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Synthesis of *trans*-1,2-Difluoroethenediylbis(phosphonic acid) and Other Unsaturated Phosphonic Acids

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Abstract: The phosphonic acids $(HO)_2P(O)CF{=}CFP(O)(OH)_2$, $CF_2{=}CFCH_2CH_2P(O)(OH)_2$, and $(HO)_2P(O)C{=}CP(O)(OH)_2(CF_2)_nCF_2$ (n = 1, 3) have been synthesized for the first time. *trans*-1,2-Difluoroethenediylbis(phosphonic acid) was prepared from $(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2$, which had been obtained via coupling of the corresponding sulfinate salt, $(C_2H_5O)_2P(O)CFBrSO_2Na$, by adding 30% aqueous hydrogen peroxide to a solution of $(C_2H_5O)_2P(O)CFBrSO_2Na$ and iron(II) sulfate. The X-ray crystal structure of the salt $[Zn(H_2O)_6]^{2+}[O(HO)P(O)CF{=}CFP(O)(OH)O]^{2-}$ indicates a network of $[Zn(H_2O)_6]^{2+}$ dications and the acid dianions linked together with water molecules via hydrogen bonding. The phosphorus, fluorine, and carbon atoms are coplanar.

The synthesis and characterization of perfluoro- and polyfluorophosphonic acids is a topic that continues to receive a great deal of attention, as evidenced by the large number of reports found in the literature. For example, several routes to a variety of perfluoroalkylphosphonic and bis(perfluoroalkylphosphonic acids)[1-3] as well as to the polyfluoroalkyl acids[4-6] have been published. The cyclic polyfluoroalkanediylbis(phosphates)[7] and the mixed phosphonic/sulfonic[8] and sulfonic/carboxylic and phosphonic/carboxylic[9] acids have also been reported. Much of the interest in these compounds stems from their potential use as phosphate mimics (difluoromethylenephosphonates) in biological systems,[5] as metal chelating agents,[10,11] or as fuel cell electrolytes.[1]

Alkenephosphonates have also been studied extensively.[5,11,12] Much of the work done describes methods for the synthesis of difluoromethylenephosphonates or perfluoroalkenephosphonates. Our interest lies in the development of synthetic routes to alkenephosphonates which should be useful as precursors to the synthesis of phosphonic acid polymers or membranes of very low equivalent weight that contain varying amounts of hydrogen and fluorine. Furthermore, the monomers are expected to possess unique chelating abilities. In this paper we present methods we have developed for the synthesis of several new phosphonic and diphosphonic acids and their precursors that possess highly unusual structural moieties.

Results and Discussion

The Michael–Arbuzov reaction is a powerful method for the formation of the carbon–phosphorus bond and sometimes the carbon–sulfur bond.[13] Now we have utilized a well-known example of this reaction to prepare the precursor to one of our interesting new acids.

$$(C_2H_5O)_3P + CFBr_3 \rightarrow \underset{\mathbf{1}\ (77\%)}{(C_2H_5O)_2P(O)CFBr_2}{}^{3}$$

When **1** was treated with sodium dithionite in the presence of sodium hydrogen carbonate in acetonitrile solution, it was converted to the sulfinate salt **2**.[16]

$$\mathbf{1} \xrightarrow[NaHCO_3]{Na_2S_2O_4} \underset{\mathbf{2}\ (64\%)}{(C_2H_5O)_2P(O)CFBrSO_2Na}$$

Addition of 30% hydrogen peroxide to an aqueous solution of **2** and $FeSO_4$ resulted in the formation of compound **3**.

$$\mathbf{2} \xrightarrow[Fe^{2+}]{H_2O_2} \underset{\mathbf{3}\ (37\%)}{(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2}$$

A reasonable mechanism for the reaction is

$$H_2O_2 + Fe^{2+} \rightarrow [H_2O_2]^- + Fe^{3+}$$

$$[H_2O_2]^- \rightarrow HO^\bullet + HO^-$$

$$(C_2H_5O)_2P(O)CFBrSO_2^- + HO^\bullet \rightarrow (C_2H_5O)_2P(O)CFBrSO_2^\bullet + HO^-$$

$$(C_2H_5O)_2P(O)CFBrSO_2^\bullet \xrightarrow{-SO_2} (C_2H_5O)_2P(O)CFBr^\bullet$$

$$2(C_2H_5O)_2P(O)CFBr^\bullet \rightarrow \underset{\mathbf{3}}{(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2}$$

When **3** was treated under reflux with zinc dust in ethyl alcohol, *trans*-1,2-difluoroethenediylbis(phosphonate) (**4**) was obtained.[17]

$$\mathbf{3} \xrightarrow[C_2H_5OH]{Zn} \underset{\mathbf{4}\ (30\%)}{(C_2H_5O)_2P(O)CF{=}CFP(O)(OC_2H_5)_2}$$

An AA′XX′ system was observed in the ^{19}F NMR spectrum. The IR spectrum confirmed the presence of a carbon–carbon double bond with a band at 1630 cm^{-1}. When **1** was treated with Zn

