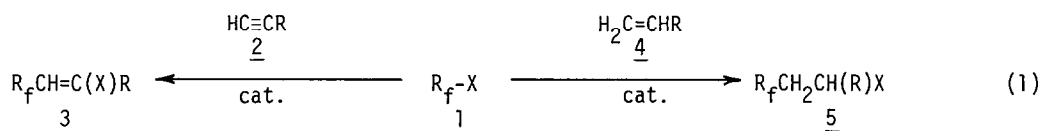TRANSITION-METAL COMPLEX CATALYZED POLYFLUOROALKYLATION. I.

FACILE ADDITION OF POLYFLUOROALKYL HALIDES TO CARBON-CARBON MULTIPLE BONDS

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Summary: Addition of polyfluoroalkyl halides to alkynes and alkenes bearing a variety of substituents is effected by the catalysis of iron, cobalt and ruthenium carbonyl complexes to give the corresponding adducts in good to excellent yields under mild conditions.

Polyfluoroalkylation of carbon-carbon multiple bonds is one of the most important and general methods for the industrial as well as laboratory synthesis of a variety of organofluorine compounds containing polyfluoroalkyl groups.[2] It has been shown that the addition of polyfluoroalkyl iodides to alkynes or alkenes is effected by photolysis,[3] pyrolysis,[4] electrolysis,[5] free radical initiators[6] or CuI-ethanolamine catalyst.[7] However, these conventional methods do not necessarily guarantee satisfactory yields, and are sometimes hampered by side reactions. In the course of our study on the functionalization of fluorine containing olefins, which gives us versatile synthetic building blocks for various organofluorine compounds of interest,[8] we have looked at the efficiency of transition-metal catalysts for the addition of polyfluoroalkyl halides to carbon-carbon multiple bonds, and have found that some of the carbonyl complexes of Group VIII transition metals exhibit good catalytic activity. We will describe here a convenient and effective method for the addition of polyfluoroalkyl halides to alkynes and alkenes bearing a variety of substituents promoted by the catalysis of transition-metal carbonyl complexes under mild conditions.[9]

$$R_fCH=C(X)R \xleftarrow[\text{cat.}]{\substack{HC\equiv CR \\ \underline{2}}} R_f\text{-}X \xrightarrow[\text{cat.}]{\substack{H_2C=CHR \\ \underline{4}}} R_fCH_2CH(R)X \qquad (1)$$
$$\underline{3} \qquad\qquad\qquad\qquad \underline{1} \qquad\qquad\qquad\qquad \underline{5}$$

In order to estimate the catalytic activity of transition-metal complexes, we fixed a very mild conditions such as 60°C for 3 h by choosing $n\text{-}C_3F_7I$ ($\underline{1a}$) and $Me_3SiC\equiv CH$ ($\underline{2a}$) as typical substrates. Then it was found that $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$ exhibited catalytic activities toward the reaction which gave $\underline{3a}$ in moderate to good yields, whereas $Fe(CO)_5$, $Rh_6(CO)_{16}$, $Cr(CO)_6$ and $Mn_2(CO)_{10}$ did not show any appreciable catalytic activities under the given reaction conditions. Although $RuCl_2(PPh_3)_3$ is known to be a good catalyst for the addition of carbon tetrachloride to olefins,[10] this complex did not display any catalytic activity toward the present reaction. It would be interesting to note that $Fe(CO)_5$ turn out to be an excellent catalyst when the reaction was carried out at 100°C as shown in Table 1. As Table 1 shows, the addition of catalytic amount of amine such as ethanolamine, diethylamine, triethylamine and pyridine remarkably accelerate the reaction to give $\underline{3a}$ in good yield even at 30 min period. The results on using other polyfluoroalkyl halides with a variety of terminal alkynes are summarized in Table 1.[11]

Table 1. Reaction of Polyfluoroalkyl Halides with Alkynes[a]

