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Direct Synthesis of Pentafluoroethyl Copper from Pentafluoropropionate as an Economical C_2F_5 Source: Application to Pentafluoroethylation of Arylboronic Acids and Aryl Bromides

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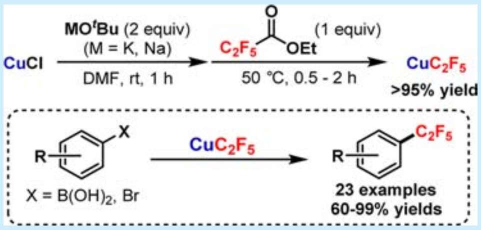
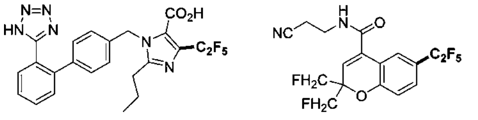
Supporting Information

ABSTRACT: The direct synthesis of pentafluoroethyl copper (CuC_2F_5) from a cuprate reagent and ethyl pentafluoropropionate as one of the most economical and useful pentafluoroethyl sources was accomplished. The advantages of this method are; all the reagents employed are low-cost and operationally simple, and the CuC_2F_5 reagent is prepared in virtually quantitative yield. Furthermore, the CuC_2F_5 reagent prepared was successfully applied to two types of pentafluoroethylations with arylboronic acids and aryl bromides to provide the pentafluoroethylated aromatic products in good-to-excellent yields, including large scale operations.



Because the introduction of fluorine into organic molecules can lead to dramatic changes in physical properties such as increased chemical and metabolic stability, enhanced lipophilicity, and changed polarity,[1] the efficient fluorinations and fluoroalkylations play an important role in the development of new pharmaceuticals and agrochemicals.[2] Over the past five years, considerable progress has been accomplished in the transition-metal-mediated and -catalyzed trifluoromethylation of the aromatic system using various trifluoromethylating reagents.[3] However, the perfluoroalkylations of aromatic compounds are still undeveloped, compared to the corresponding trifluoromethylations.[2a,c] The Swarts reaction,[4] which can industrially produce the trifluoromethylated aromatic compounds by treatment of HF or SbF_3, cannot be applied to the preparation of the perfluoroalkylated aromatic compounds, such as the pentafluoroethylated ones. Especially, the development of practical and reliable pentafluoroethylations of aromatic compounds is strongly desirable, because few biologically active compounds containing the pentafluoroethyl (C_2F_5) group, as shown in the angiotensin II receptor antagonist (DuP 532)[5] and antihypertensive K^+ channel opener (KC-515),[6] have been reported to date (Figure 1).

As a synthetic method for pentafluoroethylated aromatic compounds, the copper-mediated pentafluoroethylation of aryl iodide with CuI, $C_2F_5SiMe_3$, and KF was reported by Fuchikami, but the scope of substrates in the reaction was quite limited.[7] Recently, Hartwig demonstrated that stable (phen)CuC_2F_5 prepared and isolated from $[CuOtBu]_4$ and $C_2F_5SiMe_3$ was efficient for pentafluoroethylations of arylboronate esters and heteroaryl bromides.[8] However, perfluoroalkylsilane sources such as $C_2F_5SiMe_3$ are costly for large scale operation, despite its commercial availability. Grushin has recently disclosed that the ligandless CuC_2F_5 reagent *in situ* prepared by the direct cupration of economical C_2F_5H reacted with not only aryl iodides but also unactivated aryl bromides to provide the corresponding pentafluoroethylated products in excellent yields.[9,10] Daugulis has also succeeded in the copper-catalyzed pentafluoroethylation of ethyl-2-iodobenzoate via the *in situ* preparation of $Zn(C_2F_5)_2$ from TMP_2Zn and C_2F_5H.[11,12] In these methods, the intrinsic drawback that gaseous C_2F_5H possesses (boiling point: −48.5 °C) is hard to handle in common academic laboratories, and thus widespread synthetic applications are restricted. As an alternative approach, pentafluoroethylation of aryl iodides with CuC_2F_5 formed via decarboxylation of low-cost and easy-to-handle alkali metal pentafluoropropionates or methyl pentafluoropropionate, which are one of the most useful C_2F_5 sources, has been reported.[13] However, in this method, the too high reaction temperature (150−180 °C) facilitating the decarboxylation causes functional group incompatibility. Thus, the development of practical and reliable pentafluoroethylation processes in the aromatic system with a broad substrate scope still remains a challenge. Herein, we describe that the CuC_2F_5 reagent from cuprate and pentafluoropropionate derivatives could be prepared under mild conditions in almost quantitative yield, and consequently pentafluoroethylations of arylbronic acids and aryl bromides with the CuC_2F_5 reagent obtained proceeded to



DuP 532
(angiotensin II receptor antagonist)

KC-515
(antihypertensive K^+ channel opener)

Figure 1. Biologically active compounds with C_2F_5 group.

