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Cupration of C_2F_5H: Isolation, Structure, and Synthetic Applications of $[K(DMF)_2][(t\text{-}BuO)Cu(C_2F_5)]$. Highly Efficient Pentafluoroethylation of Unactivated Aryl Bromides

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Supporting Information

ABSTRACT: Pentafluoroethane, C_2F_5H (HFC-125), is smoothly cuprated with preisolated or in situ-generated $[K(DMF)][(t\text{-}BuO)_2Cu]$ to give $[K(DMF)_2][(t\text{-}BuO)Cu(C_2F_5)]$ (**1**) in nearly quantitative yield. Complex **1** has been isolated, structurally characterized, and demonstrated to be an exceedingly versatile pentafluoroethylating reagent for a variety of substrates, including unactivated aryl bromides.

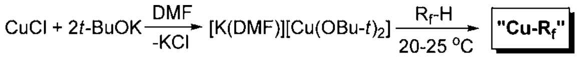
Fluoroalkylated molecules are of special importance to the development of modern agrochemicals, pharmaceuticals, and specialty materials.[1,2] A variety of methods are available for the introduction of the smallest perfluoroalkyl group, CF_3, into organic substrates. Pentafluoroethylation reactions are vastly less developed, despite the fact that in certain cases C_2F_5 derivatives exhibit properties that are superior to those of their CF_3 counterparts.[3] Since the original work of Gassman and O'Reilly[4] and more recent developments by Röschenthaler[5a−d] and others,[5e] C_2F_5Li has been successfully used for pentafluoroethylation of carbonyl compounds and some other electrophiles. Efficient alternative methods for the generation and synthetic applications of $C_2F_5^-$ carbanion equivalents have been reported.[2k,6−8]

The carbanion methodology,[2k,4−8] however, is not applicable to pentafluoroethylation of aromatic and other organic halides. Moreover, pentafluoroethylated aromatic compounds cannot be made by the Swarts-type process[9] that is used to manufacture benzotrifluorides ($ArCF_3$). Currently available synthetic routes to aromatic C_2F_5 derivatives are not only scarce but also suffer from a narrow substrate scope and limited functional group tolerance. Altogether, only two dozen or so pentafluoroethylation reactions of haloarenes have been reported in the literature. The decarboxylative pentafuoroethylation of aryl iodides with $CuI/C_2F_5CO_2M$ (M = Na, K, Me)[10] occurs at 150−180 °C, which is too high a temperature for a number of functional groups to survive. Apart from the high cost and low availability of the C_2F_5 silane source, the $CuI/C_2F_5SiMe_3/KF$ system[11] has been used for pentafluoroethylation of a handful of iodoarenes bearing only Me, NO_2, Ac, and CO_2Et substituents on the ring. A few aromatic C_2F_5 derivatives have been prepared from highly activated (hetero)aryl iodides and CuC_2F_5 produced by thermal decomposition of $CuCF_3$.[12,13] Pentafluoroethylation of unactivated bromoarenes such as bromobenzene is unknown.[14]

As is clear from the above, the area of aromatic pentafluoroethylation remains severely underdeveloped. Herein we report the facile synthesis of a new CuC_2F_5 reagent in nearly quantitative yield directly from inexpensive and readily available C_2F_5H, an ozone-friendly refrigerant and a fire suppression agent. We also describe full structural characterization of this novel CuC_2F_5 species and its remarkable ability to pentafluoroethylate a variety of substrates, including unactivated aryl bromides, in a highly efficient manner.

