Journal of Fluorine Chemistry 130 (2009) 254–258

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# The preparation of perfluoroalkenyl allenes (trienes) and pentafluorophenyl allenes

Donald J. Burton *, Greg A. Hartgraves

*Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA*

ARTICLE INFO

*Article history:*
Received 22 October 2008
Received in revised form 30 October 2008
Accepted 31 October 2008
Available online 11 November 2008

*Keywords:*
Perfluoroalkenyl allenes
Pentafluorophenyl allenes
Perfluoroalkenylcopper reagents
Pentafluorophenylcopper reagents
Organometallics

ABSTRACT

Trifluorovinyl- and (*Z*)-pentafluoropropenylcopper reagents readily react with propargylic halides or tosylates. With primary propargylic substrates, the major product is the alkyne. With secondary propargylic substrates, mixtures of alkyne/allene are obtained; the allene product is the major product. With tertiary propargylic substrates, the allene is regiospecifically and stereospecifically formed in good isolated yields. With pentafluorophenyl copper and primary propargylic substrates, the major product is pentafluorobenzene. With secondary and tertiary propargylic substrates, the allene is regiospecifically formed in good isolated yields.



## 1. Introduction

Recent reports have recently demonstrated that perfluoroalkyl allenes [1] and perfluoroalkylene diallenes [2] can be effectively prepared from perfluoroalkyl- and bis perfluoroalkylene copper reagents and propargyl halides or tosylates, as illustrated in Eqs. (1) and (2). The reaction is applicable to primary, secondary and tertiary propargylic halides or tosylates. Subsequent work with difluoromethylcadmium [3] and

$$R_FCu + HC{\equiv}CCR^1R^2X \xrightarrow[\text{or DMSO}]{\text{DMF}} R_FCH{=}C{=}CR^1R^2 \quad \text{RT, } 0^\circ C \text{ to RT} \tag{1}$$

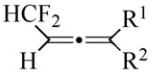
$R_F = CF_3, C_3F_7, C_6F_{13}, C_8F_{17}$; X = OTs or Cl; $R^1 = H, CH_3$; $R^2 = H, CH_3$

$$Cu\text{-}R_F\text{-}Cu + 2\ HC{\equiv}CCH_2Br \xrightarrow[15\text{-}20^\circ C]{\text{DMSO}} R_F(CH{=}C{=}CH_2)_2 \tag{2}$$

$R_F = C_6F_{12}, C_8F_{16}$

difluoromethylcopper [4] reagents and propargylic halides and tosylates afforded the corresponding difluoromethyl allenes (Eq. (3)). The difluoromethylcopper

$$\begin{matrix} HCF_2CdX \\ \text{or} \\ HCF_2Cu \end{matrix} + HC{\equiv}CCR^1R^2Y \xrightarrow[RT]{DMF} \begin{matrix} Y = Cl \text{ or } OTs \\ R^1 = H, CH_3 \\ R^2 = H, CH_3 \end{matrix} \quad \text{(3)}$$




reagent is generally more reactive and exhibits superior regioselectivity than the difluoromethylcadmium reagent. Similar to the perfluoroalkylcopper reagents, allene formation was the major or exclusive product. Thus, we were interested to determine if pentafluorophenylcopper and perfluoroalkenylcopper reagents were sufficiently reactive to accomplish a similar transformation and afford a useful preparative route to pentafluorophenyl substituted allenes and perfluoroalkenyl substituted allenes (trienes).

## 2. Results and discussion

### 2.1. Preparation of the perfluoroalkenyl and pentafluorophenylcopper reagents

Trifluorovinylcopper and (*Z*)-pentafluoropropenylcopper regents were selected as model alkenyl substrates. These reagents were generated *in situ via* the reported exchange reaction [5–7]

* Corresponding author. Tel.: +1 319 335 1363; fax: +1 319 335 1270.
*E-mail address:* donald-burton@uiowa.edu (D.J. Burton).

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.10.008

(Eq. (4)). Similarly, transmetallation of the

$$F_2C{=}CFBr \xrightarrow[DMF]{Zn} [F_2C{=}CFZnBr] \xrightarrow{Cu(I)Cl} [F_2C{=}CFCu] + ZnBrX \quad (4)$$

pentafluorophenylcadmium reagent (prepared from bromopentafluorobenzene and acid-washed cadmium powder in DMF) with Cu(I)Cl afforded *in situ* the pentafluorophenylcopper reagent [8–10] (Eq. (5)).

$$C_6F_5Br + Cd \xrightarrow[RT]{DMF} [C_6F_5CdBr] \xrightarrow{Cu(I)Cl} [C_6F_5Cu] \quad (5)$$

### 2.2. Reaction of perfluoroalkenyl- and pentafluorophenylcopper reagents with propargylic substrates

Trifluorovinyl and (*Z*)-pentafluoropropenylcopper reagents reacted with propargylic halides and tosylates to form the corresponding allene/alkyne product (Eq. (6)) in good to excellent yields. The regiochemistry is dependent on the steric environment

$$R_FCF{=}CFZnX + HC{\equiv}CCR^1R^2X \xrightarrow[DMF]{Cu(I)X} \underset{\mathbf{1}}{R_FCF{=}CFCR^1R^2C{\equiv}CH} + \underset{\mathbf{2}}{R_FCF{=}CFCH{=}C{=}CR^1R^2} \quad (6)$$

$R_F$ = F, (*Z*)-$CF_3CF{=}CF$

of the propargylic halide or tosylate (Table 1). For example, trifluorovinylcopper reacts with 3-tosyl-1-propyne (entry 1) to afford a mixture (62%) of **1** and **2** containing 4,5,5-trifluoropent-4-ene-1-yne as the major product. Similar selectivity is observed with (*Z*)-pentafluoropropenylcopper and 3-tosyl-1-propyne (entry 5).