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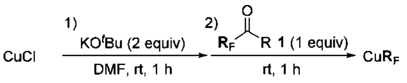
give the pentafluoroethylated aromatic compounds in good-to-excellent yields. The noteworthy advantages of this reaction system are a cost-efficient access to the CuC_2F_5 reagent, broad substrate scope, and applicability for large-scale operation.

Recently, we disclosed the direct synthesis of the $CuCF_3$ reagent from cuprate and 2,2,2-trifluoroacetophenone and its application to three types of trifluoromethylations with arylbronic acids, aryl iodides, and terminal alkynes.[14] Therefore, this synthetic method was expected to be applicable to prepare various perfluoroalkyl copper reagents. In fact, it was found that the combination of pentafluoroethyl ketone **1a** and the cuprate, $K[Cu(O^tBu)_2]$, generated from CuCl (1 equiv) and KO^tBu (2 equiv), could lead to the CuC_2F_5 reagent in 71% yield (Table 1, entry 1). Encouragingly, the yield was slightly improved when ethyl pentafluoropropionate **1b**, which is more economical as a C_2F_5 source, was employed (entry 2).[15] However, surprisingly, the formation of the copper reagents bearing longer chain perfluoroalkyl groups ($^nC_3F_7$-, $^nC_6F_{13}$-, and $^nC_8F_{17}$-) from perfluoroalkyl ketones **1c**–**e** was not observed under the same reaction conditions (entries 3–5).[16]

Table 1. Preparation of Pentafluoroethyl Copper Reagents from Cuprate and Pentafluoroethyl Ketone and Ester[a]



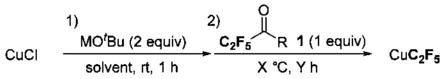
entry	R_F	R	yield (%)[b]
1	C_2F_5	Ph (**1a**)	71
2	C_2F_5	OEt (**1b**)	77
3	$^nC_3F_7$	Ph (**1c**)	0
4	$^nC_6F_{13}$	Ph (**1d**)	0
5	$^nC_8F_{17}$	Ph (**1e**)	0

[a] Conditions: After treatment of CuCl (0.5 mmol) and KO^tBu (1.0 mmol) in DMF (1.0 mL) at rt for 1 h, **1** (0.5 mmol) was added to the DMF solution at the same temperature. [b] Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

In order to increase the yield of the CuC_2F_5 reagent, we attempted to optimize the reaction conditions for its best preparation (Table 2). Treatment of **1a** at lower temperature gave ~90% yields (entries 1–2). Significantly, **1b** led to the CuC_2F_5 reagent in almost quantitative yield (>95%) (entry 3), while a higher temperature (50 °C) was required with the aim of facilitating not only the addition of cuprate to **1b** with lower electrophilicity but also the transformation from more stable tetrahedral intermediate **A′** to the CuC_2F_5, compared to the case of **1a** (see Scheme 1, eq 2). This is in sharp contrast to our previous results on the synthesis of the $CuCF_3$ reagent,[14] in which the decomposition of $CuCF_3$ was observed even at 50 °C to decrease its overall production. Moreover, it was found that the CuC_2F_5 was stable without decomposition even at 90 °C. When DMPU was used instead of DMF, a high yield was maintained under the same reaction conditions (entry 4). The employment of DMA resulted in a lower yield (entry 5), and no product was obtained in THF (entry 6). Notably, the cuprate generated from NaO^tBu or LiO^tBu can also be applicable to the reaction, despite the longer reaction time (entries 7–8). Unfortunately, the formation of the CuC_2F_5 was not observed from pentafluoropropionic anhydride **1f** and potassium pentafluoropropionate **1g** (entries 9–10).

Our previous research indicated the reaction mechanism includes perfluoroalkyl coppers being directly formed via the tetrahedral intermediate **A** (M = K or Cu or CuO^tBu).[14] Therefore, we tried to trap the tetrahedral intermediate **A** (R = Ph) by addition of TMSCl to give the *O*-silylated product **2** in 71% yield (Scheme 1, eq 1). Under the optimized reaction conditions (Table 2, entries 1 and 3), *tert*-butyl benzoate **3** and *tert*-butyl ethyl carbonate **4** generated through the tetrahedral intermediate **A′** were also isolated in 94% and 74% yields, respectively (Scheme 1, eq 2).

