cited, and these were used to identify the components in the reaction mixtures.

Reactions of $B_2H_4\cdot 2P(CH_3)_3$ with Borane Adducts. (a) With $B_4H_8\cdot PH_3$. A sample of $B_4H_8\cdot PH_3$[12] was prepared in a 10 mm o.d. Pyrex reaction tube that was equipped with a stopcock and a 10 mm o.d. side arm. A 0.54-mmol sample of B_5H_{11} and 1.41 mmol of PH_3 were used for this preparation. About 2 mL of dichloromethane was condensed into the tube to prepare a clear solution, and then the solution was frozen at −197 °C. Nitrogen gas was admitted into the tube and the side arm cut open to introduce a 0.52-mmol sample of $B_2H_4\cdot 2P(CH_3)_3$. During this procedure an outward flow of nitrogen gas was maintained through the side arm. The side arm was then resealed, and the tube was reevacuated. The contents of the tube were mixed throughly at −80 °C to give a clear solution. The tube was then placed in the chilled probe of the NMR spectrometer to monitor the reaction starting at −80 °C.

Up to −30 °C no sign of reaction could be detected; the spectrum consisted of the signals of $B_4H_8\cdot PH_3$ and $B_2H_4\cdot 2P(CH_3)_3$. At 0 °C, the signal of $BH_3\cdot P(CH_3)_3$ began to appear in the spectrum. In 1 h the signals of $BH_3\cdot P(CH_3)_3$ and $B_5H_9\cdot P(CH_3)_3$ were strong, and as the tube was allowed to warm to room temperature, the signals of $B_2H_4\cdot 2P(CH_3)_3$ and $B_4H_8\cdot PH_3$ completely disappeared. Minor quantities of several other boron compounds were present in the final solution, identifiable components being $BH_3\cdot PH_3$ and B_5H_9.

(b) With $B_4H_8\cdot P(CH_3)_3$ and $B_4H_8\cdot N(CH_3)_3$. A 0.45-mmol sample of $B_4H_8\cdot P(CH_3)_3$[3e] was prepared by the reaction of $B_3H_6\cdot 2P(CH_3)_3{}^+B_3H_8{}^-$ with $N(CH_3)_3$ in a reaction tube and was treated with 0.56 mmol of $B_2H_4\cdot 2P(CH_3)_3$ in a manner similar to that described for the $B_4H_8\cdot PH_3$ reaction in part a. The ^{11}B NMR spectrum of the reaction solution indicated there was no significant reaction after 12 h at room temperature; faint signals of $B_3H_7\cdot P(CH_3)_3$ and an unidentified borane compound (−18 ppm) were detected.

Similarly, a 0.54-mmol sample of $B_4H_8\cdot N(CH_3)_3$[13] was treated with 0.55 mmol of $B_2H_4\cdot 2P(CH_3)_3$. At 0 °C, a small amount of $BH_3\cdot N(CH_3)_3$ formed. However, no further change occurred while the tube was kept at room temperature for 5 h.

(c) With $B_5H_9\cdot P(CH_3)_3$. A sample of $B_5H_9\cdot P(CH_3)_3$[3c] was prepared by the reaction of B_5H_{11} (0.50 mmol) with $B_2H_4\cdot 2P(CH_3)_3$ (0.4 mmol). The amount of $B_5H_9\cdot P(CH_3)_3$ produced was estimated to be 0.3 mmol on the basis of the amount of B_2H_6 generated from the reaction. This sample was condensed into a reaction tube and treated with 0.4 mmol of $B_2H_4\cdot 2P(CH_3)_3$ in a manner similar to that described above.

At 0 °C slow change began to occur; the signals of $B_6H_{10}\cdot 2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$ were discernible. As the tube was allowed to warm to room temperature, the intensities of the $B_6H_{10}\cdot 2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$ signals continued to increase slowly, and in 10 h the signals of $B_5H_9\cdot P(CH_3)_3$ had diminished considerably. Weak signals of $B_2H_4\cdot 2P(CH_3)_3$ and other unidentified boron compounds were present, as determined from the final spectrum.

