NMR spectra were measured on a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer with CCl_3F as reference and $CDCl_3$ as solvent. Mass spectra were obtained with a VG 7070HS mass spectrometer operating at an ionization potential of 17 eV. Photolysis reactions were carried out in quartz reaction vessels at 3000 Å. The computer program PMR (Serena Software) was used to aid the interpretation of several of the ^{19}F NMR spectra.

Reaction of ClF with $CF_2ClN{=}CFCF{=}NCF_2Cl$ To Form $CF_2ClN(Cl)CF_2CF_2N(Cl)CF_2Cl$ (3). Five millimoles of $CF_2ClN{=}CFCF{=}NCF_2Cl$[3] and 12 mmol of ClF were condensed into a stainless-steel vessel at −196 °C, warmed to 25 °C, and allowed to stand for 10–12 h. The products were separated by trap-to-trap distillation, and **3** (70–75% yield) was isolated in the trap at −30 °C. Spectral data obtained. MS (CI) [*m*/*e* (species), intensity]: 263 ($M^+ - 3Cl$), 1.13; 229 ($C_4F_8N_2^+ + 1$), 19.61; 209 ($C_4F_7N_2^+$), 100; 114 ($C_2F_4N^+$), 91.23; 85 (CF_2Cl^+), 10.89. IR (liquid): 1319 m, 1240 s, 1191 s, 1148 s, 1087 s, 1022 s, 950 ms, 921 s, 881 s, 813 w, 787 s, 762 s cm^{-1}. ^{19}F NMR: ϕ −34.69 (CF_2Cl, t, mult), −96.31 (CF_2, t, mult); $J_{CF_2Cl-NCF_2} = 19.65$ Hz, $J_{CF_2Cl-CF_2} = 3.6$ Hz, $J_{CF_2-CF_2} = 3.1$ Hz.

Photolysis of 3 To Form $CF_2{=}NCF_2CF_2N{=}CF_2$ (4) and $CF_2ClN{=}CF_2$ (5). Ten millimoles of **3** was condensed into a quartz vessel and photolyzed for 2 h. Compound **4** (70–80% yield) was collected in a trap at −65 °C,[6] and at −90 °C, **5** (5–10% yield) was found. Compound **5** slowly decomposes at 25 °C. Spectral data obtained. MS (CI) [*m*/*e* (species), intensity]: 150 ($M^+ + 1$), 16.23; 130 ($M^+ - F$), 35.24; 114 ($M^+ - Cl$), 100; 85 (CF_2Cl^+), 25.68. IR (gas): 1796 vs ($\nu_{C=N}$), 1324 vs, 1240 vs, 1161 s, 1063 vs, 950 s cm^{-1}. ^{19}F NMR: ϕ −28.5 (br d), −47.8 (br d, $F^AF^BC{=}N$, $J_{F^A-F^B} = 91.11$ Hz), −32.4 (t, $CF_2{}^CCl$, $J_{F^A-F^C} = J_{F^B-F^C} = 9.46$ Hz).

Reaction of ClF with 4 To Form $CF_3N(Cl)CF_2CF_2N(Cl)CF_3$ (6). Five millimoles of **4** and 10–12 mmol of ClF were condensed into a stainless-steel vessel at −196 °C, warmed to 25 °C, and held for 10–12 h. Products were separated by trap-to-trap distillation, and **6** (75–80% yield) was isolated in a trap cooled at ~35 °C. Spectral data obtained. MS (CI) [*m*/*e* (species), intensity]: 317 ($M^+ - F$), 16.69; 282 ($M^+ - ClF$), 4.02; 263 ($M^+ - ClF_2$), 61.17; 229 ($C_4F_8N_2^+ + 1$), 74.50; 209 ($C_4F_7N_2^+$), 100; 168 ($C_2F_5ClN^+$), 69.13; 134 ($C_2F_5N^+ + 1$), 36.4; 114 ($C_2F_4N^+$), 100; 69 (CF_3^+), 100. IR (gas): 1392 w, 1356 w, 1336 w, 1291 vs, 1240 vs, 1206 s, 1170 vs, 1078 s, 1029 m, 952 m, 906 m, 852 ms, 820 m, 707 ms cm^{-1}. ^{19}F NMR: ϕ −59.77 (CF_3, t, mult), −94.31 (CF_2, q (mult)); $J_{CF_3-NCF_2} = 13.6$ Hz, $J_{CF_3-CF_2} = 3.8$ Hz, $J_{CF_2-CF_2} = 2.4$ Hz.

