Chain-extension reactions *via* insitu capture of the dibromofluoromethide ion with difluoromethylene fluoro-olefins

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Dedicated to Cynthia and Bruce Maryanoff

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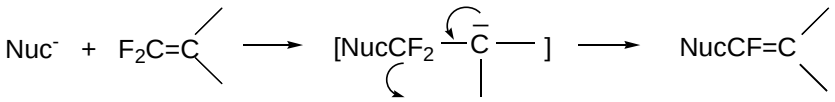
Abstract

The insitu reaction of triphenylphosphine, tribromofluoromethane, and a difluoromethylene olefin successfully allows the capture of the intermediate dibromofluoromethide ion. With fluorinated propenes, the product is an allylic dibromofluoromethyl alkene; with longer chain fluoro-olefins the major product is a 1-bromo-1,3-fluorinated diene derivative. Pentafluoropyridine yields 4-dibromofluoromethyltetrafluoropyridine.

Keywords: Dibromofluoromethide ion, fluoro-olefins, fluorodienes, ^{19}F- NMR spectroscopy, chain-extension

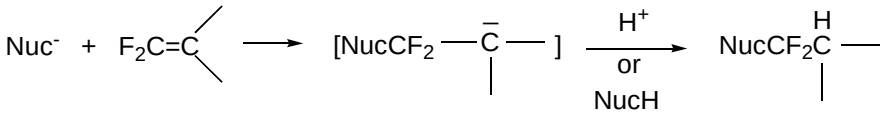
Introduction

Fluoro-olefins, especially difluoromethylene olefins, react with a wide variety of nucleophiles.[1,2] In the absence of a proton source, the intermediate carbanion can eliminate fluoride ion to re-generate the double bond (Scheme 1).



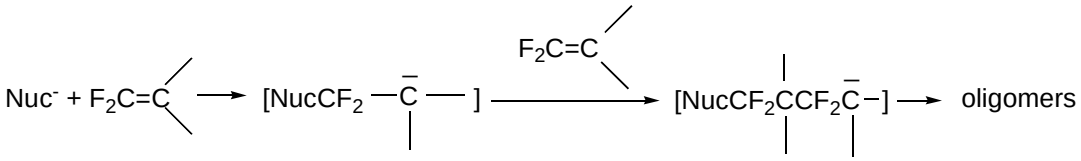
Scheme 1

If the nucleophile is a carbanion, this process provides a chain extension. Possible side reactions include proton abstraction by the intermediate carbanion (Scheme 2), attack of the intermediate carbanion on another molecule of the olefin (Scheme 3),



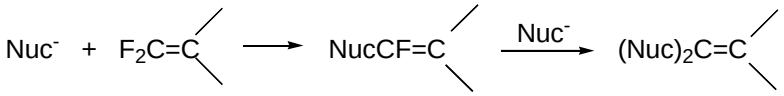
Scheme 2

which can potentially lead to oligomers or polyenes, and further reaction of the initially formed



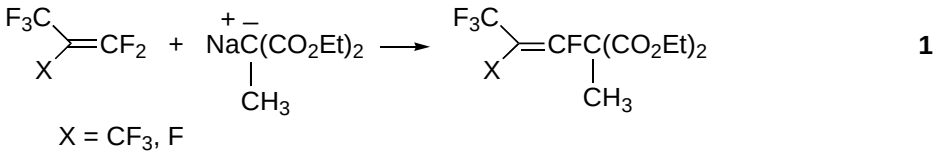
Scheme 3

product olefin with a second equivalent of the nucleophile (Scheme 4). Nevertheless, there are many examples which demonstrate that the substitution process is a viable route to chain-extended fluoro-olefins.



Scheme 4

A chain-extension reaction occurred when perfluoroisobutene or hexafluoropropene was treated with sodio-methylmalonic ester (Equation 1).[3] Phosphonium ylides can also be viewed as stabilized carbon nucleophiles and have been demonstrated to react with fluoro-olefins (Scheme 5).[4,5] Fluorine-containing ylides behave similarly (Scheme 6).[6,7]



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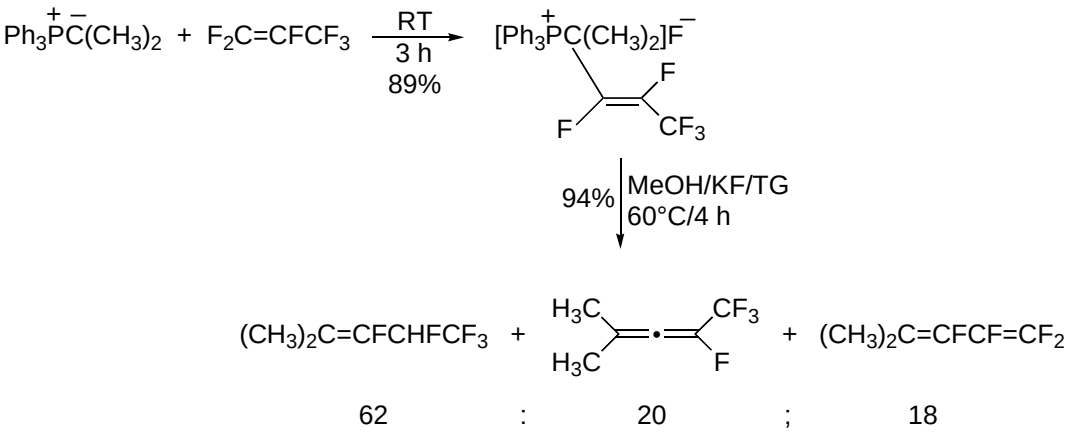
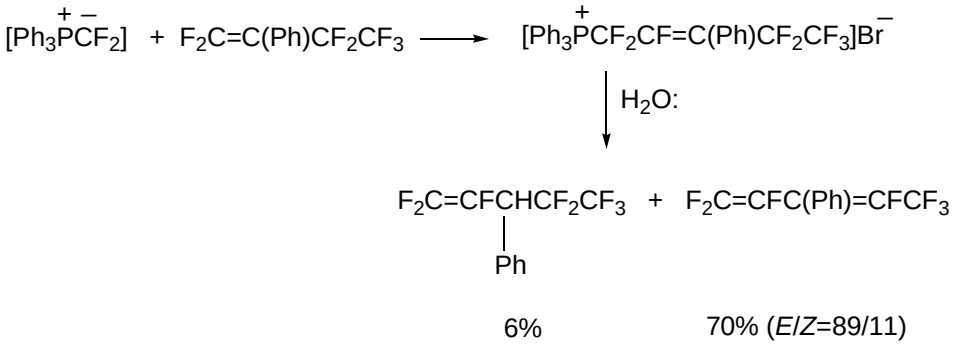
Chain-extended phosphonium salts gave fluorinated dienes as the major product (Scheme 6)

