Fluoroalkylcopper(I) Complexes Generated by the Carbocupration of Tetrafluoroethylene: Construction of a Tetrafluoroethylene-Bridging Structure

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S *Supporting Information*

ABSTRACT: We report a copper-mediated synthesis of a variety of 1,2-difunctionalized-1,1,2,2-tetrafluoroethylene derivatives via the carbocupration of tetrafluoroethylene. The key synthetic intermediates, 2-aryl-1,1,2,2-tetrafluoroethylcopper complexes, can be easily prepared, stored, and used as fluoroalkylation reagents. The molecular structure was unambiguously determined by X-ray crystallography and NMR analysis. We applied this method to the short-step synthesis of a liquid-crystalline compound bearing a tetrafluoroethylene-bridging structure.

Organofluorine compounds have attracted much attention because of their remarkable applications in pharmaceutical and materials science.[1] Thus, a great deal of effort has been directed toward the development of a method for the selective introduction of a fluorine atom into organic compounds via reaction with a fluorination reagent such as DAST.[2] In addition, the introduction of a fluoroalkyl group is regarded as an important approach to highly fluorinated compounds, which are difficult to prepare using fluorination reagents.[3] Since the pioneering work by McLoughlin and Thrower in 1969, copper-mediated fluoroalkylation has been one of the most versatile methods for the introduction of fluoroalkyl groups.[4] In the reaction, a fluoroalkylcopper(I) complex is considered to be a key intermediate. In 1986, Wiemers and Burton observed $[CF_3Cu]$ species by ^{19}F NMR analysis at low temperature.[4d] Recently, isolations of ligand-stabilized fluoroalkylcopper complexes such as $[(PPh_3)_3CuCF_3]$,[5] $[(NHC)CuCF_3]$ (NHC = N-heterocyclic carbene),[6] and $[(phen)CuC_nF_{2n+1}]$ (phen = 1,10-phenanthroline, $n = 1-3$)[7] have been reported, along with reports of outstanding performance as fluoroalkylation reagents. In general, fluoroalkylcopper complexes are prepared via transfer of a fluoroalkyl group from a fluoroalkyl halide, fluoroalkyl silane, or fluoroalkane. We assumed that the 1,2-addition of organo-copper reagents to fluoroalkenes, so-called carbocupration,[8] would afford a new class of fluoroalkylcopper complexes that would provide an important synthetic route to organofluorine compounds that are difficult to prepare by conventional methods. Except for highly strained cyclopropenes,[9] alkenes are not considered to be applicable to carbocupration, but fluoroalkenes should be able to undergo carbocupration because of their electrophilic nature.[10]

Tetrafluoroethylene (TFE), which is used in the production of PTFE and other copolymers in the fluorine industry, is one of the ideal starting materials for the synthesis of fluorinated compounds because it is an economical and environmentally benign feedstock with a negligible global warming potential.[11] We recently developed the transformations of TFE into trifluorovinyl compounds by Pd(0)-catalyzed cross-coupling reactions via C−F bond activation[12a−c] or by reactions using Grignard reagents or $ZnEt_2$ in the presence of a lithium salt.[12d] In addition, TFE has the potential to be a straightforward building block for the construction of a tetrafluoroethylene-bridging structure $(R-CF_2CF_2-R')$, which has garnered a great deal of attention as a key structure in liquid-crystalline compounds because of its potential to influence the physical properties of these materials: clearing point, mesophase sequence, and rotational viscosity.[1a,13] Tetrafluoroethylene-bridging structures typically are constructed via the fluorination of a carbon−carbon triple bond with F_2 gas or via the deoxofluorination of 1,2-diketones with fluorination reagents.[14,15] However, these methods have low functional group tolerance and use toxic or costly reagents. Thus, the development of an efficient and straightforward method has been in high demand.

Herein we describe a copper-mediated transformation of TFE into aromatic compounds bearing a tetrafluoroethylene-bridging structure in which carbocupration of TFE is a key step (Scheme 1). Novel 2-aryl-1,1,2,2-tetrafluoroethylcopper (ATFE−Cu)

**Scheme 1. Construction of a Tetrafluoroethylene-Bridging Structure via Carbocupration of TFE**

complexes generated by the carbocupration of TFE were isolated and characterized by X-ray crystallography and NMR analysis. With the ATFE−Cu complexes, a variety of 1,2-disubstituted-1,1,2,2-tetrafluoroethanes were synthesized in high yields. The short-step synthesis of a liquid-crystalline compound via carbocupration of TFE is also described.