Reaction of ClF with 5 To Form CF_3NCl_2 and $(CF_3)_2NCl$. Five millimoles of $CF_2ClN{=}CF_2$ and 6 mmol of ClF were condensed into a 75-mL stainless-steel vessel at −196 °C. The contents were held at 25 °C for 6–8 h. After distillation, CF_3NCl_2[11,12] and $(CF_3)_2NCl$[13,14] were found in a 2:1 ratio.

Photolysis of 6 To Form $CF_3N{=}CF_2$ (7). Five millimoles of **6** was condensed into a quartz vessel and photolyzed for 2–3 h. The major products were Cl_2 and $CF_3N{=}CF_2$.[1,6-9]

Photolysis of 8 and 9 To Form $CF_2{=}NCF_2CFCl_2$ (10) or $CF_2{=}NCF_2CF_2Cl$ (11). Five millimoles of **8** or **9** was condensed into a 500-mL quartz vessel and was photolyzed at 3000 Å for 2–3 h to give **10** or **11** in 60–70% yield. Each was purified by trap-to-trap distillation and identified by using the literature data.[5]

Reaction of $CF_2{=}NCF_2CFXCl$ (10 (X = Cl), 11 (X = F)) with CsF To Form $CF_3N{=}CFCFXCl$ (12 (X = Cl), 13 (X = F)). Five millimoles of **10** or **11** was condensed onto 5–10 mmol of anhydrous CsF and stirred for 8–10 h at 25 °C. Isomerization of $CF_3N{=}CFCFXCl$ (**12** or **13**) occurred in ~80% yield. Compound **13** stopped in a trap at −110 °C. Although the synthesis of this compound has not been detailed previously,[1] ^{19}F NMR studies are reported.[10] Both **12** and **13** were obtained also by stirring 5 mmol of $CF_3N(Cl)CF_2CFXCl$ (X = Cl, F)[2] with 10 mmol of $(C_6H_5)_3P$ at 25 °C for 4–6 h. Compound **12** has not been reported previously.

Properties of $CF_3{}^AN{=}CF^BCF^CCl_2$ (12). This colorless liquid was stopped in a trap cooled at −60 °C in 65% yield. Spectral data obtained. MS (CI) [*m*/*e* (species), intensity]: 216 ($M^+ + 1$), 41.04; 196 ($M^+ - F$), 100; 180 ($M^+ - Cl$), 94.12; 101 ($CFCl_2^+$), 86.65; 69 (CF_3^+), 94.59. IR (gas): 1770 vs ($\nu_{C=N}$), 1293 vs, 1255 vs, 1207 vs, 1135 s, 1088 m, 984 m, 896 m, 862 s, 797 s, 703 s, 658 m, 633 s cm^{-1}. ^{19}F NMR: ϕ −31.04 (B, p), −56.47, −56.58 (A, d), −65.67, −65.85 (C, d); $J_{A-B} = 13.67$ Hz, $J_{B-C} = 14.04$ Hz.

Properties of $CF_3N{=}CFCF_2Cl$ (13). Spectral data obtained. MS (CI) [*m*/*e* (species), intensity]: 200 ($M^+ + 1$), 48.9, 180 ($M^+ - F$), 100; 164 ($M^+ - Cl$), 49.3; 114 ($C_2F_4N^+$), 58.8; 85 (CF_2Cl^+), 43.6; 69 (CF_3^+), 76.7. IR (gas): 1780 vs ($\nu_{C=N}$), 1322 s, 1258 vs, 1213 vs, 1111 s, 988 s, 829 s, 668 w, 631 w, 560 w cm^{-1}.