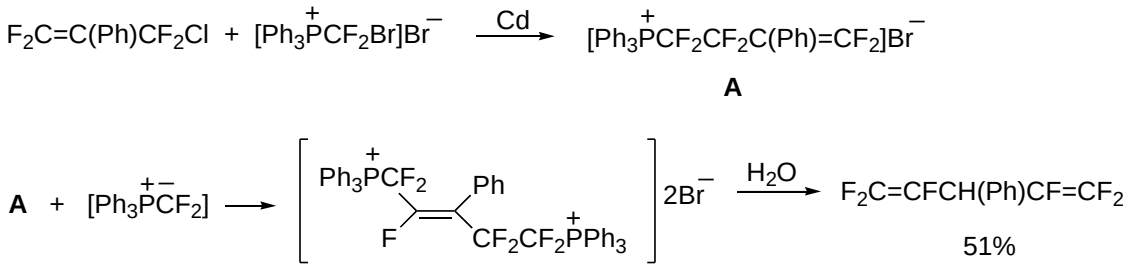


Scheme 5



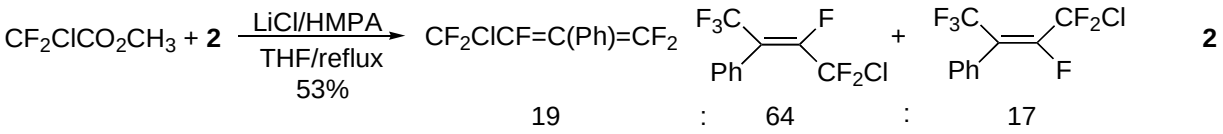
Scheme 6

If the initial ylide/olefin reaction generated a new difluoromethylene olefin center, the initially formed phosphonium salt could react with a second equivalent of the ylide to produce a bis-phosphonium salt, which on hydrolysis gave a two carbon chain-extended diene product, as illustrated in Scheme 7.[7] Halofluoromethide ions constitute another class of fluorine-containing



Scheme 7

carbon nucleophiles which can readily react with fluoro-olefins. Chlorodifluoromethide ion **1** (or possibly a complex with HMPA) was successfully trapped by Wheaton with 2-phenylpentafluoropropene **2**, as illustrated in Equation 2.[8] Bromodifluoromethide ion **3**, generated in an analogous manner from $BrCF_2CO_2CH_3$ gave $BrCF_2CF{=}C(Ph)CF_3$ in 25% yield from the olefin 2-pentafluoropropene, **2**.

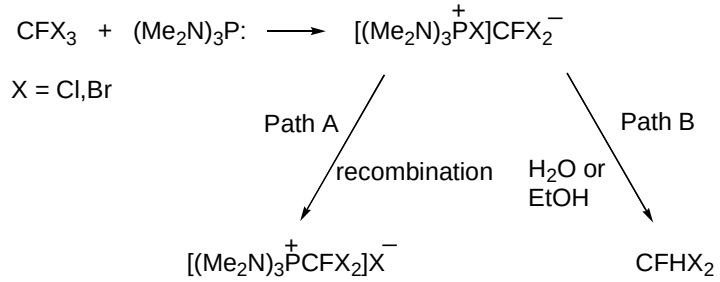


The bromodifluoromethide ion **3** was also formed by treatment of bromodifluoromethyltriphenylphosphonium bromide **4** with KF and again trapped with olefin **2** (Eq. 3).[9] Thus, there is reasonable evidence that halofluoromethide ions can be trapped by appropriate fluoro-olefins to yield chain-extended olefins.

Results and Discussion

An initial attempt was made to carry out the chain-extension of olefin **2** with $LiCFBr_2$, generated from n-BuLi and $CFBr_3$ **5** in THF/hexane at -110°C.[10] Subsequent addition of olefin **2** and analysis of the reaction mixture (after warming to RT) gave no evidence for any reaction of olefin **2**. Apparently, $LiCFBr_2$ decomposed faster than reaction with the olefin.

Tertiary phosphines react with fluorotrihalomethanes to form phosphonium salts.[11] The mechanism of phosphonium salt formation is not an SN_2 process, but involves halophilic attack on the halogen (other than fluorine) by the tertiary phosphines to form an ion-pair, followed by recombination of the ion-pair, as illustrated in Scheme 8. This mechanistic interpretation is supported by the observation that **only** the phosphonium salt is obtained when dry solvent is utilized (Path A); but the product is $CFHX_2$ when water or ethanol are present (Path B).



