeF}_6$ . A series of photolysis reactions starting from 150.7 g of  $\text{TeF}_5\text{Cl}$  produced 82.3 g of the crude product mixture. Distillation on a 100-cm spinning band column at 76 torr gave 59.7 g (186.9 mmol, 32% yield) of  $\text{TeF}_5\text{N}=\text{CCl}_2$  at 63.5–65 °C and 10.7 g (9% yield) of  $\text{Cl}_2\text{C}=\text{N}=\text{N}=\text{CCl}_2$ <sup>18</sup> at 89–90 °C.

$\text{TeF}_5\text{N}=\text{CCl}_2$ : IR (gas) 1800 (w), 1630 (vs), 1588 (w sh), 975 (w), 910 (vs), 730 (vs), 695 (m)  $\text{cm}^{-1}$ ; Raman (liquid) 1605 (2, p), 907 (5, p), 724 (11, p), 705 (7, p), 678 (29, p), 634 (100, p), 565 (60, p), 357 (43, p), 329 (4, dp), 301 (5, dp), 245 (22, p), 229 (38, p), 166 (12, p)  $\text{cm}^{-1}$ ; mass spectrum (70 eV) major *m/z* = 321 ( $\text{M}^+$ , 2%), 286 ( $\text{M} - \text{Cl}^+$ , 100%), 241 ( $\text{TeF}_4\text{Cl}^+$ , 24%), 225 ( $\text{TeF}_5^+$ , 48%), 96 ( $\text{Cl}_2\text{CN}^+$ , 21%), 61 ( $\text{ClCN}^+$ , 23%); <sup>19</sup>F NMR ( $\text{AB}_4$  pattern)  $\delta_A = -42.0$ ,  $\delta_B = -47.0$  ( $J_{\text{AB}} = 177.3$  Hz,  $J_{125\text{Te}-A} = 3460$  Hz,  $J_{125\text{Te}-B} = 3875$  Hz,  $J_{125\text{Te}-C} = 3220$  Hz). Anal. Calcd for  $\text{CNCl}_2\text{F}_5\text{Te}$ : C, 3.76; N, 4.38. Found: C, 3.89; N, 4.49.

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**Preparation of  $\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_3$ .** A mixture of  $\text{TeF}_5\text{Cl}$  (27 g, 105 mmol) and  $\text{CF}_3\text{CN}$  (9.5 g, 100 mmol) was loaded into a 5-L round-bottomed Pyrex flask and photolyzed for  $4\frac{1}{2}$ –5 h with an internal low-pressure mercury lamp. The volatile products were then distilled through traps at  $-65$  and  $-196$  °C, and the contents of the trap at  $-196$  °C were once again subjected to photolysis. After four successive photolysis reactions and distillations 10.7 g of the crude product mixture was collected in the  $-65$  °C trap. The imine  $\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_3$  could not be separated from the other side products, including  $\text{CF}_3(\text{Cl})\text{C}=\text{N}-\text{N}=\text{C}(\text{Cl})\text{CF}_3$ ,<sup>19</sup> when a capillary distillation column was used; however, preparative gas chromatography utilizing a 15% Halocarbon K-352 column gave an excellent separation.

$\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{CF}_3$ : vapor pressure  $\sim 50$  torr at 25 °C; IR (gas) 1670 (s), 1270 (s), 1245 (vs), 1200 (vs), 995 (w), 985 (m), 787 (m), 725 (vs), 653  $\text{cm}^{-1}$ ; mass spectrum (80 eV) major  $m/z = 355$  ( $\text{M}^+$ , 1%), 336 ( $\text{M} - \text{F}^+$ , 3%), 320 ( $\text{M} - \text{Cl}^+$ , 90%), 286 ( $\text{M} - \text{CF}_3^+$ , 67%), 241 ( $\text{TeF}_4\text{Cl}^+$ , 91%), 225 ( $\text{TeF}_5^+$ , 100%);  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}$  pattern)  $\delta_A = -45.2$ ,  $\delta_B = -46.7$ ,  $\delta_C = -72.7$  ( $J_{125\text{Te-A}} = 3425$  Hz,  $J_{125\text{Te-B}} = 3875$  Hz,  $J_{125\text{Te-C}} = 3140$  Hz). Anal. Calcd for  $\text{C}_2\text{NClF}_8\text{Te}$ : C, 6.80; N, 3.97. Found: C, 6.99; N, 3.85.

**Preparation of  $\text{TeF}_5\text{NHCF}_3$ .** Anhydrous HF (3.9 g, 195 mmol) was condensed at  $-196$  °C into an autoclave containing  $\text{TeF}_5\text{N}=\text{CCl}_2$  (3.8 g, 11.9 mmol). The reaction mixture was warmed to room temperature and heated at 40–50 °C overnight. The volatile products were then placed over a NaF scrubber for 1–2 h before being distilled under vacuum. Repeated trap-to-trap distillation gave  $\text{TeF}_5\text{NHCF}_3$  (3.3 g, 10.8 mmol) in 90% yield in the trap at  $-78$  °C. Vapor pressure data treated by least-squares methods gave  $\ln(P/P_0) = 11.89 - 3988.52 T^{-1}$  (between  $-47$  and  $+24$  °C), bp = 62.3 °C,  $\Delta H_v = 7.93$  kcal/mol, and  $\Delta S_v = 23.63$  cal  $\text{K}^{-1}$  mol $^{-1}$ . IR (gas): 3408 (m), 1410 (s), 1270 (vs), 1180 (vs), 735 (vs), 715 (s sh)  $\text{cm}^{-1}$ . Raman (liquid): 3383 (30, p), 3325 (5, p), 1408 (2, p), 1388 (2, p), 1282 (1, p), 1179 (2, dp), 937 (7, p), 773 (13, p), 703 (63, p), 681 (63, p), 660 (100, p), 528 (11, p), 341 (13, p), 329 (10, dp), 293 (35, p), 263 (11, dp), 255 (11, dp), 178 (5, dp)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 309$  ( $\text{M}^+$ , 9%), 290 ( $\text{M} - \text{F}^+$ , 5%), 289 ( $\text{M} - \text{HF}^+$ , 17%), 270 ( $\text{M} - \text{HF} - \text{F}^+$ , 46%), 225 ( $\text{TeF}_5^+$ , 100%), 69 ( $\text{CF}_3^+$ , 2%), 65 ( $\text{CF}_2\text{NH}^+$ , 2%), 64 ( $\text{CF}_2\text{N}^+$ , 2%).  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -44.9$ ,  $\delta_B = -44.7$ ,  $\delta_C = -52.3$  ( $J_{AB} = 175$  Hz,  $J_{BC} = -5.8$  Hz,  $J_{125\text{Te-A}} = 3500$  Hz,  $J_{125\text{Te-B}} = 3500$  Hz,  $J_{125\text{Te-C}} = 2910$  Hz).  $^1\text{H}$  NMR:  $\delta$  5.33 (bs, NH). Anal. Calcd for  $\text{CHNF}_5\text{Te}$ : C, 3.91; H, 0.33; N, 4.57; F, 49.58; Te, 41.62. Found: C, 4.13; H, 0.40; N, 4.50; F, 49.7; Te, 41.51.

**Preparation of  $\text{Cs}^+[\text{N}(\text{CF}_3)_2\text{TeF}_5]^-$ .** Dried CsF (6.1 g, 40 mmol) was loaded into a 250-mL Pyrex glass reaction vessel, which was then degassed and frozen to  $-196$  °C prior to the addition of  $\text{TeF}_5\text{N}=\text{CCl}_2$  (1.93 g, 6.0 mmol). This mixture was then heated at 70 °C overnight and the volatile products (0.27 g) were removed. Dry  $\text{CH}_3\text{CN}$  was added to the flask under argon and the resulting solution was filtered under vacuum. Removal of the solvent afforded 1.32 g of the pale yellow colored salt.  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -22.0$ ,  $\delta_B = -39.2$ ,  $\delta_C = -33.0$  ( $J_{AB} = 166.8$  Hz,  $J_{BC} = 8.5$  Hz,  $J_{125\text{Te-A}} = 2860$  Hz,  $J_{125\text{Te-B}} = 3690$  Hz,  $J_{125\text{Te-C}} = 291.6$  Hz). Anal. Calcd for  $\text{CNF}_8\text{TeCs}$ : C, 2.74; N, 3.19. Found: C, 2.94; N, 3.40.

**Preparation of  $\text{Hg}[\text{N}(\text{CF}_3)_2\text{TeF}_5]_2$ .** An improved route to the mercurial  $\text{Hg}[\text{N}(\text{CF}_3)_2\text{TeF}_5]_2$  was found in the reaction between  $\text{TeF}_5\text{N}=\text{CCl}_2$  and  $\text{HgF}_2$ . Typically,  $\text{TeF}_5\text{N}=\text{CCl}_2$  (14.24 g, 44.6 mmol) was condensed into a 100-mL-capacity stainless steel autoclave containing  $\text{HgF}_2$  (48.0 g, 201.2 mmol). The reaction mixture was heated at 60 °C for 4 days with stirring. The autoclave was then chilled to  $-25$  °C, and any materials volatile at that temperature were removed under vacuum. From the remaining solid mixture  $\text{Hg}[\text{N}(\text{CF}_3)_2\text{TeF}_5]_2$  (17.8 g, 98% yield; mp 67–68 °C) was sublimed onto a  $-25$  °C cold finger while it was heated at 60 °C. Raman (solid): 1211 (5), 1204 (3), 1164 (1), 1132 (1), 957 (6), 853 (5), 713 (9), 702 (16), 683 (17), 674 (100), 639 (19), 601 (1), 550 (2), 363 (2), 350 (11), 331 (10), 325 (7), 313 (12), 302 (9), 265 (19), 221 (9), 210 (22), 194 (4), 149 (4), 116 (5)  $\text{cm}^{-1}$ . Mass spectrum (70 eV): major  $m/z = 818$  ( $\text{M}^+$ , 2%), 799 ( $\text{M} - \text{F}^+$ , 1%), 593 ( $\text{M} - \text{TeF}_5^+$ , 1%), 574 ( $\text{M} - \text{TeF}_6^+$ , 1%), 555 ( $\text{M} - \text{TeF} - \text{F}^+$ , 1%), 529 ( $\text{M} - \text{TeF}_5\text{NCF}_2^+$ , 2%), 510 ( $\text{M} - \text{TeF}_5\text{NCF}_3^+$ , 15%), 427 ( $\text{HgTeF}_5^+$ , 1%), 225 ( $\text{TeF}_5^+$ , 100%).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -34.4$ ,  $\delta_B = -41.6$ ,  $\delta_C = -39.2$  ( $J_{AB} = 172.7$  Hz,  $J_{BC} = -7.5$  Hz,  $J_{125\text{Te-A}} = 3200$  Hz,  $J_{125\text{Te-B}} = 3535$  Hz,  $J_{125\text{Te-C}} = 64.0$  Hz). Anal. Calcd for  $\text{C}_2\text{N}_2\text{F}_{16}\text{HgTe}_2$ : C, 2.96; N, 3.45; F, 37.44. Found: C, 3.07; N, 3.49; F, 37.4.

