# Preparation of Pentafluorophenyl-Substituted Fluorinated Dienes *via* Internal Vinyl- and Dienylcopper Reagents

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Vinylcopper reagent **1** can be prepared from the stereospecific *syn* addition of (pentafluorophenyl)-copper ($C_6F_5Cu$) to hexafluoro-2-butyne. Reagent **1** undergoes a coupling reaction with either *E*- or *Z*-pentafluoropropenyl iodide to result in a mixture of isomeric dienes. Prolonged heating in the presence of CsF converts the mixture to the corresponding *E,Z* diene, which is the thermodynamic isomer. When reagent **1** is prepared in the presence of excess hexafluoro-2-butyne, the vinyl copper intermediate undergoes a second addition to the alkyne to produce a conjugated dienylcopper reagent, the formation of which is confirmed by protonation with acid. The double addition phenomenon has also been observed in the reaction of *p*-H-$C_6F_4Cu$ with 2 equiv of hexafluoro-2-butyne.

## Introduction

We recently reported[1] that $C_6F_5Cu$, prepared from the corresponding cadmium reagent in DMF, undergoes a stereospecific *syn* addition to hexafluoro-2-butyne, to produce the internal vinylcopper intermediate **1** in $^{19}F$ NMR yields of 60–80% based on the starting bromopentafluorobenzene. Reagent **1** can be functionalized with a variety of electrophiles, including aryl, alkyl, allyl, and acyl halides, typically with complete retention of stereochemistry, to produce tetrasubstituted fluoroalkenes.

$$C_6F_5Br + Cd\ (xs) \xrightarrow[RT]{DMF} [C_6F_5CdX] \qquad X = Br, C_6F_5$$

$$[C_6F_5CdX] + Cu(I)Y \xrightarrow[RT]{DMF} [C_6F_5Cu] \qquad Y = Cl, Br$$

$$[C_6F_5Cu] + CF_3C{\equiv}CCF_3 \longrightarrow \underset{\mathbf{1}}{(C_6F_5)(Cu)(CF_3)C{=}C(CF_3)}$$

60-80%

$$\mathbf{1} \xrightarrow{E^+} (C_6F_5)(E)(CF_3)C{=}C(CF_3)$$

In this paper, we wish to describe the reaction of **1** with iodoperfluoroalkenes and the reaction of $C_6F_5Cu$ with 2 or more equiv of hexafluoro-2-butyne.

## Discussion and Results

When a solution of vinylcopper reagent **1** is treated with *Z*-pentafluoropropenyl iodide, the product **2** is isolated as a mixture of isomers (**2a** and **2b**), although only approximately 15% of the unexpected *E,E* isomer (**2b**) is formed. The isomers can be easily distinguished by $^{19}F$ NMR, because the characteristic *cis*–vinyl $CF_3$–$CF_3$ coupling constant of 12 Hz is absent in the *E,E* isomers, replaced with the corresponding *trans* coupling constant of 0 Hz. The isomerization is not suppressed by the utilization of lower reaction temperatures. When a sample of the mixture is heated in an NMR tube from 50–130 °C with CsF, **2a** is converted to the more stable *E,E* diene (**2b**); however, when heating is continued overnight, further isomerization occurs, to result in the formation of 87% of the *E,Z* diene, **3a** (See Table 1). The *E,E* and *E,Z* isomers can also be distinguished by $^{19}F$ NMR, because the *trans*–vinyl fluorines have a characteristically large coupling constant of 143 Hz, whereas the *cis*–vinyl fluorines only have a coupling constant of 3 Hz.

**Table 1. Isomerization of 2a to 3a**[a]

| temperature, °C | percent composition ($^{19}F$ NMR) |
|---|---|
| rt | 85, **2a**; 15, **2b** |
| 40 | 79, **2a**; 21, **2b** |
| 60 | 76, **2a**; 24, **2b** |
| 60 | 65, **2a**; 35, **2b** |
| 70 | 61, **2a**; 39, **2b** |
| 80 | 57, **2a**; 43, **2b** |
| 90 | 37, **2a**; 63, **2b** |
| 90 | 36, **2a**; 64, **2b** |
| 100 | 28, **2a**; 72, **2b** |
| 100 | 22, **2a**; 78, **2b** |
| 100 | 21, **2a**; 79, **2b** |
| 110 | 19, **2a**; 81, **2b** |
| 110 | 19, **2a**; 81, **2b** |
| 120 | 16, **2a**; 84, **2b** |
| 125 | 15, **2a**; 85, **2b** |
| 130 | 15, **2a**; 85, **2b** |
| 130 | 13, **2a**; 87, **2b** |
| 100 (overnight) | 6, **2a**; 7, **2b**; 87, **3a** |

[a] All data were collected at 10 min intervals except where indicated otherwise.