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Secondary (Polyfluoroalkyl)chloroamines: Precursors to Fluoroazaalkenes

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There are a very large number of fluorinated azaalkenes, and there is an excellent review of synthetic methods for and reported chemistry of these compounds.[1] A facile, nearly quantitative route to azaalkenes provided by the photolysis of $R_fN(CF_2CFXCl)Cl$ ($R_f = CF_3, C_2F_5$; X = Cl, F) has been reported.[2] We now have extended this reaction by taking advantage of recently synthesized precursors to synthesize azaalkenes.

Results and Discussion

Chlorine fluoride can be reacted smoothly with $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ to saturate the carbon–nitrogen double bond and partially fluorinate the compound. Repeated photolysis and reaction with chlorine fluoride provide a high-yield route to $CF_3N{=}CF_2$

$$Cl_2C{=}NCCl_2CCl_2N{=}CCl_2 + ClF \rightarrow \underset{\mathbf{1}}{CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl}^{3}$$

$$\mathbf{1} \xrightarrow[-2Cl_2]{h\nu} \underset{\mathbf{2}}{CF_2ClN{=}CFCF{=}NCF_2Cl}^{3}$$

$$\mathbf{2} + 2ClF \rightarrow \underset{\mathbf{3}}{CF_2ClN(Cl)CF_2CF_2N(Cl)CF_2Cl}$$

$$\mathbf{3} \xrightarrow[-Cl_2]{h\nu} \underset{\mathbf{4}}{F_2C{=}NCF_2CF_2N{=}CF_2} + \underset{\mathbf{5}}{CF_2ClN{=}CF_2}$$

$$\mathbf{4} + 2ClF \rightarrow \underset{\mathbf{6}}{CF_3N(Cl)CF_2CF_2N(Cl)CF_3}$$

$$\mathbf{6} \xrightarrow[-Cl_2]{h\nu} CF_3\dot{N}{-}CF_2{-}CF_2{-}\dot{N}CF_3 \rightarrow \underset{\mathbf{7}}{2CF_3N{=}CF_2}$$

Olefins, such as $CF_2{=}CFCl$, can be inserted into the N—Cl bond of $Cl_2NCF_2CF_2NCl_2$[4] to give a bis(secondary chloroamine)[3] similar to **1**

$$Cl_2NCF_2CF_2NCl_2 + CF_2{=}CFX \rightarrow \underset{\substack{\mathbf{8}\ (X = Cl)\\ \mathbf{9}\ (X = F)}}{CFXClCF_2N(Cl)CF_2CF_2N(Cl)CF_2CFXCl}$$

$$X = Cl, F$$

which can be photolyzed to the azaalkenes **10** and **11**

$$\mathbf{8}\text{ or }\mathbf{9} \xrightarrow[-Cl_2]{h\nu} \underset{\substack{\mathbf{10}\ (X = Cl)\\ \mathbf{11}\ (X = F)}}{2CF_2{=}NCF_2CFXCl}^{5}$$

and in the presence of fluoride ion isomerization to **12** and **13** occurs:

$$\mathbf{10}\text{ or }\mathbf{11} \xrightarrow{CsF} \underset{\substack{\mathbf{12}\ (X = Cl)\\ \mathbf{13}\ (X = F)}}{CF_3N{=}CFCFXCl}$$

Dechlorofluorination of certain secondary chloroamines with triphenylphosphine also gives rise to azaalkenes:

$$CF_3N(Cl)CF_2CFXCl^{2} + Ph_3P \rightarrow \mathbf{12}\text{ or }\mathbf{13}$$

$$X = Cl, F$$

Experimental Section

Materials. The reagents $CF_2ClN(Cl)CFClCFClN(Cl)CF_2Cl$,[3] $CF_2ClN{=}CFCF{=}NCF_2Cl$,[3] and $Cl_2NCF_2CF_2NCl_2$[4] were prepared according to the literature; $Cl_2C{=}NCCl_2CCl_2N{=}CCl_2$ was a gift of Dr. E. Klauke (Bayer AG, Laverkusen, FRG). Other chemicals were purchased and used as received: chlorine fluoride (Ozark-Mahoning); $CF_2{=}CF_2$ and $CF_2{=}CFCl$ (PCR); and CsF (American Potash).

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system fitted with a Heise Bourdon tube and Televac thermocouple gauges. Volatile starting materials and products were quantitated by using *PVT* techniques. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform infrared spectrometer with a 10-cm gas cell equipped with KBr windows. ^{19}F

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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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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, $0.30 (3) \times 10^{-6}$); 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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