With an α-alkyl substituted propargylic substrate, steric hindrance at the α-carbon increases (relative to $HC{\equiv}CCH_2OTs$); as a result the regioselectivity favors the formation of **2** (allene). For example, trifluorovinylcopper and (*Z*)-pentafluoropropenylcopper reacts with 3-tosyl-1-butyne (entries 2 and 6) to afford a 64–67% yield of **2/1** in ~75/25 ratio; respectively (Eq. (7)). With increased steric

$$\mathbf{2/1}\ (75/25) \xleftarrow[DMF,\ 64\%]{F_2C{=}CFCu} HC{\equiv}CCH(CH_3)OTs \xrightarrow[DMF,\ 67\%]{(Z)CF_3CF{=}CFCu} \mathbf{2/1}\ (77/23) \quad (7)$$

hindrance, regiospecific formation of perfluorovinyl substituted allenes is observed (entries 3, 4, 7, 8) (Eq. (8)). With the (*Z*)-pentafluoropropenylcopper reagent, complete retention of stereochemistry is observed (as confirmed by $^{19}F$ NMR analysis, $J_{FF\ (trans)}$ = 127–134 Hz).

$$R_FCF{=}CFZnX + HC{\equiv}CCR^1R^2X \xrightarrow[DMF]{Cu(I)Cl} \underset{100\%\quad \mathbf{2}}{R_FCF{=}CFCH{=}C{=}CR^1R^2} \quad (8)$$

$R_F$ = F, (*Z*)-$CF_3CF{=}CF$; $R^1 = R^2 = CH_3$; $R^1R^2$ = cyclohexyl; X = Cl

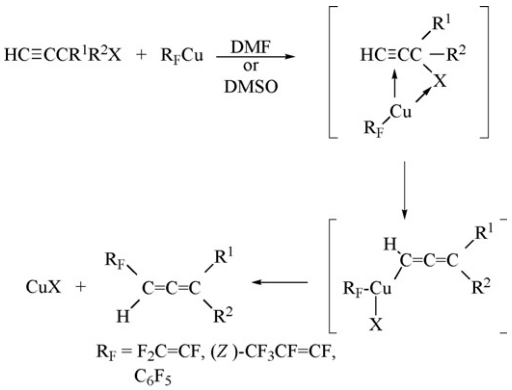
The pentafluorophenylcopper reagent was reacted with the same series of propargylic substrates. With 3-tosyl-1-propyne, a low yield (10%) of a mixture containing 32% 1-(pentafluorophenyl)-1,2-propadiene, 21% 3-1(pentafluorophenyl)-1-propyne and 47% $C_6F_5H$ was obtained. The pentafluorobenzene was formed *via* an exchange reaction between the arylcopper reagent and the acidic alkynyl hydrogen. Similarly, $C_6F_5Cu$ and 1-chloro-1-ethynylcyclohexane afforded only a 20% isolated yield of a mixture containing 60% 3-(pentafluorophenyl)-1-pentamethylene-1,2-propadiene and 40% $C_6F_5H$. However, with other secondary and tertiary propargylic chlorides or tosylates, the corresponding allenes are obtained regiospecifically (Eqs. (9) and (10)).

$$C_6F_5Cu + HC{\equiv}CCH(CH_3)OTs \xrightarrow[RT,\ 61\%]{DMF} \begin{array}{c} C_6F_5 \quad\quad H \\ \diagdown \quad / \\ C{=}C{=}C \\ / \quad \diagdown \\ H \quad\quad CH_3 \end{array} \quad (9)$$

$$C_6F_5Cu + HC{\equiv}CC(CH_3)_2Cl \xrightarrow[RT,\ 61\%]{DMF} \begin{array}{c} C_6F_5 \quad\quad CH_3 \\ \diagdown \quad / \\ C{=}C{=}C \\ / \quad \diagdown \\ H \quad\quad CH_3 \end{array} \quad (10)$$

### 2.3. Mechanism

In the reaction between diorganocuprates with propargylic halides, Landor and coworkers [11] proposed an initial complexation of the copper reagent with the triple bond to form a pi-complex. Similar complexation of organocopper reagents and alkynes has also been suggested by Pasto et al. [12]. MacNeil has also reported pi-complex formation in the addition of pentafluorophenylcopper reagents to perfluoro-2-butyne [13]. Thus, we propose that the formation of fluorinated allenes from perfluoroalkenyl- or pentafluorophenylcopper reagents and propargylic halides or tosylates involves an initial complexation of the copper reagent with the triple bond and leaving group to form a pi-complex, as illustrated in Scheme 1.




**Scheme 1.** Mechanism for the reaction of perfluoroalkenyl and perfluorophenylcopper reagents and propargylic substrates.

Complexation of the fluorinated copper reagent with the alkyne would be expected to be stronger for the fluorinated copper reagents than for a hydrocarbon copper reagent. The perfluoroalkenyl and pentafluorophenyl groups are strongly electron-withdrawing and as a result the copper atom of the fluorinated copper reagent is more electron deficient than the copper atom of a hydrocarbon copper reagent. Thus, the greater electron deficiency of the copper atom of the perfluoroalkenyl- and pentafluorophenylcopper reagent results in a stronger complex to the electron-rich alkyne. After initial complexation, oxidative addition occurs to form a copper (III) intermediate, which subsequently undergoes a reductive elimination to give the fluorinated allene and regenerates the copper (I) salt. The regeneration of the copper (I) salt allows for a catalytic process to occur between the perfluoroalkenylzinc and the pentafluorophenylcadmium reagents and propargylic halides or tosylates. The regiospecificity observed in the formation of the allenes is due to the complexation of the copper reagent and the proximity of the copper atom to the γ-carbon as a result of the complexation. In addition, the γ-carbon is always the least hindered site when the propargylic halide or tosylate is a terminal alkyne. Thus, substitution at the γ-carbon by a perfluoroalkenyl or pentafluorophenyl group occurs by oxidative addition at the γ-carbon to form a copper (III) intermediate; reductive elimination of the Cu(I) halide or tosylate affords the fluorinated allene.