## Thermodynamic Isomer

Table 1 illustrates the fluoride-ion conversion of **2a** to **3a**.

In the isomerization of **2a** to **2b**, two mechanistic pathways can be envisioned, both of which result from fluoride ion attack. The first possibility involves attack of fluoride ion on either end of the conjugated dienic system to result in the corresponding allylic anion. The second pathway involves the attack of fluoride ion on the

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(1) MacNeil, K. J.; Burton, D. J. *J. Org. Chem.* **1993**, *58*, 4411.

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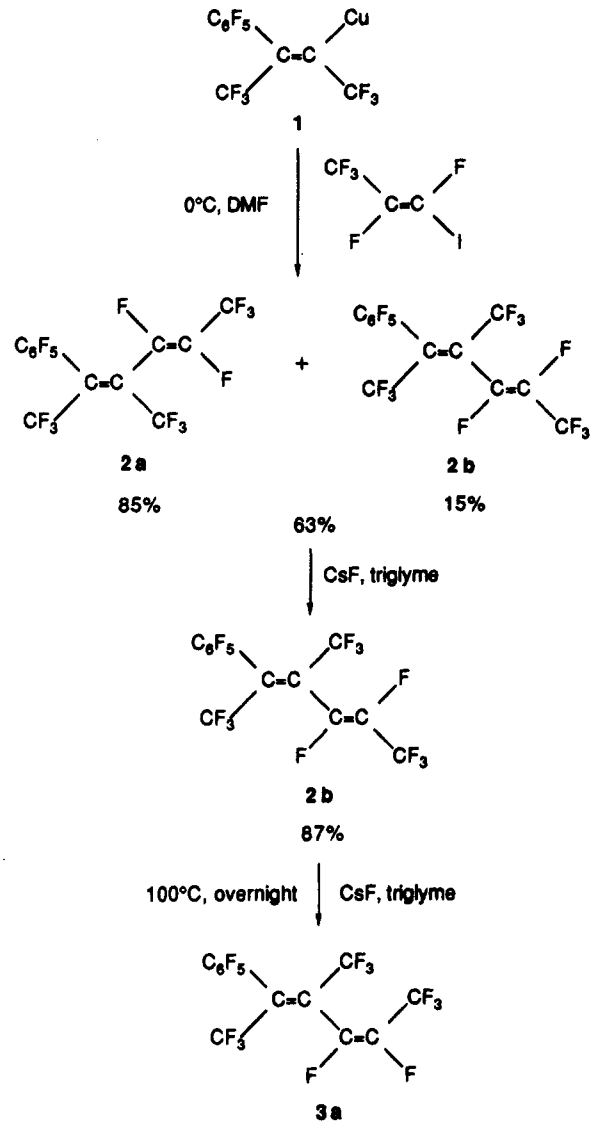
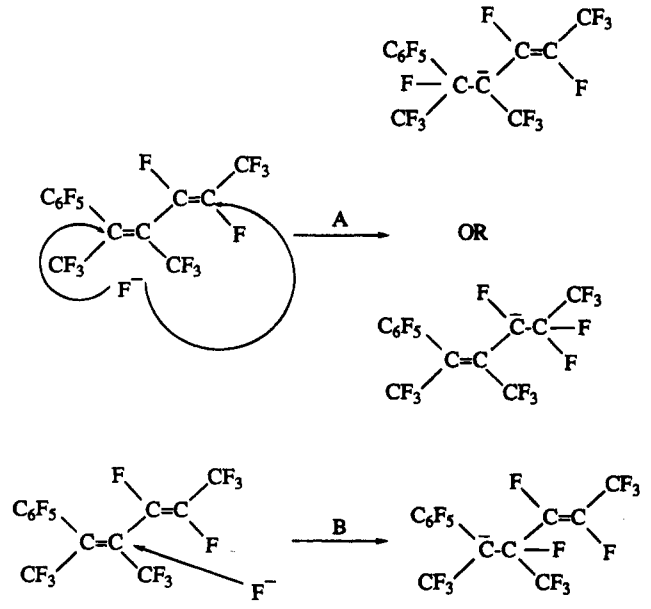
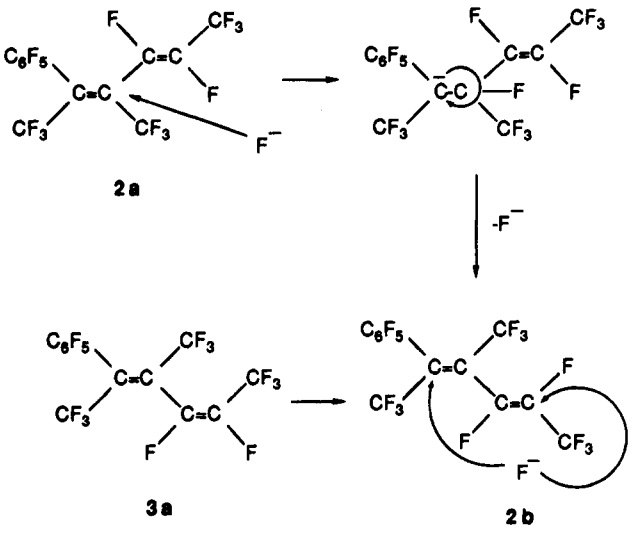



