

Synthesis of functionalized long-chain perfluoroalkanes from methyl halodifluoroacetates: a process of difluorocarbene insertion into copper–carbon bonds

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Abstract

Treatment of $\text{XCF}_2\text{CO}_2\text{Me}$ ($\text{X}=\text{Cl}, \text{Br}$) with organic halides in the presence of KF and catalytic amounts of CuI at 80–120 °C for 3–8 h in DMF gave long-chain perfluoroalkylated compounds which are considered to be former by the insertions of CF_2 into carbon–copper bonds.

Introduction

Long-chain perfluoroalkanes ($\text{C}_6\text{--C}_{10}$) containing functional groups are commercial products which, for example, can be used as surfactants and textile chemicals [1, 2]. Currently, they are prepared either by electrochemical fluorination or from the telomerization of tetrafluoroethylene with fluoroalkyl iodides under initiation by ultraviolet light, peroxide, heat or in the presence of copper [3]. Recently, a new method for synthesizing such compounds has been claimed by Burton *et al.* in which a mixture of perfluorinated oligomeric, copper reagents, $\text{CF}_3(\text{CF}_2)_n\text{Cu}$ ($n=1\text{--}13$), has been obtained, starting from CF_2Br_2 and excess of copper powder in DMF at a temperature above 65 °C [4, 5]. During our studies of the trifluoromethylation [6] of alkyl halides **2** with methyl halodifluoroacetates, $\text{XCF}_2\text{CO}_2\text{Me}$ [$\text{X}=\text{Cl}$ (**1a**), Br (**1b**)], in the presence of copper(I) iodide, we also found some perfluorinated oligomers when the quantity of copper(I) iodide used was decreased. Because of advantages, e.g. avoiding the use of tetrafluoroethylene and its telomerization reaction, using cheaper starting materials and mild reaction conditions, it was of interest to investigate our system in greater detail.

Experimental

All boiling points are uncorrected. ^1H NMR spectra were obtained on EM-360A (60 MHz) and XL-200

(200 MHz) NMR spectrometers. Chloroform-*d* was used as a solvent with TMS as the external reference. ^{19}F NMR spectra were obtained on an EM-360L (60 MHz) NMR spectrometer with $\text{CF}_3\text{CO}_2\text{H}$ as the external reference (positive for upfield shifts).

Mass spectra were recorded with a GC-MS 4021 mass spectrometer. All reagents and solvents were purified prior to use. Methyl halodifluoroacetates were prepared according to the method reported in ref. 7.

Syntheses of long-chain perfluoroalkylated compounds $R(\text{CF}_2)_n\text{CF}_3$ (**3**)

These compounds were synthesized from iodobenzene (**2a**), bromobenzene (**2b**), idonaphthalene (**2c**), benzyl bromide (**2d**) or allyl bromide (**2e**) and methyl chlorodifluoroacetate (**1a**) or methyl bromodifluoroacetate (**1b**), respectively. A typical procedure was as follows.

A mixture consisting of 2.89 g (20 mmol) of $\text{Cl-CF}_2\text{CO}_2\text{Me}$ (**1a**), 0.58 g (10 mmol) of dry KF , 0.2 g (1 mmol) CuI , 2.04 g (10 mmol) of $\text{C}_6\text{H}_5\text{I}$ (**2a**) and 30 ml DMF was placed in a 50 ml three-necked round-bottom flask fitted with a magnetic stir bar, Dry Ice condenser and thermometer. The solution was heated to 120 °C for 8 h under a nitrogen atmosphere. The mixture was filtered and poured into ice water. The aqueous layer was extracted three times with ethyl ether (20 ml \times 3). The combined extracts were washed with water (30 ml) and dried over Na_2SO_4 . After the ether had been evaporated off, distillation *in vacuo* gave 2.0 g of $\text{R}_F\text{C}_6\text{H}_5$ and 1.2 g of **2a** (conversion 43%). ^{19}F NMR δ : -66 (s, PhCF_3); -83 (m, $\text{R}_F\text{-CF}_3$); -113 (m, $\text{Ph-CF}_2\text{-R}_F$); -117 (m, $\text{CF}_2\text{-CF}_2\text{-R}_F$) ppm. ^1H NMR δ : 6.6–6.8 (m) ppm.