## 3. Experimental

### 3.1. General experimental procedures

The $^{19}$F NMR spectra were recorded on a JEOL FX90Q Spectrometer operated at 83.81 MHz. Chemical shifts have been reported relative to $CFCl_3$ and were generally determined in $CDCl_3$ solvent (unless otherwise noted). Quantitative measurements were carried out by integration relative to internal benzotrifluoride. Routine $^1$H NMR spectra were recorded on a JEOL FX90Q Spectrometer operated at 89.09 MHz. Typically $CDCl_3$ was used as the NMR lock solvent and chemical shifts are reported in ppm relative to internal TMS. The $^{13}$C NMR spectra were recorded on a Bruker WM 360X Spectrometer operated at 90.56 MHz. The spectra were run unlocked with neat samples and an internal TMS capillary. Mass spectra of liquid samples were recorded on a Hewlett-Packard 5985 GC–MS system operated at 30 eV in the electron impact mode. The GC contained an 8 ft. × 1/8 in. glass column packed with 5% ov101 Chromosorb P.

Infrared spectra were recorded on a Mattson Cygnus 25 FTIR Spectrometer as solutions in $CCl_4$. Analytical GLPC were performed on a Hewlett-Packard model 5890 equipped with a TCD. Capillary GLPC was performed using a FID. All bp were determined during fractional distillation and are incorrected. The propargyl tosylates and halo-substituted alkynes were prepared by the procedure reported by Brandsma and VerKuijsse [13] from the corresponding alcohols.

**Table 1**
Isolated yields and isomeric ratios for the reaction of perfluorovinylcopper and (*Z*)-pentafluoropropenylcopper with propargylic substrates $R_FCF{=}CFZnX + HC{\equiv}CCR^1R^2X \xrightarrow[DMF]{Cu(I)Cl}$ **1** + **2**.

| Entry | $R_F$ | $R^1$ | $R^2$ | X | Yield (%) | **1** | **2** |
|---|---|---|---|---|---|---|---|
| 1 | F | H | H | OTs | 62 | 94 | 6 |
| 2 | F | H | $CH_3$ | OTs | 64 | 25 | 75 |
| 3 | F | $CH_3$ | $CH_3$ | Cl | 59 | 0 | 100 |
| 4 | F | $-(CH_2)_5-$ | | Cl | 75 | 0 | 100 |
| 5 | $CF_3$ | H | H | OTs | 60 | 87 | 13 |
| 6 | $CF_3$ | H | $CH_3$ | OTs | 67 | 23 | 77 |
| 7 | $CF_3$ | $CH_3$ | $CH_3$ | Cl | 79 | 0 | 100 |
| 8 | $CF_3$ | $-(CH_2)_5-$ | | Cl | 67 | 0 | 100 |

### 3.2. Preparation of the trifluorovinyl and (*Z*)-pentafluoropropenylzinc reagents

A 100-ml three-neck flask equipped with a septum, magnetic stir bar and dry ice/isopropyl alcohol condenser with a nitrogen inlet was charged with 6.5 g (100 mmol) of acid-washed zinc powder and 50 ml of dry DMF. The appropriate vinyliodide, trifluorovinyliodide [14] or (*Z*)-pentafluoropropenyliodide [15] (50 mmol) was then added dropwise to the solution. After approximately one-third of the vinyliodide had been added, an exotherm occurred, which was controlled by the rate of addition of the remaining vinyliodide. After the addition of the vinyliodide was completed, the reaction mixture was stirred at room temperature for 2 h and the precipitate allowed to settle. Aliquots of the desired quantity of trifluorovinyl and (*Z*)-pentafluoropropenylzinc reagents were syringed into a reaction flask. Typical $^{19}$F NMR yields of trifluorovinyl and (*Z*)-pentafluoropropenylzinc reagents were 90–95%.

#### 3.2.1. Preparation of 4,5,5-trifluoropent-4-ene-1-yne

A 34-ml aliquot of a 1.76-M trifluorovinylzinc reagent (60 mmol) in DMF was syringed into a three-neck 100 ml flask equipped with a septum, magnetic stir bar and nitrogen inlet. The solution was cooled in a dry ice/isopropyl alcohol bath to −30 °C and then 10.5 g (50 mmol) of 3-tosyl-1-propyne was added, followed by the addition of 0.9 g Cu(I)Br (12 mol%). The reaction mixture was slowly warmed to room temperature over 3 h and stirred at room temperature for two additional hours. The nitrogen inlet was replaced with a flash distillation head equipped with a 100-ml receiving flask. The receiver was cooled with liquid $N_2$ and the product(s) distilled under vacuum at 80 °C to near dryness. The flash distillate was poured into a separatory funnel which contained an equal volume of ice water, the organic layer separated, washed with (2 × 100 ml) $H_2O$ and dried over 4 Å molecular sieves. The crude product was decanted from the molecular sieves and distilled through a 15-cm vigreaux column at 20–21 °C/118 mm Hg to give 3.69 g (62% of a mixture, which contained 94% of 4,5,5-trifluoropent-4-ene-1-yne and 6% of 4,5,5-trifluoro-1,2,4-pentatriene (as determined by GLPC analysis): $^{19}$F NMR: ($F_2C{=}CFCH_2{-}C{\equiv}CH$): ($\delta$ −103.9 (ddt, $^2J_{FF}$ = 83.0 Hz, $^3J_{FF}$ = 34.3 Hz, $^4J_{FH}$ = 2.5 Hz), −122.6 (ddt, $^3J_{FF}$ = 115.6 Hz, $^2J_{FF}$ = 83.0 Hz, $^4J_{FH}$ = 3.9 Hz), −174.4 (ddt, $^3J_{FF}$ = 115.6 Hz, $^3J_{FF}$ = 34.3 Hz, $^3J_{FH}$ = 19.1 Hz); $^1$H NMR: $\delta$ 2.09 (t, $^4J_{FH}$ = 2.7 Hz), 3.23 (dddd, $^3J_{FH}$ = 19.1 Hz, $^4J_{FH}$ = 3.9 Hz, $^4J_{FH}$ = 2.5 Hz,