**Reaction of  $\text{TeF}_5\text{N}=\text{CCl}_2$  with  $\text{NaOCH}_3$ .**  $\text{TeF}_5\text{N}=\text{CCl}_2$  (3.36 g, 10.5 mmol) was condensed at  $-196$  °C into a 250-mL Pyrex glass reaction flask containing freshly prepared  $\text{NaOCH}_3$  (25.0 mmol) in 150 mL of

dry diethyl ether. The reaction mixture was then allowed to warm slowly to room temperature and stirred. After 3 days the reaction mixture was filtered through a glass frit and the ether removed under vacuum, leaving a solid residue. A fairly nonvolatile liquid later identified as  $\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{OCH}_3$  (0.10 g, 3% yield) was then stripped from this residue into a detachable U-trap held at  $-35$  °C. The remaining solid was then sublimed in a vacuum sublimator at room temperature to give  $\text{TeF}_5\text{N}=\text{C}(\text{OCH}_3)_2$  (1.90 g, 6.1 mmol) in 58% yield.

$\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{OCH}_3$ : mp 16–18 °C; IR (gas) 2980 (w), 1625 (vs), 1440 (w), 1242 (s), 1183 (w), 970 (w), 900 (w), 720 (s)  $\text{cm}^{-1}$ ; Raman (liquid, 2000–100  $\text{cm}^{-1}$ ) 1598 (3, p), 1560 (2, p), 1452 (5, dp), 1436 (5, p), 1302 (1, p), 1250 (1, p), 1180 (3, dp), 1158 (2, p), 1005 (1, p), 946 (8, p), 895 (6, p), 885 (6, p), 775 (1, p), 700 (19, p), 683 (42, p), 630 (100, p), 621 (45, p), 581 (69, p), 466 (8, dp), 431 (38 p), 398 (2, p), 335 (10, dp), 300 (12, dp), 247 (20, p), 203 (29, p), 168 (16, dp)  $\text{cm}^{-1}$ ; mass spectrum (80 eV) major  $m/z = 298$  ( $\text{M} - \text{F}^+$ , 16%), 286 ( $\text{M} - \text{OCH}_3^+$ , 28%), 282 ( $\text{M} - \text{Cl}^+$ , 100%), 248 ( $\text{TeF}_4\text{NCO}^+$ , 67%), 225 ( $\text{TeF}_5^+$ , 48%), 187 ( $\text{TeF}_3^+$ , 90%), 92 ( $\text{NCClOCH}_3^+$ , 23%);  $^{19}\text{F}$  NMR ( $\text{AB}_4$  pattern)  $\delta_A = -38.3$ ,  $\delta_B = -47.5$  ( $J_{AB} = 173.3$  Hz,  $J_{125\text{Te-A}} = 3235$  Hz,  $J_{125\text{Te-B}} = 3735$  Hz);  $^1\text{H}$  NMR  $\delta$  4.25 (s,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_2\text{H}_5\text{NOCIF}_5\text{Te}$ : C, 7.62; H, 0.96; N, 4.45. Found: C, 7.45; H, 0.99; N, 4.51.

$\text{TeF}_5\text{N}=\text{C}(\text{OCH}_3)_2$ : mp 76–78 °C; IR (mull) 2980 (m), 1600 (sb), 1480 (s), 1450 (s), 1430 (ss), 1320 (sb), 1205 (s), 1180 (m), 1105 (s), 1000 (s), 810 (m), 750–650 (sb), 610 (s)  $\text{cm}^{-1}$ ; Raman (solid) 1586 (1), 1454 (12), 1211 (2), 1185 (3), 1116 (2), 1000 (3), 910 (6), 747 (1), 689 (11), 667 (100), 623 (76), 610 (33), 495 (12), 340 (10), 330 (10), 305 (5), 295 (7), 250 (17), 216 (12), 171 (10)  $\text{cm}^{-1}$ ; mass spectrum (80 eV) major  $m/z = 294$  ( $\text{M} - \text{F}^+$ , 15%), 282 ( $\text{M} - \text{OCH}_3^+$ , 6%), 248 ( $\text{TeF}_4\text{NCO}^+$ , 13%), 225 ( $\text{TeF}_5^+$ , 15%), 187 ( $\text{TeF}_3^+$ , 41%), 57 ( $\text{CH}_3\text{OCN}^+$ , 100%);  $^{19}\text{F}$  NMR ( $\text{AB}_4$  pattern, acetone- $d_6$ )  $\delta_A = -33.0$ ,  $\delta_B = -44.8$  ( $J_{AB} = 171.5$  Hz,  $J_{125\text{Te-B}} = 3740$  Hz);  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.90 (s,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  164.9 (quintet, NC,  $J_{\text{TeF}_4-\text{C}} = 3.7$  Hz), 54.6 (q,  $\text{OCH}_3$ ,  $J_{\text{C-H}} = 151.2$  Hz). Anal. Calcd for  $\text{C}_3\text{H}_6\text{NO}_2\text{TeF}_5$ : C, 11.60; H, 1.95; N, 4.51. Found: C, 11.82; H, 2.00; N, 4.66.

**Preparation of  $\text{TeF}_5\text{N}=\text{CF}_2$ .** The pyrolysis of the salt formed between  $\text{TeF}_5\text{NHCF}_3$  and  $\text{KF}^{10}$  was an unreliable method for preparing  $\text{TeF}_5\text{N}=\text{CF}_2$  in high yield. A better route to  $\text{TeF}_5\text{N}=\text{CF}_2$  was the reaction of  $\text{Hg}[\text{N}(\text{CF}_3)_2\text{TeF}_5]_2$  with  $(\text{CH}_3)_3\text{SiCl}$ . In a typical reaction,  $(\text{CH}_3)_3\text{SiCl}$  (6.17 g, 56.9 mmol) was added by vacuum transfer to an autoclave containing the mercurial (25.15 g, 31 mmol). The autoclave was then placed in a slush bath at  $-40$  °C which was allowed to warm slowly to room temperature. After the mixture was stirred for 2 days, the volatile products were removed and separated on a 30-cm spinning band column with the outlet being protected against moisture by a trap at  $-78$  °C. The distillation gave 7.8 g of  $\text{TeF}_5\text{N}=\text{CF}_2$  (27.2 mmol, 48% yield) at 50 °C. IR (gas): 1770 (vs), 1300 (s), 1031 (w), 735 (vs), 705 (w sh)  $\text{cm}^{-1}$ . Raman (liquid): 1740 (6, p), 1311 (1, p), 1031 (3, p), 840 (4, p), 725 (4, p), 695 (51, p), 650 (100, p), 610 (6, p), 511 (2, p), 375 (36, p), 330 (5, dp?), 306 (11, p), 267 (4, dp?), 190 (3, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 289$  ( $\text{M}^+$ , 15%), 270 ( $\text{M} - \text{F}^+$ , 26%), 260 ( $\text{Te}_2^+$ , 99%), 225 ( $\text{TeF}_5^+$ , 100%), 69 ( $\text{CF}_3^+$ , 10%), 64 ( $\text{NCF}_2^+$ , 4%).  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -43.5$ ,  $\delta_B = -43.3$ ,  $\delta_C = -22.0$  ( $J_{AB} = 175$  Hz,  $J_{BC} = -8.0$  Hz,  $J_{125\text{Te-A}} = 3435$  Hz,  $J_{125\text{Te-B}} = 3595$  Hz,  $J_{125\text{Te-C}} = 2970$  Hz). Anal. Calcd for  $\text{CNF}_7\text{Te}$ : C, 4.19; N, 4.89. Found: C, 4.20; N, 4.86.

**Preparation of  $\text{TeF}_5\text{N}=\text{C}(\text{F})\text{N}(\text{CF}_3)\text{TeF}_5$ .** Anhydrous HF (8.7 g, 435 mmol) was condensed into a 300-mL stainless steel cylinder containing  $\text{TeF}_5\text{N}=\text{CCl}_2$  (15.80 g, 49.5 mmol). The reaction mixture was heated at 80 °C for 2 h and allowed to sit at room temperature overnight. The volatile materials were then transferred to another pressure vessel containing 50 g of dried, powdered NaF. This vessel was shaken for 30 h at room temperature followed by heating at 60 °C for several hours. The volatile products were then distilled through traps at  $-50$ ,  $-95$ , and  $-196$  °C. The trap at  $-196$  °C stopped primarily  $\text{TeF}_6$  (2.55 g), while a mixture of  $\text{TeF}_5\text{NHCF}_3$  and  $\text{TeF}_5\text{N}=\text{CF}_2$  (6.00 g) was found in the trap at  $-95$  °C. The contents of the trap at  $-50$  °C were redistilled through  $-40$  and  $-196$  °C traps. The trap at  $-40$  °C stopped 2.80 g of  $\text{TeF}_5\text{N}=\text{C}(\text{F})\text{N}(\text{CF}_3)\text{TeF}_5$  (20% yield; mp 5–7 °C). IR (gas): 1725 (vs), 1340 (w), 1325 (w), 1295 (m), 1258 (w), 1240 (m), 1227 (m), 1198 (m), 1180 (m), 1045 (vw), 978 (vw), 747 (s), 730 (s)  $\text{cm}^{-1}$ . Raman (liquid): 1703 (10, p), 1685 (7, p), 1298 (2, p), 1058 (11, p), 973 (5, p), 786 (8, p), 769 (23, p), 713 (38, p), 700 (21, p), 670 (85, p), 647 (100, p), 627 (12, p), 546 (1, p), 459 (2, p), 396 (2, p), 325 (9, p), 310 (9, p), 302 (8, p), 269 (7, p), 253 (8 p), 223 (8, p), 208 (13, p), 198 (11, p), 142 (9, p), 128 (21, p), 112 (5, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 578$  ( $\text{M}^+$ , 2%), 559 ( $\text{M} - \text{F}^+$ , 1%), 334 ( $\text{M} - \text{TeF}_5^+$ , 10%), 315 ( $\text{M} - \text{TeF}_6 - \text{F}^+$ , 16%), 225 ( $\text{TeF}_5^+$ , 100%), 69 ( $\text{CF}_3^+$ , 42%).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{CD}_3\text{E}_4\text{F}$  pattern):  $\delta_A = -45.0$ ,  $\delta_B = -43.8$ ,  $\delta_C = -1.0$ ,  $\delta_D = -54.3$ ,

(19) (a) Grayston, M. W.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 1278. (b) Barlow, M. G.; Bell, D.; O'Reilly, N. J.; Tipping, A. E. *J. Fluorine Chem.* **1983**, *23*, 293.

$\delta_E = -33.3$ ,  $\delta_F = -48.7$  ( $J_{CD} = 15.1$  Hz,  $J_{DE} = -10.7$  Hz,  $J_{EF} = 174.4$  Hz).