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(1) Mahmood, T.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 3128.
(2) Burton, D. J.; Pietrzyk, D. J.; Ishihara, T.; Fonong, T.; Flynn, R. M. *J. Fluorine Chem.* **1982**, *20*, 617.
(3) Burton, D. J.; Flynn, R. M. *J. Fluorine Chem.* **1980**, *15*, 263.
(4) Blackburn, G. M.; Brown, D.; Martin, S. J.; Parratt, M. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, *181*.
(5) Chambers, R. D.; Jaouhari, R.; O'Hagan, D. *J. Fluorine Chem.* **1989**, *44*, 275.
(6) Burton, D. J.; Takei, R.; Shin-Ya, S. *J. Fluorine Chem.* **1981**, *18*, 197.
(7) Mahmood, T.; Shreeve, J. M. *Inorg. Chem.* **1986**, *25*, 4081.
(8) Burton, D. J.; Modak, A. S.; Guneratne, R.; Su, D.; Cen, W.; Kirchmeier, R. L., Shreeve, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 1773.
(9) Burton, D. J.; Sprague, L. G.; Pietrzyk, D. J.; Edelmuth, S. H. *J. Org. Chem.* **1984**, *49*, 3437; *J. Org. Chem.* **1988**, *53*, 1523.
(10) Fonong, T.; Burton, D. J.; Pietrazyk, D. J. *Anal. Chem.* **1983**, *55*, 1089.
(11) Frank, A. W. *J. Org. Chem.* **1965**, *30*, 3663. Frank, A. W. *J. Org. Chem.* **1966**, *31*, 1521.
(12) Burton, D. J.; Sprague, L. G. *J. Org. Chem.* **1989**, *54*, 613 and references therein.
(13) Kumar, R. C.; Kinkead, S. A.; Shreeve, J. M. *Inorg. Chem.* **1984**, *23*, 3112.
(14) Keller, T. M.; Tarrant, P. *J. Fluorine Chem.* **1975**, *6*, 105.
(15) Krespan, C. G.; Harder, R. J.; Drysdale, J. J. *J. Am. Chem. Soc.* **1961**, *83*, 3424.
(16) Su, D. B.; Cen, W. B.; Kirchmeier, R. L.; Shreeve, J. M. *Can. J. Chem.* **1989**, *67*, 1795.
(17) Henne, A. L.; Nager, M. *J. Am. Chem. Soc.* **1951**, *73*, 1042.

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Table I. NMR Spectrum for *trans*-$(HO)_2(O)PCF{=}CFP(O)(OH)_2$

calcd freq, Hz (intensity)[a]	measd freq, Hz (intensity)
12831 (1.5)	12833 (1.5)
12877 (3)	12881 (3)
12944 (67)	12964 (80)
12985 (37)	12983 (27)
12989 (38)	12988 (28)
13008 (38)	13010 (28)
13012 (37)	13018 (27)
13053 (67)	13047 (80)
13123 (3)	13130 (3)
13167 (1.5)	13178 (1.5)

[a] PMR program—Serena Software.

dust in an ethyl acetate–methylene chloride solution, the coupling reaction to give $(C_2H_5O)_2P(O)CF{=}CFP(O)(OC_2H_5)_2$ (**4**) did not occur.[14] Attempts to couple **1** with copper at 180 °C followed by debromination did not yield **4**.[15]

Compound **4** has been reported as a byproduct (mixture of *E* and *Z* isomers) from the reaction between $(C_2H_5O)_2P(O)CF_2ZnBr$ and ethylchloroformate in the presence of CuBr when no cosolvent (i.e., acetonitrile) was present.[9] The boiling point and carbon and hydrogen analysis were reported; however, further characterization was not presented. In a subsequent publication,[12] compound **4** was again mentioned in the context of an expected decomposition product that was not obtained in a reaction between $(C_2H_5O)_2P(O)CF_2ZnBr$ and 3-bromo-1-propene in the absence of a coordinating solvent.

The ethyl ester **3** was treated with Me_3SiBr for 2 days at 25 °C followed by heating at 50–60 °C for 8 h to give a quantitative yield of the bis(silyl) ester **5**.[2]

$$\mathbf{3} + Me_3SiBr \rightarrow \underset{\mathbf{5}\ (96\%)}{(Me_3SiO)_2P(O)CFBrCFBrP(O)(OSiMe_3)_2}$$

Debromination of **5** with zinc dust in dioxane at 90 °C[15] resulted in $(Me_3SiO)_2P(O)CF{=}CFP(O)(OSiMe_3)_2$ (**6**). Complete purification of **6** is difficult. The yield was obtained by integration of peak areas in the ^{19}F NMR spectra.

$$\mathbf{5} \xrightarrow[\text{dioxane}]{\text{Zn}} \underset{\mathbf{6}\ (52\%)}{(Me_3SiO)_2P(O)CF{=}CFP(O)(OSiMe_3)_2}$$

Hydrolysis of **6** at 25 °C for 12 h resulted in the nearly quantitative formation of the acid **7**.

$$\mathbf{6} + H_2O \xrightarrow{CH_3CN} \underset{\mathbf{7}\ (93\%)}{(HO)_2P(O)CF{=}CFP(O)(OH)_2}$$

Reaction of **7** with zinc dust in the aqueous solution above, followed by a 70% reduction in the volume of solvent and subsequent storage at ~4 °C for 24 h resulted in the formation of the salt $[Zn(H_2O)_6]^{2+}[O(HO)P(O)CF{=}CFP(O)(OH)O]^{2-}$ (**8**).