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Registry No. **2**, 124443-27-2; **3**, 124443-28-3; **4**, 16627-43-3; **5**, 124443-29-4; **6**, 124461-05-8; **7**, 371-71-1; **8**, 124443-30-7; **9**, 124443-31-8; **10**, 87533-02-6; **11**, 25688-36-2; **12**, 124443-32-9; **13**, 18696-80-5; ClF, 7790-89-8; F_3CNCl_2, 13880-73-4; $(F_3C)_2NCl$, 431-94-7; $F_3CN(Cl)CF_2CCl_2F$, 120417-58-5; $F_3CN(Cl)CF_2CF_2Cl$, 120417-57-4.

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(6) Ogden, P. H.; Mitsch, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 3868.

(7) Yakubovich, A. Ya.; Makarov, S. P.; Ginsberg, V. A.; Privezentseva, N. F.; Martynova, L. L. *Dokl. Akad. Nauk SSSR* **1961**, *141*, 125; *Chem. Abstr.* **1962**, *56*, 11429.

(8) Muller, N.; Lauterbur, P. C.; Svatos, G. F. *J. Am. Chem. Soc.* **1957**, *79*, 1807.

(9) Barr, R. A.; Hazeldine, R. N.; Willis, C. J. *J. Chem. Soc.* **1964**, 1351.

(10) Cavalli, L.; Piccardi, P. *Chem. Commun.* **1969**, 1132.

(11) Hynes, J. B.; Bishop, B. C.; Bigelow, L. A. *Inorg. Chem.* **1967**, *6*, 417.

(12) De Marco, R. A.; Fox, W. B.; Moniz, W. B.; Sojka, S. A. *J. Magn. Reson.* **1975**, *18*, 522.

(13) Dobbie, R. C.; Emeléus, H. J. *J. Chem. Soc. A* **1966**, 367.

(14) Young, J. A.; Tsoukalas, S. N.; Dresdner, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3604.

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Structure of $Mn(H_2dapd)Cl_2$: Corrigendum

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The crystal structure of this compound (dapd = 2,6-diacetylpyridine dioxime), which was originally[1] described in space group *Cc* (monoclinic; *a* = 17.843 (3) Å, *b* = 10.422 (2) Å, *c* = 6.809 (1) Å, β = 106.49 (1)°, *Z* = 4), is better described in *C*2/*c*. Least-squares refinement in *C*2/*c* proceeded routinely to an *R* of 0.039 for the 1017 reflections recovered from the supplementary material, the same *R* value (and number of reflections) as reported for the *Cc* model,[1] but with 102 parameters rather than the 170 or so required by the *Cc* model. In the *C*2/*c* refinement, the hydrogen atoms were refined independently and a secondary extinction parameter was included (final value, 0.30 (3) × 10^{-6}); in the *Cc* refinement the "hydrogens were varied by using a riding model", and no extinction correction was applied. The final *C*2/*c* coordinates are given in Table I.

A major difference between the results of the two refinements is in the environment of the seven-coordinate pentagonal-bipyramidal Mn atom. The coordination was markedly distorted in the *Cc* structure, with two axial Mn–Cl distances of 2.468 (3) and 2.581 (3) Å and two equatorial Mn–Cl distances of 2.760 (4) and 2.828 (4) Å; in the *C*2/*c* structure the axial distances are equal (by symmetry) at 2.526 (1) Å and the equatorial distances are equal at 2.793 (1) Å. The distances within the dapd ligand also are more equal, more believable, and more precise in the *C*2/*c* model. The general features of the structure, discussed earlier,[1] are unchanged.

The earlier authors made initial attempts to derive a structure in *C*2/*c*, but "refinement did not proceed smoothly". They then report, surprisingly, that "the Mn atomic parameters were subsequently refined in the space group *Cc*, after which a difference Fourier map yielded all other non-hydrogen atom positions." In fact, the Mn atom alone cannot distinguish between *Cc* and *C*2/*c*, since its *x* and *z* coordinates are arbitrary in *Cc* (*a* and *c* are polar directions) and define the position of a 2-fold axis in *C*2/*c*; as a result, any Fourier map phased only by the Mn atom must have

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(1) Unni Nair, B. C.; Sheats, J. E.; Ponteciello, R.; Van Engen, D.; Petroulas, V.; Dismukes, G. C. *Inorg. Chem.* **1989**, *28*, 1582.