**Preparation of  $\text{TeF}_5\text{NHC(F)=NCF}_3$ .** The amine  $\text{TeF}_5\text{NHC(F)=NCF}_3$  (9.38 g, 30.6 mmol) was condensed into a 300-mL Pyrex glass reaction cylinder containing dried powdered KF (1.78 g, 30.7 mmol). The vessel containing the reaction mixture was placed in a  $-78^\circ\text{C}$  cool bath which was allowed to warm slowly to  $0^\circ\text{C}$  over a period of 12 h. The reaction mixture was then held at room temperature for 6 h before being distilled through traps at  $-105$  and  $-196^\circ\text{C}$ . The trap at  $-196^\circ\text{C}$  stopped primarily  $\text{TeF}_6$  (3.2 g), while the contents of the trap at  $-105^\circ\text{C}$  were redistilled through traps at  $0$ ,  $-40$ , and  $-196^\circ\text{C}$ . The  $-40^\circ\text{C}$  trap stopped 2.63 g of a colorless, fairly nonvolatile liquid later identified as  $\text{TeF}_5\text{NHC(F)=NCF}_3$  (49% yield; mp  $2-3^\circ\text{C}$ ). IR (liquid): 3410 (m), 1690 (vs), 1530 (s), 1480 (w), 1387 (w), 1305 (m), 1257 (s), 1200 (vs), 1057 (m), 1015 (vw), 926 (m), 897 (w), 778 (w), 755 (w), 710 (vs), 630 (w)  $\text{cm}^{-1}$ . Raman (liquid): 3408 (22, p), 1683 (9, p), 1668 (sh, 6, p), 1252 (2, p), 1055 (2, p), 920 (10, p), 892 (11, p), 749 (28, p), 695 (26, p), 682 (32, p), 637 (100, p), 615 (53, p), 507 (20, p), 399 (5, p), 333 (8, p), 301 (10, p), 284 (23, p), 273 (70, p), 261 (9, p), 231 (6, p), 207 (7, p), 193 (13, p), 130 (20, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 334$  ( $\text{M} - \text{HF}^+$ , 73%), 315 ( $\text{M} - \text{HF} - \text{F}^+$ , 100%), 246 ( $\text{TeF}_4\text{NCN}^+$ , 11%), 225 ( $\text{TeF}_3^+$ , 80%), 187 ( $\text{TeF}_2^+$ , 99%), 109 ( $\text{CF}_3\text{NCN}^+$ , 33%), 90 ( $\text{CF}_2\text{NCN}^+$ , 29%), 69 ( $\text{CF}_3^+$ , 70%). Chemical ionization mass spectrum (isobutane):  $m/z = 355$  ( $\text{M} + \text{H}^+$ , 100%), 335 ( $\text{M} + \text{H}_2 - \text{HF}^+$ , 4%), 315 ( $\text{M} + \text{H} - 2\text{HF}^+$ , 21%), 287 ( $\text{M} + 2\text{H} - \text{CF}_3^+$ , 24%).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{CD}_3$  spectrum):  $\delta_A = -39.7$ ,  $\delta_B = -43.3$ ,  $\delta_C = -14.2$ ,  $\delta_D = -60.2$  ( $J_{AB} = 175.6$  Hz,  $J_{BC} = -7.5$  Hz,  $J_{CD} = 11.3$  Hz,  $J_{125\text{Te-A}} = 3235$  Hz,  $J_{125\text{Te-B}} = 3615$  Hz).  $^1\text{H}$  NMR:  $\delta$  7.08 (bs, NH) ( $J_{125\text{Te-H}} = 26.5$  Hz). Anal. Calcd for  $\text{C}_2\text{H}_2\text{N}_2\text{F}_9\text{Te}$ : C, 6.83; H, 0.29; N, 7.97; F, 48.63. Found: C, 6.81; H, 0.40; N, 8.06; F, 48.5.

**Reaction of  $\text{TeF}_5\text{NHC(F)=NCF}_3$  with KF.** Dried, powdered KF (1.16 g, 20.0 mmol) was loaded into a 250-mL Pyrex glass reaction flask in an inert-atmosphere box. The flask was degassed and frozen to  $-196^\circ\text{C}$  before  $\text{TeF}_5\text{NHC(F)=NCF}_3$  (1.10 g, 3.1 mmol) was added by vacuum transfer. The reaction flask was placed in a slush bath at  $-40^\circ\text{C}$ , and stirring was begun. The cool bath was allowed to warm slowly to room temperature overnight, and following an additional 24 h at room temperature the volatile products were separated by trap-to-trap distillation. A small quantity of  $\text{TeF}_6$  was found in the trap at  $-196^\circ\text{C}$ , while  $\text{TeF}_5\text{N}=\text{C}=\text{NCF}_3$  (0.10 g, 0.3 mmol; 10% yield) stopped in the trap at  $-75^\circ\text{C}$ . The remaining salts were washed with dry  $\text{CH}_3\text{CN}$  and filtered under vacuum. Both IR and NMR spectroscopic analyses of the filtrate gave evidence for the salt  $\text{K}^+[\text{TeF}_5\text{NC(F)NCF}_3]^-$ .

$\text{TeF}_5\text{N}=\text{C}=\text{NCF}_3$ : IR (gas) 2190 (vs), 1455 (w), 1230 (s), 1155 (s), 735 (s), 690 (w)  $\text{cm}^{-1}$ ; mass spectrum (80 eV) major  $m/z = 334$  ( $\text{M}^+$ , 32%), 315 ( $\text{M} - \text{F}^+$ , 73%), 246 ( $\text{M} - \text{CF}_4^+$ , 4%), 225 ( $\text{TeF}_3^+$ , 57%), 187 ( $\text{TeF}_2^+$ , 100%), 109 ( $\text{M} - \text{TeF}_5^+$ , 15%), 90 ( $\text{M} - \text{TeF}_6^+$ , 13%), 69 ( $\text{CF}_3^+$ , 40%);  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{C}_3$  pattern)  $\delta_A = -49.1$ ,  $\delta_B = -38.9$ ,  $\delta_C = -52.4$  ( $J_{AB} = 173.4$  Hz,  $J_{125\text{Te-B}} = 3710$  Hz).

$\text{K}^+[\text{TeF}_5\text{NC(F)NCF}_3]^-$ : IR ( $\text{CH}_3\text{CH}$  solution) 1620 (vs), 1390 (m), 1250 (s), 1150 (m), 1115 (m), 990 (m), 735 (s)  $\text{cm}^{-1}$ ;  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{CD}_3$  pattern)  $\delta_A = -28.8$ ,  $\delta_B = -42.2$ ,  $\delta_C = -7.2$ ,  $\delta_D = -53.0$  ( $J_{AB} = 173$  Hz).

**Preparation of  $\text{TeF}_5\text{N(F)CF}_3$ .** The mercurial,  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  (3.25 g, 4.0 mmol) was loaded into a 400-mL Monel autoclave in an inert-atmosphere box. The autoclave was then attached to a metal vacuum line, chilled to  $-78^\circ\text{C}$ , and degassed. While the autoclave was held at  $-78^\circ\text{C}$ , small aliquots of  $\text{F}_2$  were added over a period of 1 h until the total pressure reached 375 torr (8 mmol). The valve to the autoclave was shut and the cool bath was allowed to warm slowly to room temperature overnight. The autoclave was then cooled to  $-196^\circ\text{C}$  and the noncondensable materials (80 torr) were removed under vacuum. The condensable products were then removed to the vacuum line where the repeated trap-to-trap distillation gave  $\text{TeF}_5\text{N(F)CF}_3$  (1.62 g, 5.0 mmol; 62% yield) stopping in the trap at  $-110^\circ\text{C}$ . Vapor pressure data treated by least-squares methods gave  $\ln(P/P_0) = 11.69 - 3532.21T^{-1}$  ( $-73$  to  $+10^\circ\text{C}$ ), bp  $28.9^\circ\text{C}$ ,  $\Delta H_v = 7.02$  kcal/mol, and  $\Delta S_v = 23.24$  cal  $\text{K}^{-1}$  mol $^{-1}$ . IR (gas): 1276 (vs), 1240 (vs), 1200 (vs), 1003 (w), 735 (vs), 718 (m sh)  $\text{cm}^{-1}$ . Raman (liquid): 999 (6, dp), 707 (51, p), 663 (66, p), 623 (61, p), 595 (4, dp), 491 (26, p), 450 (10, p), 328 (13, p), 298 (14, p), 285 (9, p), 262 (100, p), 254 (69, p), 203 (5, p), 159 (11, p)  $\text{cm}^{-1}$ . Mass spectrum (70 eV): major  $m/z = 327$  ( $\text{M}^+$ , 3%), 308 ( $\text{M} - \text{F}^+$ , 7%), 289 ( $\text{TeF}_5\text{NCF}_2^+$ , 1%), 270 ( $\text{TeF}_5\text{NCF}^+$ , 1%), 239 ( $\text{M} - \text{CF}_4^+$ , 4%), 225 ( $\text{TeF}_3^+$ , 100%), 83 ( $\text{NCF}_3^+$ , 16%), 69 ( $\text{CF}_3^+$ , 30%).  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3\text{D}$  pattern):  $\delta_A = -55.1$ ,  $\delta_B = -53.3$ ,  $\delta_C = -71.2$ ,  $\delta_D = -81.7$  ( $J_{AB} \approx 175$  Hz,  $J_{AD} \approx 2.5$  Hz,  $J_{BC} \approx -5.2$  Hz,  $J_{BD} \approx 4.8$  Hz,  $J_{CD} \approx 21.6$  Hz,  $J_{125\text{Te-A}} = 3547$  Hz,  $J_{125\text{Te-B}} = 3923$  Hz).

**Preparation of  $\text{TeF}_5\text{N(Cl)CF}_3$ .** Chlorine fluoride (1.1 g, 20.2 mmol) was condensed at  $-196^\circ\text{C}$  into a 200-mL-capacity stainless steel autoclave containing  $\text{Hg}[\text{N}(\text{TeF}_5)\text{CF}_3]_2$  (3.95 g, 4.9 mmol). The autoclave

was placed in a slush bath at  $-78^\circ\text{C}$  which was allowed to warm slowly to room temperature overnight. Repeated trap-to-trap distillation of the product mixture gave  $\text{TeF}_5\text{N(Cl)CF}_3$  (3.14 g, 9.2 mmol) in 95% yield in the  $-95^\circ\text{C}$  trap. Although the chloroamine is a colorless liquid at  $-95^\circ\text{C}$ , it has a very pale yellow color at room temperature.  $\text{TeF}_5\text{N(Cl)CF}_3$  was also prepared from the reaction of  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  and  $\text{Cl}_2$ . Vapor pressure data treated by least-squares methods gave  $\ln(P/P_0) = 12.41 - 4131.76T^{-1}$  ( $-54$  to  $+15^\circ\text{C}$ ), bp =  $59.8^\circ\text{C}$ ,  $\Delta H_v = 8.21$  kcal/mol, and  $\Delta S_v = 24.66$  cal  $\text{K}^{-1}$  mol $^{-1}$ . IR (gas): 1257 (s), 1220 (vs), 1189 (vs), 735 (vs), 711 (m sh)  $\text{cm}^{-1}$ . Raman (liquid): 1264 (1, ?), 1213 (1, ?), 940 (1, p), 892 (4, p), 722 (5, p), 701 (67, p), 657 (79, p), 602 (19, p), 571 (2, p), 458 (19, p), 397 (26, p), 332 (14, p), 307 (11, p), 285 (100, p), 255 (25, p), 225 (13, p), 204 (34, p), 188 (23, p), 168 (5, p), 128 (6, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 343$  ( $\text{M}^+$ , 10%), 324 ( $\text{M} - \text{F}^+$ , 3%), 308 ( $\text{M} - \text{Cl}^+$ , 1%), 289 ( $\text{M} - \text{ClF}^+$ , 15%), 270 ( $\text{M} - \text{Cl} - \text{F}^+$ , 25%), 260 ( $\text{Te}_2^+$ , 13%), 225 ( $\text{TeF}_3^+$ , 100%), 118 ( $\text{NClCF}_3^+$ , 17%), 99 ( $\text{NClCF}_2^+$ , 28%).  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -49.3$ ;  $\delta_B = -50.5$ ,  $\delta_C = -61.7$  ( $J_{AB} = 180.8$  Hz,  $J_{AC} = 0.1$  Hz,  $J_{BC} = -6.7$  Hz,  $J_{125\text{Te-A}} = 3450$  Hz,  $J_{125\text{Te-B}} = 3760$  Hz,  $J_{125\text{Te-C}} = 3080$  Hz). Anal. Calcd for  $\text{CNCIF}_8\text{Te}$ : C, 3.52; N, 4.11; Cl, 10.40; F, 44.56. Found: C, 3.62; N, 4.13; Cl, 10.26; F, 44.5.