Scheme 8

The phosphonium salt is **not** hydrolyzed to $CFHX_2$ by H_2O or EtOH.[11-13] Since the dibromofluoromethide ion **6** could be generated readily (from **5**) by the process described in Scheme 8, it was of interest to determine whether the carbanion **6** generated in this manner could be captured by a fluoro-olefin faster than recombination of the ion-pair to form the phosphonium salt. The dibromofluoromethide ion **6** differs from chlorodifluoromethide **1** and bromodifluoromethide **3** in two important ways. Carbanions **1** and **3** are unstable and rapidly lose halide ion to form difluorocarbene, Equation 4. Although this process was initially proposed to be irreversible, subsequent work demonstrated that this α-halide elimination reaction was reversible.[14-15]

$$[CF_2X]^- \rightleftharpoons [:CF_2] + X^- \qquad \mathbf{4}$$

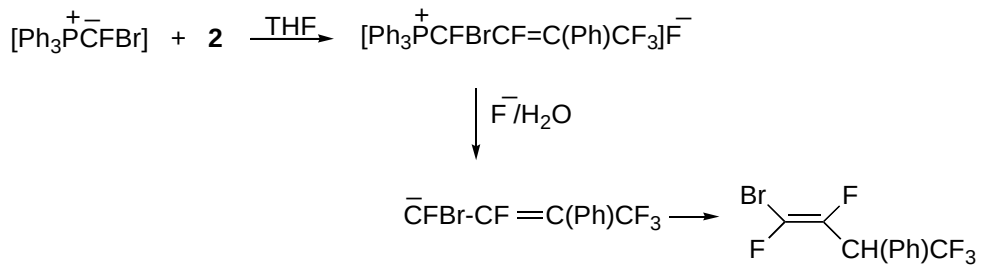
X = Cl,Br

It has also been demonstrated that dibromofluoromethide carbanion **6** loses halide in a irreversible process.[16] Secondly, it is known that halogens stabilize carbanions in the order $I^- \sim Br^- > Cl^- > F^-$, but that dihalocarbenes are stabilized by halogens in the reverse order: F > Cl > Br > I.[17] Thus, it seemed reasonable that carbanion **6** should have a better opportunity to be captured by a fluoro-olefin than carbanions **1** or **3**.

It is also been demonstrated that the initially formed phosphonium salt (from $CFBr_3$ **5**) reacts with a second equivalent of tertiary phosphine to produce the bromofluoromethylene ylide and a dihalophosphorane, as illustrated in Equation 5.[11,13] Thus, an alternative mechanism might involve attack by the ylide on the fluoro-olefin, as shown in Scheme 9.

$$[Ph_3\overset{+}{P}CFBr_2]Br^- + Ph_3P: \rightleftharpoons [Ph_3\overset{+}{P}\overset{-}{C}FBr] + Ph_3PBr_2 \qquad \mathbf{5}$$

However, when 2-phenylpentafluoropropene **2** was present during the addition of $CFBr_3$ **5** to a solution of Ph_3P: **7**, 92% of (*Z*)-$CFBr_2CF{=}C(Ph)CF_3$ was observed *via* ^{19}F NMR analysis of the reaction mixture.



Scheme 9

Apparently, carbanion **6** was trapped faster by olefin **2** before recombination of the ion-pair. Thus, this alternative mechanism either does not compete for fluoro-olefin or is only a minor pathway.[18]

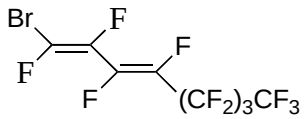
The success of the trapping of carbanion **6** depended on the presence of a terminal difluoromethylene group in the olefin, and a carbanion-stabilizing group(s) on the β-carbon of the fluoro-olefin. But it was also important that the fluoro-olefin not be so reactive that it would react directly with Ph_3P **7**.[19] For example, $F_2C=C(Ph)CF_2Cl$, $F_2C=CFCF_2Cl$. $F_2C=CFC(CF_3)=C(CF_3)H$ and perfluorocyclobutene[20] reacted directly with Ph_3P and failed to give chain-extended product.

The fluoro-ethylenes, iodo- and bromo-trifluoro-ethylenes, did not react at all at RT, and $F_2C=CCl_2$ gave only a 16% yield of $CFBr_2CF=CCl_2$ (as determined by ^{19}F- NMR). However, hexafluoropropene **8** gave an 80% isolated yield of (*E*)- and (*Z*)-$CFBr_2CF=CFCF_3$ (*E*/*Z* = 89/11). Similarly, the olefin **2** gave a 62% isolated yield of (*Z*)-$CFBr_2CF=C(Ph)CF_3$ and 2-(p-methoxyphenyl)pentafluoropropene gave a 90% yield of

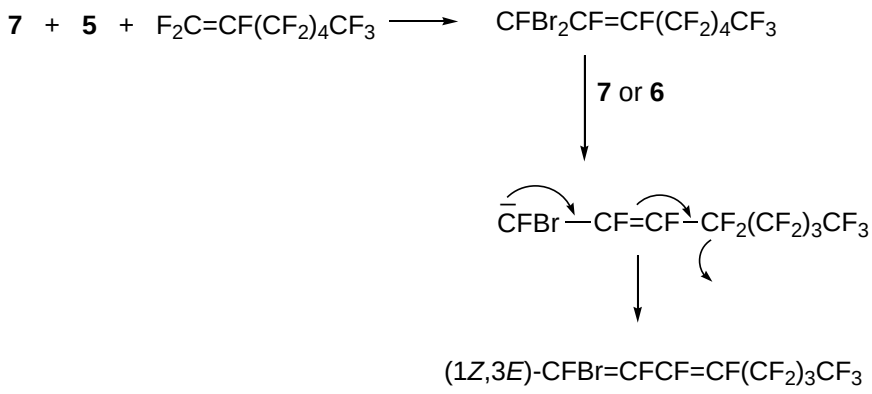
(*Z*)-$CFBr_2CF=C(CF_3)C_6H_4OCH_3$-p) (as determined by ^{19}F- NMR). Table 1 summarizes these results. Longer chain analogs of olefin **2** reacted with **7** and **5** to give 1-bromo-1,3-diene products, as illustrated in Equation 6, cf. to Table 1, entries 4-6. With perfluoro-1-olefins, the isolated product was also the (1-*Z*,3-*E*)-1-bromo-1,3-diene derivative and not the simple addition-elimination product, as shown with F-1-heptene in Equation 7.