The carbocupration of TFE proceeded with $[CuO^tBu]$, 1,10-phenanthroline (Phen) as the ligand, and arylboronates **1** as aryl transfer reagents (Scheme 2). First, a phenylcopper complex

Scheme 2. Synthesis of ATFE−Cu Complexes 3
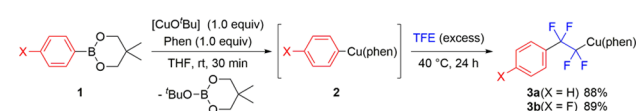
[(phen)CuPh] (**2a**)[16] was prepared by the reaction of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**1a**), [CuO^{t}Bu], and Phen in tetrahydrofuran (THF). The reaction was completed within 10 min at room temperature, and the quantitative formation of **2a** and 2-$tert$-butoxy-5,5-dimethyl-1,3,2-dioxaborinane was confirmed by ^{1}H and ^{11}B NMR analysis. Then the THF solution of **2a** was exposed to TFE (3.5 atm) and heated at 40 °C for 24 h. After the removal of TFE and THF under reduced pressure, the resultant solid was washed with ether to give the ATFE−Cu complex [(phen)CuCF$_2$CF$_2$Ph] (**3a**) in 88% yield as a brown solid (1.86 g, 4.43 mmol). This is the first example of the preparation of a fluoroalkylcopper complex via carbocupration of a fluoroalkene.[17] It is worth noting that **3a** was stable under N$_2$ at room temperature and could be stored for at least a few months without decomposition. An analogous complex bearing a fluorine substituent at the 4-position, [(phen)CuCF$_2$CF$_2$(4-C$_6$H$_4$F)] (**3b**), was also prepared in 89% yield. ^{19}F NMR monitoring indicated that the transformation of **1b** into **3b** proceeded through complex **2b** (Figure 1).
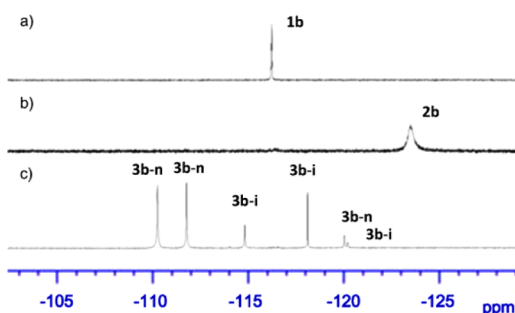

Figure 1. ^{19}F NMR spectra (in THF-d_8) of (a) **1b**, (b) **2b**, and (c) **3b**.

The molecular structure of **3b** was determined by X-ray crystallography (Figure 2). A single crystal suitable for X-ray
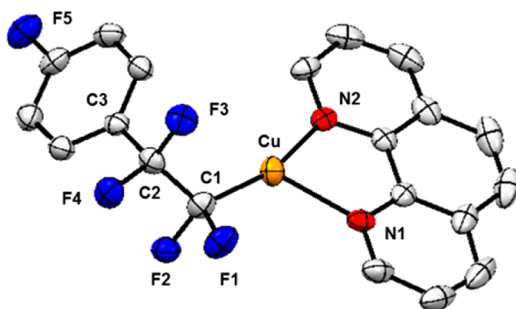

Figure 2. ORTEP structure of **3b** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

diffraction analysis was obtained by recrystallization from a saturated solution of **3b** in THF at room temperature. The revealed monomeric structure clearly shows the formation of Cu−C and C−C bonds. The sum of the three bond angles around the Cu atom is 359.78°. Thus, Cu, C1, N1, and N2 are in the same plane, and **3b** has a trigonal-planar molecular geometry.

