Synthesis and Chemistry of Cyclic and Acyclic Polyfluorosiloxanes of 2,2,3,3-Tetrafluorobutanediol and 2,2,3,3,4,4-Hexafluoropentanediol

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The acyclic disiloxanes $[CF_2CH_2OSiMe_3]_2$ (**1**) and $CF_2[CF_2CH_2OSiMe_3]_2$ (**2**) and the cyclic siloxanes $[CF_2CH_2O]_2SiMe_2$ (**3**), $CF_2[CF_2CH_2O]_2SiMe_2$ (**4**), and $[CF_2CH_2O]_2SiPh_2$ (**5**) are synthesized by the reactions of the respective diols with hexamethyldisilazane or by the condensation reactions with silyl chlorides in the presence of triethylamine. Reactions of compounds **1–4** with C_6F_6, $(CNF)_3$, and $CF_3C(O)F$ are found to proceed readily in the presence of catalytic amounts of fluoride ion that liberate Me_3SiF, Me_2SiF_2, or Ph_2SiF_2 to form cyclic and acyclic fluorinated ethers $CC_4F_4COCH_2(CF_2)_2CH_2O$ (**6**), $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_5$ (**7**), $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_5$ (**8**), $C_3N_3F_2OCH_2(CF_2)_2CH_2OC_3N_3F_2$ (**9**), $C_3N_3F_2OCH_2(CF_2)_3CH_2OC_3N_3F_2$ (**10**), $CF_3C(O)CH_2(CF_2)_2CH_2C(O)CF_3$ (**11**), and $CF_3C(O)CH_2(CF_2)_3CH_2C(O)CF_3$ (**12**). **1** reacts with $PhPCl_2$ even in the absence of catalyst to form the cyclic phosphite $(CF_2CH_2O)_2PPh$ (**13**). The new compounds are characterized by spectral (IR, ^1H and ^{19}F NMR, MS) and analytical methods. The X-ray crystal structure of the bicylic ether **6** is determined. **6** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 9.393(3)$ Å, $b = 10.588(3)$ Å, $c = 11.110(4)$ Å, $\beta = 111.42(2)°$, $V = 1028.7(5)$ Å^3, $d_{calc} = 1.990$ Mg m^{-3}, $Z = 4$, and $R = 0.0351$.

Introduction

The stability and strength of silicon–oxygen bonds (~106 kcal/mol) are well-known in organic as well as inorganic synthetic chemistry, and these properties are used fully in the versatile practical applications of siloxanes.[1] The use of siloxane functional groups as protecting groups[2] as well as their role in forming stable volatile side products in chemical reactions (e.g., $Me_3SiOSiMe_3$,[3] $CF_3CH_2OSiMe_3$[4]) is also well documented. A closer look at the literature reveals that reactions involving cleavage of a Si–O bond are rather scarce in contrast to the plethora of reactions reported on breaking of Si–X (X = Cl, Br, I), Si –N, Si–S and Si –C bonds.[3] Frequently, Si–O bond breakage requires extreme reaction conditions[5] or highly reactive reagents like strong acids or metal halides.[6] However, they do break under rather mild conditions such as those observed in the reactions of silyl enol ethers[3] and in some reactions with compounds having P–F,[7] S–F,[8] M–F,[9] and C–F[10] bonds. Recent studies show that some organotrifluoro- and diorganodifluorosilanes also react with siloxanes liberating small stable silyl fluorides, such as Me_3SiF and Me_2HSiF.[11] The formation of a bond of higher stablility, i.e., the Si–F bond (142 kcal/mol),[3] as well as easily displaceable and highly volatile side products such as Me_3SiF is the driving force in these reactions.

We have embarked upon the synthesis and chemistry of polyfluoroalkoxysilanes as part of our continuing search for new more stable reagents for the introduction of fluoroalkoxy substituents on fluorinated substrates as well as in our studies on the exploration of the chemistry of polyfluorinated diols of the type $HOCH_2(CF_2)_nCH_2OH$ ($n = 2–4$). We have reported on the reactions of the diols and their dilithium and disodium derivatives with various S,[12] P,[13] and C[14]-containing compounds. A marked difference in reactivity and product formation is observed in these cases with respect to the length of the alkyl chain and the method used to activate the hydroxy group. In the present work, the synthesis of cyclic and acyclic siloxane derivatives of two polyfluorodiols and their reactions with a variety of fluorinated compounds in realizing new cyclic and acyclic polyfluoroethers is reported. The siloxanes were found to react readily with perfluoro compounds in the presence of fluoride ion catalysts and with $PhPCl_2$ with the facile elimination of silyl fluorides.