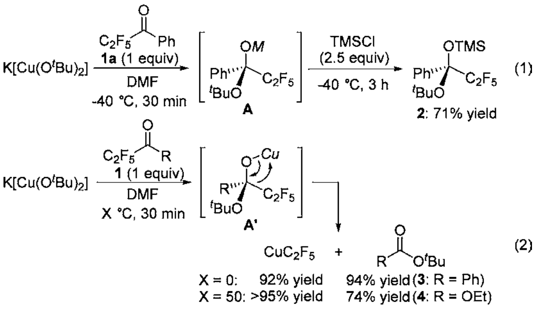
Table 2. Preparation of Pentafluoroethyl Copper Reagent Using Various Pentafluoroethyl Sources[a]



entry	R	M	solvent	*X*	*Y*	yield (%)[b]
1	Ph (**1a**)	K	DMF	0	0.5	**92**
2		K	DMF	−10	0.5	89
3	OEt (**1b**)	K	DMF	50	0.5	**>95**
4		K	DMPU	50	0.5	92
5		K	DMA	50	0.5	52
6		K	THF	50	0.5	0
7		Na	DMF	50	2	**>95**
8		Li	DMF	50	4	75
9	$OCOC_2F_5$ (**1f**)	K	DMF	50	0.5	0
10	OK (**1g**)	K	DMF	50	0.5	0

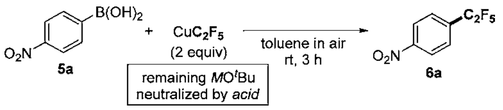
[a] Conditions: After treatment of CuCl (0.5 mmol) and KO^tBu (1.0 mmol) in solvent (1.0 mL) at rt for 1 h, pentafluoroethyl source **1** (0.5 mmol) was added to the solution, and then the solution was stirred at *X* °C for *Y* h. [b] Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

Scheme 1. Isolation of Compounds 2, 3, and 4



To test the usefulness of the CuC_2F_5 reagent *in situ* prepared from **1b** in DMF, we explored the representative reaction providing the perfluoroalkylated aromatic ring,[2a,c] the oxidative pentafluoroethylations of arylboronic acids[17] (Table 3). Initially, it was found that the desired coupling product **6a** was produced in 20% yield, when the reaction was conducted by treatment of arylboronic acid **5a**, CuC_2F_5 (2 equiv, ~0.5 M in DMF), and air (1 atm) as an oxidant in toluene at rt for 3 h (entry 1). The inefficiency of the reaction stemmed from the competing reaction between **5a** and remaining MO^tBu in preparation of the CuC_2F_5 reagent to produce a *tert*-butoxylated side product (4-*tert*-butoxy nitrobenzene) in 47% yield.[9,10d] Therefore, the neutralization of remaining MO^tBu by the addition of $Et_3N{\cdot}HCl$ dramatically enhanced the yields of product **6a** (entries 2–4). Further improvement by using $Et_3N{\cdot}3HF$ was accomplished to provide the product **6a** in 83%–90% yields following Grushin's protocol[9,10] (entries 5–7). With HCl in Et_2O, the yield was decreased, compared to that of $Et_3N{\cdot}3HF$ (entry 8).

Table 3. Effect of Acids for Neutralization[a]

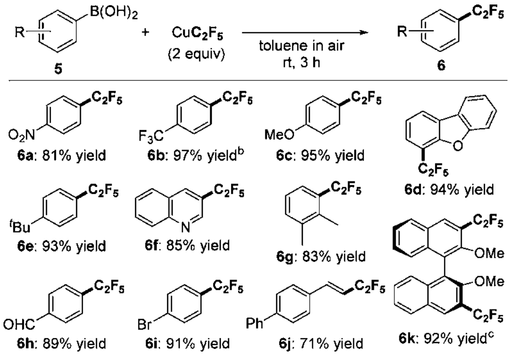


entry	M	acid	yield (%)[b]
1	K	–	20
2	K	$Et_3N{\cdot}HCl$ (2.4 equiv)	76
3	Na	$Et_3N{\cdot}HCl$ (2.4 equiv)	67
4	Li	$Et_3N{\cdot}HCl$ (2.4 equiv)	62
5	K	$Et_3N{\cdot}3HF$ (0.8 equiv)	**84**
6	Na	$Et_3N{\cdot}3HF$ (0.8 equiv)	**90**
7	Li	$Et_3N{\cdot}3HF$ (0.8 equiv)	**83**
8	K	HCl in Et_2O (2.4 equiv)	67