Entry	R_f	X	R	Cat.[b] (mol%)	Additive[c] (mol%)	Temp. (°C)	Time (h)	Adduct[d] (% yield)	E/Z
1	C_3F_7	I	$SiMe_3$	Ru_3(0.3)	——	60	3	<u>3a</u> (23)	3[e]
2				Ru_3(0.3)	Py(4)	60	0.5	(50)	
3				Fe_3(1.7)	——	60	3	(59)	3[e]
4				Fe_3(1.3)	Py(4)	60	0.5	(78)	3[e]
5				Fe_3(1.3)	EA(12)	60	0.5	(69)	
6				Fe_3(1.3)	Et_3N(12)	60	0.5	(53)	
7				Fe_3(1.3)	Et_2NH(4)	60	0.5	(64)	
8				Fe_2(3.0)	——	60	3	(32)	3[e]
9				Fe_2(2.0)	Py(4)	60	0.5	(72)	
10				Co_2(2.5)[f]	——	60	3	(77)	3[e]
11				Fe (7.0)	——	100	3	(93)	3[e]
12	C_8F_{17}	I	$SiMe_3$	Fe (7.0)	——	100	3	<u>3b</u> (92)	3[e]
13	CF_2CF_2Br	I	$SiMe_3$	Fe_3(1.3)	EA(12)	60	1	<u>3c</u> (83)	5[e]
14	$CFClCF_2Br$	Br	$SiMe_3$	Fe_3(2.0)	EA(12)	60	8	<u>3d</u> (26)	>20[e]
15	C_8F_{17}	I	C_5H_{11}	Fe_3(2.8)	——	60	3	<u>3e</u> (87)	8.9[d]
16	C_3F_7	I	Ph	Fe (7.0)	——	100	5	<u>3f</u> (78)	11.9[d]
17	C_3F_7	I	CH_2SiMe_3	Fe_3(2.0)	EA(24)	60	16	<u>3g</u> (58)	9.8[d]
18	C_3F_7	I	CH_2CH_2OH	Fe_3(1.3)	EA(12)	60	2	<u>3h</u> (66)	3.7[d]

[a] All reactions were run with 2.0 mmol of polyfluoroalkyl halide and 2.0 mmol of alkyne.
[b] $Ru_3=Ru_3(CO)_{12}$, $Fe_3=Fe_3(CO)_{12}$, $Fe_2=Fe_2(CO)_9$, $Fe=Fe(CO)_5$, $Co_2=Co_2(CO)_8$. [c] Py=pyridine, EA= ethanolamine. [d] Determined by GLC. [e] Determined by ^{19}F NMR. [f] Ethanol (0.6 ml) was used as solvent.

As Table 2 shows, the corresponding polyfluoroalkylation of $Me_3SiCH=CH_2$ (<u>4a</u>) and other various alkenes also proceeded smoothly under similar conditions and even more marked acceleration of the reaction was observed by adding amines and using ethanol as solvent.

As exemplified by the reaction using mixed halides, there is a clear difference in the reactivity of halide used, i.e., the reactivity of carbon-halogen bond decrease in the order R_f-I >> R_f-Br >> R_f-Cl. It should be noted that polyfluoroalkyl bromides can be used success-fuly in the present reactions. It is also noteworthy that extremely high regioselectivity was observed in the reaction of $BrCF_2CF(Cl)Br$ or $CF_3CF(Br)CF_2Br$ with <u>4a</u>, viz., the adducts arising from the reaction of carbon-bromine bond at less fluorine-substituted carbon atom across carbon-carbon double bond were formed exclusively in these reactions.

As for the perfluoroalkylation of $Me_3SiC\equiv CSiMe_3$ (<u>6</u>), Baum et al. recently reported the di-tert-butyl peroxide—promoted addition of <u>1a</u> to <u>6</u> (120°C, 48 h), which gave <u>8</u> as sole product in 84 % yield.[6d] In contrast with this, we have found that the same perfluoroalkylation cata-lyzed by $Fe_3(CO)_{12}$—ethanolamine (60°C, 28 h) gives <u>7</u>[12] as major product (57%) accompanied by <u>8</u> (24 %), which are isolated by a column chromatography on silica gel.[13]
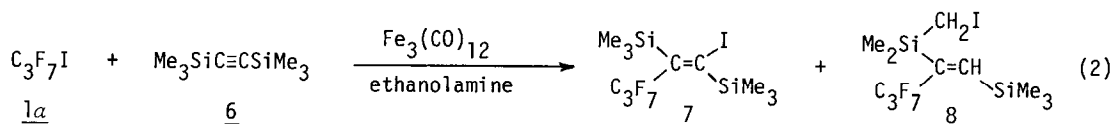
$$C_3F_7I + Me_3SiC\equiv CSiMe_3 \xrightarrow[\text{ethanolamine}]{Fe_3(CO)_{12}} \underset{C_3F_7}{\overset{Me_3Si}{>}}C=C\underset{SiMe_3}{\overset{I}{<}} + \underset{C_3F_7}{\overset{Me_2Si}{>}}C=CH\underset{SiMe_3}{\overset{CH_2I}{<}} \quad (2)$$