Results and Discussion

Reactions of the acyclic siloxanes $Me_3SiOCH_2(CF_2)_nCH_2OSiMe_3$ ($n = 2, 3$) as well as of the cyclic siloxanes $(CF_2)_n(CF_2CH_2O)_2SiMe_2$ ($n = 0, 1$) are found to proceed readily with C_6F_6, $(CNF)_3$, and $CF_3C(O)F$ according to the Schemes 1–4. Although the yields of the monomeric ether products **6–8** are moderate to

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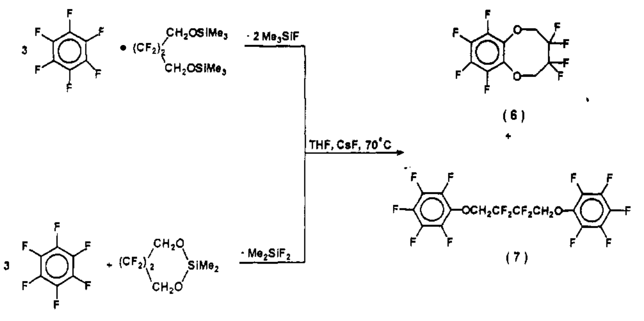
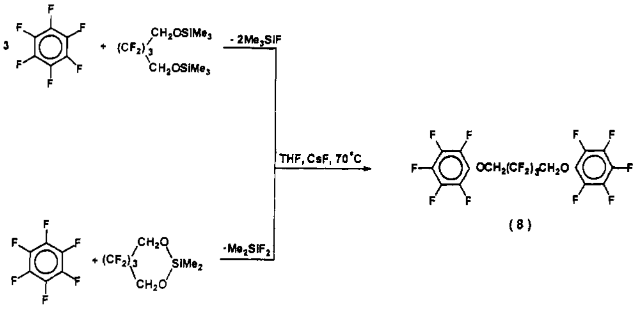
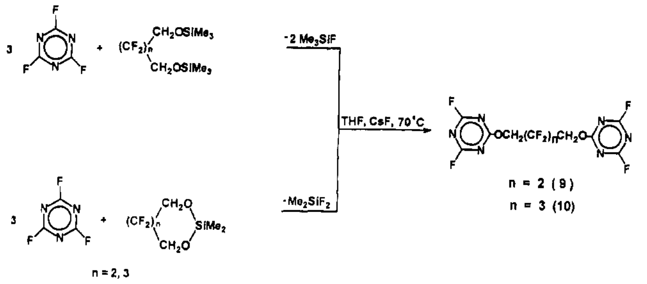
Scheme 1



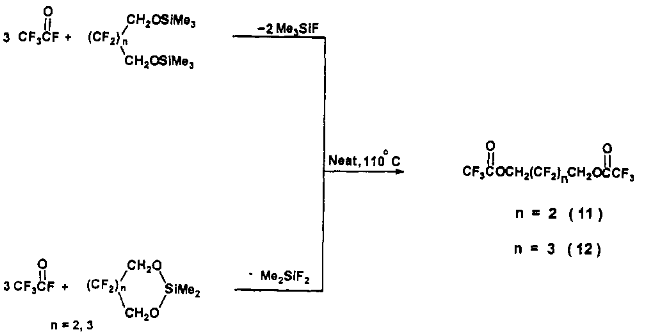
Scheme 2



Scheme 3



Scheme 4



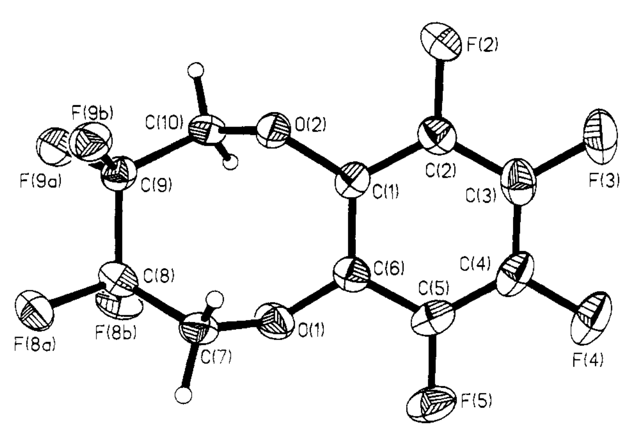


Figure 1. X-ray crystal structure of **6**.