electrophilic carbon that is attached to the propenyl system, thus affording a stable benzylic anion.

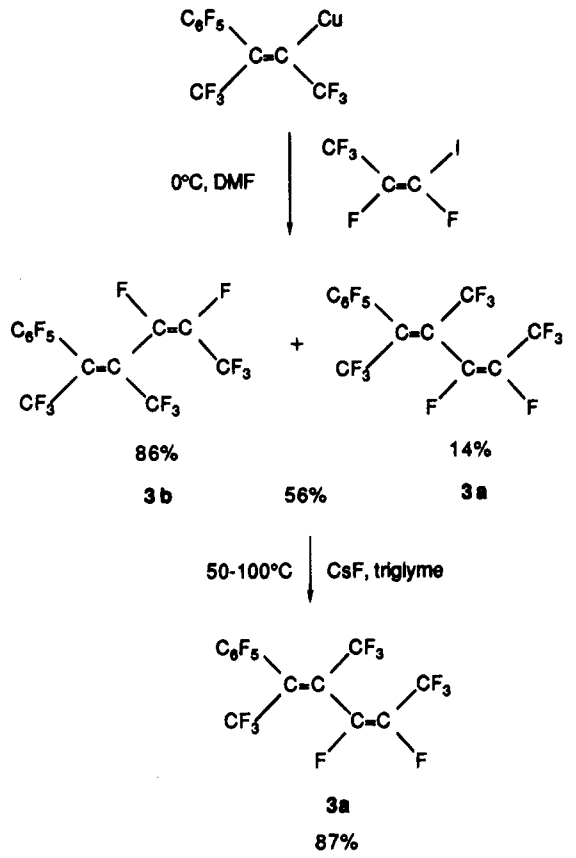



Although either scheme is possible, it is expected that if the first pathway were followed, the propenyl moiety of the intermediate anion would have partial single bond character, and that isomerization might occur at that end of the dienic system as well. Instead, the *E*-configuration of the propenyl group remains stable to relatively mild reaction conditions. This observation suggests that the overall transformation from **2a** to **3a** involves a stepwise mechanism that depends on the reaction conditions utilized. As illustrated below, the first step consists of fluoride ion attack and formation of the benzylic anion. Subsequent rotation and fluoride ion elimination produces **2b**. Upon prolonged heating with fluoride ion, however, alternative sites of fluoride attack compete, including the attack of fluoride ion on either end of the conjugated dienic system to result in the corresponding allylic anion. Again, rotation and fluoride ion elimination result in the formation of **3a**, which appears to be the thermodynamically most stable isomer. It was somewhat surprising that **2b** isomerized to **3a**. One would have expected **2b** to be the thermodynamic isomer based on the naive assumption that steric hindrance in **2b** is reduced relative to **3a**. Obviously, our assumptions are incorrect and additional work will be necessary to clarify this point.

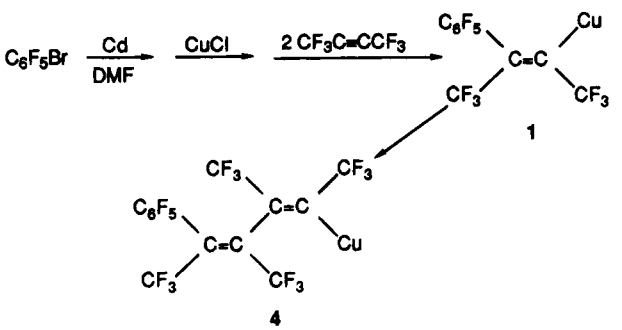



This mechanism was further supported by the results of quenching vinylcopper reagent **1** with *E*-pentafluoropropenyl iodide. Again, after isolation, the stereochemistry of the propenyl group remained intact, and the ratio of isomers was almost identical to that observed for **2**. The product mixture **3** was subsequently treated with fluoride ion and heated from 50 to 100 °C. Although fluoride ion did promote nearly complete (87%) isomerization from the *Z,Z* isomer to the *E,Z* isomer, the stereochemistry of the propenyl moiety was unaffected, again suggesting that the *Z*-configuration of the group is more stable.