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It was found that GC-MS gave a clear trace of the oligomers. Each peak had a good response in n of $\text{CF}_3(\text{CF}_2)_n\text{R}$, thus enabling the individual yields of the components to be determined from their corresponding GC peak areas. The total number of moles of oligomer could be determined by ^{19}F NMR spectroscopy through measurement of the total number of moles of CF_3 [Quartz capillary column 25 m \times 0.2 mm, column temperature programed to rise from 40 °C to 220 °C at a rate of 5 °C min

The MS data for the various compounds **3** are listed below.

$\text{C}_6\text{H}_5(\text{CF}_2)_n\text{CF}_3$:

Compound **3a** ($n=0$) m/e : 146 (M^+ , 72.8); 145 ($\text{M}^+ - 1$, 39.2); 127 ($\text{M}^+ - \text{F}$, 95.2); -77 (C_6H_5^+ , 42.5); 69 (CF_3^+ , 100).

Compound **3a** ($n=1$) m/e : 196 (M^+ , 15.7); 197 ($\text{M}^+ + 1$, 1.2); 177 ($\text{M}^+ - \text{F}$, 2.0); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.5); 96 ($\text{M}^+ - \text{C}_2\text{F}_4$, 27.4); 77 (C_6H_5^+ , 30.4).

Compound **3a** ($n=2$) m/e : 246 (M^+ , 14.4); 227 ($\text{M}^+ - \text{F}$, 2.4); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 77 ($\text{M}^+ - \text{C}_3\text{F}_7$, 17.0); 69 (CF_3^+ , 5.7); 50 (CF_2^+ , 7.1).

Compound **3a** ($n=3$) m/e : 296 (M^+ , 10.0); 277 ($\text{M}^+ - \text{F}$, 3.2); 227 ($\text{M}^+ - \text{CF}_3$, 1.3); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 0.9); 77 (C_6H_5^+ , 15.1); 69 (CF_3^+ , 7.2); 50 (CF_2^+ , 5.3).

Compound **3a** ($n=4$) m/e : 346 (M^+ , 6.1); 327 ($\text{M}^+ - \text{F}$, 2.7); 277 ($\text{M}^+ - \text{CF}_3$, 1.1); 169 (C_3F_7^+ , 0.3); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.2); 77 (C_6H_5^+ , 14.6); 69 (CF_3^+ , 7.8); 50 (CF_2^+ , 5.0).

Compound **3a** ($n=5$) m/e : 396 (M^+ , 4.4); 377 ($\text{M}^+ - \text{F}$, 2.4); 177 ($\text{C}_6\text{H}_5\text{CF}_2\text{CF}_2^+$, 0.4); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.4); 77 (C_6H_5^+ , 9.6); 69 (CF_3^+ , 7.5); 50 (CF_2^+ , 2.9).

Compound **3a** ($n=6$) m/e : 446 (M^+ , 6.4); 427 ($\text{M}^+ - \text{F}$, 3.2); 327 ($\text{M}^+ - \text{C}_2\text{F}_5$, 2.9); 177 ($\text{C}_6\text{H}_5\text{CF}_2\text{CF}_2^+$, 0.8); 169 (C_3F_7^+ , 0.7); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.6); 77 (C_6H_5^+ , 7.5); 69 (CF_3^+ , 7.4); 50 (CF_2^+ , 2.2).

Compound **3a** ($n=7$) m/e : 496 (M^+ , 2.7); 477 ($\text{M}^+ - \text{F}$, 2.2); 169 (C_3F_7^+ , 0.7); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 11.7); 77 (C_6H_5^+ , 6.4); 69 (CF_3^+ , 8.5); 50 (CF_2^+ , 1.5).