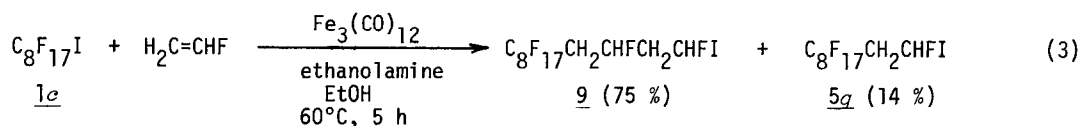<u>1a</u>   <u>6</u>   <u>7</u>   <u>8</u>

Table 2. Reaction of Polyfluoroalkyl Halides with Alkenes[a]

Entry	R_f	X	R	Cat.[b] (mol%)	Additive[c] (mol%)	Temp. (°C)	Time (h)	Adduct[d] (% yield)
1	C_3F_7	I	$SiMe_3$	$Ru_3(0.3)$	——	60	3	$\underline{5a}$ (91)
2				Fe (7.0)	——	100	3	(95)
3				$Fe_2(3.0)$	——	60	3	(81)
4				$Fe_3(1.3)$	——	60	3	(71)
5				$Fe_3(1.3)$	Py(4)	60	0.5	(75)
6				$Fe_3(1.3)$	$Et_2NH(4)$	60	0.5	(75)
7				$Fe_3(0.2)^e$	(+)-PEA(5)	60	0.2	(97)
8				$Fe_3(1.3)^e$	EA(40)	25	0.25	(91)
9				Fe (4.0)^e	EA(40)	25	0.5	(92)
10				$Co_2(0.8)^e$	EA(12)	25	0.2	(89)
11	CF_3	I	$SiMe_3$	$Ru_3(0.3)$	——	60	18	$\underline{5b}$ (89)
12	C_8F_{17}	I	$SiMe_3$	$Fe_3(2.0)$	——	60	3	$\underline{5c}$ (90)
13	CF_2CF_2Br	I	$SiMe_3$	$Fe_3(1.3)$	EA(8)	60	1	$\underline{5d}$ (88)
14	$CFClCF_2Cl$	I	$SiMe_3$	$Fe_3(1.3)$	EA(12)	60	0.5	$\underline{5e}$ (93)
15	$CFHCF_2Cl$	I	$SiMe_3$	$Fe_3(1.3)$	EA(12)	60	3	$\underline{5f}$ (89)
16	$CFClCF_2Br$	Br	$SiMe_3$	$Fe_3(1.3)$	EA(12)	60	5	$\underline{5g}$ (77)
17	$CF(CF_2Br)CF_3$	Br	$SiMe_3$	$Fe_3(4.0)$	EA(60)	60	20	$\underline{5h}$ (38)
18	CF_3	I	C_4H_9	$Fe_3(1.3)$	Py(4)	60	3	$\underline{5i}$ (78)
19	C_8F_{17}	I	H	$Ru_3(0.8)^f$	——	60	20	$\underline{5j}$ (75)
20	C_3F_7	I	CH_2OH	$Ru_3(0.3)$	——	60	15	$\underline{5k}$ (85)
21	C_3F_7	I	CH_2CH_2OH	$Fe_3(1.3)$	Py(4)	60	2	$\underline{5l}$ (85)
22	C_3F_7	I	CH_2OAc	$Ru_3(0.3)$	——	60	3	$\underline{5m}$ (88)
23	C_3F_7	I	CH_2OSiMe_3	$Fe_3(1.3)$	——	60	15	$\underline{5n}$ (85)
24	C_3F_7	I	$CH(OEt)_2$	$Fe_3(2.0)$	EA(12)	60	3	$\underline{5o}$ (78)
25	$CFClCF_2Br$	Br	$C(Me)_2CH_2COOMe$	$Fe_3(1.3)$	EA(12)	60	4	$\underline{5p}$ (78)

a All reactions were run with 2.0 mmol of polyfluoroalkyl halide and 2.0 mmol of alkene.
b $Ru_3=Ru_3(CO)_{12}$, $Fe_3=Fe_3(CO)_{12}$, $Fe_2=Fe_2(CO)_9$, $Fe=Fe(CO)_5$, $Co_2=Co_2(CO)_8$. c Py=pyridine, EA= ethanolamine, PEA=α-phenylethylamine. d Determined by GLC. e Ethanol (0.6 ml) was used as solvent. f Reaction was run with excess of ethylene in a stainless steel autoclave.