The −CF$_2$CF$_2$(4-C$_6$H$_4$F) group leans to one side as a result of the crystal packing, with one N−Cu−C angle larger than the other [N1−Cu−C1 = 117.43(11)°, N2−Cu−C1 = 161.65(11)°] and one N−Cu distance longer than the other [N1−Cu = 2.157(3) Å, N2−Cu = 1.981(2) Å].

NMR analysis (Figure 1c) showed that in solution **3b** exists as a mixture of a neutral form, [(phen)CuCF$_2$CF$_2$(4-C$_6$H$_4$F)] (**3b-n**), and an ionic form, [(phen)$_2$Cu][Cu(CF$_2$CF$_2$(4-C$_6$H$_4$F))$_2$] (**3b-i**). In the ^{19}F NMR spectrum of **3b** in THF-d_8, broad signals assigned to **3b-n** were observed at −110.4, −112.0 (for −CF$_2$CF$_2$−), and −120.1 ppm (for Ar−F). Those assigned to **3b-i** were observed at −115.0, −118.3, and −120.3 ppm. The **3b-n**:**3b-i** peak-area ratio was ca. 5:2 but depended on the concentration of **3b** and the polarity of the solvent. The dynamic behavior of **3b** in solution is consistent with previous studies of fluoroalkylcopper complexes.[6,7,18]

Although organoboron compounds are less common in the preparation of organocopper reagents,[19] their use confers great advantages with regard to ease of handling and functional group tolerance. Furthermore, the weak Lewis acidic nature of both **1** and 2-$tert$-butoxy-5,5-dimethyl-1,3,2-dioxaborinane is quite important for the synthesis of **3** because Lewis acidic species can cause decomposition of the complex through α- or β-fluorine elimination. In fact, the reaction using phenylmagnesium bromide instead of **1a** did not produce **3a** at all, and trifluorostyrene (**4**) was obtained in 70% yield as a result of β-fluorine elimination. Moreover, **3a** was immediately converted into **4** by treatment with magnesium bromide at room temperature. We assumed that the Lewis acidic metal species were involved in the β-fluorine elimination step through interaction with a fluorine atom. Although organoboron compounds also have a potential Lewis acidic nature, their Lewis acidity might be very low to avoid the β-fluorine elimination during the synthesis of **3**.

Next, we investigated the reactivity of **3a** (Scheme 3). As mentioned above, treatment of **3a** with magnesium bromide

Scheme 3. Transformations of 3a
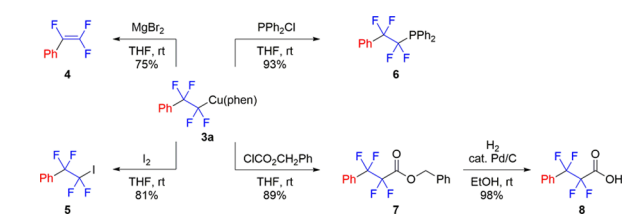
afforded **4** via β-fluorine elimination. Iodonolysis of **3a** at room temperature gave (1,1,2,2-tetrafluoro-2-iodoethyl)benzene (**5**) in 81% yield. A phosphine compound bearing a fluoroalkyl group (**6**) was obtained by the reaction of **3a** with PPh$_2$Cl. Moreover, the reaction of **3a** with benzyl chloroformate generated a C−C bond to give the corresponding ester **7** in 89% yield, and subsequent hydrogenation catalyzed by 10% Pd/C afforded the corresponding carboxylic acid **8** quantitatively.

Furthermore, the ATFE−Cu complex was also applicable for the coupling reaction with iodoarenes **9** to give 1,2-diaryl-1,1,2,2-tetrafluoroethanes **10** (Table 1). After the preliminary screening of the reaction conditions, we found that the reaction of iodobenzene (**9a**) with 1.2 equiv of **3a** in THF proceeded at 60 °C to afford 1,1,2,2-tetrafluoro-1,2-diphenylethane (**10aa**) in 98% yield. Under the reaction conditions, electron-deficient 4-iodobenzotrifluoride (**9b**) reacted with **3a** smoothly to give **10ab**