$$Ph_3P + CFBr_3 + F_2C=C(Ph)CF_2CF_3 \xrightarrow[82\%]{TG} (E,Z:Z,Z)\text{-}CFBr=CFC(Ph)=CFCF_3 \quad \mathbf{6}$$

$$Ph_3P + CFBr_3 + F_2C=C(CF_2)_4CF_3 \xrightarrow[46\%]{TG} \quad \mathbf{7}$$



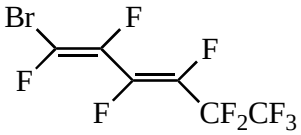
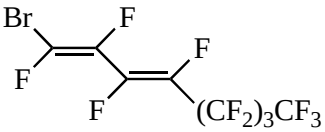
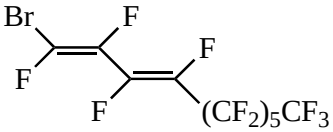
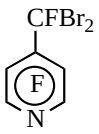
Similar results were obtained with F-1-pentene and F-1-nonene, (see Table 1, entries 7-9). Mechanistically, the bromodienes can be rationalized *via* further reaction of the initially formed addition-elimination product(s)[21] with either Ph_3P **7** or $CFBr_2^-$ **6**, as illustrated in Scheme 10. The stereochemistry of the dienes was determined from ^{19}F- NMR coupling constants, and the (*E*)- and (*Z*)-$^3J_{FF}$ are readily distinguished by the magnitude of the vinyl coupling constants.[22]



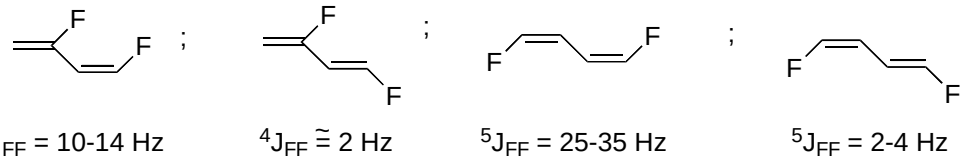
Scheme 10

The stereochemistry of the internal double bond of $CFBr=CFC(Ph)=CFCF_3$ and similar compounds was determined from the following long range coupling constants.[6,23-24]

Table 1. Yields of $CFBr_2$ olefins and 1-bromo-1,3-dienes.

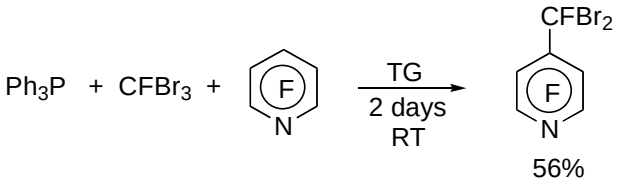
Reactant	Product Structure	% Yields
$F_2C=CFCF_3$	$CFBr_2CF=CFCF_3$ (E/Z) = 89/11	80[a]
$F_2C=C(Ph)CF_3$	(Z)-$CFBr_2CF=C(Ph)CF_3$	62[a] (85)[b]
$F_2C=C(CF_3)C_6H_4OCH_3$-p	(Z)-$CFBr_2CF=C(CF_3)C_6H_4OCH_3$-p	90[b]
$F_2C=C(Ph)CF_2CF_3$	$CFBr=CFC(Ph)=CFCF_3$ E/Z: Z/Z = 90/10	82[a] (92)[b]
$F_2C=C(Ph)CF_2CF_2CF_3$	$CFBr=CFC(Ph)=CFCF_2CF_3$ Z/E: Z/Z = 60/40	65[a] (70)[b]
$F_2C=C(Bu)CF_2CF_3$	$CFBr=CFC(Bu)=CFCF_3$ Z/Z = Z/E = 60/40	40[b]
$F_2C=CF(CF_2)_2CF_3$		36[b]
$F_2C=CF(CF_2)_4CF_3$		46[a](85)[b]
$F_2C=CF(CF_2)_6CF_3$		82[b]
		56[a](62)[b]

[a]isolated yield. [b] ^{19}F NMR yield *vs.* $PhCF_3$.



$^4J_{FF}$ = 10-14 Hz $^4J_{FF} \cong$ 2 Hz $^5J_{FF}$ = 25-35 Hz $^5J_{FF}$ = 2-4 Hz

As with chlorodifluoromethide **1**, and bromodifluoromethide **3**, dibromofluoromethide **6** can be readily trapped with pentafluoropyridine, Equation 8.



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Conclusions

When triphenylphosphine and tribromofluoromethene are allowed to react in the presence of an appropriate difluoromethylene fluoro-olefin, the intermediate dibromofluoromethide ion is captured by the fluoro-olefin. With hexafluoropropene and 2-substituted trifluoropropenes, the addition-elimination product is formed. With longer chain 2-substituted difluoromethylene olefins, the 1-bromo-1,3-substituted dienes are the major product(s). Similar diene formation is observed with perfluoro-1-alkenes. The capture of the dibromofluoromethide ion results in a chain-extension process. With pentafluoropyridine, 4-dibromofluoromethyltetrafluoropyridine is formed in moderate yield.

Experimental Section

General. RT denotes room temperature. ^{1}H- NMR spectra were recorded on a Jeol FX90Q spectrometer in $CDCl_3$. Chemical shifts are in ppm relative to internal TMS. ^{19}F-NMR spectra were recorded either on a Varian HA-100 (CW) or Jeol FX90Q (FT) spectrometer. Chemical shifts are given in ppm upfield from internal $CFCl_3$, and were generally recorded in $CDCl_3$, neat or triglyme (TG). ^{13}C NMR spectra were recorded on a Bruker HX-90E or JEOL FX90Q spectrometer, with chemical shifts reported in ppm relative to TMS. Infrared spectra were recorded for liquid films between sodium chloride plates on a Beckman Accu Lab 8 instrument. Low resolution mass spectra were recorded on a Hitachi-Perkin Elmer RMU-6E mass spectrometer or a Hewlett-Packard 5985 GC/MS system at 70 eV. High resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska, Lincoln, NE. GLPC analyses were carried out on either a Hewlett-Packard 5840A or an F & M 720 instrument with columns packed with OV-101, SE-30 or Carbowax.