During the course of the exploration of the synthetic utility of vinylcopper reagent **1**, it was discovered that under certain conditions, **1** can undergo reaction with excess hexafluoro-2-butyne. For example, if 2 or more equiv of the alkyne are condensed into a flask containing $C_6F_5Cu$ in DMF, **1** is formed, but is gradually converted



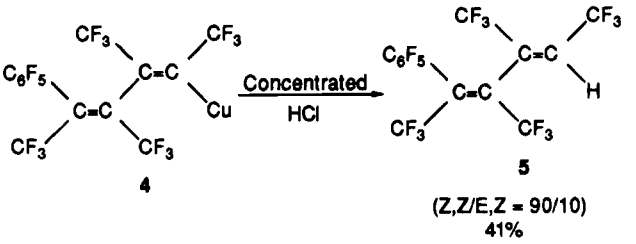

entirely to dienylcopper reagent **4** over a period of approximately five days.




Copper species **4** is formed in $^{19}F$ NMR yields of 55–65%, presumably *via* the *syn* addition of **1** to hexafluoro-2-butyne. A significant byproduct of the "double addition" is decafluorobiphenyl, which typically accounts for 3–15% of the product mixture, although the mechanism for its formation is not known. The $^{19}F$ NMR spectrum of the reaction mixture indicates that all of the $C_6F_5Cu$ is converted to **1** before **4** appears, which suggests that the second addition is much slower than the initial addition.

Reagent **4** is considerably less reactive than **1**. When another 1 equiv of $CF_3C{\equiv}CCF_3$ is added to a flask containing **4**, there does not appear to be a "triple addition", even after several additional days of stirring. This reduction in reactivity may be due in part to the decreased solubility in DMF of **4** as compared to that of **1**, or the reduced reactivity of **4** may be due to increased steric hindrance in **4** compared to **1**.

The lesser reactivity of **4** is also exemplified by its resistance to hydrolysis. A 10% aqueous solution of HCl was added to **4** in DMF, and, although **1** is protonated easily under these conditions, the $^{19}F$ NMR spectrum of the resultant bottom layer indicated that no hydrolysis had taken place, and that the copper reagent was still intact. However, when concentrated HCl was added, the corresponding protonated diene **5** could be isolated in a 41% yield.

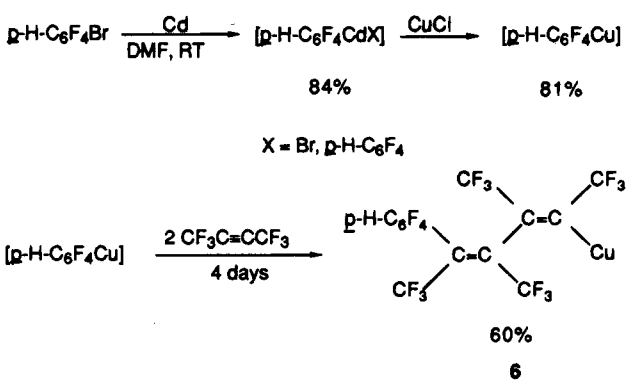



Because the $^{19}F$ NMR signals of **4** were broad (due to limited solubility) and the spectrum was complex, it was difficult to ascertain whether the reaction mixture was composed of more than one stereoisomer; however, the $^{19}F$ NMR spectrum of **5** revealed that 0–10% of the isolated protonated diene is actually a stereoisomer of **5**. It is possible that isomerization of **4** was promoted because of the longer reaction time required for the complete conversion of **1** to **4**. In addition, the somewhat harsher conditions needed for hydrolysis may have contributed to the isomerization.

The double addition can be slightly accelerated by an increase in the temperature of the system. Two equivalents of hexafluoro-2-butyne were condensed into a reaction mixture that contained $C_6F_5Cu$ in DMF, and the mixture was heated at 30–40 °C. After a period of only 6 h, the $^{19}F$ NMR spectrum revealed that both the single (**1**) and double (**4**) addition products had already formed.