0020-1669/90/1329-0572$02.50/0

Table I. Coordinates, Space Group *C2/c* (*x*, *y*, *z* and U_{eq}[a] × 10^4)

atom	*x*	*y*	*z*	U_{eq}
Mn	0	1052 (0.8)	2500	269 (2)
Cl	733 (0.5)	1042 (1)	6265 (2)	341 (2)
O	-1802 (2)	1213 (3)	3056 (6)	487 (9)
N(1,3)	-1166 (2)	1938 (3)	2929 (5)	308 (8)
C(1,7)	-1314 (2)	3134 (4)	2714 (6)	302 (9)
C(2,6)	-645 (2)	3936 (4)	2565 (6)	263 (8)
N(2)	0	3282 (4)	2500	250 (10)
C(3,5)	-662 (3)	5271 (4)	2556 (6)	335 (10)
C(4)	0	5939 (6)	2500	371 (17)
C(8,9)	-2093 (3)	3712 (6)	2602 (12)	505 (14)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$.

the symmetry of *C*2/*c*. The problem lay in recognizing the symmetry.

Supplementary Material Available: Tables SI–SIII, listing anisotropic U_{ij}'s for the heavy atoms, coordinates and isotropic *B*'s for the hydrogens, and bond distances for the *C*2/*c* refinement (1 page); Table SIV, listing observed and calculated *F*'s for the *C*2/*c* refinement (4 pages). Ordering information is given on any current masthead page.

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Trifluoroamine Oxide: Reactions with Phosphorus Compounds and Selected Elements

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Earlier, we reported the utilization of carbonyl difluoride (COF_2) as a versatile and nondestructive fluorine-transfer reagent[1,2] and compared it with sulfinyl fluoride in a similar role.[3] The conversion of inorganic oxides to fluorides under mild conditions was also demonstrated by using carbonyl difluoride. Carbon dioxide is the only volatile product, and it is removed easily from the reaction vessel and absorbed in aqueous alkali.[4] Although this procedure has definite advantages over other methods, it also suffers from the fact that inorganic oxides that have high melting points could not be converted to fluorides and, in other cases, only oxyfluorides are formed. While fluorides have also been prepared by using vigorous fluorinating reagents, such as elemental fluorine or bromine trifluoride, or milder reagents, such as anhydrous hydrogen fluoride or sulfur tetrafluoride, none of these reagents is invariably the reagent of choice. Neither COF_2 nor SOF_2 reacts with the elements to form fluorides.

We now report the results obtained when trifluoroamine oxide, NF_3O, is reacted with main-group elements to give binary fluorides. Trifluoroamine oxide was found to fluorinate P(III) and P(V) compounds, also. The relative effectiveness of NF_3O, COF_2, and SOF_2 as fluorinating agents is examined.

Results and Discussion

Since its synthesis,[5-7] the physical, chemical, and spectral properties of trifluoroamine oxide have been studied extensively.[8,9] However, fluorination reactions of NF_3O have not been explored.[9]

Trifluoroamine oxide was found to react with phosphines at 110 °C to form difluorophosphoranes in good yields

$$R_3P + NF_3O \xrightarrow[4\ h]{110\ °C} R_3PF_2 + FNO + R_3PO$$

$$R\ (\%\ yield) = C_6H_5\ (80),\ CH_3\ (85)$$

Phosphites also reacted under similar conditions and formed the analogous oxidatively fluorinated products

$$(RO)_3P + NF_3O \xrightarrow[4\ h]{110\ °C} (RO)_3PF_2 + (RO)_2P(O)F + RF + (RO)_3PO$$

$$R\ (\%\ yield) = CH_3\ (80),\ C_2H_5\ (50),\ n\text{-}C_4H_9\ (70)$$

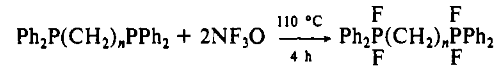
At higher temperatures, an Arbuzov–Michael reaction occurs, forming the respective fluoroalkane and monofluorophosphite. The extent of this latter reaction can be controlled but cannot be prevented, even when the reaction is carried out at low temperature; i.e., no reaction takes place at room temperature, but after 4 h at 50 °C, the difluorophosphorane is formed and the products due to the Arbuzov reaction are formed in small amounts. Products such as R_3PO and $(RO)_3PO$ resulted from reactions of NO_2 with the respective starting materials. The fluorinated products were isolated in high yield.

