Dalton Transactions

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c6dt00277c

A class of effective decarboxylative perfluoroalkylating reagents: [(phen)$_2$Cu](O$_2$CR$_F$)†

Yangjie Huang,[a] Manjaly J. Ajitha,[b] Kuo-Wei Huang,*[b] Zhongxing Zhang[c] and Zhiqiang Weng*[a]

Received 20th January 2016,
Accepted 13th April 2016

DOI: 10.1039/c6dt00277c

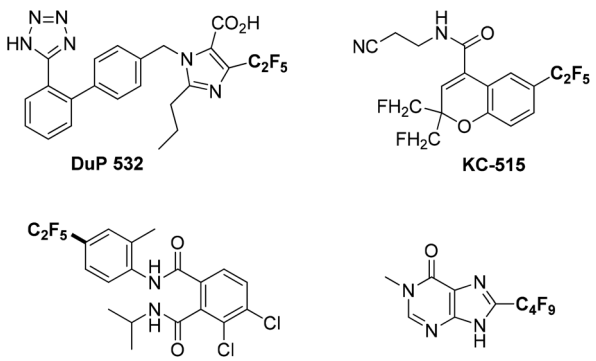
www.rsc.org/dalton

This article describes the invention of a class of effective reagents [(phen)$_2$Cu](O$_2$CR$_F$) (**1**) for the decarboxylative perfluoroalkylation of aryl and heteroaryl halides. Treatment of copper *tert*-butyloxide with phenanthroline ligands, with subsequent addition of perfluorocarboxylic acids afforded air-stable copper(I) perfluorocarboxylato complexes **1**. These complexes reacted with a variety of aryl and heteroaryl halides to form perfluoroalkyl(hetero)arenes in moderate to high yields. Computational studies suggested that the coordination of the second phen ligand may reduce the energy barrier for the decarboxylation of perfluorocarboxylate to facilitate perfluoroalkylation.

Introduction

The development of efficient methods for organofluorine compound synthesis is a highly active research area in organic chemistry.[1–3,4–7] The incorporation of perfluoroalkyl groups into bioactive molecules often dramatically alters their physical and chemical properties, and biological activities which has led to the widespread use of fluorine-containing compounds in the fields of medicinal chemistry[8–10,11,12] and materials science.[13] For instance, pentafluoroethyl groups are present in many bioactive compounds and drugs, such as the angiotensin II receptor antagonist (DuP 532),[14] the antihypertensive K^+ channel opener (KC-515),[15] perfluoroalkyl substituted aniline insecticides[16] and nucleobases[17] (Scheme 1). The exploration of efficient perfluoroalkylation reactions is therefore of great urgency.

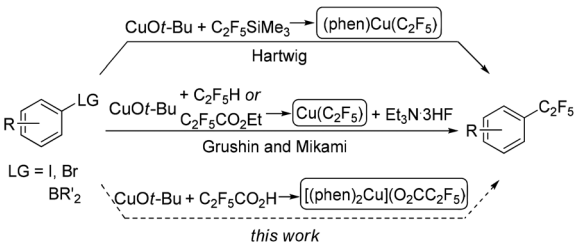
Transition metal-mediated or -catalyzed trifluoromethylation has emerged as an attractive new strategy for C–CF$_3$ bond formation from arenes, aryl halides, arenediazonium salts, and the corresponding boronic acids.[18–25,26–35] There are, however, few examples of the introduction of longer-chain perfluoroalkyl moieties, such as the C_2F_5 group, into organic molecules (Scheme 2).[36–38] For instance, Hartwig and coworkers successfully employed stable (phen)Cu(C_2F_5), prepared from the reaction of CuO*t*-Bu with $C_2F_5SiMe_3$, for pentafluoroethylation of arylboronate esters and heteroaryl bromides.[39–41] Grushin's group reported the ligandless Cu(C_2F_5) *in situ* prepared by the direct cupration of economical C_2F_5H[42] and Mikami's group later reported the same reagent synthesized from ethyl pentafluoropropionate.[43] The CuC_2F_5 reagent was demonstrated as an exceedingly versatile pentafluoroethylating reagent for a variety of substrates, including arylboronic acids and aryl bromides. Despite the popularity of these methods, some of them suffered from the use of expensive perfluoroalkylsilane sources such as $C_2F_5SiMe_3$ or gaseous C_2F_5H (boiling point: −48.5 °C), or the requirement of the addition of Et$_3$N·3HF to enhance the reaction efficiency. An alternative approach to CuC_2F_5 is the decarboxylation of low-cost and easy-to-handle alkali metal



Scheme 1 Bioactive compounds containing perfluoroalkyl groups.