$^4J_{HH}$ = 2.7 Hz); $^{13}$C NMR (Neat): δ 152.6 (ddd, $^1J_{CF}$ = 285.7 Hz, $^1J_{CF}$ = 274.1 Hz, $^2J_{CF}$ = 45.5 Hz), 124.5 (ddd, $^1J_{CF}$ = 235.8 Hz, $^2J_{CF}$ = 53.0 Hz, $^2J_{CF}$ = 18.2 Hz), 75.2 (s), 69.1 (s), 15.6 (d, $^2J_{CF}$ = 23.7 Hz). GC–MS, *m/z* (relative intensity): 120 (100.0), 119 (51.9). IR: 3317 (≡C) (s), 1804 ($F_2C$=CF) (s), 1765 ($F_2C$=CF) (m), 1301 (vs), 1216 (s), 1096 (s).

### 3.2.2. Reaction of trifluorovinylcopper with 3-tosyl-1-butyne

Similar to Section 3.2.1, a 30-ml aliquot of a 1.45-M trifluorovinylzinc reagent (43 mmol), 6.17 g (43 mmol) of Cu(I)Br and 10.1 g (45 mmol) of 3-tosyl-1-butyne gave 3.67 g (64%) of a mixture after distillation. The mixture (94% GLPC purity) contained 32% of 3-methyl-4,5,5-trifluoropent-4-ene-1-yne and 68% of 5,6,6-trifluoro-2,3,5-hexatriene (as determined by GLPC analysis), $^{19}$F NMR: ($F_2$=CFCH($CH_3$)C≡CH): δ −105.1 (dd, $^2J_{FF}$ = 84.2 Hz, $^3J_{FF}$ = 34.1 Hz), −122.3 (ddd, $^3J_{FF}$ = 114.7 Hz, $^2J_{FF}$ = 84.2 Hz, $^4J_{FH}$ = 3.1 Hz), −182.7 (ddd, $^3J_{FF}$ = 114.7 Hz, $^3J_{FF}$ = 34.1 Hz, $^3J_{FH}$ = 26.8 Hz); $^1$H NMR: δ 1.44 (d, $^3J_{HH}$ = 7.2 Hz), 2.16 (d, $^4J_{HH}$ = 2.4 Hz), 3.50 (m); $^{13}$C NMR (Neat): δ 153.6 (ddd, $^1J_{CF}$ = 289.6 Hz, $^1J_{CF}$ = 280.5 Hz, $^2J_{CF}$ = 46.0 Hz), 128.2 (ddd, $^1J_{CF}$ = 239.5 Hz, $^2J_{CF}$ = 50.7 Hz, $^2J_{CF}$ = 16.1 Hz), 80.2 (d, $^3J_{CF}$ = 3.0 Hz), 68.9 (s), 23.4 (d, $^2J_{CF}$ = 23.2 Hz), 16.6 (s). GC–MS, *m/z* (relative intensity): 134 (19.4), 119 (74.8), 69 (100.0). $^{19}$F NMR: ($F_2C$=CFCH=C=$CHCH_3$): δ −103.0 (dddd, $^2J_{FF}$ = 73.5 Hz, $^3J_{FF}$ = 30.0 Hz, $^4J_{FH}$ = 2 Hz, $^6J_{FH}$ = 2 Hz), −121.5 (dddd, $^3J_{FF}$ = 109.2 Hz, $^2J_{FF}$ = 73.5 Hz, $^4J_{FH}$ = 3.1 Hz, $^6J_{FH}$ = 3.1 Hz), −177.3 (ddd, $^3J_{FF}$ = 109.2 Hz, $^3J_{FF}$ = 30.0 Hz, $^3J_{FH}$ = 22.7 Hz); $^1$H NMR: δ 1.74 (dd, $^3J_{HH}$ = 7.0 Hz, $^5J_{HH}$ = 3.5 Hz), 5.56 (m), 5.80 (m); $^{13}$C NMR (Neat): δ 150.4 (ddd, $^1J_{CF}$ = 286.6 Hz, $^1J_{CF}$ = 275.1 Hz, $^2J_{CF}$ = 46.2 Hz), 123.6 (ddd, $^1J_{CF}$ = 229.6 Hz, $^2J_{CF}$ = 49.3 Hz, $^2J_{CF}$ = 19.0 Hz), 203.8 (dd, $^3J_{CF}$ = 10.4 Hz, $^4J_{CF}$ = 3.8 Hz), 91.5 (s), 80.6 (dd, $^2J_{CF}$ = 22.6 Hz, $^3J_{CF}$ = 3.4 Hz), 12.4 (s), GC–MS, *m/z* (relative intensity): 134 (100.0), 133 (41.7). IR: Mixture of $F_2C$=CFCH=C=$CHCH_3$ and $F_2C$=CFCH($CH_3$)C≡CH): 3313 (≡CH)(m), 2337 (C≡C) (w), 1830 ($F_2C$=CF) (w), 1796 ($F_2C$=CF) (vs), 1306 (s), (1283 (vs), 1267 (s), 1081 (vs).