poor due to the polymeric reactions involving C_6F_6, reactions that involve $(CNF)_3$ and $CF_3C(O)F$ give very good yields of the products **9**–**12**. The observable side product in the reactions of the trimethylsilylated compounds is Me_3SiF, and that of the cyclic siloxanes, Me_2SiF_2. Although THF and a fluoride ion catalyst are required for the reactions of C_6F_6 and $(CNF)_3$, reactions of $CF_3C(O)F$ are found to proceed even in the absence of solvent and fluoride ion catalyst. Reactions of **5** with $CF_3C(O)F$ proceed in the presence of CsF to give, in addition to **11**, a white solid residue that on analysis is found to be a mixture of Ph_2SiF_2 and $Ph_2SiF_3^-Cs^+$.[16]

The stoichiometry of the reactants plays an important role in deciding the nature of products formed in these reactions. However, in the present study, a slight excess of perfluorinated substrate is found to give smaller amounts of polymerization products. The fact that the nature and yields of the polyfluoro ether derivatives obtained from the acyclic and cyclic siloxanes are similar for the same parent diol indicates that the nature and the distribution of the products of these reactions are independent of the silyl group. It is also noteworthy that **2** and **4** did not yield any cyclic ethers in their reactions with C_6F_6 or $(CNF)_3$.

The ^{19}F NMR spectra of the seven-membered cyclic siloxanes **3** and **5** and the phosphite **13** show an unusual upfield shift in the chemical shifts of the CF_2 groups adjacent to the CH_2 group (δ -127.67 ± 0.33 ppm). Interestingly, the same CF_2 group is deshielded in the case of the eight-membered siloxane **4** (δ -117.75 ppm). Similar shifts are found in our previous studies with cyclic polyfluoroalkoxy compounds.[12,13] In compounds **9** and **10** the fluorine atoms on the cyanuric group show a small upfield shift in comparison to cyanuric fluoride. The infrared spectra of **11** and **12** show carbonyl groups at 1805 ± 2 cm^{-1} shifted about 100 cm^{-1} to lower energy compared to $CF_3C(O)F$.

The crystal structure of **6** (Figure 1) shows an almost planar C_6F_4 ring attached to a highly puckered eight-membered dialkoxy ring. The torsion angle at the fusion bond (O(2)C(1)C(3)O(1)) is 11.2°. The C–C bond distances of the aromatic ring vary from 1.371(3) to 1.404(3) Å, the latter being the C(1)–C(6) fusion bond. The ring angles of the C_6F_4 ring also vary from 118.5(2) to 122.2(2)° indicating a slight distortion in this ring.

The conventional methods of reacting alcohols with active halogenated compounds include direct reactions and reactions in the presence of a base or after metalation, especially as sodium or lithium salts. The latter method, although widely used, is not free from disadvantages in that the metalated alkoxides are only moderately stable and the procedure involves filtration and purification of products from metal salts. As observed by Johncock *et al.*, polymerization products of reactions involving perfluorinated aromatics and metalated polyfluorinated diols contain around 10–20% inorganic salts.[17] To overcome these difficulties, silicon-mediated synthesis of polymers was attempted by Kircheldorf[10b] initially on silylated diphenols and was later extended to polyfluoro diols by Farnham, who used this method to prepare macrocyclic polyfluoro ethers in a stepwise manner.[10a] The comparatively less reactive siloxy compounds plus their stability and ease of isolation coupled with ease of purification of reaction products make this alternative route attractive. In the present study, we carry out the reactions of both acyclic and cyclic polyfluorinated siloxanes with C_6F_6, $(CNF)_3$, and $CF_3C(O)F$. The fact that the cyclic siloxanes also behave in a similar fashion indicates the scope and possibilities of extending these reactions to siloxy polymers with polyfluoro and aromatic substituents.

The reaction of **1** with $PhPCl_2$ is indicative of the ease of removal of Me_3SiCl from P(III) halides in reactions with polyfluorosi-

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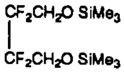
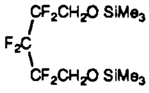
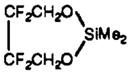
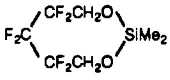
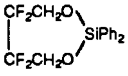
Table 1. Physical and Spectral Characteristics of Compounds **1–5**

siloxane	synth route[a]	^1H NMR[b]	^{19}F NMR[b]	^{29}Si NMR[b]	bp
	A, 94%	0.12 (Me_3Si), 3.94 (CH_2)	−123.90 (4F)	22.7	45 °C/0.35 mm
	A, 95%	0.20 (Me_3Si), 4.08 (CH_2)	−122.10 (4F),[c] −126.21 (2F)	22.8	46 °C/0.1 mm
	B, 26%	0.18 (Me_2Si), 3.98 (CH_2)	−127.99 (4F)	8.6	40 °C/10 mm
	B, 27%	0.21 (Me_2Si), 4.13 (CH_2)	−117.75 (4F), −123.90 (2F)	6.8	50 °C/10 mm
	B, 80%	4.16 (CH_2), 7.37–7.70 (Ph)	−127.34 (4F)	−23.2	117 °C/0.02 mm (mp 58 °C)