**Preparation of  $\text{TeF}_5\text{N(Br)CF}_3$ .** The preparation of the bromoamine was analogous to that of  $\text{TeF}_5\text{N(Cl)CF}_3$ . A mixture of  $\text{Br}_2$  (7.39 g, 46.2 mmol) and  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  (18.78 g, 23.1 mmol) was stirred at room temperature for a period of 1 week. Reaction workup gave  $\text{TeF}_5\text{N(Br)CF}_3$  (8.70 g) as a yellow colored liquid in the  $-70^\circ\text{C}$  trap. The unreacted  $\text{Br}_2$  was returned to the autoclave for further reaction. Additional product (3.33 g) was obtained following the second reaction workup, thus giving an overall yield of 68%. The bromoamine was also obtained in a reaction between the mercurial and a mixture of  $\text{Br}_2$  and  $\text{BrF}$ . An excitation energy of 10 mW had to be used to obtain the Raman spectrum without sample decomposition. Vapor pressure data treated by least squares methods gave  $\ln(P/P_0) = 11.25 - 4047.97T^{-1}$  ( $-15$  to  $+23^\circ\text{C}$ ; limited temperature range due to observed decomposition), bp  $86.7^\circ\text{C}$ ,  $\Delta H_v = 8.04$  kcal/mol, and  $\Delta S_v = 22.35$  kcal  $\text{K}^{-1}$  mol $^{-1}$ . IR (gas): 1240 (s), 1220 (vs), 1182 (vs), 735 (vs), 705 (m), 330 (s)  $\text{cm}^{-1}$ . Raman (liquid): 697 (81, p), 635 (100, p), 600 (19, p), 453 (14, p), 325 (19, p), 272 (67, p), 253 (28, dp?), 165 (34, dp?), 157 (21, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 387$  ( $\text{M}^+$ , 21%), 368 ( $\text{M} - \text{F}^+$ , 18%), 308 ( $\text{M} - \text{Br}^+$ , 1%), 289 ( $\text{TeF}_5\text{NCF}_2^+$ , 14%), 270 ( $\text{TeF}_5\text{NCF}^+$ , 19%), 225 ( $\text{TeF}_3^+$ , 100%), 162 ( $\text{BrNCF}_3^+$ , 39%).  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -47.2$ ,  $\delta_B = -49.5$ ,  $\delta_C = -58.2$  ( $J_{AB} = 178.8$  Hz,  $J_{125\text{Te-A}} = 3445$  Hz,  $J_{125\text{Te-B}} = 3715$  Hz,  $J_{125\text{Te-C}} = 3050$  Hz). Anal. Calcd for  $\text{CNBrF}_8\text{Te}$ : C, 3.11; N, 3.63; Br, 20.73. Found: C, 3.22; N, 3.71; Br, 20.79.

**Preparation of  $\text{TeF}_5\text{N(I)CF}_3$ .** A mixture of  $\text{ICl}$  (1.6 g, 9.9 mmol) and  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  (4.1 g, 5 mmol) was sealed in a thick-walled glass ampule. The mixture was allowed to react at room temperature overnight with magnetic stirring. The ampule was then broken open under vacuum, and the volatile products were transferred to the vacuum line for distillation through a series of traps at  $-15$ ,  $-50$ , and  $-196^\circ\text{C}$ . The trap at  $-15^\circ\text{C}$  stopped 0.47 g of  $\text{I}_2$ , while the trap at  $-196^\circ\text{C}$  contained primarily  $\text{TeF}_5\text{N}=\text{CF}_2$ . Both a red liquid and a colorless solid were found in the  $-50^\circ\text{C}$  trap. This mixture was redistilled several times through the above series of traps, but each time  $\text{I}_2$  was found in every trap except the one held at  $-196^\circ\text{C}$ . Finally, the remaining contents of the trap at  $-50^\circ\text{C}$  (1.33 g) were examined by  $^{19}\text{F}$  NMR spectroscopy. Both  $\text{TeF}_5\text{N}=\text{CF}_2$  and  $\text{IF}_5^{20}$  were found in the mixture as well as a new  $\text{AB}_4\text{C}_3$  pattern attributed to  $\text{TeF}_5\text{N(I)CF}_3$ . Unfortunately, further analyses by infrared and mass spectrometry gave no further evidence for the iodoamine; however, it was still present in the original NMR sample even after several weeks.

$\text{TeF}_5\text{N(I)CF}_3$ :  $^{19}\text{F}$  NMR (degenerate  $\text{AB}_4\text{C}_3$  pattern)  $\delta_A = -43.4$ ,  $\delta_B = -48.4$ ,  $\delta_C = -53.0$  ( $J_{AB} = 177.9$  Hz,  $J_{BC} = -7.1$  Hz,  $J_{AC} = 0.1$  Hz).

**Preparation of  $\text{TeF}_5\text{N}(\text{CF}_3)\text{C(O)CH}_3$ .** Acetyl bromide (1.18 g, 9.6 mmol) was condensed at  $-196^\circ\text{C}$  into a 250-mL Pyrex glass reaction flask containing  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  (4.87 g, 6.0 mmol). The reaction mixture was warmed slowly to room temperature and magnetically stirred for a period of 24 h. Multiple trap-to-trap distillation of the volatile products gave 2.44 g of  $\text{TeF}_5\text{N}(\text{CF}_3)\text{C(O)CH}_3$  stopping in the trap at  $-55^\circ\text{C}$  (73% yield; mp  $-41$  to  $-42^\circ\text{C}$ ). IR (gas): 1713 (s), 1295 (s), 1242 (vs), 1180 (s), 1045 (w), 960 (s), 835 (w), 744 (vs), 738 (vs)  $\text{cm}^{-1}$ . Raman (liquid): 3042 (1, p), 3000 (2, p), 2951 (20, p), 1708 (9, p), 1436 (2, dp), 1381 (2, dp), 1286 (1, p), 1232 (8, p), 1169 (2, p), 1029 (10, p), 993 (1, p), 949 (12, p), 834 (12, p), 736 (4, p), 721 (5, p), 710 (9, p), 675 (100, p), 663 (99, p), 587 (2, p), 553 (18, p), 497 (2, p), 406 (18, p), 325 (5, dp), 309 (10, p), 295 (5, p), 252 (3, p), 198 (6, p), 142

(6, dp)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 351$  ( $\text{M}^+$ , 14%), 336 ( $\text{M} - \text{CH}_3^+$ , 15%), 289 ( $\text{TeF}_5\text{NCF}_2^+$ , 1%), 270 ( $\text{TeF}_5 - \text{NCF}^+$ , 2%), 267 ( $\text{TeF}_5\text{NCO}^+$ , 6%), 248 ( $\text{TeF}_4\text{NCO}^+$ , 11%), 225 ( $\text{TeF}_5^+$ , 78%), 69 ( $\text{CF}_3^+$ , 44%), 43 ( $\text{CH}_3\text{CO}^+$ , 100%).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -46.6$ ,  $\delta_B = -41.2$ ,  $\delta_C = -57.3$  ( $J_{\text{AB}} = 181.3$  Hz,  $J_{125\text{Te-A}} = 3350$  Hz,  $J_{125\text{Te-B}} = 3820$  Hz).  $^1\text{H}$  NMR:  $\delta$  2.40 (bs,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $\delta$  206.1 (m, CO), 122.8 (q,  $\text{CF}_3$ ,  $^1J_{\text{C-F}} = -259.4$  Hz), 18.4 (q of octets,  $\text{CH}_3$ ,  $^1J_{\text{C-H}} = 133.4$  Hz,  $^3J_{\text{CF}_3-\text{C}} = ^5J_{\text{TeF}_4-\text{C}} = 2.2$  Hz). Anal. Calcd for  $\text{C}_3\text{H}_3\text{NOF}_8\text{Te}$ : C, 10.34; H, 0.87; N, 4.02. Found: C, 10.42; H, 0.84; N, 4.16.

**Preparation of  $(\text{TeF}_5)_2\text{NCF}_3$ .** A 6-L round-bottomed flask chilled to  $-196^\circ\text{C}$  was loaded with  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  (3.88 g, 11.4 mmol). After being warmed to room temperature, the contents of the Pyrex flask were photolyzed for 1 h with an internal low-pressure Hg lamp. Distillation of the product mixture gave 0.1 g of a material subsequently identified as  $(\text{TeF}_5)_2\text{NCF}_3$  (3% yield) in the trap at  $-60^\circ\text{C}$ . The material in the trap at  $-196^\circ\text{C}$ , containing unreacted  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$ , was photolyzed for an additional 4 h; however, reaction workup yielded no additional  $(\text{TeF}_5)_2\text{NCF}_3$ . Other volatile products produced included  $\text{TeF}_5\text{Cl}$ ,  $\text{TeF}_6$ , and most likely  $\text{Cl}_2$  as evidence by its color and volatility. A photolysis of  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  in the liquid phase in Pyrex glass with a high-pressure Hg lamp gave no evidence for the new  $\text{TeF}_5\text{-N}$  compound as mostly  $\text{TeF}_5\text{Cl}$  was generated. IR (gas): 1258 (vs), 1215 (vs), 1160 (vs), 945 (w), 856 (m), 753 (vs), 720 (vs)  $\text{cm}^{-1}$ . Mass spectrum (70 eV): major  $m/z = 533$  ( $\text{M}^+$ , 2%), 514 ( $\text{M} - \text{F}^+$ , 1%), 445 ( $\text{TeF}_5\text{NTeF}_4$ , 2%), 308 ( $\text{TeF}_5\text{NCF}_3$ , 1%), 289 ( $\text{TeF}_5\text{NCF}_2^+$ , 21%), 270 ( $\text{TeF}_5\text{NCF}^+$ , 73%), 260 ( $\text{Te}_2^+$ , 1%), 225 ( $\text{TeF}_5$ , 100%).  $^{19}\text{F}$  NMR ( $\text{AA}'\text{B}_4\text{B}'_4\text{C}_3$  pattern):  $\delta_A \approx \delta_{A'} = -43.6$ ,  $\delta_B \approx \delta_{B'} = -27.3$ ,  $\delta_C = -42.8$  ( $J_{\text{AB}} \approx J_{A'B'} = 178.1$  Hz,  $J_{\text{BC}} \approx J_{B'C'} = -11.5$  Hz,  $J_{125\text{Te-B}} \approx J_{125\text{Te-B}'} = 3660$  Hz). Anal. Calcd for  $\text{CNF}_3\text{Te}_2$ : C, 2.27. Found: C, 2.39.