The ^{19}F NMR spectrum of either **7** or **8** in D_2O showed an AA′XX′ pattern. Coupling constants were calculated, and the actual spectrum and theoretical spectrum are shown in Table I. The ^1H NMR spectrum of the analogous nonfluorinated *trans*-dimethylphosphonate has been reported[17] and shows a similar AA′XX′ pattern. The reported phosphorus–phosphorus coupling constant was 37.2 Hz, while the coupling constant we have calculated for *trans*-1,2-difluoroethenediylbis(phosphonic acid) is 24 Hz.

From the crystal structure of **8**, the compound may be described as a network of $[Zn(H_2O)_6]^{2+}$ dications and $[H_2P_2O_6C_2F_2]^{2-}$ dianions, linked together with water molecules via hydrogen bonding. The structure is shown in Figure 1. The zinc atom sits at a center of inversion in a nearly octahedral field of water molecules. The average Zn–O distance is 2.072 Å, and the bond angles are all within 2° of a perfect octahedral geometry.

The anion also sits at a center of inversion. The phosphorus atom possesses approximately tetrahedral geometry with P–O bonds of 1.569, 1.492, and 1.496 Å. The longest P–O bond, P1–O1, results from O1 being protonated. The atoms P1, C1, and C1a are perfectly planar. The C1–C1a double bond length is 1.289 Å and has a trans coordination geometry.

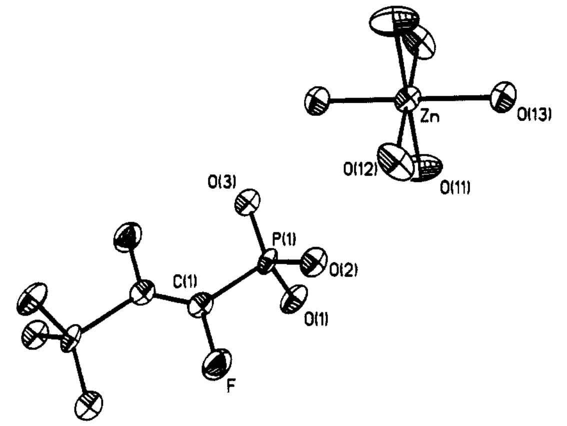

Figure 1. Structure of $[Zn(H_2O)_6]^{2+}[O(HO)P(O)CF{=}CFP(O)(OH)O]^{2-}$ (**8**).

Table II. Selected Structural Parameters for **8**

	Bond Distances (Å)		
Zn–O(11)	2.066 (6)	P(1)–O(1)	1.569 (4)
Zn–O(12)	2.051 (9)	P(1)–O(2)	1.492 (5)
Zn–O(13)	2.098 (5)	P(1)–O(3)	1.496 (6)
Zn–O(11A)	2.066 (6)	P(1)–C(1)	1.825 (9)
Zn–O(12A)	2.052 (9)	C(1)–F	1.371 (10)
Zn–O(13A)	2.098 (5)	C(1)–C(1A)	1.289 (12)
	Bond Angles (deg)		
O(1)–P(1)–O(2)	108.0 (2)	O(3)–P(1)–C(1)	109.0 (3)
O(1)–P(1)–O(3)	110.5 (3)	P(1)–C(1)–F	110.9 (4)
O(2)–P(1)–O(3)	117.2 (3)	P(1)–C(1)–C(1A)	132.1 (11)
O(1)–P(1)–C(1)	104.8 (3)	F–C(1)–C(1A)	117.0 (11)
O(2)–P(1)–C(1)	106.5 (3)		

The cations and anions are hydrogen bonded to a common H_2O molecule. The oxygen of the water molecule is 2.864 Å from O1 (anion) and 2.785 Å from O11 (cation). The O1–H_2O–O11 angle is 97.7°. Thus a fairly strong hydrogen bonding network exists.

The zinc atom coordinates were found by Patterson methods, and the positions of the other non-hydrogen atoms were located from subsequent difference maps. Final refinement included variation of all positional parameters and anisotropic thermal parameters on all non-hydrogen atoms. The isotropic thermal parameters for all hydrogens, except H1, were set at 0.08. The H1 thermal parameter was set at 1.2 times the equivalent isotropic μ of O1. All hydrogen atoms were fixed at bond distances of 0.96 Å and constrained to tetrahedral geometries. A list of bond angles and distances may be found in Table II.