[a] A: $HO(R_f)OH + (Me_3Si)_2NH \rightarrow NH_3$ + siloxane. B: $HO(R_f)OH + R_2SiCl_2 + Et_3N \rightarrow Et_3N{\cdot}HCl$ + siloxane. [b] δ, ppm. [c] Reference 10a.

loxanes. Similar observations are reported for aromatic siloxanes with P(III) halides,[18] as well as for polyfluorinated siloxanes and $P(O)Cl_3$ where a single chlorine is eliminated.[19]

Experimental Section

Materials. $[CF_2CH_2OH]_2$ (gift from 3M Co.) and $CF_2[CF_2CH_2OH]_2$ (PCR) are purified by sublimation before use. Hexamethyldisilazane, Me_2SiCl_2, Ph_2SiCl_2, $PhPCl_2$, Et_3N, CsF, C_6F_6 (Aldrich), and $CF_3C(O)F$ (PCR) are used as received. Tetrahydrofuran (THF) and hexane are dried and distilled by standard techniques prior to use. $[CNF]_3$ (Alfa) is freshly distilled before use.

General Procedures. A conventional vacuum system, comprised of a Pyrex glass vacuum line equipped with a Heise Bourdon tube and Televac thermocouple gauges, is used to handle gases and volatile liquids. Reactions are performed in thick-walled 50-mL round-bottomed flasks fitted with Teflon stopcocks or in 25-mL stainless steel vessels. Products are separated and purified by distillation or vacuum sublimation. Infrared spectra are recorded on a Perkin-Elmer 1710 FTIR spectrometer equipped with an IBM PS–2 data station by using KBr plates for neat samples or Nujol mulls or with a 10-cm gas cell equipped with KBr disks. ^1H, ^{19}F, and ^{29}Si NMR spectra are obtained with a Bruker AC200 Fourier transform NMR spectrometer by using $CDCl_3$ or CD_3CN as solvent and Me_4Si, CCl_3F, and 85% H_3PO_4 as references. Mass spectra are obtained with a VG 7070HS GC/MS by using electron impact or chemical ionization techniques. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Synthesis of Siloxanes 1–5. The acyclic siloxanes $Me_3SiOCH_2(CF_2)_nCH_2OSiMe_3$ (n = 2, 3[10a]) are prepared by the reaction of $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 3) (40 mmol) with $(Me_3Si)_2NH$ (46 mmol) in a 50-mL round-bottomed flask fitted with a reflux condenser. After the initial evolution of ammonia subsides, the mixture is heated to 80 °C and maintained at that temperature for 8 h. A pinch of sodium saccharin is added as catalyst in the preparation of **1** to drive the reaction to completion. The siloxanes are obtained as colorless air-stable liquids upon vacuum distillation. The physical and spectral characteristics of these compounds are given in Table 1.

Since polymerization is found to dominate in the reactions of the diols with $(Me_2SiNH)_3$, the cyclic siloxanes $[CF_2CH_2O]_2SiMe_2$ (**3**), $CF_2[CF_2CH_2O]_2SiMe_2$ (**4**), and $[CF_2CH_2O]_2SiPh_2$ (**5**) are prepared by the reactions of Me_2SiCl_2 (30 mmol) and the diols $HOCH_2(CF_2)_nCH_2OH$ (n = 2, 3) (30 mmol) in the presence of Et_3N (61 mmol) in a solvent system comprised of 50 mL of THF and 250 mL of hexane at 0 °C. The cyclic siloxanes are obtained as colorless liquids upon vacuum distillation of the polymeric residue obtained from the reaction mixture after filtration through a frit containing a thin layer of Celite and removal of the solvents by distillation.