**Preparation of  $\text{TeF}_5\text{N}(\text{SF}_5)\text{CF}_3$ .** A mixture of  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  (3.97 g, 11.6 mmol) and  $\text{SF}_5\text{Cl}$  (4.0 g, 24.6 mmol) was photolyzed as in the preceding reaction. Repeated trap-to-trap distillation gave an approximately 60:40 mixture of  $\text{TeF}_5\text{N}(\text{SF}_5)\text{CF}_3$  and  $(\text{TeF}_5)_2\text{NCF}_3$  (0.20 g) stopping in the trap at  $-80^\circ\text{C}$ . Attempted analysis by gas chromatography-mass spectrometry was unsuccessful; however, the following data from the mixture strongly supports the existence of  $\text{TeF}_5\text{N}(\text{SF}_5)\text{CF}_3$ . IR (gas; not coinciding with  $(\text{TeF}_5)_2\text{NCF}_3$ ): 1270 (vs), 1176 (vs), 990 (m), 923 (s), 883 (m), 843 (vs), 803 (w), 740 (s), 608 (m)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 435$  ( $\text{M}^+$ ), 416 ( $\text{M} - \text{F}^+$ ), 328 ( $\text{TeF}_5\text{NSF}_3^+$ ), 191 ( $\text{SF}_5\text{NCF}_2^+$ ), 171 ( $\text{SF}_5\text{NCF}^+$ ), 127 ( $\text{SF}_5^+$ ).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{XY}_4\text{Z}_3$  pattern):  $\delta_A = 62.3$ ,  $\delta_B = 81.1$ ,  $\delta_X = -44.3$ ,  $\delta_Y = -30.3$ ,  $\delta_Z = -49.5$  ( $J_{\text{AB}} = 147$  Hz,  $J_{\text{XY}} = 178$  Hz,  $J_{\text{BZ}} \approx J_{\text{YZ}} = -15.5$  Hz).

**Photolysis of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$ .**  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  (3.25 g, 8.5 mmol) was photolyzed in a 6-L Pyrex flask with an internal low-pressure Hg lamp for two successive periods of 1 h. The product mixture was examined after each photolysis, but no evidence was found for  $(\text{TeF}_5)_2\text{NCF}_3$ . Both  $\text{TeF}_5\text{Br}^{21}$  and  $\text{CF}_3\text{N}=\text{NCF}_3^{22}$  were found as the major volatile products along with some unreacted  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  (0.9 g).

**Reaction of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  with CO.** The bromoamine (2.60 g, 6.75 mmol) was reacted at room temperature with an excess of CO (10 mmol) in a 250-mL glass reaction vessel. After a reaction period of 16 h, the glass vessel was chilled to  $-196^\circ\text{C}$  and the unreacted CO was pumped away. Fractional distillation of the condensable products gave unreacted  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  (0.70 g) stopping in the trap at  $-75^\circ\text{C}$ , primarily  $\text{TeF}_5\text{Br}$  (1.25 g) in the trap at  $-110^\circ\text{C}$ , and  $\text{CF}_3\text{NCO}^{23}$  (0.54 g) in the trap at  $-196^\circ\text{C}$ . The contents of both traps at  $-110$  and  $-196^\circ\text{C}$  were slightly orangish red, indicating the presence of  $\text{Br}_2$  and/or  $\text{BrF}$ .

**Reaction of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  with  $\text{C}_2\text{H}_2$ .** Both  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  (1.01 g, 2.6 mmol) and  $\text{C}_2\text{H}_2$  (4.0 mmol) were condensed at  $-196^\circ\text{C}$  into a 25-mL-capacity thick-walled glass ampule, equipped with a magnetic stirring bar. The ampule was sealed and then warmed slowly to room temperature, by which time a white solid had formed. The mixture was stirred for a period of 16 h before the ampule was refrozen to  $-196^\circ\text{C}$  and broken open under vacuum. The compounds  $\text{CHBr}_2\text{CHF}_2^{24}$  and  $\text{TeF}_5\text{N}=\text{CF}_2$  were identified as principal components of the product mixture by IR and NMR spectroscopy. The white solid was not identified.

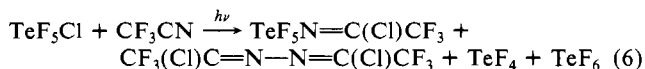
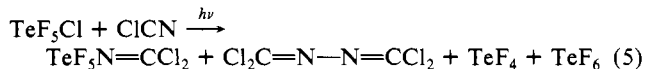
**Preparation of  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Br}$ .** A mixture of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  (1.08 g, 2.8 mmol) and  $\text{C}_2\text{H}_4$  (5.0 mmol) was reacted in a sealed glass ampule as in the preceding reaction. Within a period of 1 h at room temperature the reaction mixture had become completely colorless. After being stirred overnight, the volatile products were removed to the vacuum

line for distillation. Repeated fractionation gave  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Br}$  (1.05 g, 91% yield) stopping in the trap at  $-45^\circ\text{C}$ ; mp  $-18$  to  $-17^\circ\text{C}$ . IR (gas): 3010 (vw), 1760 (vw), 1465 (w), 1373 (w), 1330 (w), 1265 (vs), 1172 (vs), 1070 (w), 915 (w), 730 (vs), 715 (s sh), 608 (w)  $\text{cm}^{-1}$ . Raman (liquid): 3045 (4, p), 3011 (12, p), 2990 (28, p), 2977 (38, p), 2916 (6, p), 2877 (4, p), 1466 (2, dp), 1448 (5, dp?), 1372 (1, p), 1330 (2, p), 1255 (4, p), 1227 (7, p), 1153 (1, pe), 1062 (5, p), 910 (3, dp), 767 (6, p), 734 (15, p), 699 (75, p), 652 (100, p), 603 (6, p), 578 (3, p), 510 (6, p), 450 (4, p), 345 (6, p), 3332 (5, dp?), 308 (12, dp?), 270 (9, dp?), 258 (5, dp?), 243 (7, p), 210 (23, p), 175 (2, dp), 147 (31, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 415$  ( $\text{M}^+$ , 1%), 335 ( $\text{M} - \text{HBr}^+$ , 1%), 322 ( $\text{M} - \text{CH}_2\text{Br}^+$ , 100%), 225 ( $\text{TeF}_5^+$ , 2%), 187 ( $\text{TeF}_3^+$ , 53%), 171 ( $\text{CF}_3\text{NCH}_2\text{CH}_2\text{Br}^+$ , 9%), 107 ( $\text{CH}_2\text{CH}_2\text{Br}^+$ , 24%), 93 ( $\text{CH}_3\text{Br}^+$ , 33%), 69 ( $\text{CF}_3^+$ , 29%).  $^{19}\text{F}$  NMR ( $\text{AB}_4\text{C}_3$  pattern):  $\delta_A = -41.1$ ,  $\delta_B = -47.3$ ,  $\delta_C = -54.6$  ( $J_{\text{AB}} = 176.2$  Hz,  $J_{\text{BC}} = -7.3$  Hz,  $J_{125\text{Te-A}} = 3450$  Hz,  $J_{125\text{Te-B}} = 3575$  Hz).  $^1\text{H}$  NMR ( $\text{A}_2\text{B}_2$  pattern):  $\delta$  3.8 (bm,  $\text{CH}_2\text{Br}$ ,  $J_{\text{H-H}} \approx 8$  Hz), 4.2 (bm,  $\text{NCH}_2$ ,  $J_{\text{H-H}} \approx 8$  Hz). Anal. Calcd for  $\text{C}_2\text{H}_4\text{NBrF}_8\text{Te}$ : C, 8.71; H, 0.97; N, 3.39; Br, 19.32. Found: C, 9.12; H, 1.05; N, 3.53; Br, 20.02.

**Reaction of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  with  $\text{C}_3\text{F}_6$ .** The bromoamine (1.24 g, 3.2 mmol) was reacted with an excess of  $\text{C}_3\text{F}_6$  (1.4 g, 9.3 mmol) in a sealed glass ampule. Because no reaction was found to take place at room temperature, the mixture was heated at  $100^\circ\text{C}$  for 16 h. The ampule was broken open under vacuum, and the product mixture was separated by trap-to-trap distillation. The trap at  $-60^\circ\text{C}$  stopped  $\text{TeF}_5\text{N}(\text{CF}_3)\text{-C}_3\text{F}_6\text{Br}$  (1.0 g) as a colorless liquid in 58% yield. The product was found to be a mixture of the isomers  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}_2\text{CF}(\text{CF}_3)\text{Br}$  and  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}(\text{CF}_3)\text{CF}_2\text{Br}$  in an approximate ratio of 90:10 as determined by NMR spectroscopy. The following characterization data was obtained on the isomer mixture. IR (gas): 1305 (vs), 1280 (vs), 1250 (vs), 1230 (vs), 1218 (vs), 1172 (m), 1130 (m), 965 (w), 930 (m), 825 (w), 794 (vw), 738 (vs), 715 (vs)  $\text{cm}^{-1}$ . Raman (liquid): 1302 (4, p), 1276 (3, dp?), 1223 (4, dp?), 1183 (4, p), 1170 (3, p), 1122 (3, p), 1053 (1, p), 978 (5, p), 965 (2, p), 936 (4, p), 822 (3, p), 745 (28, p), 708 (63, p), 669 (100, p), 641 (19, p), 555 (4, p), 473 (5, p), 412 (4, p), 367 (5, p), 345 (9, p), 324 (26, p), 311 (27, p), 296 (18, p), 279 (12, p), 263 (14, p), 214 (18, p), 202 (11, p), 182 (6, p), 163 (8, p), 135 (8, p), 125 (11, p)  $\text{cm}^{-1}$ . Mass spectrum (80 eV): major  $m/z = 430$  ( $\text{M} - \text{F} - \text{CF}_2^+$ , 1%), 408 ( $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}(\text{CF}_3)^+$ , 1%), 358 ( $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}_2^+$ , 19%), 293 ( $\text{M} - \text{TeF}_6^+$ , 18%), 274 ( $\text{M} - \text{TeF}_6 - \text{F}^+$ , 15%), 229 ( $\text{C}_3\text{F}_6\text{Br}^+$ , 15%), 225 ( $\text{TeF}_5^+$ , 20%), 214 ( $\text{CF}_3\text{NCF}_3\text{F}_5^+$ , 14%), 187 ( $\text{TeF}_3^+$ , 100%), 179 ( $\text{CF}_3\text{CFBr}^+$ , 43%), 129 ( $\text{CF}_2\text{Br}^+$ , 54%), 114 ( $\text{CF}_3\text{NCF}^+$ , 83%), 69 ( $\text{CF}_3^+$ , 90%). Chemical ionization mass spectrum (isobutane): major  $m/z = 518$  ( $\text{M} - \text{F}^+$ , 24%), 430 ( $\text{M} - \text{F} - \text{CF}_4^+$ , 11%), 408 ( $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}(\text{CF}_3)^+$ , 3%), 358 ( $\text{TeF}_5\text{N}(\text{CF}_3)\text{CF}_2^+$ , 69%), 274 ( $\text{M} - \text{TeF}_6 - \text{F}^+$ , 75%), 229 ( $\text{C}_3\text{F}_6\text{Br}^+$ , 60%), 215 ( $\text{CF}_3\text{NHC}_3\text{F}_5^+$ , 15%), 187 ( $\text{TeF}_3^+$ , 35%), 179 ( $\text{CF}_3\text{CFBr}^+$ , 23%), 129 ( $\text{CF}_2\text{Br}^+$ , 48%), 115 ( $\text{CF}_3\text{NHC}_3\text{F}_5^+$ , 100%), 69 ( $\text{CF}_3^+$ , 62%).  $^{19}\text{F}$  NMR ( $\text{F}^A\text{TeF}_5^B\text{N}(\text{CF}_3^C)\text{C}(\text{F}^D)\text{F}^E\text{CF}^F(\text{CF}_3^G)\text{Br}$ ):  $\delta_A = -44.3$ ,  $\delta_B = -31.0$ ,  $\delta_C = -48.5$ ,  $\delta_D = -77.2$ ,  $\delta_E = -81.2$ ,  $\delta_F = -133.4$ ,  $\delta_G = -76.9$  ( $J_{\text{AB}} = 178$  Hz,  $J_{\text{DE}} = 235$  Hz,  $J_{125\text{Te-A}} = 3480$  Hz,  $J_{125\text{Te-B}} = 3610$  Hz).  $^{19}\text{F}$  NMR ( $\text{F}^A\text{TeF}_5^B\text{N}(\text{CF}_3^C)\text{C}(\text{F}^D)\text{CF}_3^E\text{C}(\text{F}^F)\text{CF}^G\text{Br}$ ):  $\delta_A = -43.4$ ,  $\delta_B = -28.0$ ,  $\delta_C = -47.9$ ,  $\delta_D = -131.9$ ,  $\delta_E = -73.7$ ,  $\delta_F = -56.5$ ,  $\delta_G = -58.2$  ( $J_{\text{AB}} = 178$  Hz,  $J_{\text{FG}} \approx 175$  Hz). Anal. Calcd for  $\text{C}_4\text{NBrF}_{14}\text{Te}$ : C, 8.97; N, 2.62; Br, 14.92; F, 49.67. Found: C, 9.13; N, 2.69; Br, 15.17; F, 50.2.