Compound **3a** ($n=8$) m/e : 546 (M^+ , 1.0); 527 ($\text{M}^+ - \text{F}$, 2.3); 177 ($\text{C}_6\text{H}_5\text{CF}_2\text{CF}_2^+$, 0.5); 169 (C_3F_7^+ , 0.7); 127 ($\text{C}_6\text{H}_5\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.4); 77 (C_6H_5^+ , 7.3); 69 (CF_3^+ , 8.5); 50 (CF_2^+ , 1.5).

1- R_F -naphthalene ($\text{C}_{10}\text{H}_7(\text{CF}_2)_n\text{CF}_3$):

Compound **3c** ($n=0$) m/e : 196 (M^+ , 100); 177 ($\text{M}^+ - \text{F}$, 18.1); 146 ($\text{M}^+ - \text{CF}_2$, 32.9); 127 ($\text{M}^+ - \text{CF}_3$, 6.3); 69 (CF_3^+ , 1.6).

Compound **3c** ($n=1$) m/e : 247 ($\text{M}^+ + 1$, 17.3); 246 (M^+ , 17.0); 177 ($\text{M}^+ - \text{CF}_3$, 100); 127 ($\text{M}^+ - \text{C}_2\text{F}_5$, 10.8); 69 (CF_3^+ , 3.8).

Compound **3c** ($n=2$) m/e : 297 ($\text{M}^+ + 1$, 2.0); 296 (M^+ , 16.1); 246 ($\text{M}^+ - \text{CF}_2$, 38.7); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 127 ($\text{M}^+ - \text{C}_3\text{F}_7$, 8.8); 119 (C_2F_5^+ , 1.4); 69 (CF_3^+ , 1.9).

Compound **3c** ($n=3$) m/e : 346 (M^+ , 3.8); 196 ($\text{M}^+ - \text{C}_3\text{F}_6$, 100); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 25); 169 (C_3F_7^+ , 2.0); 127 ($\text{C}_{10}\text{H}_7^+$, 6.1); 69 (CF_3^+ , 1.5).

Compound **3c** ($n=4$) m/e : 396 (M^+ , 23.8); 196 ($\text{M}^+ - \text{C}_4\text{F}_8$, 2.7); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 127 ($\text{C}_{10}\text{H}_7^+$, 5.7); 69 (CF_3^+ , 8.5).

Compound **3c** ($n=5$) m/e : 446 (M^+ , 17.5); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 127 ($\text{C}_{10}\text{H}_7^+$, 4.4); 119 (C_2F_5^+ , 0.8); 69 (CF_3^+ , 8.3).

Compound **3c** ($n=6$) m/e : 496 (M^+ , 16.4); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 127 ($\text{C}_{10}\text{H}_7^+$, 3.5); 119 (C_2F_5^+ , 1.0); 69 (CF_3^+ , 8.7).

Compound **3c** ($n=7$) m/e : 546 (M^+ , 9.9); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 119 (C_2F_5^+ , 1.1); 69 (CF_3^+ , 9.4).

Compound **3c** ($n=8$) m/e : 596 (M^+ , 5.2); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 127 ($\text{C}_{10}\text{H}_7^+$, 2.6); 119 (C_2F_5^+ , 1.0); 69 (CF_3^+ , 10.4).

Compound **3c** ($n=9$) m/e : 646 (M^+ , 9.5); 227 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 1.3); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 169 (C_3F_7^+ , 0.4); 127 ($\text{C}_{10}\text{H}_7^+$, 2.4); 119 (C_2F_5^+ , 1.4); 69 (CF_3^+ , 8.1).

Compound **3c** ($n=10$) m/e : 696 (M^+ , 1.3); 677 ($\text{M}^+ - \text{F}$, 1.5); 227 ($\text{C}_{10}\text{H}_7\text{CF}_2\text{CF}_2^+$, 1.7); 219 (C_4F_9^+ , 0.6); 177 ($\text{C}_{10}\text{H}_7\text{CF}_2^+$, 100); 169 (C_3F_7^+ , 0.4); 127 ($\text{C}_{10}\text{H}_7^+$, 4.2); 119 (C_2F_5^+ , 1.2); 69 (CF_3^+ , 10.0).