Reaction of 1 with C_6F_6 in THF To Form 6 and 7. To a solution of C_6F_6 (2.66 g, 14.30 mmol) in THF (40 mL) kept at 0 °C is added CsF (0.2 g) and **1** (1.96 g, 6.41 mmol). On increase of the solution temperature to 25 °C, it becomes pale yellow. After being stirred at 70 °C for 12 h, the reaction mixture is monitored by ^{19}F NMR, which shows the presence of Me_3SiF (δ −158.5 ppm). It is distilled, and the semisolid residue is subjected to careful vacuum sublimation. Two solid fractions are obtained. The first, subliming at 45 °C (0.025 Torr), is identified as **6** (0.28 g, 15%, mp 60 °C). IR (Nujol): 1512 vs, 1447 s, 1362 m, 1320 m, 1272 m, 1239 m, 1211 m, 1141 s, 1110 m, 1078 s, 1028 s, 980 s, 951 m, 916 m, 743 w, 710 w, 672 m, 607 w, 566 w, 544 m cm^{-1}. NMR: ^1H, δ 4.55 (mult, 4 H, CH_2); ^{19}F, δ −121.46 (mult, 4 F), −157.63 (mult, 2 F), −161.83 (mult, 2 F). MS (EI) [m/e (species), intensity]: 183 ($C_6F_5O^+$), 85; 149 ($C_6F_4H^+$), 50. MS (CI) [m/e (species), intensity]: 308 (M^+), 15; 289 ($M^+ - F$), 15; 149 ($C_6F_4H^+$), 35; 71 ($C_3H_3O_2^+$), 100. Anal. Calcd for $C_{10}H_4F_8O_2$: C, 38.98; F, 49.33. Found: C, 38.93; F, 49.00. The second fraction subliming at 65 °C is identified as $C_6F_5OCH_2CF_2CF_2CH_2OC_6F_5$ (**7**) (0.93 g, mmol, mp 88 °C). Yield: 0.75 g, 30%. IR (Nujol): 1515 vs, 1473 s, 1413 w, 1319 m, 1285 s, 1192 vs, 1161 s, 1135 vs, 1062 vs, 1022 vs, 991 vs, 956 s, 912 s, 789 m, 773 m, 662 w, 602 m, 565 m, 529 m, 461 w cm^{-1}. NMR: ^1H, δ 4.607 (mult, 4 H, CH_2); ^{19}F, δ −122.75 (t, 4 F), −156.25 (d, 4 F), −161.02 (t, 2 F), −162.37 (mult, 4 F). MS (EI) [m/e (species), intensity]: 494 (M^+), 15; 311 ($M^+ - C_6F_5O$), 45; 183 ($C_6F_5O^+$), 100; 155 ($C_5F_5^+$), 25. MS (CI) [m/e (species), intensity]: 494 (M^+) 100; 475 ($M^+ - F$), 10; 455 ($M^+ - HF_2$), 45; 311 ($M^+ - C_6F_5O^+$), 100; 196 ($C_6F_5OCH_3^+$), 50; 183 ($C_6F_5O^+$), 100; 155 ($C_5F_5^+$), 72. Anal. Calcd for $C_{16}H_4F_{14}O_2$: C, 38.80; H, 0.81; F, 53.80. Found: C, 38.51; H, 0.85; F, 53.30.

Reaction of 2 with C_6F_6 in THF To Form 8. In THF, 2.0 g (5.62 mmol) of $CF_2[CF_2CH_2OSiMe_3]_2$ (**2**) and 2.1 g (11.35 mmol) of C_6F_6 are reacted under identical conditions to those above. On working up the reaction and separation of the products, only one isolable product is observed, $C_6F_5OCH_2CF_2CF_2CF_2CH_2OC_6F_5$ (**8**) (1.19 g, 39%, mp 46 °C). IR (Nujol): 1538 s, 1506 vs, 1331 m, 1319 m, 1297 m, 1194 s, 1156 vs, 1117 m, 1093 s, 1068 vs, 1001 vs, 866 m, 817 m, 762 s, 606 m, 538 m, 461 w, 417 w cm^{-1}. NMR: ^1H, δ 4.59 (mult, 4 H, CH_2); ^{19}F, δ −121.36 (s, 4 F), −125.65 (s, 2 F), −156.25 (d, 4 F), −161.06 (s, 2 F), −162.42 (s, 4 F). MS (EI) [m/e (species), intensity]: 544 (M^+), 36; 361 ($M^+ - C_6F_5O$), 35; 215 ($C_6F_5OCHF^+$), 20; 197 ($C_6F_5OCH_2^+$), 100; 183 ($C_6F_5O^+$), 82; 167 ($C_6F_5^+$), 20; 155 ($C_5F_5^+$), 30. MS (CI) [m/e (species), intensity]: 544 (M^+), 75; 505 ($M^+ - HF_2$), 58; 361 ($M^+ - C_6F_5O$), 100. Anal. Calcd for $C_{17}H_4F_{16}O_2$: C, 37.52; F, 55.86. Found: C, 35.87; F, 53.90.

Reactions of 3 and 4 with C_6F_6 To Form 6–8. Reactions of the cyclic siloxanes with C_6F_6 are performed under conditions identical to those described above in the presence of catalytic amounts of CsF. The formation of Me_2SiF_2 is monitored by its typical infrared and ^{19}F NMR (δ −133.5 ppm) spectral features. On removal of the solvent, separation, and purification of products, compounds **6–8** are obtained in 12, 45, and 41% yields, respectively.