Similarly, the reaction between triethylphosphite and $CF_2{=}CFCH_2CH_2Br$ resulted in the formation of the expected phosphonate $CF_2{=}CFCH_2CH_2P(O)(OC_2H_5)_2$ (**9**). The phosphonate was converted to the silyl ester with trimethylsilylbromide and subsequently hydrolyzed to give an overall yield of 46% of $CF_2{=}CFCH_2CH_2P(O)(OH)_2$ (**10**). The ^{19}F NMR, ^1H NMR, and mass spectral data obtained are consistent with this compound.

The cyclic alkene phosphonates $(C_2H_5O)_2(O)PC{=}CP(O)(OC_2H_5)_2(CF_2)_nCF_2$ (n = 1 (**11**), 2 (**12**), 3 (**13**)) were synthesized from the corresponding cyclic dichloroalkenes $ClC{=}CCl(CF_2)_nCF_2$ (n = 1, 2, 3). The synthesis of these phosphonates has been reported;[11] however, they were only characterized by IR, UV, and elemental analysis. We report here the NMR and mass spectral data for these compounds as well. Only the hydrolysis of the five-membered ring bis(phosphonate) **12** to the bis(phosphonic acid) **15** has been noted in the literature.[11b] We have obtained the three cyclic bis(phosphonic acids) (**14**, **15**, and **16**) by conversion to the silyl esters and hydrolysis.

In summary, we have developed a facile method for the preparation of the interesting new bis(phosphonic acid) $(HO)_2P(O)CF{=}CFP(O)(OH)_2$ (**7**) as well as for $CF_2{=}CFCH_2CH_2$-

Table III. Crystal and Data Collection Parameters for **8**

formula	$[O(HO)(O)PCF{=}CFP(O)(OH)O]^{2-}[Zn(H_2O)_6]^{2+}$
M_+	980
space group	$P\bar{1}/2$
a, Å[a]	6.484 (1)
b, Å	6.651 (1)
c, Å	10.358 (2)
α, deg	74.97 (1)
β, deg	74.58 (1)
γ, deg	61.18 (1)
V, $Å^3$	373
Z	2
F(000)	214
crystal size	0.084 × 0.25 × 0.38 mm
radiation	Cu Kα (λ = 1.54178 Å)
temp, K	298
hkl values scanned	$+h,\pm k,\pm l$
scan type	ω
scan speed, deg min^{-1}	4.0–29.3
2θ max, deg	110
no. of reflcns collcd	1029
no. of unique reflcns	926
no. of obsd reflcns with $F > 3\sigma(F)$	857
abs cor	none
R	0.0655
R_w	0.0770
total parameters refined	94

[a] Estimated standard deviations in the least significant figures are given in parentheses.

$P(O)(OH)_2$ (**10**). The cyclic acids and their precursors (**11**, **12**, **13**, **14**, **15**, and **16**) have been completely characterized. Both the chelating ability of these compounds and their potential use in the preparation of very low equivalent weight ionomers provide areas for future study.

Experimental Section

Materials. Literature methods were used to prepare $(C_2H_5O)_2P(O)CFBr_2$[3] and $(C_2H_5O)_2P(O)CFBrSO_2Na$.[16] The other chemicals were obtained as follows: $Na_2S_2O_4$, CH_3CN, and $CHCl_3$ (Merck); $NaHCO_3$, H_2O_2 (30%), and $FeSO_4{\cdot}7H_2O$ (J. T. Baker); and Me_3SiBr (Aldrich).

General Procedures. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform NMR spectrometer operating at 84.26 MHz. Chloroform-*d*, D_2O, or CD_3CN were used as solvent with $CFCl_3$ as the external reference. The ^{31}P NMR spectra were obtained at an operating frequency of 36.20 MHz with H_3PO_4 as the external reference, and ^1H NMR spectra were recorded at 89.56 MHz. Mass spectra were recorded with a VG7070HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

Theoretical ^{19}F NMR spectra and coupling constants for **7** or **8** were calculated by using the PMR program from Serena Software. For the crystal structure determination of **8** an approximately rectangular, transparent crystal of dimensions 0.084 × 0.25 × 0.38 mm was mounted in a glass capillary. The data collection was carried out on a Nicolet R3m/E system with Cu Kα radiation and graphite monochromator.[19] The orientation matrix and lattice parameters were optimized from the least-squares refinement to the angular settings of 25 carefully centered reflections with high Bragg angles. The SHELXTL 5.1 software package was used for data reduction and refinement.[20] Crystal and data collection parameters may be found in Table III.