## Results and Discussion

The photolytic addition of  $\text{TeF}_5\text{Cl}$  to the nitriles  $\text{ClCN}$  and  $\text{CF}_3\text{CN}$  has given the first  $\text{TeF}_5\text{N}=\text{C}<$  systems:



Even though these reactions represent the first successful incorporation of the  $\text{TeF}_5$  group photolytically, the percent conversions are comparable to those observed with the related sulfur systems (30–40%).<sup>5,6</sup> The azine byproducts probably result from photolytic degradation of the  $\text{Te}-\text{N}$  bond. Although  $\text{S}_2\text{F}_{10}$  is observed in the analogous reactions of  $\text{SF}_5\text{Cl}$ ,<sup>5</sup> we see no evidence for the formation of the unknown  $\text{Te}_2\text{F}_{10}$ ; both  $\text{TeF}_4$  and  $\text{TeF}_6$  are formed instead. In fact, photolysis of a mixture of  $\text{TeF}_5\text{Cl}$  and  $\text{H}_2$  gives the same result.

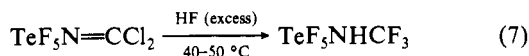
**Reactions of  $\text{TeF}_5\text{N}=\text{CCl}_2$ .** The amine  $\text{TeF}_5\text{NHCF}_3$  is produced in 90% yield as a colorless, stable liquid from the reaction of  $\text{TeF}_5\text{N}=\text{CCl}_2$  with excess HF:

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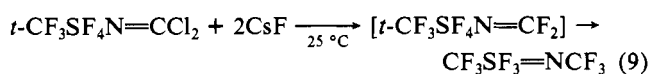
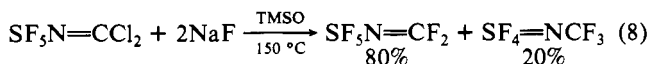
(22) Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 2337.

(23) Lutz, W.; Sundermeyer, W. *Chem. Ber.* **1979**, *112*, 2158.

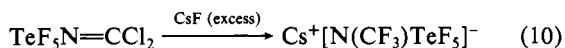
(24) Abraham, R. J.; Cooper, M. A.; Siverns, T. M.; Swinton, P. F.; Weder, H. G.; Cavalli, L. *Org. Magn. Reson.* **1974**, *6*, 331.



On the other hand, a reproducible, high-yield synthesis of the imine  $\text{TeF}_5\text{N}=\text{CF}_2$  was not so easily found. In the sulfur systems, the chlorine atoms of the azomethines are readily replaced by fluoride ion from alkali-metal fluorides (see eq 8 and 9).<sup>5,6</sup> The reaction

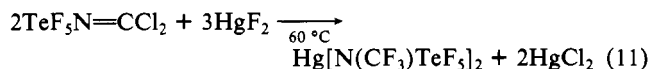


of  $\text{TeF}_5=\text{CCl}_2$  with NaF in tetramethylene sulfone (TMSO) gave  $\text{TeF}_6$  as the primary volatile product, while the reaction with excess CsF produced the salt  $\text{Cs}^+[\text{N}(\text{CF}_3)\text{TeF}_5]^-$ :



The crystalline salt was found to be highly soluble in acetonitrile and was identified by its <sup>19</sup>F NMR spectrum and elemental analysis.

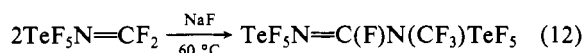
The mercurial  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  is formed almost quantitatively in the direct reaction between  $\text{TeF}_5\text{N}=\text{CCl}_2$  and  $\text{HgF}_2$ :



This represents a substantial improvement over the 20% yield obtained in the reaction between  $\text{TeF}_5\text{NHCF}_3$  and  $\text{HgF}_2$ .<sup>10</sup> This colorless, sublimable mercurial was identified by various spectroscopic methods, including mass spectrometry, which gave a molecular ion at *m/z* 818 for <sup>202</sup>Hg. In contrast, reaction temperatures of 100–125 °C were required to prepare  $\text{Hg}[\text{N}(\text{CF}_3)\text{SF}_5]_2$  from  $\text{SF}_5\text{N}=\text{CF}_2$  and  $\text{HgF}_2$ .<sup>5</sup>

The (dichloromethylene)amine  $\text{TeF}_5\text{N}=\text{CCl}_2$  was also found to react with nucleophilic reagents such as  $\text{NaOCH}_3$  to give both mono- and disubstituted products. The disubstituted derivative  $\text{TeF}_5\text{N}=\text{C}(\text{OCH}_3)_2$  is a white, crystalline solid, while  $\text{TeF}_5\text{N}=\text{C}(\text{Cl})\text{OCH}_3$  is a colorless liquid. The imine carbon resonance in the carbon-13 NMR spectrum of  $\text{TeF}_5\text{N}=\text{C}(\text{OCH}_3)_2$  appeared as a quintet due to coupling with the four basal fluorines of the  $\text{TeF}_5$  group. A similar coupling has been observed in many *N*-pentafluorosulfanylimine derivatives.<sup>8,25</sup>

**Attempts to Dehydrofluorinate  $\text{TeF}_5\text{NHCF}_3$ .** The first attempts to dehydrofluorinate  $\text{TeF}_5\text{NHCF}_3$  were made by prolonged exposure of the amine to NaF with heating. This procedure produced a mixture of unreacted  $\text{TeF}_5\text{NHCF}_3$ ,  $\text{TeF}_5\text{N}=\text{CF}_2$ , and a third heavier component. This less volatile component was fractionated from the mixture and identified as the imine dimerization product  $\text{TeF}_5\text{NC}(\text{F})\text{N}(\text{CF}_3)\text{TeF}_5$ :



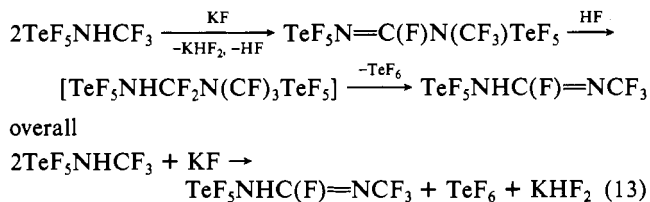
The identity of the product was verified by its mass, infrared, Raman, and <sup>19</sup>F NMR spectra. The NMR spectrum revealed the presence of two distinct  $\text{TeF}_5$  groups, a  $\text{CF}_3$  group, and a CF group in approximately a 5:5:3:1 intensity ratio.

Salt formation was once again observed when  $\text{TeF}_5\text{NHCF}_3$  was placed over the more active metal fluoride KF. The resulting solid material was heated gently with a Bunsen burner, and the imine  $\text{TeF}_5\text{N}=\text{CF}_2$  was separated from the volatile products in 35% yield.<sup>10</sup> However, this method proved to be unreliable as it generally gave only trace quantities of  $\text{TeF}_5\text{N}=\text{CF}_2$ .

An equimolar reaction between  $\text{TeF}_5\text{NHCF}_3$  and KF was then carried out with the hope that there would be no free metal fluoride available for salt formation. The major products observed in this reaction were not  $\text{TeF}_5\text{N}=\text{CF}_2$  and unreacted  $\text{TeF}_5\text{NHCF}_3$  but instead  $\text{TeF}_6$  and  $\text{TeF}_5\text{NHC}(\text{F})=\text{NCF}_3$ . A plausible route to these two products is given in Scheme I. The loss of  $\text{TeF}_6$  from

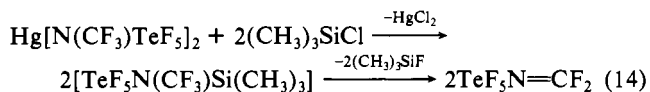
the intermediate shown is most likely fluoride ion promoted. At first it was not certain whether the product shown in eq 13 was indeed  $\text{TeF}_5\text{NHC}(\text{F})=\text{NCF}_3$  or perhaps  $\text{TeF}_5\text{N}=\text{C}(\text{F})\text{NHCF}_3$  instead. The tellurium-125 satellites observed in the proton NMR spectrum indicated that our assignment was correct.