Reaction of 1 with Cyanuric Fluoride To Form 9. Freshly distilled cyanuric fluoride (1.32 g, 9.77 mmol) is condensed into a 50-mL flask fitted with a Teflon stopcock that contains 30 mL of dry THF, 0.1 g of CsF, and **1** (1.00 g, 3.27 mmol) at 0 °C. The mixture is brought to 25 °C and stirred for 12 h at 70 °C, and then the volatile materials are pumped off. The semisolid residue on sublimation yields $F_2C_3N_3OCH_2CF_2CF_2CH_2ON_3C_3F_2$ (**9**) (1.12 g, 87%, mp 122 °C). IR (Nujol): 3051 w, 1631 s, 1608 s, 1562 vs, 1490 m, 1447 m, 1419 s, 1306 m, 1243 m, 1185 s, 1163 m, 1124 s, 1081 vs, 1022 w, 954 w, 922 w, 814 s, 766 m,

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700 w, 623 w, 572 w, 523 w cm^{-1}. NMR: ^1H, δ 5.08 (mult, 4 H, CH_2); ^{19}F, δ –36.06 (t, 4 F), –120.64 (mult, 4 F). MS (EI) [*m/e* (species), intensity]: 372 ($M^+ - HF$), 18; 246 ($M^+ - F_2C_3N_3OCH_2$), 8; 146 ($F_2C_3N_3OCH_2^+$), 100; 116 ($F_2N_3C_3^+$), 30. MS (CI) [*m/e* (species), intensity]: 393 ($M^+ + 1$), 60; 372 ($M^+ - HF$), 20; 260 ($M^+ - F_2C_3N_3O$), 100. Anal. Calcd for $C_{10}H_4F_8O_2N_6$: C, 30.60; H, 1.02; F, 38.77; N, 21.40. Found: C, 30.29; H, 0.92; F, 39.30; N, 20.92.

Reaction of 2 with Cyanuric Fluoride To Form 10. In HF, 1.14 g (8.42 mmol) of cyanuric fluoride and 1.50 g (4.21 mmol) of **2** are reacted with CsF as catalyst similar to the reaction described for **9**. On working up the reaction mixture, a viscous liquid is obtained (bp 162 °C/0.25 Torr) that crystallizes slowly on standing and is identified as $CF_2[CF_2CH_2O(F_2N_3C_3]_2$ (**10**) (yield 1.39 g, 75%). IR (Nujol mull): 3052 w, 1641 vs, 1621 vs, 1566 vs, 1495 s, 1433 vs, 1410 vs, 1320 w, 1285 m, 1243 m, 1207 m, 1162 s, 1125 vs, 1105 s, 1085 vs, 1014 w, 971 m, 909 w, 814 vs, 782 m, 703 w, 684 w, 647 w, 620 m, 590 w, 545 w, 528 w, 479 w cm^{-1}. NMR: ^1H, δ 5.11 (mult, 4 H, CH_2); ^{19}F, δ –35.97 (s, 4 F), –119.21 (mult, 4 F), –124.6 (s, 2 F). MS (EI) [*m/e* (species), intensity]: 442 (M^+), 5; 422 ($M^+ - HF$), 45; 403 ($M^+ - HF_2$), 5; 310 ($M^+ - F_2C_3N_3O$), 4; 196 [$(F_2C_3N_3)OCH_2CF_2^+$], 44; 146 [$(F_2C_3N_3)OCH_2^+$], 100; 116 ($F_2C_3N_3^+$), 54.

Reactions of 3 and 4 with Cyanuric Fluoride To Form 9 and 10. Reactions of **3** and **4** with cyanuric fluoride in a 1:3 ratio under conditions descibed above proceed readily with the evolution of Me_2SiF_2 (monitored by IR and ^{19}F NMR) to give **9** and **10** in 79 and 70% yields, respectively.