Preparation of $(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2$ (3). Water (110 mL), $(C_2H_5O)_2P(O)CFBrSO_2Na$ (19.95 g, 17.8 mol), and $FeSO_4{\cdot}7H_2O$ (16.66 g) were placed in a 250-mL three-necked, round-bottomed flask, and 6.74 g of H_2O_2 (30%) was added at 0 °C under nitrogen. The mixture was stirred at 0 °C for 4 h and at 25 °C for 4 h. The reaction mixture consisted of two phases. The water phase was extracted with $CHCl_3$ (3 × 15 mL). The chloroform extract was added to the organic phase, and the solution was washed with H_2O (3 × 10 mL). After removal of solvent, 5.49 g (37%) of $(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2$ was obtained (bp 136–138 °C/10^{-3} mm Hg). Spectral data obtained are as follows: ^{19}F NMR ($CDCl_3$) ϕ −127.1 d (1 F) (J_{F-P} = 83 Hz, J_{F-F} = 29.3 Hz), −127.5 d (1 F) (J_{F-P} = 78.1 Hz, J_{F-F} = 24.4 Hz); $^{31}P\{H\}$ δ 2.67 d; ^1H ($CDCl_3$) δ 1.27 t (6 H, J_{H-H} = 6.35 Hz), 4.18 q (2 H), 4.25 q (2 H) (J_{H-P} = 6.35 Hz); MS (CI) [*m/e* (species) %] 499 (M^{81+} + 1) 0.99, 495 (M^{79+} + 1) 1.18, 249 ($(C_2H_5O)_2P(O)CFBr^{81+}$) 1.39, 247 ($(C_2H_5O)_2P(O)CFBr^{79+}$) 1.09, 168 ($(C_2H_5O)_2P(O)CF^+$) 1.28, 149 ($(C_2H_5O)_2P(O)C^+$) 4.04, 137 ($(C_2H_5O)_2P(O)^+$) 7.44, 121 ($(C_2H_5O)_2P^+$) 58.21, 109 ($C_2H_6O_3P^+$) 38.19, 65 ($PO_2H_2^+$) 100, 64 ($PO_2H^+$) 1.13, 63 ($PO_2^+$) 1.20.

Preparation of $(C_2H_5O)_2P(O)CF{=}CFP(O)(OC_2H_5)_2$ (4). The flask was loaded with 0.125 g (1.9 mmol) of zinc dust, 0.5 g (1 mmol) of $(C_2H_5O)_2P(O)CFBrCFBrP(O)(OC_2H_5)_2$ (**3**), and 2 mL of anhydrous ethanol. The solution was heated at reflux for 10 h and filtered to remove the excess zinc. The solvent was removed under vacuum. The residue was extracted with $CHCl_3/H_2O$ to remove impurities. Concentration of the organic layer led to isolation of 0.1 g (30%) of $(C_2H_5O)_2P(O)CF{=}CFP(O)(OC_2H_5)_2$ (**4**). Spectral data obtained for *trans*-$(C_2H_5O)_2P(O)CF{=}CFP(O)(OC_2H_5)_2$ are as follows: ^{19}F NMR ($CDCl_3$) ϕ −151.93 mult; $^{31}P\{H\}$ ($CDCl_3$) δ 0.73; ^1H ($CDCl_3$) δ 1.34 t (3 H, J_{H-H} = 6.96 Hz), 4.16 q (1 H), 4.25 q (1 H); J_{H-P} = 8.03 Hz; MS (CI) [*m/e* (species) %] 337 (M^+ + 1) 2.51, 169 ($M^+/2$ + 1) 3.62, 155 ($C_3F_2P_2OH_3^+$) 100, 149 ($CP(O)(OC_2H_5)_2^+$) 2.05, 137 ($P(O)(OC_2H_5)_2^+$) 28.84, 65 ($PO_2H_2^+$) 58.15, 64 (PO_2H^+) 2.62, 62 ($C_2F_2^+$, CFP^+) 1.98; IR (liquid film) 1630 cm^{-1} ($\nu_{C=C}$).

Preparation of $(Me_3SiO)_2P(O)CFBrCFBrP(O)(OSiMe_3)_2$ (5). Compound **3** (2 g, 4 mmol) was placed in a 25-mL, dry, round-bottomed flask, and 7.4 g (48 mmol) of Me_3SiBr was added slowly at 25 °C. The reaction mixture was then stirred at 25 °C for 2 days and at 50–60 °C for 8 h. The remaining Me_3SiBr and C_2H_5Br were removed under vacuum to leave the silyl ester as a brown viscous oil (2.6 g, 96% yield). Spectral data obtained are as follows: ^{19}F NMR ($CDCl_3$) ϕ −124.09 d (1 F) (J_{F-F} = 92.78 Hz, J_{F-F} = 19.54 Hz), −126.81 d (1 F) (J_{F-P} = 83.01 Hz, J_{F-F} = 34.18 Hz); $^{31}P\{H\}$ ($CDCl_3$) δ −14.92 d (1 P), −15.76 d (1 P); ^1H ($CDCl_3$) δ 0.344 s; MS (CI) [*m/e* (species) %] 585 (M^{81+} − $OSi(CH_3)_3$) 0.15, 581 (M^{79+} − $OSi(CH_3)_3$) 0.11, 497 (M^{81+} + 1 − $O_2Si_2(CH_3)_6$) 3.15, 493 (M^{79+} + 1 − $O_2Si_2(CH_3)_6$) 2.80, 225 ($((CH_3)_3SiO)_2P(O)^+$) 10.59, 93 (CBr^{81+}) 2.36, 91 (CBr^{79+}) 1.99, 73 ($(CH_3)_3Si^+$) 100.