[a] Conditions: **5a** (0.1 mmol) and CuC_2F_5 reagent (0.2 mmol) in air (1 atm) in toluene (1 mL) at rt for 3 h. CuC_2F_5 reagent, which was prepared from CuCl, MO^tBu, and ethyl pentafluoropropionate in DMF, was neutralized by acid before being used in the reaction. [b] Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

Under the optimized reaction conditions in hand, pentafluoroethylation of various boronic acids **5** with the CuC_2F_5 reagent without any ligands, such as 1,10-phenantroline and 2,2′-bipyridine, was examined (Scheme 2). A wide range of electronically varied arylboronic acids underwent this oxidative reaction in good-to-excellent yields with high efficiency. A methyl substituent on the *ortho*-position of **5g** did not interfere with the reaction. The use of **5h** bearing a formyl group also led to the corresponding product **6h** in high yield but did not give the pentafluoroethylated alcohol at all. Moreover, the formation of **6i** with intact bromide in high yield could provide a convenient platform for further functionalization. The reactions of vinylbronic acid **5j** and naphthylbronic acid **5k** with the backbone of Me-protected 2,2′-binaphthol also proceeded smoothly in excellent yield.

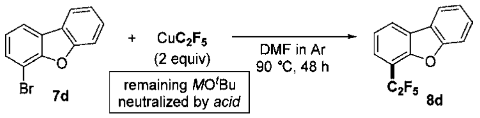
Scheme 2. Pentafluoroethylation of Arylboronic Acids[a]



[a] Conditions: **5** (0.1 mmol) and CuC_2F_5 reagent (0.2 mmol) in air (1 atm) in toluene (1 mL) at rt for 3 h. Yield of the isolated product after column chromatography. CuC_2F_5 reagent (2 equiv), which was prepared from CuCl, KO^tBu, and ethyl pentafluoropropionate in DMF, was neutralized by $Et_3N{\cdot}3HF$ (0.8 equiv) before being used in the reaction. [b] Yield was determined by ^{19}F NMR analysis using (trifluoromethoxy)benzene as an internal standard. [c] CuC_2F_5 reagent of 4 equiv was used.

Additionally, the CuC_2F_5 reagent prepared by our method was successfully applied to pentafluoroethylation with aryl bromides which are more economical and useful but less reactive than aryl iodides, while the reaction mixture needed to be heated up to 90 °C with the aim of gaining high conversion (Table 4). In contrast to the case of arylboronic acids, the reaction was found to be extremely sensitive to not only additional acids but also the metal cation (K, Na, and Li) of the remaining bases (MO^tBu) in preparation of the CuC_2F_5 reagent. Initially, the reactions in the presence of each of metal cation led to low yields of the product, whether $Et_3N{\cdot}HCl$ as an acid was used or not (entries 1−4). The reaction with $Et_3N{\cdot}3HF$ for neutralization of KO^tBu also resulted in a low yield (entry 5); however, switching KO^tBu to NaO^tBu dramatically increased the reactivity to give the desired product **8d** in 95% yield (entry 6). In the presence of the Li cation, the yield was moderate (entry 7). While the influence of the metal cation on the product yields was not well understood, the change in solution phases from heterogeneous to homogeneous was observed on addition of $Et_3N{\cdot}3HF$ when NaO^tBu was used for preparation of the CuC_2F_5 reagent (entry 6). Contrary to NaO^tBu, the CuC_2F_5 solution prepared with KO^tBu or LiO^tBu remained heterogeneous so that KF or LiF settled at the bottom of the flask, even after the addition of $Et_3N{\cdot}3HF$ (entries 5 and 7).

Table 4. Effect of Additional Bases and Acids[a]



entry	M	acid	yield (%)[b]
1	K	–	12
2	K	$Et_3N{\cdot}HCl$ (2.4 equiv)	33
3	Na	$Et_3N{\cdot}HCl$ (2.4 equiv)	44
4	Li	$Et_3N{\cdot}HCl$ (2.4 equiv)	32
5	K	$Et_3N{\cdot}3HF$ (0.8 equiv)	44
6	Na	$Et_3N{\cdot}3HF$ (0.8 equiv)	**95**
7	Li	$Et_3N{\cdot}3HF$ (0.8 equiv)	75