Materials. Triglyme (TG) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Fluoroethylenes and hexafluoropropene were obtained from commercial sources and used as received. 2-phenylpentafluoropropene and substituted 2-phenyl difluoromethylene olefins were prepared by the literature procedure.[25,26] F-1-pentene, F-1-heptene and F-1-nonene were prepared by the literature procedure.[27] Tribromofluoromethane was prepared by the literature procedure.[28] Triphenylphosphine, pentafluoropyridine, potassium fluoride, and n-BuL/hexane were purchased from commercial sources.

(*Z*)-1,1-dibromo-3-phenyl-1,2,4,4,4-pentafluoro-2-butene. A 3-neck, 250 ml flask was equipped with a septum port, a nitrogen inlet tee and a magnetic stir bar. Triphenylphosphine PhP_3 **7** (22 g, 84 mmol) and THF (100 ml) were added to the flask; then $CFBr_3$ **5** (21.6 g, 80 mmol) and 2-phenylpentafluoropropene **2** (10.4 g, 50 mmol) were added *via* syringe. After stirring at RT overnight, ^{19}F NMR analysis showed a significant amount of unreacted **2,** so additional **7** (17.8 g, 67 mmol) and **5** (13.8 g, 51 mmol) were added and the reaction mixture stirred an additional 8 h at RT. The reaction mixture was pressure filtered under N_2 through a fritted glass filter (medium frit), the solids rinsed with 15 ml THF. Most of the THF was removed by vacuum distillation, the distillation continued at 0.3 mm Hg (oil bath temp. of 160°C). The oily distillate was fractionally distilled under vacuum to give 11.8 g (62%) of (*Z*)-$CFBr_2CF{=}C(Ph)CF_3$, bp 82° C/0.5 mm Hg. GC/MS *m*/*z* (relative intensity): 382 (0.9 M + 4), 380 (2.0, M + 2), 378 (1.0, M), 220 (18, M-2Br), 151 (100, M-2Br, CF_3). IR (cm^{-1}): 1680 (s), 1496 (m), 1449 (m), 1332 (s), 1240-1100 (vs), 981 (m). ^{19}F NMR (ppm, TG): δ -60.5 (d, $^4J_{FF}$ = 24 Hz), -63.6 (d, $^3J_{FF}$ = 38 Hz), -101.0 (dq, $^3J_{FF}$ = 38 Hz, $^4J_{FF}$ = 24 Hz). ^1H NMR (ppm. $CDCl_3$): δ 7.40 (m). ^{13}C NMR (ppm, neat): 80.8 (d, $^1J_{CF}$ = 322.5 Hz), 112.2 (dq, $^2J_{CF}$ = 33.4 Hz, $^2J_{CF}$ = 10.0 Hz), 121.9 (q, $^1J_{CF}$ = 276.3 Hz), 126.9 (s), 128.1 (s), 128.6 (s), 129.8 (s), 154.7 (ddq, $^1J_{CF}$ = 273.2 Hz, $^2J_{CF}$ = 23.9 Hz, $^3J_{CF}$ = 2.9 Hz).

(*E*)- and (*Z*)-1,1-dibromo-1,2,3,4,4,4-hexafluoro-2-butenes. A three-neck 1-liter flask was equipped with a septum port, a Dry Ice/isopropyl alcohol-cooled cold finger condenser, thermometer and magnetic stir bar. Ph_3P **7** (78.7 g, 300 mmol) was dissolved (with stirring) in TG (340 ml) at RT. $CFBr_3$ **5** (78.8 g, 291 mmol) was added *via* syringe followed by **8** (19.5 g, 130 mmol) *via* the cold finger condenser. The reaction mixture was stirred overnight at RT, then vacuum distilled (~ 60°C/0.2 mm Hg). The distillate was ~ equal amounts of $CFBr_2CF{=}CFCF_3$ and **5**. These two components could not be separated by spinning band distillation; a constant boiling (93°C) mixture was obtained. However, $CFBr_3$ could be removed by selective fluorination. The constant boiling mixture was added to a 100 ml flask equipped with a Claisen head, a mechanical stirrer, and a water-cooled condenser topped by a nitrogen inlet tee. SbF_3 (49.7 g, 278 mmol) and Br_2 (4.4 g, 27.5 mmol) were added and the mixture refluxed for 40 h. The reaction mixture was then distilled under nitrogen at atmospheric pressure (bp 105°C). The distillate was washed with 5% tartaric acid (2 x 25 ml), H_2O (25 ml) to give a clear colorless liquid, which was dried over 4Å molecular sieves, then flash distilled (RT @ 02 mm Hg) to give 33.5 g (80% based on **8**) of $CFBr_2CF{=}CFCF_3$ (*E*/*Z* = 89/11). ^{19}F NMR (ppm, $CDCl_3$): (*E*)-isomer: δ -80.4 (ddd, $^5J_{FF}$ = 10.8 Hz, $^3J_{FF}$ = 7.4 Hz, $^4J_{FF}$ = 4.0 Hz); -105.3 (ddq, $^3J_{FF}$ = 140.8 Hz,

$^3J_{FF}$ = 46.9 Hz, $^4J_{FF}$ = 4.0 Hz); -139.9 (ddq, $^3J_{FF}$ = 46.9 Hz, $^4J_{FF}$ = 27.4 Hz, $^5J_{FF}$ = 10.8 Hz); -144.3 (ddq, $^3J_{FF}$ = 140.8 Hz, $^4J_{FF}$ = 27.4 Hz, $^3J_{FF}$ = 7.4 Hz). (*Z*)-isomer: δ -79.5 (dd, $^3J_{FF}$ = 10.6 Hz, $^4J_{FF}$ = 9.4 Hz); -85.2 (dd, $^3J_{FF}$ = 14.4 Hz, $^4J_{FF}$ = 2.8 Hz); -130.1 (ddq $^3J_{FF}$ = 26.4 Hz, $^3J_{FF}$ = 14.4 Hz, $^4J_{FF}$ = 9.4 Hz); -132.4 (ddq, $^3J_{FF}$ = 26.4 Hz, $^3J_{FF}$ = 10.6 Hz, $^4J_{FF}$ = 2.8 Hz). IR (cm^{-1}): 1702 (s), 1290-1190 (*vs*), 1128 (s), 1170 (m), 813 (m), 747 (m), 678 (m). HRMS (mixture of isomers): Calc'd for $C_4F_6{}^{81}Br^{79}Br$: 321.8250, observed 321.8248.