Preparation of $(Me_3SiO)_2P(O)CF{=}CFP(O)(OSiMe_3)_2$ (6). A 25-mL, round-bottomed flask was loaded with 0.38 g (6 mmol) of zinc dust, 2.6 g (3.9 mmol) of **5**, and 7.2 mL of dry dioxane. The mixture was stirred under reflux at 90 °C for 10 h and was then filtered to remove any excess zinc dust. The solvent was removed under vacuum to leave **6** which was dissolved in $CHCl_3$ and filtered to remove inorganic impurities. After the chloroform was removed, the residue was taken up in CH_3CN. The yield based on ^{19}F NMR ($CDCl_3$) was 51.5%. Spectral data obtained are as follows: ^{19}F NMR ($CDCl_3$) ϕ −150.9 mult; $^{31}P\{H\}$ ($CDCl_3$) δ −19.22 mult; ^1H ($CDCl_3$) δ −2.21 s; MS (EI) [*m/e* (species) %] 231 ($C_3H_3F_2O_4P_2Si^+$) 28, 149 ($C_2H_6O_2PSi_2^+$) 0.2, 89 ($(CH_3)_3SiO^+$) 4.77, 88 ($C_3H_8SiO^+$) 100, 87 ($C_3H_7SiO^+$) 8.02, 58 $(CH_3)_2Si^+$, 79.77.

Preparation of $(HO)_2P^A(O)CF^B{=}CF^CP^D(O)(OH)_2$ (7) and $[Zn(H_2O)_6]^{2+}[OP(O)(OH)CF{=}CFP(O)(OH)O]^{2-}$ (8). The acetonitrile solution of **6** was maintained in a moist environment for a week. The crystals of **7** appeared very slowly (0.42 g). They were dissolved in 2 mL of H_2O and extracted with $CHCl_3$ (2 × 5 mL). On treatment with additional zinc, in aqueous solution, and removal of 70% of the water followed by standing at 4 °C for 24 h, a nearly quantitative yield of the zinc salt, $[Zn(H_2O)_6]^{2+}[O(HO)P(O)CF{=}CF(O)P(OH)O]^{2-}$ (**8**), was obtained. Spectral data obtained for **7** or **8** are as follows: ^{19}F NMR (D_2O) ϕ −154.6 mult (J_{A-B} = 96.5 Hz, J_{A-C} = 13.5 Hz, J_{A-D} = 24 Hz, J_{B-C} = 134 Hz, J_{B-D} = 13.5 Hz, J_{C-D} = 96.5 Hz); $^{31}P\{H\}$ (D_2O) δ −0.12 mult; ^1H (DMSO-d_6) δ 8.3 s; MS (FB^-, glycerol) [*m/e* (species) %] 224 (M^-) 1.10, 223 (M^- − 1) 22.5, 221 (M^- − 3) 3.4, 205 (M^- − F) 4.3, 183 (M^- − 3 − 2(F)) 12.7, 175 (M^- + 2 − 3(OH)) 7.8, 144 (M^- + 1 − PO_3H_2) 10.4, 134 (M^- − 1 − 2(F) − 3(OH)) 16.0, 105 (M^- − 2(F) − PO_3H_2) 13.8, 103 (M^- − 2 − 2(F) − PO_3H_2) 16.9, 93 ($C_2F_2P^-$) 86.2, 91 (C_2FPOH^-) 32.2, 81 ($PO(OH)_2^-$) 100, 79 (PO_3^-) 34.0.

Preparation of $CF^AF^B{=}CF^CCH_2CH_2P(O)(OC_2H_5)_2$ (9). A mixture of $CF_2{=}CFCH_2CH_2Br$ (4 g, 21.2 mmol) and triethylphosphite (5.27 g, 31.8 mmol) was heated at 130 °C for 10 h in a 75-mL stainless steel vessel. Distillation of the mixture under vacuum gave 3.1 g (60%) of **9**, a colorless liquid with a boiling point of 118–119 °C/0.4 mm. Spectral data obtained are as follows: ^{19}F NMR ϕ −106.52 dd (A, J_{A-B} = 29.3,

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(18) Ionin, B. I.; Lebedev, V. B. *J. Gen. Chem. USSR* (*Engl.*) **1967**, *37*, 1117.

(19) Campana, C. F.; Shephard, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039.

(20) Sheldrick, G. SHELXTL; Nicolet Analytical Instruments: Madison, WI, 1984.

Hz, J_{A-C} = 83.0 Hz), −124.54 dd (B, J_{B-C} = 112.3 Hz), −176.35 ddt (C, J_{F-H} = 19.4 Hz); $^{31}P\{H\}$ NMR δ 28.42 s; ^{1}H NMR δ 1.19 t (CH_3, $J_{CH_3-CH_2}$ = 6.8 Hz), 3.98 dq (OCH_2), 1.82 m (CH_2P), 2.43 m (CH_2F); MS (EI) [*m/e* (species) %] 246 (M^+) 8, 219 ($M^+ + 1 - C_2H_4$) 21, 191 ($M^+ + 1 - C_4H_8$) 13, 171 ($M^+ - C_4H_8F$) 29, 138 ($P(O)(OC_2H_5)_2^+ +$ 1) 15, 108 ($M^+ - P(O)(OC_2H_5)_2 - 1$) 38, 82 ($PO_3H_3^+$) 100, 65 ($PO_2H_2^+$) 25.