#### Scheme I



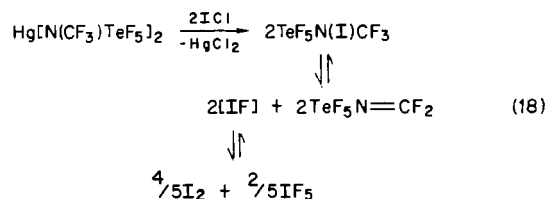
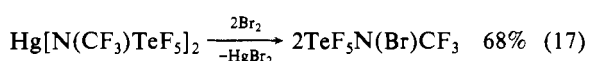
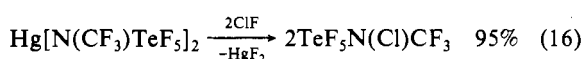
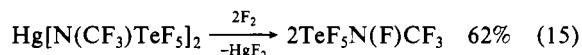
Following purification, a sample of  $\text{TeF}_5\text{NHC}(\text{F})=\text{NCF}_3$  was placed over fresh potassium fluoride. Since the expected carbodiimide  $\text{TeF}_5\text{N}=\text{C}=\text{NCF}_3$  was obtained in only 10% yield, the remaining salts were washed with acetonitrile and the resulting filtrate was examined by infrared and NMR spectroscopy. Both analyses gave evidence for the salt  $\text{K}^+[\text{TeF}_5\text{NC}(\text{F})\text{NCF}_3]^-$ . The compound  $\text{TeF}_5\text{N}=\text{C}=\text{NCF}_3$ , characterized by an intense  $\text{N}=\text{C}=\text{N}$  absorption at 2190  $\text{cm}^{-1}$ , is one of the few examples of carbodiimides with perfluorinated substituents. Other examples include  $\text{CF}_3\text{N}=\text{C}=\text{NCF}_3$ <sup>26</sup> and  $\text{SF}_5\text{N}=\text{C}=\text{NSF}_5$ .<sup>27</sup> An analogy to the KF addition product was found in the addition products of carbodiimines and organomagnesium halides reported in 1907.<sup>28</sup> The infrared absorption at 1620  $\text{cm}^{-1}$  in  $\text{K}^+[\text{TeF}_5\text{NC}(\text{F})\text{NCF}_3]^-$  favors delocalization of the negative charge over the entire N–C–N system. As with the aforementioned salts, one sees evidence of the great stabilizing effect of the  $\text{TeF}_5\text{N}<$  group.<sup>3,4</sup>

**$\text{TeF}_5\text{N}(\text{CF}_3)$ -Derivatives.** A convenient route to  $\text{TeF}_5\text{N}=\text{CF}_2$  was finally found in the reaction of  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  with  $(\text{CH}_3)_3\text{SiCl}$ . The reaction is envisioned as proceeding through a  $\text{TeF}_5\text{N}(\text{CF}_3)$ -intermediate as shown in eq 14. The yield of



pure product is low (~50%) due to the difficulty in separating the imine from the byproduct  $(\text{CH}_3)_3\text{SiF}$ . Unlike the corresponding sulfur compounds shown in eq 8 and 9,  $\text{TeF}_5\text{N}=\text{CF}_2$  does not isomerize to a five-coordinated species, namely  $\text{TeF}_4=\text{NCF}_5$ . This can be rationalized by the fact that no tellurium(VI) compound containing a multiple bond and thus a coordination number less than 6 has been reported.<sup>29</sup>

Reactions of the mercurial with halogens or interhalogens have led to the trisubstituted amines  $\text{TeF}_5\text{N}(\text{X})\text{CF}$ , where X = F, Cl, Br, and I. Of these only the *N*-iodo compound is unstable and decomposes according to the equilibrium shown in eq 18.



(26) (a) Mitch, R. A.; Ogden, P. H. *J. Chem. Soc., Chem. Commun.* **1967**, 59. (b) Ogden, P. H.; Mitch, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 5007.

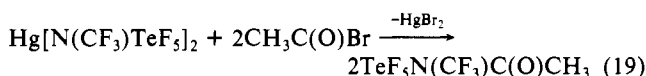
(27) Thrasher, J. S.; Howell, J. L.; Clifford, A. F. *Inorg. Chem.* **1982**, *21*, 1616.

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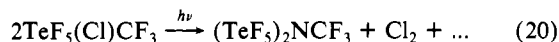
(25) Thrasher, J. S.; Howell, J. L.; Clifford, A. F. *Chem. Ber.* **1984**, *117*, 1707.

A *N*-pentafluorotellurium trisubstituted amide was prepared in the reaction of  $\text{Hg}[\text{N}(\text{CF}_3)\text{TeF}_5]_2$  with acetyl bromide:

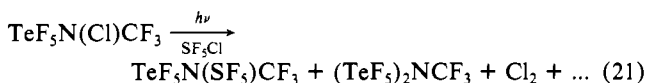


This reaction parallels the reported preparation of  $\text{SF}_5\text{N}(\text{CF}_3)\text{C}(\text{O})\text{C}_6\text{H}_5$ .<sup>5</sup> With the exception of  $\text{TeF}_5\text{N}(\text{I})\text{CF}_3$ , these derivatives were characterized by their mass, infrared, Raman, and  $^{19}\text{F}$  NMR spectra and by their physical properties.

A variety of other  $\text{TeF}_5\text{N}(\text{CF}_3)$ - derivatives were prepared through reactions of the haloamines  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  and  $\text{TeF}_5\text{N}(\text{Br})\text{CH}_3$ . Photolysis of the *N*-chloro compound  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  gave  $(\text{TeF}_5)_2\text{NCF}_3$  in low yield:

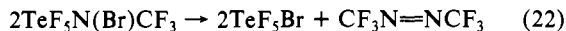


This compound is the first known material with two  $\text{TeF}_5$  groups bonded to the same nitrogen. In fact, the first examples of bis-(pentafluorosulfanyl)amines,  $(\text{SF}_5)_2\text{NX}$ , appeared only a short time ago.<sup>30</sup> The formation of  $(\text{TeF}_5)_2\text{NCF}_3$  most likely proceeds through several steps with the final step being the combination of  $\text{TeF}_5\cdot$  and  $\text{TeF}_5(\text{CF}_3)\text{N}\cdot$  radicals. The presence of  $\text{TeF}_5\text{Cl}$ ,  $\text{TeF}_6$ , and  $\text{Cl}_2$  in the product mixture supports this conclusion. Next the photolysis of  $\text{TeF}_5\text{N}(\text{Cl})\text{CF}_3$  was repeated in the presence of  $\text{SF}_5\text{Cl}$ . As expected, the trisubstituted amine  $\text{TeF}_5\text{N}(\text{SF}_5)\text{CF}_3$  was obtained, along with  $(\text{TeF}_5)_2\text{NCF}_3$ :

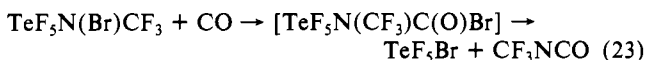


Although the two compounds could not be separated, sufficient evidence was obtained to support the existence of  $\text{TeF}_5\text{N}(\text{SF}_5)\text{CF}_3$ .

Photolysis of the bromoamine led only to the degradation products  $\text{TeF}_5\text{Br}$  and  $\text{CF}_3\text{N}=\text{NCF}_3$ ; no evidence was observed for  $(\text{TeF}_5)_2\text{NCF}_3$ :

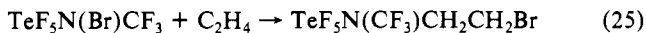
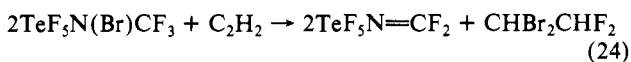


This was somewhat unexpected in view of the fact that  $\text{SF}_5\text{Br}$  generally enters free radical reactions more readily than either  $\text{SF}_5\text{Cl}$  or  $\text{S}_2\text{F}_{10}$ .<sup>31</sup> Other reactions of  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  were then studied without UV irradiation. The reaction with carbon monoxide gave  $\text{TeF}_5\text{Br}$  and  $\text{CF}_3\text{NCO}$  instead of the expected carbamoyl bromide  $\text{TeF}_5\text{N}(\text{CF}_3)\text{C}(\text{O})\text{Br}$ :

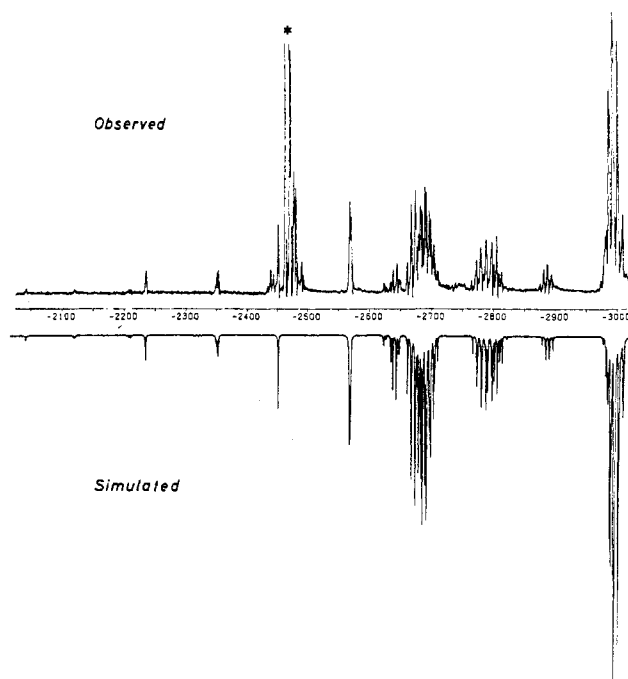
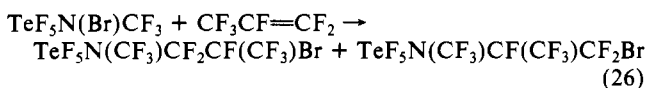


This is in contrast to the corresponding reaction of  $(\text{CF}_3)_2\text{NBr}$ , which yields  $(\text{CF}_3)_2\text{NC}(\text{O})\text{Br}$  as a stable product.<sup>32</sup>

With acetylene,  $\text{BrF}$  was effectively removed from  $\text{TeF}_5\text{N}(\text{Br})\text{CF}_3$  as shown in eq 24. However, the reaction with ethylene



proceeded smoothly upon warming to room temperature to give the addition product  $\text{TeF}_5\text{N}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{Br}$  in over 90% yield. Reaction with hexafluoropropylene occurred at 100 °C. The addition product, which was isolated in 58% yield, was found to be a mixture of two isomers:



**Figure 1.** Fluorine-19 NMR spectra of  $\text{TeF}_5\text{N}(\text{I})\text{CF}_3$  (56.4 MHz): experimental (above) and simulated (below) as an  $\text{AB}_4\text{C}_3$  spin system with  $\delta_A = -43.4$ ,  $\delta_B = -48.4$ ,  $\delta_C = -53.0$ ,  $J_{AB} = 177.9$  Hz,  $J_{AC} = 0.1$  Hz, and  $J_{BC} = -7.1$  Hz. The asterisk denotes the  $\text{AB}_4$  portion of  $\text{TeF}_5\text{N}=\text{CF}_2$ .

The distribution of isomers is as expected on the basis of the results of other addition reactions of  $\text{CF}_3\text{CF}=\text{CF}_2$ . Generally attack is favored at the  $\text{CF}_2$  position not only because it is sterically advantageous but because a more stable anionic or radical intermediate (depending on the mechanism) is formed.<sup>33</sup> In comparison, the related reaction of  $(\text{CF}_3)_2\text{NBr}$  gave only one isomer thought to be  $(\text{CF}_3)_2\text{NCF}_2\text{CF}(\text{CF}_3)\text{Br}$ ,<sup>34</sup> while the reaction with  $\text{SF}_2=\text{NBr}$  gave both possible isomers.<sup>35</sup>

**Spectral Parameters.** This investigation has demonstrated synthetic methods that allow the preparation of a variety of *N*-pentafluorotellurium derivatives. The identity of each new compound is strongly supported by the data given in the experimental section. The compounds typically boil at 20–40 °C higher than their  $\text{SF}_5$  analogues<sup>5</sup> as do the corresponding  $\text{CF}_3\text{SF}_4$  derivatives.<sup>6</sup> The infrared spectrum of each  $\text{TeF}_5\text{N}(\text{CF}_3)\text{X}$  derivative, where  $\text{X} = \text{H, F, Cl, Br, SF}_5, \text{TeF}_5, \text{C}(\text{O})\text{CH}_3, \text{C}(\text{F})=\text{N}-\text{TeF}_5$ , and  $\text{CH}_2\text{CH}_2\text{Br}$ , generally exhibits three strong CF stretching frequencies in the region of 1150–1300  $\text{cm}^{-1}$ . As in the related  $(\text{CF}_3)_2\text{NX}$  derivatives,<sup>33,36</sup> one can readily observe progressive shifts in these stretching frequencies with respect to the mass and electron-withdrawing power of X. Complex fluorine-19 NMR spectra were observed for many of the new tellurium–nitrogen derivatives due to the close proximity of the chemical shifts in relationship to the magnitude of the coupling constants. The sign of the  $J_{BC}$  coupling in the  $\text{TeF}_5\text{N}(\text{CF}_3)\text{X}$  derivatives was determined to be negative from the computer simulations<sup>37</sup> carried out on the complex  $\text{AB}_4\text{C}_3$  spectra. These NMR simulations were also helpful in the verification of structure, especially in the case of  $\text{TeF}_5\text{N}(\text{I})\text{CF}_3$ , as shown in Figure 1.