### 3.2.3. Preparation of 2-methyl-5,6,6-trifluoro-2,3,5-hexatriene

Similar to Section 3.2.1, a 39-ml aliquot of a 1.55-M trifluorovinylzinc reagent (60 mmol), 7.9 g Cu(I)Br (55 mmol) and 4.6 g (45 mmol) of 3-chloro-3-methyl-1-butyne gave 3.96 g (59%) of 2-methyl-5,6,6-trifluoro-2,3,5-hexatriene after flash distillation (97% GLPC purity). $^{19}$F NMR: δ −103.6 (ddd, $^2J_{FF}$ = 75.7 Hz, $^3J_{FF}$ = 29.3 Hz, $^4J_{FH}$ = 1.7 Hz), −122.2 (ddd, $^3J_{FF}$ = 112.3 Hz, $^2J_{FF}$ = 75.7 Hz, $^4J_{FH}$ = 3.9 Hz), −176.9 (ddd, $^3J_{FF}$ = 112.3 Hz, $^3J_{FF}$ = 29.3 Hz, $^3J_{FH}$ = 23.3 Hz); $^1$H NMR: δ 1.77 (d, $^5J_{FH}$ = 3.0 Hz), 5.56 (m); $^{13}$C NMR (Neat): δ 151.9 (ddd, $^1J_{CF}$ = 289.4 Hz, $^1J_{CF}$ = 280.4 Hz, $^2J_{CF}$ = 46.7 Hz), 124.0 (ddd, $^1J_{CF}$ = 229.6 Hz, $^2J_{CF}$ = 48.6 Hz, $^2J_{CF}$ = 18.4 Hz), 201.0 (d, $^3J_{CF}$ = 10.4 Hz), 101.6 (s), 79.1 (d, $^2J_{CF}$ = 23.0 Hz), 18.6 (s). GC–MS, *m/z* (relative intensity): 148 (100.0), 133 (38.8). IR: 1964 (C=C=C) (w), 1763 ($F_2C$=CF) (s), 1274 (vs), 1086 (vs).

### 3.2.4. Preparation of 1-pentamethylene-4,5,5-trifluoro-1,2,4-pentatriene

Similar to Section 3.2.1, a 46-ml aliquot of a 1.42-M trifluorovinylzinc reagent, 0.6 g Cu(I)Cl (10 mol%) and 8.5 g (60 mmols) of 1-chloro-1-ethynylcyclohexane gave 8.5 g (75%) of 1-pentamethylene-4,5,5-trifluoro-1,2,4-pentatriene after distillation, bp 34–35 °C/0.5 mm Hg (GLPC purity = 91%). $^{19}$F NMR: δ −103.8 (dd, $^2J_{FF}$ = 75.7 Hz, $^3J_{FF}$ = 29.7 Hz), −122.4 (dd, $^3J_{FF}$ = 109.5 Hz, $^2J_{FF}$ = 75.7 Hz), −176.8 (ddd, $^3J_{FF}$ = 109.5 Hz, $^3J_{FF}$ = 29.7 Hz, $^3J_{FH}$ = 22.5 Hz); $^1$H NMR: δ 1.59 (m), 2.15 (m), 5.45 (dm, $^3J_{FH}$ = 22.5 Hz); $^{13}$C NMR (Neat): δ 151.8 (ddd, $^1J_{CF}$ = 290.0 Hz, $^1J_{CF}$ = 280.5 Hz, $^2J_{CF}$ = 47.0 Hz), 124.0 (ddd, $^1J_{CF}$ = 229.5 Hz, $^2J_{CF}$ = 48.1 Hz, $^2J_{CF}$ = 17.8 Hz), 197.5 (d, $^3J_{CF}$ = 10.2 Hz), 108.5 (s), 78.8 (dd, $^2J_{CF}$ = 22.7 Hz, $^3J_{CF}$ = 3.5 Hz), 30.6 (s), 26.7 (s), 25.4 (s). GC–MS: *m/z* (relative intensity): 188 (100.0). IR: 2937 (s), 1960 (C=C=C) (w), 1765 ($F_2C$=CF) (s), 1687 ($F_2C$=CF) (m), 1277 (vs), 1274 (vs), 1088 (vs), 1066 (s).

### 3.2.5. Preparation of (E)-4,5,6,6,6-pentafluorohex-4-ene-1-yne

Similar to Section 3.2.1, a 19-ml aliquot of a 0.76-M (*Z*)-pentafluoropropenylzinc reagent (14.3 mmol) in DMF, 2.1 g Cu(I)Br) (14.3 mmol), and 3.15 g of 3-tosyl-1-propyne (15 mmol) gave after distillation and washing with water 1.46 g (60%) of a mixture which contained 87% (*E*)-4,5,6,6,6-pentafluorohex-4-ene-1-yne and 13% (*E*)-4,5,6,6,6-pentafluoro-1,2,4-hexadiene (as determined by GLPC analysis). $^{19}$F NMR: [(E)-$CF_3CF$=$CFCH_2C$=CH]: δ-68.6 (dd, $^4J_{FF}$ = 20.9 Hz, $^3J_{FF}$ = 11.0 Hz), −171.6 dqt, $^3J_{FF}$ = 133.7 Hz, $^3J_{FF}$ = 11.0 Hz, $^4J_{FH}$ = 5.6 Hz), −139.8 (dqt, $^3J_{FF}$ = 133.7 Hz, $^4J_{FF}$ = 20.9 Hz, $^3J_{FH}$ = 18.5 Hz); $^1$H NMR: δ 2.14 (t, $^4J_{HH}$ = 2.7 Hz), 3.14 (dm, $^3J_{FH}$ = 18.5 Hz); GC–MS, *m/z* (relative intensity): 170 (53.9), 101 (100.0). IR (mixture): 1382 (s), 1251 (s), 1217 (s), 1199 (s), 1155 (vs). GC–MS, *m/z* (relative intensity): [(*E*) $CF_3CF$=CFCH=C=$CH_2$]: 170 (59.3), 101 (100.0).