$\text{C}_6\text{H}_5\text{CH}_2(\text{CF}_2)_n\text{CF}_3$:

Compound **3d** ($n=0$) m/e : 160 (M^+ , 100); 141 ($\text{M}^+ - \text{F}$, 20.4); 140 ($\text{M}^+ - \text{HF}$, 6.3); 91 ($\text{M}^+ - \text{CF}_3$, 100); 90 ($\text{M}^+ - \text{CF}_3\text{H}$, 5.9); 83 ($\text{M}^+ - \text{C}_6\text{H}_5$, 7.6); 77 (C_6H_5^+ , 5.9); 69 (CF_3^+ , 16.8).

Compound **3d** ($n=1$) m/e : 210 (M^+ , 9.5); 160 ($\text{M}^+ - \text{CF}_2$, 100); 141 ($\text{M}^+ - \text{CF}_3$, 26.6); 140 ($\text{M}^+ - \text{CF}_3\text{H}$, 9.0); 119 (C_2F_5^+ , 6.8); 109 ($\text{M}^+ - \text{C}_2\text{F}_4\text{H}$, 25.1); 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$, 100); 77 (C_6H_5^+ , 9.4); 69 (CF_3^+ , 34.9); 50 (CF_2^+ , 37.2).

Compound **3d** ($n=2$) m/e : 260 (M^+ , 10.3); 210 ($\text{M}^+ - \text{CF}_2$, 11.3); 160 ($\text{M}^+ - \text{C}_2\text{F}_4$, 2.9); 169 (C_3F_7^+ , 2.7); 141 ($\text{M}^+ - \text{C}_2\text{F}_5$, 44.3); 119 (C_2F_5^+ , 15.5); 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$, 3.0); 69 (CF_3^+ , 100); 50 (CF_2^+ , 12.2).

Compound **3d** ($n=3$) m/e : 310 (M^+ , 4.9); 260 ($\text{M}^+ - \text{CF}_2$, 7.8); 210 ($\text{M}^+ - \text{C}_2\text{F}_4$, 2.3); 169 (C_3F_7^+ , 10.1); 119 (C_2F_5^+ , 28.6); 69 (CF_3^+ , 100); 50 (CF_2^+ , 8.8).

Compound **3d** ($n=4$) m/e : 361 ($\text{M}^+ + 1$, 5.2); 360 (M^+ , 5.6); 259 ($\text{M}^+ - \text{C}_2\text{F}_4\text{H}$, 1.1); 141 ($\text{C}_6\text{H}_5\text{CH}_2\text{CF}_2^+$, 2.4); 119 (C_2F_5^+ , 1.8); 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$, 100); 69 (CF_3^+ , 9.8); 50 (CF_2^+ , 8.6).

Compound **3d** ($n=5$) m/e : 411 ($\text{M}^+ + 1$, 1.37); 141 ($\text{C}_6\text{H}_5\text{CH}_2\text{CF}_2^+$, 1.3); 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$, 100); 77 (C_6H_5^+ , 8.0); 69 (CF_3^+ , 3.0); 50 (CF_2^+ , 35.1).



Compound **3e** ($n=0$) m/e : 110 (M^+ , 16.38); 91 ($\text{M}^+ - \text{F}$, 6.38); 90 ($\text{M}^+ - \text{HF}$, 2.90); 71 ($\text{M}^+ - \text{HF} - \text{F}$, 3.96); 69 (CF_3^+ , 17.04); 41 ($\text{M}^+ - \text{CF}_3$, 100).

Compound **3e** ($n=1$) m/e : 160 (M^+ , 10.5); 139 ($\text{M}^+ - \text{HF} - \text{H}$, 7.0); 119 (C_2F_5^+ , 4.8); 110 ($\text{M}^+ - \text{CF}_2$, 89.5); 69 (CF_3^+ , 66.3); 50 (CF_2^+ , 51.7); 41 (C_3H_5^+ , 100).