Table 1. Substrate Scope of Iodoarenes[a]
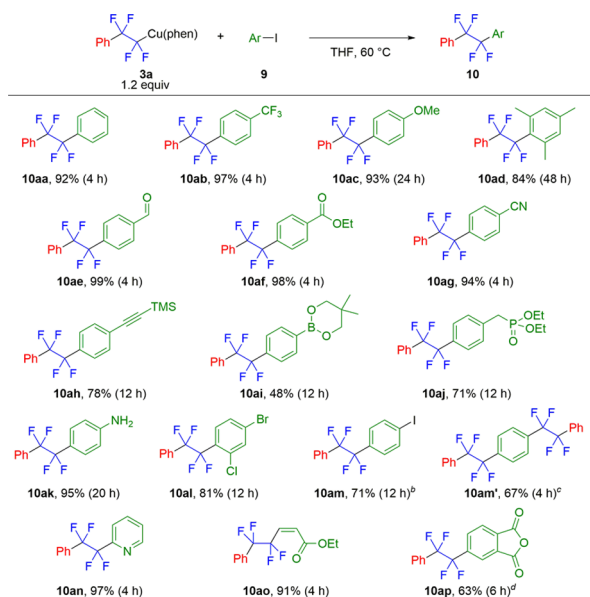
[a]Isolated yields are shown. [b]Conducted with **3a** (0.30 mmol) and **9m** (1.50 mmol). [c]Conducted with **3a** (0.72 mmol) and **9m** (0.30 mmol). [d]Conducted with **9p** instead of the corresponding iodide.

in 97% yield. The reactions with electron-rich 4-iodoanisole (**9c**) and sterically hindered iodomesitylene (**9d**) were sluggish, but the corresponding coupling products **10ac** and **10ad** were obtained in high yields. Functional groups such as formyl, ester, and cyano were tolerant of the reaction conditions (**10ae**–**ag**). Substrates bearing a C–C triple bond or a boronate, phosphate, amino, bromo, or chloro group were converted to the corresponding products (**10ah**–**al**), which are potential substrates for further functionalization by, for example, Suzuki–Miyaura or Horner–Wadsworth–Emmons reaction. In addition, 1,4-diiodobenzene (**9m**) was selectively converted to either the mono- or disubstituted product depending on the stoichiometric proportions: the reaction using excess **9m** relative to **3a** gave the monosubstituted product (**10am**) in 71% yield, and that using excess **3a** relative to **9m** gave the disubstituted product (**10am′**) in 67% yield. We found that 2-iodopyridine (**9n**) and alkenyl iodide (**9o**) also reacted with **3a** to give the products **10an** and **10ao** in excellent yields. The coupling reaction of **3a** with bromobenzene did not occur, but electron-deficient 4-bromophthalic anhydride (**9p**) reacted with **3a** to afford the corresponding coupling product **10ap**.

In addition to the above-mentioned stepwise reaction using **3a**, we conducted a one-pot synthesis of 1,2-diaryl-1,1,2,2-tetrafluoroethanes **10** from **1**, TFE, and **9** without isolation of the corresponding ATFE–Cu complexes. First, **2a** was generated in situ by the reaction of **1a**, [CuO^{t}Bu], and Phen, and the resultant solution was transferred to an autoclave reactor. TFE (3.5 atm) was charged into the reactor, and the reaction mixture was heated at 40 °C for 24 h. After the removal of TFE under reduced pressure, the reaction mixture was heated with a small excess amount of **9b** at 60 °C for 4 h. The target compound **10ab** was isolated in 92% yield after separation by silica gel column chromatography. In the one-pot reaction, no significant side product was obtained. On the other hand, when all of the starting materials, including **9b**, were mixed at once before the heating, a complicated mixture was obtained, and **10ab** was observed in only 15% yield by ^{19}F NMR spectroscopy.[20]

Various substituted arylboronates were converted into 1,2-diaryl-1,1,2,2-tetrafluoroethanes **10** (Table 2). Fluorine, chlor-