### 3.2.6. Reaction of (Z)-pentafluoropropenylcopper reagent with 3-tosyl-1-butyne

Similar to Section 3.2.1, a 32-ml aliquot of a 0.94-M (*Z*)-pentafluoropropenylzinc reagent (30 mmol) in DMF, 0.3 g (10 mol%) Cu(I)Br and 6.7 g (30 mmol) of 3-tosyl-1-butyne gave after distillation 4.0 g (67%), bp 40–45 °C/90 mm Hg, a mixture (GLPC purity, 96%) which contained 23% of (*E*)-3-methyl-4,5,6,6,6-pentafluorohex-4-ene-1-yne and 77% of (*E*)-5,6,7,7,7-pentafluoro-2,3,5-heptatriene (as determined by GLPC analysis). $^{19}$FNMR: [(E)-$CF_3CF$=CFCH($CH_3$)C=CH)]: δ−68.6 (dd, $^4J_{FF}$ = 21.5 Hz, $^3J_{FF}$ = 11.1 Hz), −149.0 (ddq, $^3J_{FF}$ = 132.9 Hz, $^3J_{FH}$ = 27.5 Hz, $^4J_{FF}$ = 21.5 Hz), −172.6 (dqd, $^3J_{FF}$ = 132.9 Hz, $^3J_{FF}$ = 11.1 Hz, $^4J_{FH}$ = 4.0 Hz); $^1$H NMR: δ 1.47 (d, $^3J_{HH}$ = 7.2 Hz), 2.18 (d, $^4J_{HH}$ = 2.4 Hz), 3.69 (dm, $^3J_{FH}$ = 27.5 Hz); $^{13}$C NMR (Neat): δ 154.4 (dd, $^1J_{CF}$ = 266.2 Hz, $^2J_{CF}$ = 41.8 Hz), 136.5 (ddq, $^1J_{CF}$ = 247.6 Hz, $^2J_{CF}$ = 44.9 Hz, $^2J_{CF}$ = 40.7 Hz), 118.9 (qd, $^1J_{CF}$ = 270.3 Hz, $^2J_{CF}$ = 33.8 Hz), 79.1 (s), 70.1 (s), 24.5 (d, $^2J_{CF}$ = 23.1 Hz), 16.6 (s). GC–MS, *m/z* (relative intensity): 184 (4.8), 119 (74.4), 115 (100.0), 69 (90.7). $^{19}$F NMR: [(*E*)-$CF_3CF$=CFCH=C=$CHCH_3$)]: δ −67.9 (dd, $^4J_{FF}$ = 20.8 Hz, $^3J_{FF}$ = 12.2 Hz), −174.1 (dqdd, $^3J_{FF}$ = 127.5 Hz, $^3J_{FF}$ = 12.2 Hz, $^4J_{FH}$ = 3.3 Hz, $^6J_{FH}$ = 3.3 Hz), −146.0 (ddq, $^3J_{FF}$ = 127.5 Hz, $^3J_{FH}$ = 22.8 Hz, $^4J_{FF}$ = 20.8 Hz); $^1$H NMR: 1.78 (dd, $^3J_{HH}$ = 7.2 Hz, $^5J_{HH}$ = 3.3 Hz) 5.76 (m), 6.09 (dddq, $^3J_{FH}$ = 22.8 Hz, $^4J_{HH}$ = 6.4 Hz, $^4J_{FH}$ = 3.3 Hz, $^5J_{HH}$ = 3.3 Hz); $^{13}$C NMR (Neat): δ 148.6 (dd, $^1J_{CF}$ = 253.0 Hz, $^2J_{CF}$ = 39.1 Hz), 136.5 (ddq, $^1J_{CF}$ = 247.6 Hz, $^2J_{CF}$ = 44.9 Hz, $^2J_{CF}$ = 40.7 Hz), 119.3 (qdd, $^1J_{CF}$ = 270.2 Hz, $^2J_{CF}$ = 34.7 Hz, $^3J_{CF}$ = 4.0 Hz), 207.3 (d, $^3J_{CF}$ = 5.1 Hz), 81.7 (d, $^2J_{CF}$ = 23.2 Hz), 92.2 (s), 12.0 (s). GC–MS, *m/z* (relative intensity): 184 (13.6), 115 (76.7), 69 (100.0). IR (mixture of isomers): 3313 (≡CH) (m), 1957 (C=C=C) (m), 1734 (FC=CF) (w), 1702 (FC=CF) (w), 1380 (vs), 1370 (vs), 1261 (vs), 1250 (s), 1202 (vs), 1147 (vs).

### 3.2.7. Preparation of (E)-2-methyl-5,6,7,7,7-pentafluoro-2,3,5-heptatriene

Similar to Section 3.2.1, a 58-ml aliquot of 0.89 M (*Z*)-pentafluoropropenylzinc reagent (52 mmol), 7.5 g Cu(I)Br (52 mmol) and 5.12 g (50 mmol) of 3-chloro-3-methyl-1-butyne gave after distillation 7.85 g (79%), bp 37–38 °C/21 mm Hg, of (*E*)-2-methyl-5,6,7,7,7-pentafluoro-2,3,5-heptatriene (GLPC purity, 100%). $^{19}$F NMR: δ −67.8 (dd, $^4J_{FF}$ = 21.2 Hz, $^3J_{FF}$ = 11.7 Hz), −146.6 (ddq, $^3J_{FF}$ = 126.9 Hz, $^3J_{FH}$ = 23.7 Hz, $^4J_{FF}$ = 21.2 Hz), −175.0 (dqd, $^3J_{FF}$ = 126.9 Hz, $^3J_{FF}$ = 11.7 Hz, $^4J_{FH}$ = 3.7 Hz); $^1$H NMR: δ 1.80 (d, $^5J_{HH}$ = 2.9 Hz), 5.86 (ddhept), $^3J_{FH}$ = 23.7 Hz,