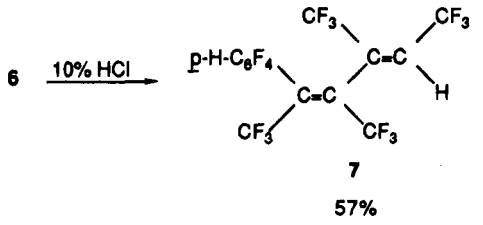
A combination of increased temperature and pressure also accelerates the double addition. A DMF solution of **1** was syringed into a NMR tube, which was immediately sealed, evacuated, and cooled to −78 °C. Excess $CF_3C{\equiv}CCF_3$ was condensed into the tube, and the contents of the tube were allowed to warm slowly to room temperature. Upon heating in a 60 °C $H_2O$ bath for 24 h, all of **1** was converted to **4**. Although excess hexafluoro-2-butyne was still apparent in the $^{19}F$ NMR spectrum of the reaction mixture, no "triple addition" occurred, and the excess alkyne was still present after 3 days.

(*p*-Hydrotetrafluorophenyl)copper was similar to (pentafluorophenyl)copper with regards to its reactivity toward hexafluoro-2-butyne. As described previously,[1] treatment of *p*-H-$C_6F_4Cu$ with 1 equiv of hexafluoro-2-butyne resulted in the corresponding vinyl copper reagent, whereas treatment with 2 equiv of the alkyne afforded the dienyl copper reagent **6**.



Even after the mixture is stirred for six days, the formation of **6** is not entirely complete, and approximately 10% of the single addition vinyl copper reagent can still be detected in the $^{19}F$ NMR spectrum of the reaction mixture.

The structure of **6** was confirmed by hydrolysis to produce protonated diene **7**.




**7**

**57%**

## Conclusion

We have described herein a novel procedure for the preparation of previously unknown highly fluorinated substituted dienes. In the case of compounds **2** and **3**, all four stereoisomers have been observed and characterized, and fluoride-ion-induced isomerization can be performed in order to selectively obtain the thermodynamic isomer. These results have suggested a stepwise fluoride ion addition/elimination reaction that involves a carbanionic intermediate. Finally, preliminary results have been obtained in unique "double additions" of copper reagents to fluorinated alkynes, and it is hoped that these efforts can be used to further extend the conjugated carbon chain in the future.

## Experimental Section

**General**. All reactions were performed in an oven-dried apparatus that consisted of a two- or three-necked flask equipped with a Teflon-coated magnetic stir bar and a nitrogen tee connected to a nitrogen source and mineral oil bubbler. Reported boiling points were determined during fractional distillation by means of a partial immersion thermometer and are uncorrected. $^{19}F$, $^{1}H$, and $^{13}C$ NMR spectra were generated on 90 and 300 MHz multinuclear spectrometers. $^{19}F$ NMR spectra were referenced against internal $CFCl_3$; $^{1}H$ and $^{13}C$ NMR spectra were referenced against internal TMS. All chemical shifts are reported in parts per million downfield of the standard. FTIR spectra were recorded in $CCl_4$ solution and absorbance frequencies reported in $cm^{-1}$; GC-MS spectra were obtained at 70 eV, in the electron impact mode. High resolution mass spectral data were collected at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. Where indicated, final purifications were performed on a preparative scale gas chromatograph using a 1 m × 1/2 in. OV-101 column.

**Materials**. Cadmium powder was activated by stirring with dilute acid, washing with water and acetone, and drying *in vacuo* overnight. DMF was purified and dried by vacuum distillation from calcium hydride. Cuprous chloride was purified by dissolving in concentrated HCl, diluting with 1 L of water, suction filtering, rinsing with acetone, and removing the acetone *in vacuo*. $C_6F_5Br$ and $CF_3C{\equiv}CCF_3$ were obtained from PCR Specialty Chemicals, Gainesville, FL, and utilized without further purification. *p*-H-$C_6F_4Br$ was prepared according to the method of Tamborski and Soloski.[2] CsF was dried by heating to 150 °C overnight at full vacuum. *E*- and *Z*-$CF_3CF{=}CFI$ were prepared according to the method of Shin-Ya.[3]