(*Z*)-1,1-dibromo-3-(p-methoxyphenyl)-1,2,4,4,4-pentafluoro-2-butenes. As in the preparation of (*Z*)-$CFBr_2CF{=}C(Ph)CF_3$, **7** (3.2 g, 12 mmol), $CFBr_3$ (3.26 g, 12.0 mmol) and $F_2C{=}C(CF_3)C_6H_4OCH_3$-p (0.95 g, 4.0 mmol) gave a 90% yield of (*Z*)-$CFBr_2CF{=}C(CF_3)C_6H_4OCH_3$-p (as determined by ^{19}F- NMR). The reaction mixture was flash distilled and the flash distillate analyzed by GC/MS and ^{19}F- NMR spectroscopy. ^{19}F- NMR (ppm, TG): δ –60.4 (d, $^4J_{FF}$ = 24 Hz), -63.2 (d, $^3J_{FF}$ = 38 Hz), -100.4 (dq, $^3J_{FF}$ = 38 Hz, $^4J_{FF}$ = 24 Hz). GC/MS, *m*/*z* (relative intensity): 412 (1.6, M+ 4), 410 (3.2, M+2), 408 (1.5, M), 250 (100, M-2Br).

(*Z*:*E*:*Z*:*Z*-1-bromo-3-phenyl-1,2,4,5,5,5-hexafluoropenta-1,3-diene. Ph_3P **7** (78.6 g, 300 mmol), 350 ml TG, $F_2C{=}C(Ph)CF_2CF_3$ (25.7 g, 100 mmol), and $CFBr_3$ **5** (81.3 g, 300 mmol) was stirred at RT for 20 h. ^{19}F- NMR analysis of the reaction mixture showed complete conversion of the olefin to the diene. Flash distillation (0.2 mm Hg) gave two 50 ml fractions containing a mixture of diene and triglyme; each fraction was washed with water to remove tiglyme and the fractions combined. The remaining TG was distilled from the reaction mixture and washed with 350 ml H_2O. The combined organic layers were washed with 2 x 150 ml H_2O, dried over $MgSO_4$, filtered and vacuum distilled. Unreacted **5** was recovered as a low-boiling fraction. The higher boiling fraction (bp ~ 40°C/0.2 mm Hg) was the bromodiene (>95% purity); yield 27.0 g (82%); *Z*:*E*:*Z*:*Z* = 90/10. ^{19}F- NMR (ppm, $CDCl_3$): (*Z*:*E*)-isomer. δ-69.3 (ddd, $^3J_{FF}$ = 9.7 Hz, $^5J_{FF}$ = 4.4 Hz, $^6J_{FF}$ = 4.4 Hz); -112.8 (dqd, $^3J_{FF}$ = 140.9 Hz, $^6J_{FF}$ = 4.4 Hz, $^5J_{FF}$ = 3.1 Hz); 119.5 (qdd, $^3J_{FF}$ = 9.7 Hz, $^4J_{FF}$ = 3.5 Hz, $^5J_{FF}$ = 3.1 Hz), -132.4 (ddq, $^3J_{FF}$ = 140.9 Hz, $^5J_{FF}$ = 4.4 Hz, $^4J_{FF}$ = 3.5 Hz). (*Z*:*Z*)-isomer δ -65.7 (ddd, $^3J_{FF}$ = 8.8 Hz, $^5J_{FF}$ = 1.9 Hz, $^6J_{FF}$ = 1.0 Hz), -107.1 (ddq, $^3J_{FF}$ = 137.2 Hz, $^5J_{FF}$ = 29.0 Hz, $^6J_{FF}$ = 1.0 Hz), -113.2 (ddq, $^5J_{FF}$ = 29.0 Hz), $^4J_{FF}$ = 10.9 Hz, $^3J_{FF}$ = 8.8 Hz), -140.1 (ddq, $^3J_{FF}$ = 137.2 Hz, $^4J_{FF}$ = 10.9 Hz, $^5J_{FF}$ = 1.9 Hz). GC/MS, *m*/*z* (relative intensity): (mixture): 332 (3.1, $^{81}BrM^+$), 330 (3.1, $^{79}BrM^+$, 251 (100, M-Br). HRMS (mixture): Calc'd. For $C_{11}H_5{}^{81}BrF_6$: 331.9459, observed 331.9470; Calc'd for $C_{11}H_5{}^{79}BrF_6$: 329.9479, observed 369.9485.