**Acknowledgment.** We wish to thank the Fonds der Chemischen Industrie and especially the Deutsche Forschungsgemeinschaft. The latter is also acknowledged for a postdoctoral fellowship to J.S.T.

(30) Waterfeld, A.; Oberhammer, H.; Mews, R. *Angew. Chem.* **1982**, *94*, 390; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 355; *Angew. Chem. Suppl.* **1982**, 834.  
 (31) Steward, J.; Kegley, L.; White, H. F.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 760.  
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(33) Banks, R. E. "Fluorocarbons and their Derivatives"; MacDonald & Co., Ltd.: London, 1970; Chapter 2.  
 (34) Young, J. A.; Tsoukalas, S. N.; Dresner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.  
 (35) Mews, R.; Glemser, O. *Chem. Ber.* **1969**, *102*, 4188.  
 (36) Mason, J. *J. Chem. Soc.* **1963**, 4531.  
 (37) Computer simulation with LACON III program.



**Registry No.** TeF<sub>5</sub>N=CCl<sub>2</sub>, 87191-36-4; TeF<sub>5</sub>N=C(Cl)CF<sub>3</sub>, 87191-37-5; TeF<sub>5</sub>NHCF<sub>3</sub>, 87206-80-2; Cs<sup>+</sup>[N(CF<sub>3</sub>)TeF<sub>5</sub>]<sup>-</sup>, 98720-66-2; Hg[N(CF<sub>3</sub>)TeF<sub>5</sub>]<sub>2</sub>, 98720-67-3; TeF<sub>5</sub>N=CF<sub>2</sub>, 98720-68-4; TeF<sub>5</sub>N=C(F)N(CF<sub>3</sub>)TeF<sub>5</sub>, 98720-69-5; TeF<sub>5</sub>NHC(F)=NCF<sub>3</sub>, 98720-70-8; TeF<sub>5</sub>N(F)CF<sub>3</sub>, 98720-71-9; TeF<sub>5</sub>N(Cl)CF<sub>3</sub>, 87191-40-0; TeF<sub>5</sub>N(Br)CF<sub>3</sub>, 87191-41-1; TeF<sub>5</sub>N(I)CF<sub>3</sub>, 98720-72-0; TeF<sub>5</sub>N(CF<sub>3</sub>)C(O)CH<sub>3</sub>, 98720-73-1; (TeF<sub>5</sub>)<sub>2</sub>NCF<sub>3</sub>, 87191-42-2; TeF<sub>5</sub>N(SF<sub>5</sub>)CF<sub>3</sub>, 98720-74-2; TeF<sub>5</sub>N(CF<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Br, 98720-75-3; TeF<sub>5</sub>N=C(Cl)OCH<sub>3</sub>, 98720-76-4; Te-

F<sub>5</sub>N=C(OCH<sub>3</sub>)<sub>2</sub>, 98720-77-5; TeF<sub>5</sub>N=C=NCF<sub>3</sub>, 98720-78-6; K<sup>+</sup>[TeF<sub>5</sub>NC(F)NCF<sub>3</sub>]<sup>-</sup>, 98735-50-3; TeF<sub>5</sub>N(CF<sub>3</sub>)CF<sub>2</sub>CF(CF<sub>3</sub>)Br, 98720-79-7; TeF<sub>5</sub>N(CF<sub>3</sub>)CF(CF<sub>3</sub>)CF<sub>2</sub>Br, 98720-80-0; TeF<sub>5</sub>Cl, 21975-44-0; HgF<sub>2</sub>, 7783-39-3; ClCN, 506-77-4; CF<sub>3</sub>CN, 353-85-5; HF, 7664-39-3; CsF, 13400-13-0; (CH<sub>3</sub>)<sub>3</sub>SiCl, 75-77-4; KF, 7789-23-3; F<sub>2</sub>, 7782-41-4; ClF, 7790-89-8; Cl<sub>2</sub>, 7782-50-5; Br<sub>2</sub>, 7726-95-6; BrF, 13863-59-7; ICl, 7790-99-0; CH<sub>3</sub>COBr, 506-96-7; SF<sub>5</sub>Cl, 13780-57-9; CO, 630-08-0; C<sub>2</sub>H<sub>2</sub>, 74-86-2; C<sub>2</sub>H<sub>4</sub>, 74-85-1; C<sub>3</sub>F<sub>6</sub>, 116-15-4.

Contribution from the Laboratoire de Cristallographie aux Rayons-X, Université de Genève, CH-1211 Genève 4, Switzerland, and Labor für Neutronenstreuung, ETH Zürich, CH-5303 Würenlingen, Switzerland

## Dimagnesium Cobalt(I) Pentahydride, Mg<sub>2</sub>CoH<sub>5</sub>, Containing Square-Pyramidal CoH<sub>5</sub><sup>4-</sup> Anions

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Received March 13, 1985

Mg<sub>2</sub>CoH<sub>5</sub> and its deuteride have been prepared as black crystalline solids by a sintering technique at temperatures between 620 and 770 K and hydrogen (deuterium) pressures between 40 and 60 bar. X-ray and neutron powder diffraction data recorded at room temperature suggest a tetragonally distorted CaF<sub>2</sub>-type metal atom structure (for the deuteride  $a = 4.463$  (4) Å,  $c = 6.593$  (6) Å, space group  $P4/nmm$ , and  $Z = 2$ ). The D atoms surround the Co atoms in an ordered square-pyramidal configuration ( $d[\text{Co}-\text{D}] = 1.590$  (17) Å (apical) and 1.515 (3) Å (basal)). The structure transforms at 488 (5) K into a disordered cubic modification ( $a = 6.453$  (6) Å, at 498 K). The heat of dissociation of the hydride as measured from pressure-composition isotherms is 86 (5) kJ/mol of H<sub>2</sub>. The electrical resistivity suggests nonmetallic behavior.

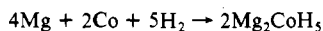
### Introduction

During a search for new hydrogen storage materials that contain 3d transition-metal elements, we have recently discovered a ternary metal hydride of composition Mg<sub>2</sub>FeH<sub>6</sub> in which the iron atoms were surrounded octahedrally by hydrogen atoms.<sup>1</sup> In this paper we report the synthesis, structure, and properties of a ternary metal hydride of composition Mg<sub>2</sub>CoH<sub>5</sub> in which the cobalt atoms are surrounded by hydrogen atoms in a square-pyramidal configuration. The compound is structurally related to, but not isostructural with, the reported tetragonal low-temperature modification of Sr<sub>2</sub>IrD<sub>5</sub>.<sup>2</sup> It can be considered as an intermediate member in the isoelectronic structural series Mg<sub>2</sub>NiH<sub>4</sub>-Mg<sub>2</sub>CoH<sub>5</sub>-Mg<sub>2</sub>FeH<sub>6</sub>. A preliminary account of the results presented in this article has appeared elsewhere.<sup>3</sup>

### Experimental Section

**Synthesis.** The hydride was prepared according to the sintering technique described previously.<sup>1</sup> Magnesium powder (Ventron, 50 mesh, M2N8) and cobalt powder (Puratronic, 99.998% purity) were mixed in a 2:1 atomic ratio of Mg:Co, pressed under 6 kbar to cylindrical pellets, placed in a steel autoclave, and treated for several days at temperatures between 690 and 720 K and hydrogen pressures between 40 and 60 bar. The synthesis of the deuteride was identical with that of the hydride except that it required a lower sintering temperature (670-700 K).

**Purification.** Under the above experimental conditions the reaction



did not proceed to completion (see Results). The unreacted phases (mainly MgH<sub>2</sub> and Co metal) were removed as follows. The powders were suspended in chloroform and magnetically stirred. The free cobalt adhered to the magnetic stirrer and was removed mechanically. The products were then dried and suspended in purified 1,2-dibromoethane (density 2.15 g/cm<sup>3</sup>) such that MgH<sub>2</sub> (density 1.42 g/cm<sup>3</sup>) floated to the surface of the tube and could be removed. The remaining black powders were dried and analyzed. They were stable in air over a period of several weeks.

**Structure Analysis.** The structure analysis was performed by X-ray powder diffraction methods (Guinier photographs) at room temperature (Co Kα<sub>1</sub> radiation,  $\lambda = 1.7889$  Å) and in the temperature range between 300 and 550 K (Cu Kα<sub>1</sub> radiation,  $\lambda = 1.5405$  Å), and by neutron powder diffraction at 498, 298, and 9 K (powder diffractometer DMC,

equipped with a multidetector at the reactor SAPHIR at Würenlingen,<sup>4</sup>  $\lambda = 1.184$  (1) Å,  $[(\sin \theta)/\lambda]_{\text{max}} = 0.77$  Å<sup>-1</sup>; scattering lengths used (10<sup>-12</sup> cm) were 0.538 (Mg), 0.253 (Co) and 0.667 (D)). A purified sample (ca. 3 cm<sup>3</sup>) was placed in a cylindrical vanadium container of 10 mm diameter. The structure refinement was performed by the Rietveld profile fitting method,<sup>5</sup> using the neutron diffraction data recorded at 298 K, and a computer program written,<sup>6</sup> for the simultaneous treatment of two phases.

**Pressure-Composition Isotherms.** The thermal stability of Mg<sub>2</sub>CoH<sub>5</sub> was determined from pressure-composition isotherms as measured on unpurified samples in the temperature range between 620 and 720 K. The experimental setup was identical with that described in ref 7.

**Magnetization Measurements.** The magnetic susceptibility of the purified deuteride sample was measured as a function of an applied magnetic field (up to 80 kG) and temperature (60-300 K) by using a SQUID magnetometer described in ref 8.

**Electrical Resistivity.** The electrical resistivity was measured as a function of temperature (4-24 K, 300 K) using the four-point method. For this purpose two purified hydride samples were pressed under 10 kbar pressure into cylindrical pellets and cut into slabs of about 5-mm length and 1-1.5-mm width.

### Results

The Mg-Co mixtures that were sintered in hydrogen (deuterium) atmosphere showed a weight increase of up to 3.5% (7%). The reaction products consisted of fine black powders, which contained small concentrations of white particles (MgH<sub>2</sub>). X-ray analysis confirmed the formation of a new ternary hydride (deuteride) phase and revealed the presence of about 25% impurity phases (mainly MgH<sub>2</sub> or MgD<sub>2</sub>, and elemental Co). After purification the fraction of impurity phases was reduced to less than 8% (estimated from neutron data and magnetization measurements). An attempt was made to measure the compositional ratio Mg:Co by X-ray fluorescence analysis as well as by atomic absorption. Although the results were consistent with the expected

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