**Preparation of 1**. (Pentafluorophenyl)cadmium was prepared on a 100 mmol scale according to the procedure reported by Burton and Heinze.[4] The solid material in the flask was allowed to settle, and the remaining liquid was carefully decanted *via* syringe and added to another flask. To the stirred cadmium reagent was added 9.9 g (100 mmol) of CuCl. The $^{19}F$ NMR yield of the resultant (pentafluorophenyl)copper reagent was 88%, based on bromopentafluorobenzene. $^{19}F$ NMR (DMF) −112.4 (m, 2F), −164.0 (t, $J_{F,F}$ = 19 Hz, 1F), −165.3 (m, 2F). The reaction flask was fitted with a condenser containing methanol that was cooled to −100 °C with a Neslab Cryocool low temperature probe. The hexafluoro-2-butyne (17.8 g, 110 mmol) was condensed into the reaction mixture. After a period of 2−3 days at ambient temperature, the resulting vinylcopper species **1** was present in an 80% $^{19}F$ NMR yield. $^{19}F$ NMR (DMF) −54.9 (q, $^{5}J_{F,F}$ = 12 Hz, 3F), −61.1 (q, $^{5}J_{F,F}$ = 12 Hz, 3F), −142.9 (m, 2F), −159.0 (t, $^{3}J_{F,F}$ = 19 Hz, 1F), −165.5 (m, 2F).

**Preparation of 2a**. To an ice-cooled flask containing 50 mL of a 0.5 M solution of **1** (25 mmol) was added *Z*-perfluoropropenyl iodide (6.5 g, 25 mmol) dropwise *via* syringe. The mixture was allowed to warm to room temperature over a period of 2 h and filtered. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 7.2 g (63%) of **2**, which was present as an 85:15 mixture of the *Z,E* and the *E,E* isomers: GLPC purity: 97%; bp (**2a**) = 34−35 °C (10 mm/Hg); $^{19}F$ NMR ($CDCl_3$) −59.4 (qm, $^{5}J_{F,F}$ = 12 Hz, 3F), −60.8 (qm, $^{5}J_{F,F}$ = 12 Hz, 3F), −69.2 (dd, $^{4}J_{F,F}$ =21 Hz, $^{3}J_{F,F}$ = 11 Hz, 3F), −138.2 (m, 2F), −147.0 (tt, $^{3}J_{F,F}$ = 21 Hz, $^{4}J_{F,F}$ = 4 Hz, 1F), −159.1 (m, 2F), −138.5 (dq, $^{3}J_{F,F}$ = 142 Hz), $^{4}J_{F,F}$ = 21 Hz, 1F), −158.2 (dm, $^{3}J_{F,F}$ = 142 Hz, 1F), $^{13}C$ NMR ($CDCl_3$) 119.4 (q, $^{1}J_{C,F}$ = 276 Hz), 136.5−146.0 (m), 105.8 (m); FTIR ($CCl_4$-mixture of **2a** and **2b**) 2439 (w), 1381 (s), 1186 (s), 1041 (m), 874 (m); GC-MS 460 (3.9), 391 (100.0), 322 (79.3), 291 (31.3), 272 (32.3), 69 (85.3); HRMS calcd 459.9745, obsd 459.9770.

**Isomerization of 2a to 2b**. A neat sample (0.65 g) of the mixture of **2a** and **2b** was syringed into an evacuated NMR tube containing 0.05 g of CsF and 0.5 mL of dry triglyme. The NMR tube was placed in the variable temperature probe of a JEOL FX90Q NMR spectrometer and was heated from 25−130 °C at a rate of approximately 1 °C/min. The isomerization reaction was monitored by $^{19}F$ NMR and spectra were collected at 10 min intervals. After 2 h the liquid sample was distilled to afford 0.48 g (74%) of **2b** (*E,E*/*Z,E* = 87/13): GLPC purity: 97%; $^{19}F$ NMR ($CDCl_3$) −61.6 (s, 3F), −63.4 (s, 3F), −68.5 (dd, $^{4}J_{F,F}$ = 20 Hz, $^{3}J_{F,F}$ = 10 Hz, 3F), −137.0 (m, 2F), −146.9 (t, $^{3}J_{F,F}$ = 20 Hz, 1F), −159.2 (m, 2F), −133.6 (dq, $^{3}J_{F,F}$ = 143 Hz, $^{4}J_{F,F}$ = 20 Hz, 1F), −158.1 (dq, $^{3}J_{F,F}$ = 143 Hz, $^{3}J_{F,F}$ = 10 Hz, 1F); $^{13}C$ NMR ($CDCl_3$) 103.9 (m), 118.3 (qdd, $^{1}J_{C,F}$ = 273 Hz, $^{2}J_{C,F}$ = 35 Hz, $^{3}J_{C,F}$ = 5 Hz), 120.3 (q, $^{1}J_{C,F}$ = 276 Hz), 120.4 (q, $^{1}J_{C,F}$ = 277 Hz), 134.3 (q, $^{2}J_{C,F}$ = 35 Hz), 136.5−146.3 (m); GC-MS 460 (4.7), 391 (100.0), 322 (78.5), 272 (29.5), 69 (89.5), 40 (72.8); HRMS calcd 459.9745, obsd 459.9758.