Oxidative fluorination of phosphites was achieved by using COF_2 and SOF_2 as fluorinating agents where the formation of additional products due to the Arbuzov reaction did not take place and the difluorophosphorane yields are high (Table I). The difference in the behavior of NF_3O compared to COF_2 and SOF_2 toward phosphites may be due to reaction temperature because the oxidative fluorination reaction with carbonyl difluoride and sulfinyl fluoride is achieved at room temperature in CH_2Cl_2, whereas NF_3O did not react under such conditions and, in fact, requires temperatures greater than 100 °C.

As has been found with secondary amines where the abstraction of hydrogen from >NH by NF_3O at 0 °C occurs smoothly,[10] with diethyl phosphite and di-*n*-butyl phosphite the hydrogen–phosphorus bond is also broken and the stronger P–F bond is formed in the phosphorofluoridates.

$$(RO)_2P(O)H + NF_3O \rightarrow (RO)_2P(O)F$$

Compounds that contain more than one phosphorus atom also could be reacted with trifluoroamine oxide at 110 °C to form the oxidatively fluorinated products



$$Ph_2P(CH_2)_nPPh_2 + 2NF_3O \xrightarrow[4\ h]{110\ °C} Ph_2\underset{F}{\overset{F}{P}}(CH_2)_n\underset{F}{\overset{F}{P}}Ph_2$$

$$n\ (\%\ yield) = 1\ (75),\ 2\ (75)$$

Both SOF_2 and COF_2 behave similarly with phosphites and diphosphines to give products in comparable yields (Table I).

Although PF_3 and PCl_3 are oxidatively unsaturated, trifluoroamine oxide, under conditions employed in this study, did not fluorinate or react with them.[11] This lack of reactivity, also noted for COF_2 and SOF_2, arises from the reduced availability of the electron pair of phosphorus in PX_3 (X = Cl, F) compared to cases where X = RO and Ph.

Acyclic and cyclic nonaromatic secondary amines were reacted with NF_3O at ~0 °C to form *N*-fluoro and *N*-nitroso compounds.[10] With carbonyl fluoride and sulfinyl fluoride at 25 °C,

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[1] Gupta, O. D.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, *416* and references therein.

[2] Williamson, S. M.; Gupta, O. D.; Shreeve, J. M. *Inorg. Synth.* **1986**, *24*, 62.

[3] Mahmood, T.; Shreeve, J. M. *Inorg. Chem.* **1985**, *24*, 1395.

[4] Mallela, S. P.; Gupta, O. D.; Shreeve, J. M. *Inorg. Chem.* **1988**, *27*, 208.

[5] Maya, W. (Rocketdyne) U.S. 3320147, 1967.

[6] Fox, W. B.; MacKenzie, J. S.; Vanderkooi, N.; Sukornick, B.; Wamser, C. A.; Holmes, J. R.; Eibeck, R. E.; Stewart, B. B. *J. Am. Chem. Soc.* **1966**, *88*, 2604.

[7] Bartlett, N.; Passmore, J; Wells, E. J. *Chem. Commun.* **1966**, 213.

[8] Smardzewski, R. R.; Fox, W. B. *J. Chem. Phys.* **1974**, *60*, 2193 and references therein.

[9] Kinkead, S. A.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 4174 and references therein.

[10] Gupta, O. D.; Kirchmeier, R. L.; Shreeve, J. M. *J. Am. Chem. Soc.*, in press.

[11] Fox, W. B.; Wamser, C. A.; Eibeck, R.; Huggins, D. K.; MacKenzie, J. S.; Juurik, R. *Inorg. Chem.* **1969**, *8*, 1247.

0020-1669/90/1329-0573$02.50/0