We have recently found[15] the first cupration reaction of fluoroform (CHF_3) and demonstrated the synthetic value of the thus-produced $CuCF_3$ in a variety of trifluoromethylation reactions.[15−17] A logical extension of these developments was to examine whether this method could be applied to higher *H*-perfluoroalkanes. To our surprise, under the conditions leading to the highly selective cupration of fluoroform, $CF_3(CF_2)_nH$ (n = 2, 5, 7), $H(CF_2)_6H$, and $(CF_3)_2CFH$ did not produce Cu−R_f but rather gave KF/KHF_2 and complex mixtures of organofluorine products (^{19}F NMR). An even bigger surprise came when, after all these failures, C_2F_5H underwent exceedingly smooth and clean cupration to give a C_2F_5Cu derivative in nearly quantitative yield (Scheme 1). There have been no literature reports on the preparation of CuC_2F_5 compounds directly from C_2F_5H.

Scheme 1. Cupration of R_f−H



R_f	Yield of Cu-R_f, %	ref.
CF_3	>90	15
$CF_3(CF_2)_n$ (n = 2, 5, 7)	not observed	this work
$H(CF_2)_6$	not observed	this work
$(CF_3)_2CF$	not observed	this work
CF_3CF_2	***>95***	this work

Adding C_2F_5H to $[K(DMF)][(t\text{-}BuO)_2Cu]$,[15] preisolated or generated in situ from CuCl and *t*-BuOK (1:2), in *N*,*N*-dimethylformamide (DMF) at room temperature resulted in an instantaneous reaction. ^{19}F NMR analysis of the resultant solution indicated the formation of "CuC_2F_5" (ca. 95%) along with traces (<1%) of $[Cu(C_2F_5)_2]^-$.[18−20] The CuC_2F_5 product appeared to be much more robust than the $CuCF_3$ analogue prepared in a similar manner from CHF_3.[15] This difference in stability is explained by less facile α-F-elimination from higher R_fM complexes compared with their CF_3M congeners. (For

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instance, under conditions where C_2F_5Li is stable,[4,5] CF_3Li decomposes to LiF and CF_2.) The enhanced stability of the C_2F_5H cupration product allowed for its isolation and study by single-crystal X-ray diffraction. The structure of this novel compound, $[K(DMF)_2][(t\text{-BuO})Cu(C_2F_5)]$ (**1**),[21] is shown in Figure 1. Like $[M(DMF)_n][(t\text{-BuO})_2Cu]$ (M = Na, K),[15] **1** is a polymer in the solid state. Each two adjacent K atoms are bridged by two μ-DMF-κ^2O molecules and one μ-$[(t\text{-BuO})Cu(C_2F_5)]$-$\kappa^2O$ unit. The latter is similar to the μ-$[(t\text{-BuO})Cu(CF_3)]$-κ^2O link found previously[15] in the structure of $[Cu_4(CF_3)_2(C(OBu\text{-}t)_2)_2(\mu^3\text{-OBu-}t)_2]$. Only two X-ray structures of Cu−C_2F_5 compounds have been reported, one Cu(III) species, $[(C_2F_5)_2Cu(S_2CNEt_2)]$,[20] and one mixed Cu(I) ate complex, $[K(DMPU)_3][(C_2F_5)CuCl]$.[13] The Cu−C bond length in **1** (1.893(4) Å), while considerably shorter than that in the Cu(III) complex (1.981(7) Å), is close in length to that found in the $[(C_2F_5)CuCl]^-$ anion (1.916 Å). The Cu−C−C angles in the structures of **1** (115.7(3)°), the Cu(III) complex (117.4(6)°), and $[(C_2F_5)CuCl]^-$ (116.8°) are similar. The less stable and consequently nonisolable primary product of the cupration of fluoroform[15] likely has a structure similar to that of **1**.