$^4J_{FH}$ = 3.7 Hz, $^5J_{HH}$ = 2.9 Hz); $^{13}$C NMR (Neat): $\delta$ 148.7 (ddq, $^1J_{CF}$ = 251.5 Hz, $^2J_{CF}$ = 39.3 Hz, $^3J_{CF}$ = 2.5 Hz), 135.8 (ddq, $^1J_{CF}$ = 242.8 Hz, $^2J_{CF}$ = 44.9 Hz, $^2J_{CF}$ = 40.7 Hz), 118.9 (qdd, $^1J_{CF}$ = 270.2 Hz, $^2J_{CF}$ = 34.9 Hz, $^3J_{CF}$ = 4.0 Hz), 204.3 (d, $^3J_{CF}$ = 5.5 Hz), 102.2 (s), 79.7 (d, $^2J_{CF}$ = 23.2 Hz), 17.9 (s). GC–MS, *m/z* (relative intensity): 198 (46.3), 127 (100.0). IR: 1961 (C═C═C) (w), 1702 (FC═CF) (m), 1382 (vs), 1371 (vs), 1261 (vs), 1148 (vs).

### 3.2.8. Preparation of 1-pentamethylene-(Z)-4,5,6,6,6-pentafluoro-1,2,4-hexatriene

Similar to Section 3.2.1, a 38-ml aliquot of a 0.94-M (*Z*)-pentafluoropropenylzinc reagent (36 mmol), 0.4 g Cu(I)Cl (10 mol%) and 5.1 g (36 mmol) of 1-chloro-1-ethynylcyclohexane gave 5.7 g (67%) of 1-pentamethylene-(*Z*)-4,5,6,6,6-pentafluoro-1,2,4-hexatriene after distillation, bp 75–79 °C/10 mm Hg (GLPC = 95%). $^{19}$F NMR: $\delta$ −67.8 (dd, $^4J_{FF}$ = 21.2 Hz, $^3J_{FF}$ = 11.7 Hz), −146.5 (ddq, $^3J_{FF}$ = 127.4 Hz, $^3J_{FH}$ = 23.4 Hz, $^4J_{FF}$ = 21.2 Hz), −175.8 (dqd, $^3J_{FF}$ = 127.4 Hz, $^3J_{FF}$ = 11.7 Hz, $^4J_{FH}$ = 3.7 Hz); $^1$H NMR: $\delta$ 1.59 (bs, 4H), 2.18 (bs, 4H), 5.82 (dm, $^3J_{FH}$ = 23.4 Hz, 1H), $^{13}$C NMR (Neat): $\delta$ 118.8 (qdd, $^1J_{CF}$ = 270.3 Hz, $^2J_{CF}$ = 34.9 Hz, $^3J_{CF}$ = 4.1 Hz), 135.6 (ddq, $^1J_{CF}$ = 242.7 Hz, $^2J_{CF}$ = 40.8 Hz, $^2J_{CF}$ = 44.9 Hz), 148.7 (ddq, $^1J_{CF}$ = 215.4 Hz, $^2J_{CF}$ = 39.3 Hz, $^3J_{FF}$ = 2.5 Hz), 79.5 (d, $^2J_{CF}$ = 23.2 Hz), 201.1 (d, $^3J_{CF}$ = 5.3 Hz), 108.8 (s), 29.9 (s), 26.4 (s), 25.2 (s). GC–MS: *m/z* (relative intensity): 238 (11.2), 127 (100.0). IR: 1956 (C═C═C) (m), 1700 (CF═CF) (m), 1375 (vs), 1262 (vs), 1200 (s), 1144 (vs).

### 3.2.9. Preparation of the pentafluorophenylcadmium reagent

A 100-ml three-neck flask equipped with a septum, magnetic stir bar and nitrogen inlet was charged with 11.2 g of acid-washed cadmium powder, 50 ml of dry DMF and 12.4 g of bromopentafluorobenzene (50 mmol). The reaction mixture was stirred at room temperature for 5 h and the precipitate allowed to settle. Aliquots of the desired quantity of the pentafluorophenylcadmium reagent were syringed into the reaction flask. Typical $^{19}$F NMR yields of the pentafluorophenylcadmium reagent were 90–95%.

### 3.2.10. Preparation of 1-(pentafluorophenyl)-1,2-butadiene

A 40-ml aliquot of a 1.14-M pentafluorophenylcadmium reagent (46 mmol) in DMF was syringed into a three-neck 100 ml flask equipped with a septum, magnetic stir bar and nitrogen inlet. The solution was cooled in an ice-water bath and then 0.5 g Cu(I)Cl (10 mol%) was added, followed by the addition of 11.2 g (50 mmol) 3-tosyl-1-butyne. The reaction mixture was warmed to room temperature over 2 h and then stirred for an additional 1 h at rt. The nitrogen tee was replaced with a flash distillation head equipped with a 100-ml receiving flask cooled with liquid nitrogen. The product of the reaction was distilled under full vacuum at 80 °C to near dryness. An equivalent volume of ice water was added to the flash distillate, the organic layer washed with 2 × 100 ml of water, dried over 4 Å molecular sieves and distilled through a 15-cm vigreaux column equipped with a short path distillation apparatus to give 6.2 g (61%) of 1-(pentafluorophenyl)-1,2-butadiene (GLPC purity 100%), bp 55–57 °C/2 mm Hg. $^{19}$F NMR: $\delta$ −158.4 (t, $^3J_{FF}$ = 19.6 Hz), −164.1 (m), −143.9 (m); $^1$H NMR: $\delta$ 1.78 (dd, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 3.4 Hz), 5.52 (qd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 6.8 Hz), 6.08 (dq, $^4J_{HH}$ = 6.8 Hz, $^5J_{HH}$ = 3.4 Hz); $^{13}$C NMR (Neat): $\delta$ 138.7 (dm, $^1J_{CF}$ = 253.2 Hz), 136.8 (dm, $^1J_{CF}$ = 250.2 Hz), 143.4 (dm, $^1J_{CF}$ = 250.9 Hz), 109.5 (m), 77.0 (s), 208.5 (s), 87.8 (s), 11.5 (s). GC–MS, *m/z* (relative intensity): 221 (10.2), 220 (92.2), 219 (16.6), 205 (100.0). IR: 1959 (C═C═C) (w), 1521 (vs), 1508 (s), 1504 (s), 998 (s), 962 (s).