As a rather special case, the perfluorooctylation of vinyl fluoride in a stainless steel autoclave gave 1:2 adduct ($\underline{9}$) as predominant product accompanied by 1:1 adduct ($\underline{5q}$).

$$C_8F_{17}I \ + \ H_2C=CHF \ \xrightarrow[\substack{\text{ethanolamine}\\ \text{EtOH}\\ 60°C,\ 5\ h}]{Fe_3(CO)_{12}} \ C_8F_{17}CH_2CHFCH_2CHFI \ + \ C_8F_{17}CH_2CHFI \qquad (3)$$

$$\underline{1c} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underline{9}\ (75\ \%) \qquad\qquad \underline{5q}\ (14\ \%)$$

β-Polyfluoroalkylvinyl halides ($\underline{3}$) thus obtained are versatile synthetic building blocks for a variety of organofluorine compounds: Two relevant applications using palladium complex-catalyzed carbonylation are exemplified in equations 4 and 5.

$$C_8F_{17}CH=C(I)SiMe_3 \; + \; CO \; + \; EtOH \xrightarrow[\text{Et}_3\text{N/benzene}]{\text{PdCl}_2(\text{PPh}_3)_2} C_8F_{17}CH=CHCOOEt \qquad (4)$$

$$\underline{3b} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \underline{10} \; (61 \%)$$

$$C_3F_7CH=C(I)CH_2CH_2OH \; + \; CO \xrightarrow[\text{K}_2\text{CO}_3/\text{CH}_3\text{CN}]{\text{PdCl}_2(\text{PPh}_3)_2} C_3F_7CH\text{—}\overset{\text{O}}{\underset{\|}{\bigcirc}}\text{O} \qquad (5)$$

$$\underline{3h} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underline{11} \; (90 \%)$$
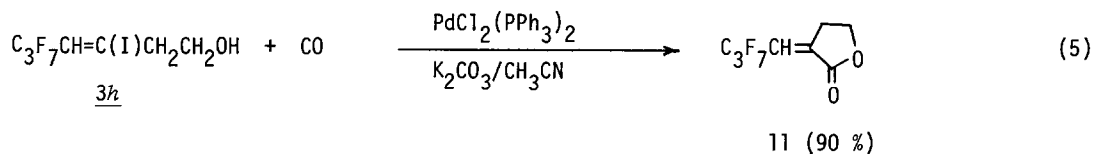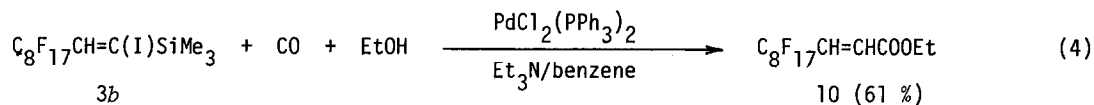
Further studies on the expansion and application of the present reaction are currently underway.

REFERENCES AND NOTES

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9. Satisfactory analytical and spectral data were obtained for all new compounds.
10. (a) H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Lett.*, 5147 (1973); (b) H. Matsumoto, T. Nakano, T. Nakaido, and Y. Nagai, *Chem. Lett.*, 115 (1978).
11. As for the stereochemistry of the adducts with trimethylsilylacetylene, the present reaction gives E-isomer preferencially (E/Z=1.5~>20), which is arising from *trans* addition, which forms a contrast to the results reported for peroxide−promoted reactions where no appreciable selectivities are observed.[6d]
12. Compound $\underline{7}$: ^{1}H NMR (CDCl$_3$:TMS): δ 0.36 (m, 9H), 0.46 (m, 9H). ^{19}F NMR (CDCl$_3$:CFCl$_3$): δ −80.3 (t, J=10 Hz, 3F), −95.9 (m, 2F), −121.4 (m, 2F). IR (neat): 1510, 1345, 1255, 1230, 1215, 1180, 1130, 1110, 980, 850, 770, 745, 700 cm^{-1}. Elemental analysis: Calcd. for $C_{11}H_{18}F_7ISi_2$: C, 28.33; H, 3.89. Found: C, 28.63; H, 3.97.
13. It has turned out that $\underline{7}$ undergoes a quite facile thermal isomerization to $\underline{8}$, e.g., the attempted collection of $\underline{7}$ by preparative GLC (column temperature: 180°C) resulted in the quantitative isolation of $\underline{8}$. Consequently, the apparent exclusive formation of $\underline{8}$ in the peroxide−promoted reaction should be ascribed to the isomerization of the initially formed $\underline{7}$ to $\underline{8}$ under the given reaction conditions rather than the isomerization of a first formed vinyl radical to a silylmethylene radical via intramolecular hydrogen abstrzction, which finally gives $\underline{8}$ by abstracting iodine, as Baum et al. proposed.[6d]