Compound **3e** ($n=2$) m/e : 210 (M^+ , 3.0); 189 ($\text{M}^+ - \text{HF} - \text{H}$, 1.5); 160 ($\text{M}^+ - \text{CF}_2$, 10.5); 119 (C_2F_5^+ , 4.8); 110 ($\text{M}^+ - \text{C}_2\text{F}_4$, 56.8); 91 ($\text{M}^+ - \text{C}_2\text{F}_5$, 56.8); 69 (CF_3^+ , 66.3); 50 (CF_2^+ , 51.7); 41 (C_3H_5^+ , 100).

Compound **3e** ($n=3$) m/e : 260 (M^+ , 1.4); 160 ($\text{M}^+ - \text{C}_2\text{F}_4$, 10.5); 119 (C_2F_5^+ , 3.7); 110 ($\text{M}^+ - \text{C}_3\text{F}_6$, 30.1); 91 ($\text{M}^+ - \text{C}_3\text{F}_7$, 40.3); 69 (CF_3^+ , 65.2); 50 (CF_2^+ , 31.6); 41 (C_3H_5^+ , 100).

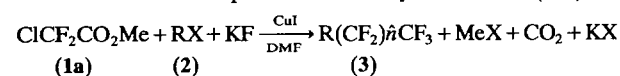
Results and discussion

As mentioned above the treatment of methyl chlorodifluoroacetate (**1a**) with organic halides in the presence of 1 equiv. of KF and CuI at 100 °C to 120 °C for 7–8 h in DMF gave the corresponding trifluoromethylated derivatives in moderate to high yield [6]. However, decreasing the quantity of copper(I) iodide from equivalent amounts to 5% resulted in the same reaction, e.g. **1a** with phenyl iodide (**2a**), phenyl bromide (**2b**), 1-iodonaphthalene (**2c**), benzyl bromide (**2d**) and allyl bromide (**2e**), giving the corresponding perfluoroalkyl products in addition to the normal substituted ones (see Table 1).

As mentioned in our previous work [6], compound **1b** reacted readily with **2** when heated at 80 °C for 3 h to give the same oligomers. The results are listed in Table 2.

The results listed in Tables 1 and 2 show that both the conversion of **2** and the yield of **3** in the reactions of **2** with **1a** or **1b** are comparable despite the different

TABLE 1. Reaction of **1a** with **2** and KF (**1a/2/KF**=1:2:1) at 120 °C for 8 h in the presence of catalytic amounts (5%) of CuI

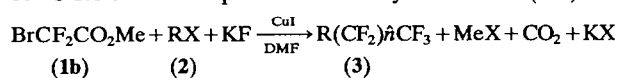


(a) $\text{RX} = \text{C}_6\text{H}_5\text{I}$; (b) $\text{RX} = \text{C}_6\text{H}_5\text{Br}$; (c) $\text{RX} = 1\text{-iodonaphthalene}$;
(d) $\text{RX} = \text{C}_6\text{H}_5\text{CH}_2\text{Br}$; (e) $\text{RX} = \text{CH}_2=\text{CHCH}_2\text{Br}$

Entry	2	Conversion of 2 (%)	Yield of 3 (%) ^a
1	2a	43	83
2	2b	24	71
3	2c	49	86
4	2d	28	72
5	2e	27	70

^aBased on the conversion of **2** [3].

TABLE 2. Reaction of **1b** with **2** and KF (**1b/2/KF**=2:1:1) at 80 °C for 3 h in the presence of catalytic amounts (5%) of CuI



Entry	2	Conversion of 2 (%)	Yield of 3 (%) ^a
1	2a	37	84
2	2b	26	73
3	2c	39	85
4	2d	28	74
5	2e	29	70

^aBased on conversion of **2**.

TABLE 3. Product distribution of $\text{R}(\text{CF}_2)_n\text{CF}_3^a$

Entry n	1 3a^b	2 3a^c	3 3b^b	4 3c^b	5 3c^c	6 3d^b	7 3e^b
0	48.2 (88) ^d	35.0 (81)	42.6 (60)	59.6 (94)	27.0 (84.2)	54.9 (84)	85.7 (82)
1	27.4	17.5	19.2	29.3		15.3	10.1
2	12.3	17.2	15.7	8.7		8.8	2.9
3	3.7	15.7	9.3	2.3		7.8	1.3
4	2.6	11.0	5.2		12.1	6.7	
5	1.7	10.5	3.6		13.4		
6	1.6	10.0	2.1		14.5	6.3	
7	1.2	7.6	1.7		12.7		
8	0.8	6.5			9.6		
9					5.4		
10					3.8		

^aAll compositions were determined by GC methods.