Reaction of 1 with $CF_3C(O)F$ To Form 11. Into a 25-mL stainless steel vessel is added 1.0 g (3.27 mmol) of **1**. The vessel is then cooled in liquid nitrogen and evacuated for 15 min. A 10-mmol amount of $CF_3C(O)F$ is condensed into the vessel, and the mixture is heated to 130 °C for 12 h. On fractionation, the reaction mixture, Me_3SiF, and unreacted $CF_3C(O)F$ are obtained in the more volatile fractions. When the vessel is heated, a less volatile viscous liquid fraction is obtained which is identified as $F_3CC(O)OCH_2CF_2CF_2CH_2OC(O)CF_3$ (**11**) (yield 0.93 g, 81%). IR (neat): 2987 w, 1800 vs, 1544 vw, 1489 vw, 1450 m, 1353 vs, 1282 m, 1234 vs, 1132 vs, 1065 s, 1039 m, 1014 m, 968 s, 931 m, 918 s, 875 m, 835 w, 773 s, 731 s, 715 m, 627m, 573 m, 523 s, 477w, 458 w, 435w cm^{-1}. NMR: ^1H, δ 4.78 (mult, 4 H, CH_2); ^{19}F, δ –75.76 (s, 6 F), –121.49 (s, 4 F). MS (EI) [*m/e* (species), intensity]: 241 ($M^+ - CF_3C(O)O$), 35; 177 ($CF_3C(O)OCH_2CF_2^+$), 8; 147 ($CF_3C(O)CF_2^+$), 70. MS (CI) [*m/e* (species), intensity]: 355 ($M^+ + 1$), 6; 335 ($M^+ - F$), 6; 241 ($M^+ - CF_3C(O)O$), 100. Anal. Calcd for $C_8H_4F_{10}O_4$: C, 27.20; F, 53.67. Found: C, 27.57; F, 51.5.

Reaction of 2 with $CF_3C(O)F$ To Form 12. In a stainless steel vessel, 0.78 g (2.19 mmol) of **2** and $CF_3C(O)F$ (6.57 mmol) are reacted as in the case described above. After 12 h at 130 °C the mixture is fractionated. Removal of Me_3SiF and excess $CF_3C(O)F$ yields a less volatile viscous product which is purified by on line distillation and is identified as $CF_2(CF_2CH_2OC(O)CF_3)_2$ (**12**) (0.80 g, 97%). IR (neat): 3042 vw, 2988 w, 1808 vs, 1544 w, 1449 m, 1410 s, 1354 vs, 1289 s, 1252 vs, 1197 vs, 1143 vs, 1188 vs, 1080 s, 1024 m, 972 s, 927 m, 898 s, 855 w, 773 s, 732 s, 674 w, 623 m, 583 w, 542 m, 524 m, 486 w, 441 w cm^{-1}. NMR: ^1H, δ 4.79 (tm, 4 H, CH_2); ^{19}F, δ –75.38 (s, 6 F), –120.28 (s, 4 F), –125.85 (s, 2 F). MS (EI) [*m/e* (species), intensity]: 291 ($M^+ - CF_3C(O)O$), 30. MS (CI) [*m/e* (species), intensity]: 405 ($M^+ + 1$), 35; 385 ($M^+ - F$), 10; 291 ($M^+ - CF_3C(O)O$), 65; 69 (CF_3^+), 100. Anal. Calcd for $C_9H_4F_{12}O_4$: C, 26.75; F, 56.42. Found: C, 26.8; F, 56.30.

Reactions of 3 and 4 with $CF_3C(O)F$ To Form 10 and 11. Identical reactions of **3** and **4** performed with $CF_3C(O)F$ give **10** and **11** in 79 and 83% yields, respectively, along with Me_2SiF_2.

Reaction of 1 with $PhPCl_2$ To Form 13. In a 50-mL side arm flask fitted with a pressure equalizing funnel is taken 1.59 g (5.19 mmol) of **1** along with CH_2Cl_2 (10 mL) under nitrogen. $PhPCl_2$ (0.93 g, 5.20 mmol) and CH_2Cl_2 (5 mL) are added to the dropping funnel and are slowly added to the stirring solution of **1** over a period of 1 h. Afterward the mixture is refluxed for 6 h and then the volatile compounds are removed in vacuum. Fractional distillation of the residue gives an air-sensitive, viscous oil which is identified as $PhP(OCH_2CF_2)_2$ (**13**) (64 °C/0.15 Torr, 1.0 g, 72%). IR (neat): 3061 w, 3010 w, 2947 m, 2881 w, 1593 m, 1574 w, 1485 w, 1452 s, 1439 s, 1387 m, 1349 m, 1333 m, 1279 s, 1230 vs, 1191 vs, 1126 vs, 954 s, 925 s, 828 s, 802 s, 750 vs, 704 s, 661 s, 618 w, 569 m, 563 m, 532 s, 513 m, 466 w, 414 w cm^{-1}. NMR: ^1H, δ 7.68–7.45 (m, 5 H, Ph), 4.10 (m, 4 H, CH_2); ^{19}F, δ 127.64 (m, CF_2); ^{31}P, δ 164.64 (s). MS (EI) [*m/e* (species), intensity]: 268 (M^+), 60; 143 ($OCH_2CF_2CF_2CH^+$), 87; 77 (Ph^+), 100. Anal. Calcd for $C_{10}H_9F_4O_2P$: C, 44.80; H, 3.38; F, 28.34. Found: C, 42.9; H, 3.7; F, 28.4.