Table 2. Substrate Scope of the One-Pot Synthesis of 10[a]
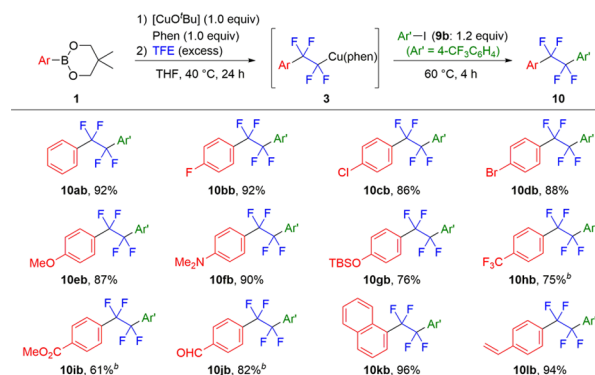
[a]Isolated yields are shown. [b]Heated at 40 °C for 48 h before the addition of **9b** to complete the formation of **3**.

ine, and bromine substituents were tolerated in the reaction (**10bb**–**db**). The reactions using electron-rich arylboronates proceeded to give the products in high yields (**10eb**–**gb**). The carbocupration reactions with electron-deficient arylboronates were relatively sluggish and required longer reaction times in order to complete the formation of the ATFE–Cu intermediates, which reacted with **9b** to give the corresponding coupling products **10hb**–**jb**. An arylboronate bearing a vinyl group and sterically hindered 1-naphthylboronate were also applicable to the carbocupration of TFE (**10kb** and **10lb**).

Finally, we applied the present method to the synthesis of a liquid-crystalline compound bearing a tetrafluoroethylene-bridging structure. Materials containing the tetrafluoroethylene-bridging structure are expected to be used in the next generation of active-matrix liquid crystal displays with reduced power consumption, and the development of an efficient and convenient synthetic method has been in high demand. A previous report[13d] detailed the synthesis of a liquid-crystalline compound bearing a tetrafluoroethylene-bridging structure in 10 steps from 4,4′-(tetrafluoroethane-1,2-diyl)diphenol bearing the tetrafluoroethylene-bridging structure.[21] By contrast, through carbocupration of TFE, **17** was synthesized in six steps from commercially available 4-pentylphenylboronic acid (**11**) (Scheme 4). Even though **17** was obtained as a mixture of geometric isomers, each of the isomers was separated by means of preparative HPLC. ATFE–Cu complex **13**, which is a key intermediate in this transformation, could be prepared and stored at room temperature under N$_2$ in a manner similar to **3a**.

In conclusion, we have demonstrated the synthesis, characterization, and synthetic application of 2-aryl-1,1,2,2-tetrafluoroethylcopper complexes, which are generated by the carbocupration of tetrafluoroethylene. The molecular structure was unambiguously determined by X-ray crystallography and NMR analysis. Using the complexes as fluoroalkylation reagents, we synthesized a variety of 1,2-difunctionalized-1,1,2,2-tetrafluoroethanes in high yields. The synthetic utility of this method was demonstrated by the short-step synthesis of a liquid-crystalline compound bearing a tetrafluoroethylene-bridging structure.

Scheme 4. Synthesis of Liquid-Crystalline Compound 17[a]
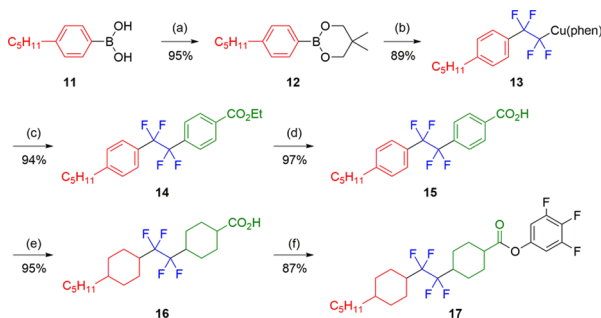
[a]Reagents and conditions: (a) 2,2-dimethyl-1,3-propanediol, toluene, reflux, 10 h; (b) [CuO^{t}Bu], Phen, TFE, THF, 40 °C, 5 h; (c) 4-(CO$_2$Et)C$_6$H$_4$I, THF, 60 °C, 4 h; (d) KOH, MeOH/H$_2$O, 60 °C, 12 h; (e) H$_2$, cat. Rh/Al, AcOH, 60 °C, 12 h; (f) 3,4,5-trifluorophenol, DCC, DMAP, CH$_2$Cl$_2$, rt, 24 h.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Procedures and analytical and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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