(*Z*:*E*:*Z*:*Z*)-1-bromo-3-phenyl-1,2,4,5,5,6,6,6-octafluorohexa-1,3-diene. Ph_3P (19.7 g, 75 mmol), 94 ml triglyme, $CFBr_3$ (20.3 g, 75 mmol), and $F_2C{=}C(Ph)CF_2CF_2CF_3$ (7.7 g, 25 mmol) were stirred for 48 h at RT; then the reaction mixture was distilled under vacuum. The first fraction (3.5 ml) was mostly **5**; the second fraction (bp 80°C/1.2 mm Hg) was mostly triglyme and product. This fraction was washed with 9 x 100 ml water to remove triglyme. The aqueous washes were extracted with Skelly B (6 x 15 ml); the Skelly B was removed by rotary evaporation and the residue combined with the rest of the organic material, dried over 4Å molecular sieves and vacuum distilled to give 6.2 g (65%) of $CFBr{=}CFC(Ph){=}CFCF_2CF_3$, bp

45°C/0.2 mm Hg; *Z*:*E*: *Z*:*Z* = 60/40. ^{19}F- NMR (ppm, Neat): (*Z*:*E*)-isomer: δ -83.0 (m), -111.7 (dm, $^{3}J_{FF}$ = 144 Hz), -115.7 (m), -117.6 (m), -129.0 (d, $^{3}J_{FF}$ = 144 Hz). (Z:Z)-isomer: ^{19}F- NMR (ppm, neat): δ -82.8 (m), -102.5 (dd, $^{3}J_{FF}$ = 139 Hz, $^{5}J_{FF}$ = 31 Hz), -109.9 (dtd, $^{5}J_{FF}$ = 31 Hz, $^{3}J_{FF}$ = 12 Hz, $^{4}J_{FF}$ = 10 Hz), -114.0 (d, $^{3}J_{FF}$ = 12 Hz), -139.5 (dd, $^{3}J_{FF}$ = 139 Hz, $^{4}J_{FF}$ = 10 Hz). GC/MS, *m/z* (relative intensity): 382 (4.0, $^{81}BrM^{+}$), 380 (4.0 $^{79}BrM^{+}$), 301 (100, M-Br). HRMS (mixture): Calc'd for $C_{12}H_5{}^{81}BrF_8$: 381.9426, observed 381.9441; Calc'd for $C_{12}H_5{}^{79}BrF_8$: 379.9447, observed 379.9440.

(*Z*:*Z*:*Z*:*E*)1-bromo-3-(n-butyl)-1,2,4,5,5,5-hexafluoropenta-1,3-diene. Similar to the reaction with F_2C=(Ph)CF_2CF_3, (8.65 g, 33 mmol), 15 ml TG, F_2C=C(n-Bu)CF_2CF_3 (7.1 mmol) and $CFBr_3$ (7.8 g, 29 mmol) were stirred for 2 weeks at RT, ^{19}F- NMR analysis of the reaction mixture indicated that most of the fluoroolefin had been consumed. Integration of the ^{19}F- NMR signals of the diene product *vs.* added $PhCF_3$ indicatd a 40% ^{19}F- NMR of the diene product CFBr=CF-C(n-Bu)=$CFCF_3$, *Z*:*Z*: *Z*:*E* = 60:40. The reaction mixture was flash distilled, and the flash distillate was evacuated at RT to remove the product from most of the TG. A pure sample of the diene was isolated by GLPC (SE-30) and analyzed by GC/MS and ^{19}F- NMR. ^{19}F- NMR (ppm, TG): (*Z*:*Z*)-isomer: δ -65.8 (dm, $^{3}J_{FF}$ = 7 Hz), -109.0 (dd, $^{3}J_{FF}$ = 140 Hz, $^{5}J_{FF}$ = 30 Hz), -113.6 (d, $^{5}J_{FF}$ = 30 Hz) -143.5 (d, $^{3}J_{FF}$ = 140 Hz). (Z:E)-isomer: δ -69.7 (m), -114.7 (dm, $^{3}J_{FF}$ = 142 Hz), -121.4 (m), -136.0 (d, $^{3}J_{FF}$ = 142 Hz). GC/MS, (mixture) *m*/*z* (relative intensity): 312, (2.6, $^{81}BrM^{+}$), 310 (2.7, $^{79}BrM^{+}$), 270 (97, ^{81}BrM-$(CH_2)_3$), 268 (100, ^{79}BrM-$(CH_2)_3$).

(1-*Z*,3-*E*)-1-bromo-1,2,3,4,5,5,6,6,6-nonafluorohexa-1,3-diene. As above, Ph_3P (16.2 g, 61.7 mmol), 65 ml THF, F-1-pentene (6.40 g, 21.6 mmol) and $CFBr_3$ (16.3 g, 60.3 mmol) were mixed at 0°C; the reaction was warmed to RT and stirred overnight at RT. ^{19}F- NMR analysis of the reaction mixture indicated a 36% ^{19}F- NMR yield of (1-*Z*,3-*E*)-1-bromo-nonafluoro-1,3-hexadiene. Flash distillation of the reaction mixture gave a distillate that was washed with 3 x 200 ml of water to give 2 ml of a lower layer. The water washings were extracted with 3 x 10 ml CH_2Cl_2. The CH_2Cl_2 extracts were combined with the lower layer, dried over $CaCl_2$ then fractionally distilled at atmospheric pressure under N_2. The product diene could not be isolated pure by distillation and was obtained as a mixture of THF, diene and $CFBr_3$. A sample of pure diene was isolated by GLPC for spectroscopic analysis. ^{19}F- NMR (ppm, THF: δ -84.5 (m), -100.6 (dm, $^{3}J_{FF}$ = 141 Hz), -119.7 (broad d, partial overlap, $^{3}J_{FF}$ = 141 Hz), -120.7 (dm, $^{3}J_{FF}$ = 14 Hz), -152.3 (dm, $^{3}J_{FF}$ = 138 Hz), -155.0 (dm, $^{3}J_{FF}$ = 138 Hz). GC/MS, *m*/*z* (relative intensity): 324 (59, $^{81}BrM^{+}$), 322 (63, $^{79}BrM^{+}$), 255 (99, ^{81}BrM-CF_3), 253 (100, 79 BrM-CF_3), 243 (15.7, M-Br), 205 (25, ^{81}BrM-CF_2CF_3), 203 (26, ^{79}BrM-CF_2CF_3). HRMS: Calc'd for $C_6{}^{81}BrF_9$: 323.9019, observed 323.9027; Calc'd for $C_6{}^{79}BrF_9$: 321.9039, observed 321.9045.