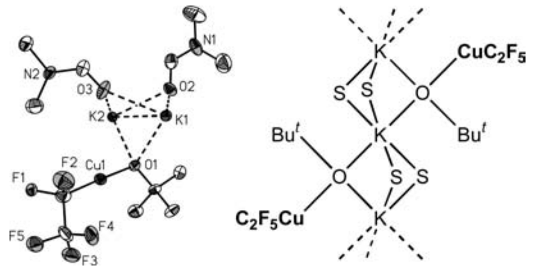


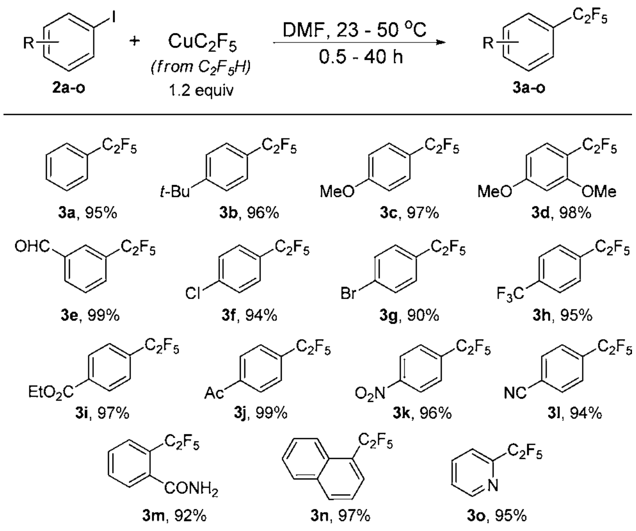
Figure 1. Structure and ORTEP drawing of $[K(DMF)_2][(t\text{-BuO})Cu(C_2F_5)]$ (**1**) (S = μ-DMF-κ^2O) with thermal ellipsoids drawn to the 50% probability level and all H atoms omitted for clarity.

We next explored the possibility of using **1** for pentafluoroethylation of various substrates. First, the reactivity of **1** toward aryl iodides was tested. For initial studies, 4-fluoroiodobenzene was chosen as a substrate in order to extract more information from monitoring the reaction by ^{19}F NMR. No reaction of **1** generated from CuCl/*t*-BuOK (1:2) and C_2F_5H in DMF was observed upon addition of 10 equiv of 4-IC_6H_4F at room temperature, and only small amounts of $4\text{-C}_2F_5C_6H_4F$ were produced after 3 h at 50 °C. After ca. 10 h at 80 °C, however, the reaction reached full conversion of **1** to $4\text{-C}_2F_5C_6H_4F$ (^{19}F NMR: δ −84.4, 3F; −106.8, 1F; −113.2, 2F) and $4\text{-}t\text{-BuOC}_6H_4F$ (^{19}F NMR: δ −120.3) in a 1:1.2 ratio. Remarkably, no side decomposition of **1** was observed. These results indicated that (i) **1** is less reactive toward aryl halides yet much more thermally stable than its CF_3 analogue[15,22] and (ii) like fluoroform-derived $CuCF_3$ prior to the stabilization,[15] **1** both fluoroalkylates and *tert*-butoxylates the substrate.

The *tert*-butoxylation side reaction was efficiently suppressed by adding $Et_3N\cdot 3HF$ (TREAT HF) or Py·*n*HF to **1** in DMF prior to use in pentafluoroethylation reactions. This technique was adopted from our previous work with fluoroform-derived $CuCF_3$.[15] Interestingly, it was found that not only HF sources but also other acids such as AcOH or HCl in dioxane could be used with **1** to eliminate the undesired *tert*-butoxylation. The best results in the current work were obtained with TREAT HF.[22,23]

A series of optimization experiments indicated that adding 1.6 equiv of HF in the form of TREAT HF to a solution of **1** produced the most efficient reagent.[22] The latter was found to pentafluoroethylate iodoarenes **2a**−**o** in 90−99% yield at 23−50 °C (Scheme 2). A slight 20% excess of CuC_2F_5 was sufficient to achieve full conversion of the starting ArI substrates. Electron-withdrawing or -donating substituents at the ortho, meta, or para position were easily tolerated, including simple alkyls (**2b**), MeO (**2c**, **2d**), CHO (**2e**), Cl (**2f**), Br (**2g**), CF_3 (**2h**), CO_2Et (**2i**), Ac (**2j**), NO_2 (**2k**), CN (**2l**), and $CONH_2$ (**2m**). The reaction of 4-IC_6H_4Br (**2g**) side-produced $1,4\text{-}(C_2F_5)_2C_6H_4$ (ca. 8%). Both 1-iodonaphthalene and 2-iodopyridine underwent smooth fluoroalkylation, giving **3n** and **3o** in yields of 97% and 95%, respectively.