^b $\text{ClCF}_2\text{CO}_2\text{Me}$.

^c $\text{BrCF}_2\text{CO}_2\text{Me}$.

^dNumbers in brackets indicate the yield of trifluoromethylated compounds obtained in the presence of 1 equiv. CuI.

reaction temperatures and times employed. Table 3 lists the product distribution of perfluoroalkylated oligomers and indicates that decreasing amounts of CuI play an important role in extending the carbon-carbon chain. For comparison, the yield of **3** from the same reaction but with 1 equiv. CuI are listed in brackets in Table 3.

Comparing the product distribution of **3** from **1a** or from **1b** (entries 1 and 2, 4 and 5 in Table 3) seems to suggest that **1b** gives longer chain products than **1a**. In the literature [8], it was reported that suppression of the oligomerization can be accomplished by the presence of KF or the presence of an equivalent volume of HMPA (to DMF). In order to test the effects of KF and HMPA, experiments using a KF/RX molar ratio of 4:1 or an additional equivalent volume of HMPA with **1b** were carried out separately. Little change in the ratio of oligomer to normal trifluoromethylated products was found in the presence of excess KF and an equivalent amount of HMPA (see Table 4). Hence,

TABLE 4. The influence of KF and HMPA on the perfluoroalkylation of **2c** with **1b** at 80 °C for 3 h in the presence of 5% CuI

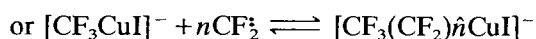
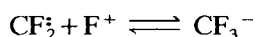
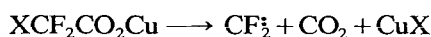
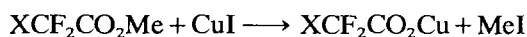
Entry	KF/2c	HMPA/2c	RCF ₃ formed (%)	R(CF ₂) _n CF ₃ (n > 0) formed (%)	R(CF ₂) _n CF ₃ /RCF ₃
1	1:1	0	27	73	2.8
2	4:1	0	35	65	1.8
3	4:1	1:1	21	79	3.8

in comparison to CuI as a donor, KF and HMPA play a less important role in the system studied.

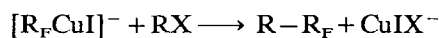
The mechanism of the formation of long-chain products may be similar to that for the simple trifluoromethylation of organic halides. Thus, nucleophilic attack of copper iodide on **1** gives copper halodifluoroacetates, which decompose in a concerted process to give difluorocarbene. In support of this mechanism, the following points should be noted.

(i) The difluorocarbene formed and added fluoride ion are in equilibrium with trifluoromethide ion. The equilibrium is readily shifted to CF₃⁻ in the presence of copper iodide, to give [CF₃CuI]⁻ which reacts with alkyl halides to yield trifluoromethylated products.

(ii) Difluorocarbene can also insert into the Cu-C bond of perfluoroalkyl copper*complexes to afford the corresponding perfluoroalkyl copper species with a longer carbon chain. Chain termination of perfluoroalkyl copper species with alkyl halides affords the final products:



*After submission of this manuscript, Z.-Y. Yang, D.M. Wiemers and D.J. Burton reported the multiple insertion of difluorocarbene into a carbon-copper bond [*J. Am. Chem. Soc.*, 114 (1992) 4402].



Decreasing the amount of copper(I) iodide used results in an increase in the difluorocarbene concentration, thus allowing more difluorocarbene to react with perfluoroalkyl copper complexes and hence generate longer perfluoroalkyl copper complexes.

The different behaviour between **1a** and **1b** may be due to the more ready decomposition of **1b** relative to that of **1a**. Thus, the concentration of [•]CF₂ generated from **1b** is higher than that from **1a** resulting in longer chain products from **1b**.

Acknowledgement

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