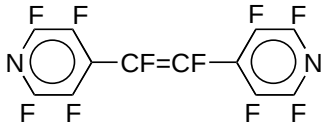
(1-*Z*,3-*E*)-1-bromo-1,2,3,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1,3-diene. Similarly, Ph_3P (23.6 g, 90 mmol), 100 ml THF, F-1-heptene (10.5 g, 30 mmol, and $CFBr_3$ (24.4 g, 90 mmol) were stirred at RT for 24 h. Flash distillation of the reaction mixture (under vacuum) gave a distillate, which was washed with 3 x 200 ml water to remove THF. The organic layer was dried over $MgSO_4$, and fractionally distilled through a 6" Vigreaux column to give 5.8 g (46%) of (1-*Z*,3-*E*)-1-bromo-tridecafluoruo-octa-1,3-diene, bp 77°C/57 mm Hg). Repetition of the reaction

indicated a ^{19}F- NMR yield of 85% diene, ^{19}F- NMR (ppm, $CDCl_3$): δ -80.9 (t, $^4J_{FF}$ = 10 Hz), -100.9 (dm, $^3J_{FF}$ = 131 Hz), -117.3 (s), -122.9 (dm, $^3J_{FF}$ = 131 Hz), -124.5 (s), -126.0 (m), -152.2 (dm, $^3J_{FF}$ = 140 Hz), -153.8 (dm, $^3J_{FF}$ = 140 Hz). GC/MS, *m*/*z* (relative intensity): 424 (32.3, $^{81}BrM^+$), 422 (33.0, $^{79}BrM^+$), 343 (21, M-Br), 255 (100, ^{81}BrM-C_3F_7), 253 (99.8,^{79} BrM-C_3F_7). HRMS: Calc'd for $C_8{}^{81}BrF_{13}$: 423.8955, observed, 423.8954; Calc'd for $C_8{}^{79}BrF_{13}$: 421.8975, observed 421.8976.

(1-*Z*,3-*E*)-1-bromo-1,2,3,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-deca-1,3-diene. Similarly, Ph_3P (3.2 g, 12 mmol), 16 ml TG, F-1-nonene (1.8 g, 4 mmol) and $CFBr_3$ (3.3 g, 12 mmol) were stirred at RT overnight. ^{19}F- NMR analysis of the reaction mixture indicated the diene was formed in 82% ^{19}F- NMR yield. Flash distillation of the reaction mixture under vacuum (80°C/0.2 mm Hg) gave a distillate, which was washed with water to remove most of the TG. The aqueous layer was extracted with Skelly B. The Skelly B was removed by rotary evaporation and the residue combined with the organic layer. GLPC analysis indicated a mixture of $CFBr_3$, diene and triglyme. A sample of pure diene was collected by GLPC for spectroscopic analysis. ^{19}F- NMR (ppm, neat): δ -81.5 (tm, $^4J_{FF}$ = 9 Hz), -101.0 (dm, $^3J_{FF}$ = 136 Hz), -116.1 (broad s), -121.4 (dm, partially overlapped, $^3J_{FF}$ = 136 Hz), -122.4 (s), -123.0 (s), -123.8 (m), -126.6 (s), -152.7 (dm, $^3J_{FF}$ = 138 Hz), -154.2 (dm, $^3J_{FF}$ = 138 Hz). GC/MS, *m*/*z* (relative intensity): 255 (98.6, ^{81}BrM-C_5F_{11}), 253 (100, ^{79}BrM-C_5F_{11}).

4-dibromofluoromethyltetrafluoropyridine. Ph_3P (9.4 g, 35.8 mmol), 35 ml triglyme, $CFBr_3$ (9.7 g, 36 mmol) and pentafluoropyridine (2.03 g, 12 mmol) were stirred at RT for 2 days; then distilled under vacuum. The first fraction (2 ml) contained mostly $CFBr_3$. The second fraction (~25 ml) contained 4-dibromofluoromethyltetrafluoropyridine and triglyme. The second fraction was washed with a large excess of water to remove triglyme. The lower layer was saved; the aqueous layer was extracted with 2 x 16 ml Skelly B. The Skelly B was removed by rotary evaporation; the residue combined with the organic layer; the combined material dried over 4Å molecular sieves, filtered, and redistilled to give 2.30 g (56%) of 4-dibromofluoromethyltetrafluoropyridine, bp 40°C/0.5mm Hg. ^{19}F- NMR (ppm, neat): δ -59.1 (t, $^4J_{FF}$ = 45 Hz, 1F), -88.7 (m, 2F), -138.9 (m, 2F). GC/MS, *m*/*z* (relative intensity): 343 (2.4, $^{81}Br^{81}BrM$), 341 (4.3, $^{81}Br^{79}BrM$), 339, (2.4, $^{79}Br^{79}BrM$), 262 (63.3, M-Br), 260 (66.4, M-Br), 201 (100, C_6HF_6N). HRMS: Calc'd for $C_6{}^{81}Br^{79}BrF_5$: 342.8277, observed: 342.8301; Calc'd for $C_6{}^{81}Br^{79}BrF_5$: 340.8297, observed: 340.8301; Calc'd for $C_6{}^{79}Br^{79}BrF_5$: 338.8318, observed: 338.8325.

A sample of 4-dibromofluoromethyltetrafluoropyridine passed through a 20% SE-30 GLPC column (200°C, 30 minutes retention time) produced white crystals at the exit port. These were collected and analyzed by GC/MS and ^{19}F NMR spectroscopy. ^{19}F- NMR (ppm, $CDCl_3$): d -87.3 (m), 4F), -136.9 (m, 4F), -138.6 (m, 2F). GC/MS, m/z (relative intensity): 363 (0.6, M+1), 362 (3.6, M), 138 (19.7, C_4F_4N), 123 (100, N_2F_5). This material is consistent with the structure:



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18. (^{19}F NMR yield) of (Z)-$CFBr_2CF{=}C(Ph)CF_3$ was observed.
19. Ph_3P: (**7**) was utilized in this work, since it reacts only with the most reactive fluoroolefins. $(Me_2N)_3P$ reacts rapidly with many fluoroolefins.
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