Preparation of $CF^AF^B{=}CF^CCH_2CH_2P(O)(OH)_2$ (10). Trimethylsilyl bromide (1.34 g, 8.76 mmol) and **9** (0.70 g, 2.85 mmol) were combined in a 100-mL, round-bottomed flask fitted with a Teflon stopcock and stirred vigorously at room temperature for 2 days. All volatile materials were removed under vacuum leaving 0.86 g (90%) of a colorless viscous liquid found to be $CF_2{=}CFCH_2CH_2P(O)(OSiMe_3)_2$. Three milliliters of water was added to the silyl ester and the resulting suspension was stirred vigorously at room temperature for 1 day and at 55 °C for 10 h. Following purification by extraction with CH_2Cl_2, water was removed under vacuum to give 0.41 g (85%) of the white solid **10** (mp 95–96 °C). Spectral data obtained for $CF^AF^B{=}CF^CCH_2CH_2P(O)(OSiMe_3)_2$ are as follows: ^{19}F NMR ϕ −106.35 dd (A, J_{A-B} = 29.3 Hz, J_{A-C} = 83.0 Hz), −124.35 dd (B, J_{B-C} = 112.3 Hz), −175.88 ddt (C, J_{F-H} = 19.4 Hz); $^{31}P\{H\}$ δ 10.19 s; ^{1}H NMR δ 0.26 s ($SiCH_3$), 1.84 m (CH_2P), 2.53 m (CH_2CF). Spectral data obtained for **10** are as follows: ^{19}F NMR ϕ −104.98 dd (A, J_{A-B} = 29.3 Hz, J_{A-C} = 83.0 Hz), −123.10 dd (B, J_{B-C} = 112.3 Hz), −175.81 ddt (C, J_{F-H} = 19.6 Hz); $^{31}P\{H\}$ NMR δ 22.92 s; ^{1}H NMR δ 4.98 s (OH), 1.75 m (CH_2P), 3.73 m (CH_2CF); MS (EI) [*m/e* (species) %] 190 (M^+) 2, 170 ($M^+ - HF$) 17, 150 ($M^+ - 2\ HF$) 9, 108 ($M^+ - PO_3H_3$) 44, 82 ($PO_3H_3^+$) 100, 65 ($PO_2H_2^+$) 30. Anal. Calcd for $C_4F_3H_6O_3P$: C, 25.27; H, 3.16. Found: C, 25.12; H, 3.33.

Preparation of $(C_2H_5O)_2(O)P\overline{C{=}CP(O)(OC_2H_5)_2(CF_2)_nCF_2}$ (*n* = 1 (11), 2 (12), 3 (13)). Twenty mmol of 1,2-dichloroperfluorocycloalkene-1, $Cl\overline{C{=}C(Cl)(CF_2)_nCF_2}$ (*n* = 1, 2, 3), was placed into a 50-mL, three-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, and a 50-mL dropping funnel. Forty mmol of triethylphosphite was added dropwise to the boiling alkene through the funnel. The mixture was stirred for 2 h after addition was complete. The tetraethyl bis(phosphonate) products **11**, **12** and **13** were purified by distillation and were obtained in 60, 84, and 52% yields, respectively. These phoshonate esters have been reported previously, along with infrared and UV data.[11] No NMR or mass spectral data were given.

Characterization of $(C_2H_5O)_2(O)P\overline{C{=}CP(O)(OC_2H_5)_2CF_2CF_2}$ (11). Compound **11** is a colorless liquid that boils at 105–106 °C/0.06 mmHg. Spectral data obtained are as follows: ^{19}F NMR ϕ −110.10 s; ^{31}P NMR δ −1.82 s; ^{1}H NMR δ 1.29 t (CH_3, $J_{CH_3-CH_2}$ = 6.89 Hz), 4.25 q (OCH_2); MS (CI) [*m/e* (species) %] 399 ($M^+ + 1$) 100, 379 ($M^+ + 1 - HF$) 37, 371 ($M^+ + 2 - C_2H_5$) 39, 353 ($M^+ - C_2H_5O$) 19, 269 ($M^+ - (OC_2H_5)_2 - HF_2$) 59, 138 ($P(O)(OC_2H_5)_2^+ + 1$) 15, 65 ($PO_2H_2^+$) 10.

Characterization of $(C_2H_5O)_2(O)P\overline{C{=}CP(O)(OC_2H_5)_2CF_2CF_2CF_2}$ (12). Compound **12** is a colorless liquid that boils at 95 °C/0.04 mmHg. Spectral data obtained are as follows: ^{19}F NMR ϕ −109.05 s (4 F), −133.60 s (2 F); $^{31}P\{H\}$ NMR δ 0.12 s; ^{1}H NMR δ 1.22 t (CH_3, $J_{CH_3-CH_2}$ = 6.84), 4.14 q (OCH_2); MS (CI) [*m/e* (species) %] 449 ($M^+ + 1$) 100, 421 ($M^+ + 2 - C_2H_5$) 33, 403 ($M^+ - OC_2H_5$) 45, 319 ($M^+ + 1 - O_2C_4H_{10} - H_2F_2$) 56, 312 ($M^+ + 1 - OP(OC_2H_5)_2$) 18, 138 ($OP(OC_2H_5)_2^+ + 1$) 19, 121 ($P(OC_2H_5)_2$) 64, 81 ($OP(OH)_2^+$) 7, 65 ($P(OH)_2$) 11.