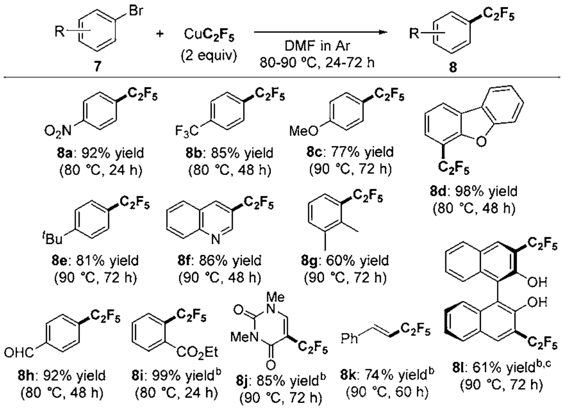
[a] Conditions: **7d** (0.2 mmol) and CuC_2F_5 reagent (0.4 mmol) at 90 °C for 48 h. CuC_2F_5 reagent, which was prepared from CuCl, MO^tBu, and ethyl pentafluoropropionate in DMF, was neutralized by acid before being used in the reaction. [b] Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) as an internal standard.

The CuC_2F_5 reagent was useful for pentafluoroethylation with a variety of aryl bromides **7** under the optimized conditions, providing the pentafluoroethylated aromatic compounds in good-to-excellent yields (Scheme 3). In general, it was found that aryl bromides **7c**, **7e**, and **7g** with electron-donating substituents showed lower reactivity than **7a**−**b** and **7h**−**i** with electron-withdrawing substituents. Quinoline **7f**, uracil **7j** derivatives, and vinyl bromide **7k** were also successfully pentafluoroethylated by the CuC_2F_5 reagent. Importantly, free hydroxyl functionality of 3,3′-Br-BINOL **7l** was compatible with the reaction.

It is valuable that these reactions could be successfully employed in a gram scale synthesis for two types of pentafluoroethylation, thus affording a practical and reliable access to pentafluoroethylated aromatic compounds (Scheme 4, eqs 3 and 4). Under the optimized reaction conditions, the reaction with arylbronic acid **5d** (2.1 g, 10 mmol) proceeded to isolate the product **6d** in 84% yield (2.4 g, 8.4 mmol). In the reaction with aryl bromide **7i** (scale: 2.2 g, 10 mmol), the product **8i** was also isolated in 98% yield (2.6 g, 9.8 mmol).

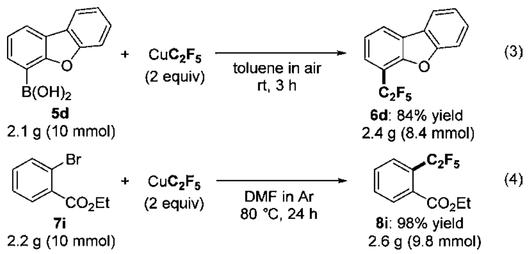
In summary, we have succeeded in the direct synthesis of the CuC_2F_5 reagent from cuprate and ethyl pentafluoropropionate as

Scheme 3. Pentafluoroethylation of Aryl Bromides[a]



[a] Conditions: 7 (0.2 mmol) and CuC_2F_5 reagent (0.4 mmol) at 80−90 °C for 24−72 h. Yield was determined by ^{19}F NMR analysis using benzotrifluoride (BTF) or (trifluoromethoxy)benzene as an internal standard. CuC_2F_5 reagent (2 equiv), which was prepared from CuCl, NaO^{t}Bu, and ethyl pentafluoropropionate in DMF, was neutralized by $Et_3N·3HF$ (0.8 equiv) before being used in the reaction. [b] Isolated yield. [c] CuC_2F_5 reagent (4 equiv) was used.

Scheme 4. Large-Scale Operation for Pentafluoroethylation



one of the most useful C_2F_5 sources. Compared with our previous work that the $CuCF_3$ reagent prepared from ethyl trifluoroacetate was obtained in ∼60% yield, ethyl pentafluoropropionate could lead to the CuC_2F_5 reagent in excellent yield even under large-scale operation. Furthermore, the CuC_2F_5 reagent prepared can be successfully applied to two types of pentafluoroethylations with arylboronic acids and aryl bromides to provide the pentafluoroethylated aromatic compounds in good-to-excellent yields, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and compound characterization 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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(15) The ^{19}F and ^{13}C NMR spectra of CuC_2F_5 obtained in DMF matched well with the spectra reported by Grushin; see ref 9.

(16) Grushin has reported the same result that perfluoroalkyl copper reagents bearing longer chain perfluoroalkyl groups than the pentafluoroethyl one could not be prepared from cuprate and the corresponding 1*H*-perfluoroalkanes; see ref 9.

(17) (a) Chu, L.; Qing, F.-L. *Org. Lett.* **2010**, *12*, 5060. (b) Senecal, T. D.; Parsons, A. T.; Buchwald, S. L. *J. Org. Chem.* **2011**, *76*, 1174.