**Preparation of 3b**. To an ice-cooled flask containing 50 mL of a 0.5 M solution of **1** (25 mmol) was added *E*-perfluoropropenyl iodide (6.5 g, 25 mmol) dropwise *via* syringe. The mixture was stirred for 2 h and filtered. The lower, organic layer was washed with water and dried over 4A molecular sieves. Distillation of the crude product resulted in 6.4 g (56%) of **3**, which was present as an 86:14 mixture of the *Z,Z* and *E,Z* isomers: GLPC purity: 98%; bp 36−39 °C (10 mm/Hg); $^{19}F$ NMR ($CDCl_3$) −59.9 (q, $^{5}J_{F,F}$ = 12 Hz, 3F), −62.1 (q, $^{5}J_{F,F}$ = 12 Hz, 3F), −70.1 (bs, 3F), −139.7 (m, 2F), −147.0 (t, $^{3}J_{F,F}$ = 19 Hz, 1F), −159.7 (m, 2F), −119.2 (s, 1F), −145.6 (q, $^{3}J_{F,F}$ = 12 Hz, 1F); FTIR ($CCl_4$-mixture of **3a** and **3b**) 1522 (s), 1239 (m), 1176 (s), 1050 (m), 729 (w); GC-MS 460 (4.9), 391 (49.3), 341 (32.0), 322 (75.7), 303 (29.3), 69 (100.0); HRMS calcd 459.9745, obsd 459.9724.

**Isomerization of 3b to 3a**. A neat sample of the mixture of **3b** and **3a** was syringed into an evacuated NMR tube containing 0.05 g of CsF and 0.5 mL of dry triglyme. The NMR

(2) Tamborski, C.; Soloski, E. *J. Org. Chem.* **1966**, *31*, 746.
(3) Burton, D. J.; Spawn, T. D.; Heinze, P. L.; Bailey, A. R.; Shin-Ya, S. *J. Fluorine Chem.* **1989**, *44*, 167. Heinze, P. L.; Spawn, T. D.; Burton, D. J.; and Shin-Ya, S. *J. Fluorine Chem.* **1988**, *38*, 131.
(4) Burton, D. J.; Heinze, P. L. *J. Fluorine Chem.* **1985**, *29*, 359.

tube was placed in the variable temperature probe of a JEOL FX90Q NMR spectrometer and was heated from 25–130 °C at a rate of approximately 1 °C/min. The isomerization reaction was monitored by $^{19}F$ NMR and spectra were collected at 10 min intervals. After 2 h, the liquid sample was distilled to afford 0.53 g (81%) of **3a** (*E,E/E,Z* = 13/87): GLPC purity: 98%; $^{19}F$ NMR ($CDCl_3$) −64.4 (s, 3F), −65.0 (s, 3F), −71.4 (bs, 3F), −140.1 (m, 2F), −151.4 (t, $^3J_{F,F}$ = 20 Hz, 1F), −163.5 (m, 2F), −147.5 (qd, $^4J_{F,F}$ = 12 Hz, $^3J_{F,F}$ = 3 Hz, 1F), −119.0 (d, $^3J_{F,F}$ = 3 Hz, 1F); $^{13}C$ NMR ($CDCl_3$) 103.7 (m), 120.1 (q, $^1J_{C,F}$ = 277 Hz), 120.2 (q, $^1J_{C,F}$ = 277 Hz), 120.3 (q, $^1J_{C,F}$ = 278 Hz); GC-MS 460 (5.8), 391 (100.0), 341 (32.6), 322 (73.4), 291 (28.1), 69 (49.5); HRMS calcd 459.9745, obsd 459.9758.

**Preparation of 4.** (Pentafluorophenyl)copper was prepared as described above on a 50 mmol scale. The reaction flask was fitted with a condenser containing methanol that was cooled to −100 °C with a Neslab Cryocool low temperature probe. The hexafluoro-2-butyne (16.2 g, 100 mmol) was condensed into the reaction mixture, and the mixture was monitored by $^{19}F$ NMR over the course of 2–5 days until all of the alkyne was consumed. Reagent **4** was formed in an overall $^{19}F$ NMR yield of 55–65%: $^{19}F$ NMR (DMF) −54.9 (q, $^5J_{F,F}$ = 10 Hz, 3F), −57.4 (q, $^5J_{F,F}$ = 10 Hz, 3F), −58.5 (q, $^5J_{F,F}$ = 12 Hz, 3F), −62.3 (q, $^5J_{F,F}$ = 12 Hz, 3F), −140.0 (m, 2F), −152.7 (t, $^3J_{F,F}$ = 20 Hz, 1F), −163.7 (m, 2F).