Scheme 2. Pentafluoroethylation of Aryl Iodides with C_2F_5H-Derived CuC_2F_5[a]

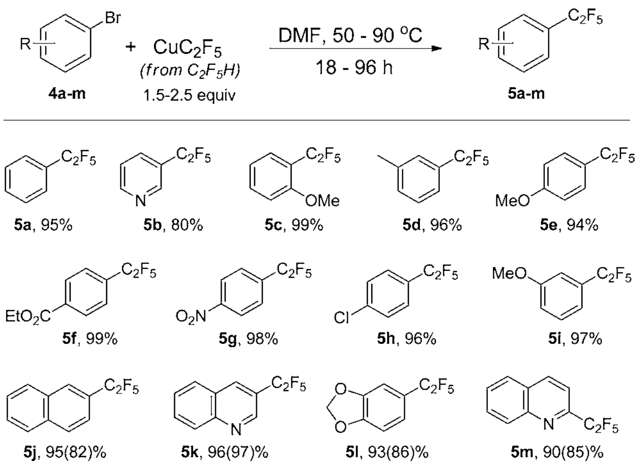


[a]Yields determined by ^{19}F NMR using an internal standard.[22]

Aryl bromides are much more cost-attractive and readily available but significantly less reactive than iodoarenes. There have been no reports of general methods for efficient trifluoromethylation or pentafluoroethylation of unactivated bromoarenes. We were pleased to find that our Cu reagent pentafluoroethylated various bromo(hetero)arenes **4a**−**m** at 80−90 °C with high selectivity in 80−99% yield (Scheme 3). Even particularly challenging bromobenzene (**4a**), *o*- and *p*-bromoanisole (**4c** and **4e**), and *m*-bromotoluene (**4d**) were smoothly converted to the corresponding C_2F_5 derivatives in ≥94% yield. 2-(Pentafluoroethyl)naphthalene (**5j**) and the three heterocyclic derivatives **5k**−**m** were produced in 90−96% yield (^{19}F NMR) and isolated in 82−97% yield (0.42−0.72 g).[22] The structure of **5j** was confirmed by single-crystal X-ray diffraction (Figure 2).

The CuC_2F_5 was found to be useful for pentafluoroethylation of not only aryl halides but also a variety of other substrates (Scheme 4), including arylboronic acids and terminal acetylenes under oxidative conditions (in air), benzylic and vinylic bromides, and metal complexes. Treatment of [(tmeda)Pd(Ph)-I] with our CuC_2F_5 reagent gave $[(tmeda)Pd(C_2F_5)(Ph)]$ (**6**), which was isolated in 90% yield and fully characterized, including by single-crystal X-ray diffraction (Figure 3). Palladium complexes bearing a σ-C_2F_5 ligand are extremely rare because of the lack of general methods for Pd−C_2F_5 bond formation.

Scheme 3. Pentafluoroethylation of Aryl Bromides with C_2F_5H-Derived CuC_2F_5[a]



[a] ^{19}F NMR (isolated) yields.[22]