Characterization of $(C_2H_5O)(O)P\overline{C{=}CP(O)(OC_2H_5)_2CF_2CF_2CF_2CF_2}$ (13). Compound **13** is a colorless liquid that boils at 94–96 °C/0.025 mmHg. Spectral data obtained are as follows: ^{19}F NMR ϕ −106.86 s (CF_2P), −134.94 s (CF_2CF_2); $^{31}P\{H\}$ NMR δ 2.55 s; ^{1}H NMR δ 1.26 t (CH_3, $J_{CH_3-CH_2}$ = 6.88), 4.04 q (OCH_2); MS (EI) [*m/e* (species) %] 499 ($M^+ + 1$) 38, 453 ($M^+ - OC_2H_5$) 45, 425 ($M^+ + 1 - OC_2H_5 - C_2H_5$) 17, 397 ($M^+ + 2 - OC_2H_5 - C_4H_{10}$) 13, 369 ($M^+ - O_2C_4H_{10} - 2\ HF$) 100, 350 ($M^+ - O_2C_4H_{10} - H_2F_3$) 18, 138 ($PO_3C_4H_{11}^+$) 19, 81 ($PO_3H_2^+$) 10, 65 ($PO_2H_2^+$) 20.

Preparation of $(HO)_2(O)P\overline{C{=}CP(O)(OH)_2(CF_2)_nCF_2}$ (*n* = 1 (14), 2 (15), 3 (16)). Approximately 2.5 mmol of the diphosphonate ester (**11**, **12**, or **13**) was stirred vigorously with 20 mmol of trimethylsilylbromide at room temperature for 2 days. Following the removal of all volatile materials under vacuum, 4 mL of water was added, and the suspension was stirred at room temperature for 1 day and heated with stirring to 60 °C for 8 h. The resulting transparent solution was extracted with CH_2Cl_2, and the water layer was removed and evaporated under vacuum to give the cyclic diphosphonic acids **14** (60%), **15** (95%), and **16** (50%). Spectral data obtained for **14** are as follows: ^{19}F NMR ϕ −110.25 s; $^{31}P\{H\}$ NMR δ −4.73 s; ^{1}H NMR δ 9.96 s (OH); MS (EI) [*m/e* (species) %] 286 (M^+) 2, 266 ($M^+ - HF$) 84, 155 ($M^+ - (P(O)(OH)_2) - CF_2$) 41, 124 ($M^+ - 2(P(O)(OH)_2)$) 52, 93 ($CP(O)(OH)_2^+$) 23, 81 ($P(O)(OH)_2^+$) 76, 65 ($P(OH)_2^+$) 100; mp 105–106 °C. Spectral data obtained for **15** are as follows: ^{19}F NMR ϕ −109.12 s (4 F), −132.17 s (2 F); $^{31}P\{H\}$ NMR δ −4.24 s; ^{1}H NMR δ 8.55 s (OH); MS (EI) [*m/e* (species) %] 335 ($M^+ - 1$) 10, 319 ($M^+ - OH$) 17, 283 ($M^+ - (OH)_2 - F$) 16, 155 ($M^+ - 2(P(O)(OH)_2) - F$) 49, 111 ($CFPO_2H^+$) 100, 93 ($CPO_2H_2^+$) 73, 81 ($PO_3H_2^+$) 64, 65 ($PO_2H_2^+$) 56; mp 192–194 °C dec. Anal. Calcd for $C_5F_6H_4O_6P_2$: C, 17.86; H, 1.19. Found: C, 17.76; H, 1.46. Spectral data obtained for **16** are as follows: ^{19}F NMR ϕ −108.90 s (PCF_2), −133.78 s (CF_2CF_2); ^{31}P NMR δ −5.82 s; ^{1}H NMR δ 9.01 s (OH); MS (EI) [*m/e* (species) %] 369 ($M^+ - OH$) 67, 368 ($M^+ - OH - 1$) 51, 269 ($M^+ - OH - P(O)(OH)_2 - F$) 100, 174 ($M^+ - 2(P(O)(OH)_2) - CF_2$) 15, 155 ($M^+ - 2(P(O)(OH)_2) - CF_2 - F$) 75, 124 ($M^+ - 2(P(O)(OH)_2) - C_2F_4$) 87, 102 ($C_2F_4H_2^+$) 37, 82 ($PO_3H_3^+$) 91, 65 ($P(OH)_2^+$) 33; mp 198–202 °C dec.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and hydrogen atom coordinates and a unit cell packing diagram (3 pages); table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.