### 3.2.11. Preparation of 3-methyl-1-(pentafluorophenyl)-1,2-butadiene

Similar to Section 3.2.10, a 48-ml aliquot of 1.13 M pentafluorophenylcadmium reagent (54 mmol), 0.5 g Cu(I)Cl (10 mol%) and 5.1 g 3-chloro-3-methyl-1-butyne (50 mmol) gave 7.9 g (68%) of 3-methyl-1-(pentafluorophenyl)-1,2-butadiene (GLPC purity = 100%), bp 39–40 °C/0.3 mm Hg after distillation. $^{19}$F NMR: $\delta$ −159.0 (t, $^3J_{FF}$ = 20.5 Hz), −164.3 (m), −144.9 (m); $^1$H NMR: $\delta$ 1.80 ($\delta$, $^5J_{HH}$ = 3.2 Hz), 5.97 (heptet, $^3J_{HH}$ = 3.2 Hz); $^{13}$C NMR (Neat): $\delta$ 138.5 (dm, $^1J_{CF}$ = 252.4 Hz), 136.7 (dm, $^1J_{CF}$ = 250.2 Hz), 143.4 (dm, $^1J_{CF}$ = 250.4 Hz), 110.3 (m), 75.7 (s), 206.1 (s), 97.9 (s), 18.0 (s). GC–MS, *m/z* (relative intensity): 234 (69.4), 169 (100.0). IR: 1964 (C═C═C) (w), 1520 (vs), 1507 (vs).

### 3.2.12. Reaction of pentafluorophenylcopper with 1-chloro-1-ethynylcyclohexane

Similar to Section 3.2.10, a 48-ml aliquot of a 0.98-M pentafluorophenylcadmium reagent (47 mmol), 0.5 g Cu(I)Cl (10 mol%) and 6.4 g 1-chloro-1-ethynylcyclohexane (40.4 mmol) afforded 1.76 g of product composed of 54.2% pentafluorobenzene, 36% 3-(pentafluorophenyl)-1-pentamethylene-1,2-propadiene and 9% of an unknown by-product, as determined by GLPC analysis. [3-(pentafluorophenyl)-1-pentamethylene-1,2-propadiene]. $^{19}$F NMR: $\delta$ −159.4 (t, $^3J_{FF}$ = 19.6 Hz), −164.4 (m), −144.6 (m); $^1$H NMR: $\delta$ 1.59 (m), 2.17 (m), 5.98 (bs). GC–MS, *m/z* (relative intensity): 274 (80.8), 232 (100.0).

## 4. Conclusions

Trifluorovinyl- and (*Z*)-pentafluoropropenylcopper reagents readily react with propargylic halides or tosylates. With primary propargylic substrates, the major product is the alkyne. With secondary propargylic substrates, mixtures of alkyne/allene are obtained; the allene product is ~75% of the mixture. With tertiary propargylic substrates, the allene is regiospecifically formed in good yields. With pentafluorophenylcopper and primary propargylic substrates, the major product is pentafluorobenzene. With secondary and tertiary propargylic substrates, the allene is regiospecifically formed in good yields.

## Acknowledgements

We gratefully appreciate the financial support from the Air Force Office of Scientific Research and the National Science Foundation.

## References

[1] D.J. Burton, G.A. Hartgraves, J. Hsu, Tetrahedron Lett. 31 (1990) 3699–3702.
[2] M.-H. Hung, Tetrahedron Lett. 31 (1990) 3703–3706.
[3] D.J. Burton, G.A. Hartgraves, J. Fluorine Chem. 49 (1990) 155–158.
[4] D.J. Burton, G.A. Hartgraves, J. Fluorine Chem. 128 (2007) 1198–1215.
[5] D.J. Burton, S.W. Hansen, J. Am. Chem. Soc. 108 (1986) 4229.
[6] C.R. Davis, D.J. Burton, in: P. Knochel, P Jones (Eds.), Organozinc Reagents: A Practical Approach, Oxford University Press, 1999, pp. 57–76.
[7] S.W. Hansen, T.D. Spawn, D.J. Burton, J. Fluorine Chem. 35 (1987) 415–420.
[8] P.L. Heinze, D.J. Burton, J. Fluorine Chem. 29 (1985) 359–361.
[9] K.J. MacNeil, D.J. Burton, J. Org. Chem. 58 (1993) 4411–4417.
[10] K.J. MacNeil, D.J. Burton, J. Org. Chem. 60 (1995) 4085–4089.
[11] M. Kalli, P.D. Landor, S.R. Landor, J. Chem. Soc., Perkin Trans. 1 (1973) 1347.
[12] D.J. Pasto, S. Chou, E. Fritzen, R.H. Schultz, A. Waterhouse, G. Hennion, J. Org. Chem. 43 (1978) 1389–1394.
[13] L. Brandsma, W.D. VerKuijsse, Synthesis of Acetylenes, Allenes and Cummulenes, Elsevier, 1981.
[14] C. Lim, D.J. Burton, C.A. Wesolowski, J. Fluorine Chem. 119 (2003) 21–26.
[15] P.L. Heinze, T.D. Spawn, D.J. Burton, S. Shin-Ya, J. Fluorine Chem. 38 (1988) 131–134.