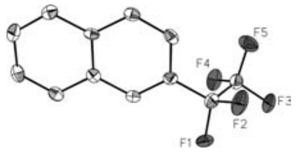
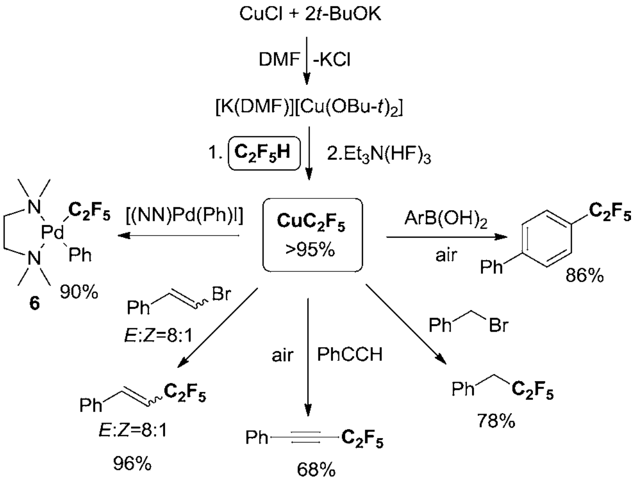


Figure 2. ORTEP drawing of 2-$C_{10}H_7C_2F_5$ (**5j**) with thermal ellipsoids drawn to the 50% probability level and all H atoms omitted for clarity.

Scheme 4. Pentafluoroethylation of Various Substrates with C_2F_5H-Derived CuC_2F_5



Only one such adequately characterized complex, [(tmeda)Pd(C_2F_5)(Me)],[24] has been reported.[25]

The trans influence and electronic effects of the CF_3 and higher R_f groups are not without controversy.[2r] The X-ray structures of **6** and its previously reported[26] CF_3 analogue **8** provided a unique opportunity to compare the structural trans influences of C_2F_5 and CF_3.[27] Table 1 lists coordination bond distances for **6** and its counterparts [(tmeda)Pd(R_f)(R)], where $R_f = C_2F_5$, R = Me (**7**)[24] and $R_f = CF_3$, R = Ph (**8**).[26] The three structures display similar, nearly undistorted square-planar geometries, suggesting no excessive steric crowding in the coordination sphere. The almost identical Pd–C(R) bond distances for R = Ph (1.990(2) Å in **6** and 1.996(1) Å in **8**) are slightly shorter than that for R = Me (2.171(4) Å in **7**). The Pd–C(R_f) bond lengths are longer for $R_f = C_2F_5$ (2.019(2) Å in **6** and 2.033(5) Å in **7**) than for $R_f = CF_3$ (1.993(1) Å in **8**). This is consistent with a decrease in the degree of s character in the carbon's hybrid orbital directed toward Pd upon replacement of one F atom in **8** with the less electronegative CF_3 to give **6** (Bent's rule).[28] The Pd–N bond distances trans to the R_f ligand are similar for $R_f = CF_3$ (2.169(1) Å in **8**) and $R_f = C_2F_5$ (2.166(2) Å in **6** and 2.180(2) Å in **7**) and are ca. 0.03–0.04 Å shorter than those trans to the Ph and Me ligands. These data show that the structural trans influences of C_2F_5 and CF_3 are indistinguishable within experimental error and somewhat weaker than those of Me and Ph.

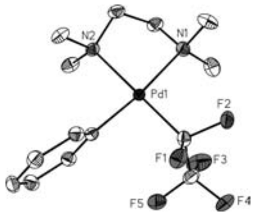


Figure 3. ORTEP drawing of [(tmeda)Pd(C_2F_5)(Ph)] (**6**) with thermal ellipsoids drawn to the 50% probability level and all H atoms omitted for clarity.

Table 1. Selected Bond Distances (Å) for [(tmeda)Pd(R_f)(R)]

bond	$R_f = C_2F_5$ R = Ph (**6**) (this work)	$R_f = C_2F_5$ R = Me (**7**) (ref 24)	$R_f = CF_3$ R = Ph (**8**) (ref 26)
Pd–C(R_f)	2.019(2)	2.033(5)	1.993(1)
Pd–C(R)	1.990(2)	2.171(4)	1.996(1)
Pd–N trans to R_f	2.166(2)	2.180(2)	2.169(1)
Pd–N trans to R	2.213(2)	2.221(4)	2.198(1)