**Preparation of 5.** To a flask containing 60 mL of a 0.5 M solution of **4** (30 mmol) was added concentrated HCl (5 mL) dropwise *via* syringe. The mixture was poured into water and filtered, and the lower organic layer was washed with water and dried over 4A molecular sieves. Purification of the crude product by preparative gas chromatography resulted in 6.1 g (41%) of **5**: GLPC purity: 90% (*Z,Z/E,Z* = 90/10); bp = 71–75 °C (20 mm/Hg); $^{19}F$ NMR ($CDCl_3$) −59.2 (q, $^5J_{F,F}$ = 10 Hz, 3F), −59.7 (q, $^5J_{F,F}$ = 11 Hz, 3F), −61.0 (q, $^5J_{F,F}$ = 11 Hz, 3F), −61.5 (q, $^5J_{F,F}$ = 10 Hz, 3F), −138.7 (m, 2F), −148.0 (t, $^3J_{F,F}$ = 20 Hz, 1F), −160.2 (m, 2F); $^1H$ NMR ($CDCl_3$) 6.28 (m); $^{13}C$ NMR ($CDCl_3$) 119.4 (q, $^1J_{C,F}$ = 274 Hz), 119.8 (q, $^1J_{C,F}$ = 277 Hz), 130.7 (q, $^2J_{C,F}$ = 38 Hz), 133.0 (q, $^2J_{C,F}$ = 41 Hz), 136.7–146.1 (m); FTIR ($CCl_4$) 3086 (w), 1522 (m), 1282 (s), 1179 (vs), 994 (m); GC-MS 492 (1.4), 423 (50.3), 354 (43.1), 285 (23.0), 69 (100.0), 44 (14.0); HRMS calcd 491.9807, obsd 491.9831.

**Preparation of 6.** *p*-H-$C_6F_4$Cu was prepared as reported previously[1] on a 25 mmol scale. The reaction flask was fitted with a condenser containing methanol that was cooled to −100 °C with a Neslab Cryocool low temperature probe. The hexafluoro-2-butyne (8.1 g, 50 mmol) was condensed into the reaction mixture, and the progress of the reaction was periodically monitored by $^{19}F$ NMR for 4–6 days, after which **6** was present in an overall $^{19}F$ NMR yield of 60%: $^{19}F$ NMR (DMF) −62.2 (m, 3F), −57.6 (m, 3F), −58.6 (m, 3F), −54.9 (m, 3F), −141.7 (m, 4F).

**Preparation of 7.** To a flask containing 50 mL of a 0.5 M solution of **6** (25 mmol) was added 10% HCl (5 mL) dropwise *via* syringe. The mixture was filtered, and the lower organic layer was washed with water and dried over 4A molecular sieves. Distillation of the crude product resulted in 8.4 g (57%) of **7**: GLPC purity: 90%; bp = 76–81 °C (30 mm/Hg); $^{19}F$ NMR ($CDCl_3$) −59.2 (q, $^5J_{F,F}$ = 10 Hz, 3F), −59.6 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.0 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.7 (qd, $^5J_{F,F}$ = 10 Hz, $^3J_{F,H}$ = 9 Hz, 3F), −136.3 (t, $^3J_{F,F}$ = 10 Hz, 2F), −137.3 (t, $^3J_{F,F}$ = 10 Hz, 2F); $^1H$ NMR ($CDCl_3$) 7.4 (t, $^3J_{H,F}$ = 8 Hz, 1H), 8.3 (qq, $^3J_{H,F}$ = 9 Hz, $^4J_{H,F}$ = 2 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) 108.9 (t, $^2J_{C,F}$ = 22 Hz), 120.0 (q, $^1J_{C,F}$ = 275 Hz), 120.4 (q, $^1J_{C,F}$ = 277 Hz), 130.5–137.7 (m), 145.2–148.6 (m), 163.2 (s); FTIR ($CCl_4$) 3081 (w), 1504 (m), 1245 (s), 1189 (vs), 746 (m); GC-MS 474 (14.2), 455 (33.4), 405 (98.2), 336 (100.0), 267 (39.4), 69 (94.7); HRMS calcd 473.9901, obsd 473.9873.

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