Table 2. X-ray Crystallography Parameters for **6**

formula	$C_{10}H_4F_8O_2$
fw	308.1
space group	$P2_1/n$
cryst system	monoclinic
a, Å	9.393(3)
b, Å	10.588(3)
c, Å	11.110(4)
β, deg	111.42 (2)
V, Å^3	1028.7(5)
d_c, Mg m^{-3}	1.990
Z	4
F(000)	608
cryst size, mm	0.3 × 0.4 × 0.6
abs coeff, mm^{-1}	0.231
2θ range, deg	0.0–50.0
scan range, ω, deg	0.80
index ranges	$0 \leq h \leq 11, 0 \leq k \leq 12, -12 \leq l \leq 12$
no. of measd reflns	2032
no. of unique reflns (R_{int}, %)	1809 (1.05)
no. of obsd reflns with $I > 6\sigma(I)$	1497
no. of params refined	182
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0085F^2$
R	0.0351
R_w	0.0648
goodness of fit	0.68
largest diff peaks, hole, e Å^{-3}	0.36, –0.22

Table 3. Selected Bond Distances (Å) and Angles (deg) of **6**

C(1)–C(2)	1.383(3)	C(1)–C(6)	1.404(3)
C(1)–O(2)	1.366(2)	C(2)–C(3)	1.375(3)
C(2)–F(2)	1.347(2)	C(3)–C(4)	1.378(3)
C(3)–F(3)	1.333(3)	C(4)–C(5)	1.371(3)
C(4)–F(4)	1.347(3)	C(5)–C(6)	1.390(3)
C(5)–F(5)	1.346(2)	C(6)–O(1)	1.367(3)
C(7)–C(8)	1.517(3)	C(8)–C(9)	1.539(3)
C(8)–F(8A)	1.352(3)	C(8)–F(8B)	1.358(3)
C(9)–C(10)	1.511(3)	C(9)–F(9A)	1.352(2)
C(9)–F(9B)	1.358(3)		
C(2)–C(1)–C(6)	118.5(2)	C(2)–C(1)–O(2)	118.5(2)
C(6)–C(1)–O(2)	122.8(2)	C(1)–C(2)–C(3)	122.2(2)
C(1)–C(2)–F(2)	119.4(2)	C(3)–C(2)–F(2)	118.4(2)
C(2)–C(3)–C(4)	119.1(2)	C(2)–C(3)–F(3)	120.5(2)
C(4)–C(3)–F(3)	120.4(2)	C(3)–C(4)–C(5)	119.9(2)
C(3)–C(4)–F(4)	120.0(2)	C(5)–C(4)–F(4)	120.1(2)
C(4)–C(5)–C(6)	121.6(2)	C(4)–C(5)–F(5)	119.4(2)
C(6)–C(5)–F(5)	119.0(2)	C(1)–C(6)–C(5)	118.7(2)
C(1)–C(6)–O(1)	123.5(2)	C(5)–C(6)–O(1)	117.5(2)
C(7)–C(8)–C(9)	116.3(2)	C(7)–C(8)–F(8A)	108.4(2)
C(9)–C(8)–F(8A)	108.3(2)	C(7)–C(8)–F(8B)	109.2(2)
C(9)–C(8)–F(8B)	107.2(2)	F(8A)–C(8)–F(8B)	107.1(2)
C(8)–C(9)–C(10)	116.7(2)	C(8)–C(9)–F(9A)	108.1(2)
C(10)–C(9)–F(9A)	108.4(2)	C(8)–C(9)–F(9B)	106.6(2)
C(10)–C(9)–F(9B)	109.2(2)	F(9A)–C(9)–F(9B)	107.5(2)

Crystallography. Crystals of **6** suitable for structural analysis are grown by slow sublimation under vacuum (50 °C, 0.05 mmHg). Data collection is carried out on a Siemens R3m/V diffractometer by using Mo Kα radiation (λ = 0.710 73) at 133 K. A highly oriented graphite crystal was used as a monochromator. The structure is solved by direct methods and refined by full-matrix least-squares method by using the Siemens SHELXTL Plus (VMS) program.[15] The quantity minimized is $\Sigma w(F_o - F_c)^2$, and hydrogen atoms are located by the riding model with a fixed isotropic *U*. Additional data on structure solution and refinement are given in Table 2, and Table 3 lists selected bond distances and angles of **6**.

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Supplementary Material Available: Listings of thermal and positional parameters and derived and rigid group positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.