A comment is due on the peculiar varying reactivity of different *H*-perfluoroalkanes toward the dialkoxycuprate. The abrupt change in reaction pathways for the $CF_3(CF_2)_nH$/[K(DMF)][(*t*-BuO)$_2$Cu] system when going from $n = 1$ (cupration) to $n > 1$ (HF elimination) is not fully understood. It is conceivable that HF elimination is preferred for C3 and higher *H*-perfluoroalkanes because the substituted olefinic products $R_fCF{=}CF_2$ are more stable than $CF_2{=}CF_2$ that would result from dehydrofluorination of C_2F_5H. Mechanistic studies of this interesting reactivity pattern are currently underway.

In conclusion, like CHF_3 but unlike other higher *H*-perfluoroalkanes, C_2F_5H undergoes smooth cupration with [K(DMF)][(*t*-BuO)$_2$Cu]. This reaction occurs at room temperature and atmospheric pressure to give quantitatively [K(DMF)$_2$] [(*t*-BuO)Cu(C_2F_5)] (**1**), which has been structurally characterized. Complex **1**, while being slightly less reactive toward electrophiles than its CF_3 counterpart, is much more thermally stable. This stability allowed for highly efficient pentafluoroethylation of not only iodoarenes (>90% yield) but also much more inert unactivated aryl bromides (80–99% yield). These reactions of bromoarenes are unprecedented. Efficient C_2F_5 transfer has also been demonstrated from **1** to benzylic and vinylic bromides, arylboronic acids, and terminal acetylenes under oxidative conditions (in air) as well as to another metal (Pd) center. This new methodology is likely to find use in both academia and industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full details of synthetic (PDF) and crystallographic (CIF) studies. 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.

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(13) One ArI substrate has been pentafluoroethylated with $[(DMPU)_2Zn(C_2F_5)_2]$ in the presence of CuCl (10%) and phen (20%). See: Popov, I.; Lindeman, S.; Daugulis, O. *J. Am. Chem. Soc.* **2011**, *133*, 9286.

(14) (a) A few examples of pentafluoroethylation of activated bromoarenes have been reported.[10b,c,12b] Attempted Cu-catalyzed perfluoroalkylation of 4-bromobiphenyl with $[(DMPU)_2Zn(R_f)_2]$ generated in situ from R_fH gave the desired product in <5% yield.[13] (b) Pd-catalyzed borylation of a few unactivated aryl bromides followed by oxidative fluoroalkylation of the resultant arylboronate esters with $[(phen)CuC_2F_5]$ has been reported. See: Litvinas, N. D.; Fier, P. S.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 536.

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(18) Reported ^{19}F NMR data for "CuC_2F_5": δ −82.8 (3F), −110.0 (2F).[12,19] For $[Cu(C_2F_5)_2]^-$: δ −82.9 (3F), −116.1 (2F).[14b,20]

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(21) In contrast with the cupration of CHF_3,[15] which cannot be efficiently carried out in THF, the reaction of preisolated $[K(DMF)][(t\text{-}BuO)_2Cu]$ with C_2F_5H in THF afforded **1**, albeit in a slightly lower yield (81%). No formation of $[Cu(C_2F_5)_2]^-$ was detected in this case.

(22) See the Supporting Information for details.

(23) In contrast with fluoroform-derived $CuCF_3$,[15] the CuC_2F_5 reagent produced upon treatment with HCl or AcOH is stable.

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(27) Although X-ray analysis has been performed for *trans*-$[(Ph_2PMe)_2Pt(R_f)Cl]$ (R_f = CF_3, C_2F_5), packing disorder in the CF_3 complex precludes comparison of the structural trans influences of C_2F_5 and CF_3. It has been suggested on the basis of the ν(Pt−Cl) values that the IR trans influences of CF_3 and C_2F_5 are similar. See: Bennett, M. A.; Chee, H.-K.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061.

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