[a]*State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, 350108, China. E-mail: zweng@fzu.edu.cn*
[b]*KAUST Catalysis Center and Division of Physical Sciences & Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia*
[c]*Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634, Singapore*

† Electronic supplementary information (ESI) available: Experimental procedures and spectral data for products and mechanistic study experiments. X-ray crystallography details. CCDC 1427126 and 1427127. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00277c



Scheme 2 Copper reagent for pentafluoroethylation of aryl halides and boronic acids.

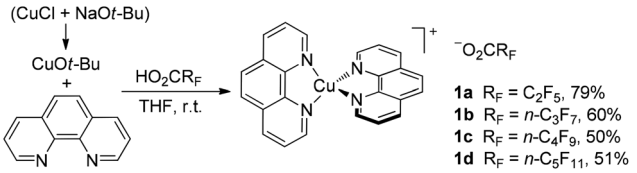
pentafluoropropionates or methyl pentafluoropropionate.[44–47] Unfortunately, these reactions have a number of limitations, such as the requirement of high temperatures (150–180 °C), lack of practicability, and poor substrate scope, despite their economical nature.[48]

Besides the C_2F_5 group, the incorporation of other higher fluorinated functional groups onto an aromatic core structure has also gained exceptional attention.[49–54] Transition metal-catalyzed perfluoroalkylation of arenes and heteroarenes has proven to be a useful and versatile method for their synthesis.[55–64] However, there still remain a number of limitations. In particular, some of the approaches reported are of limited reaction scope with respect to the even carbon number $C_nF_{2n+1}I$ (n = 2, 4, 6, 8, 10) species, and expensive reagents are typically needed. Therefore, the development of general and economical reagents for perfluoroalkylation is highly desirable.

In this context, we recently reported a copper(I) trifluoroacetate complex (phen)Cu(O_2CCF_3) for the decarboxylative trifluoromethylation of (hetero)aryl halides,[65] and the related copper reagents for the synthesis of fluorinated organic compounds.[66–69] Herein, we report the synthesis of complexes [(phen)$_2$Cu](O_2CR_F), and demonstrate their applications in the perfluoroalkylation of (hetero)aryl halides to furnish perfluoroalkylarenes in good yields.

Results and discussion

We started our studies by the synthesis of copper(I)–O_2CR_F complexes. The copper species **1a** was generated by the reaction of CuO*t*-Bu (prepared *in situ* from the reaction of CuCl with NaO*t*-Bu) with two equiv. of phen ligand, with subsequent addition of perfluoropropionic acid (1.0 equiv.) in THF at room temperature. Complex **1a** was isolated as a reddish brown solid in good yield (79%). Its higher fluorinated analogues **1b–d** were also synthesized *via* the reactions with the respective perfluorocarboxylic acids (Scheme 3). These complexes containing longer chains of fluorinated groups were isolated as reddish brown crystalline solids in slightly lower yields (50–60%), probably due to their good solubility in solvents. All of these complexes can be prepared on a multi-gram scale (4–5 g) in the laboratory. All of them are air- and moisture stable in the solid state and readily soluble in polar organic solvents such as DMF, DMSO, CH_3CN, and CH_2Cl_2.



Scheme 3 Synthesis of copper(I) perfluoroacetato complexes **1a–d**.

Crystallization of **1a** by vapor diffusion of diethyl ether into a solution of CH_3CN afforded dark red crystals suitable for X-ray analysis. Crystals of complex **1b**·C_6H_6 were obtained by slow evaporation of a CH_3CN/benzene solution at room temperature. The molecular structures of **1a** and **1b** are shown in Fig. 1 and 2, respectively. Each of these complexes contains a cationic tetrahedral Cu^I center ligated by two phen ligands and a free, unligated anionic perfluorocarboxylato group.

To evaluate the potential of these perfluorocarboxylato complexes to be reactive reagents in decarboxylative perfluoroalkylation,

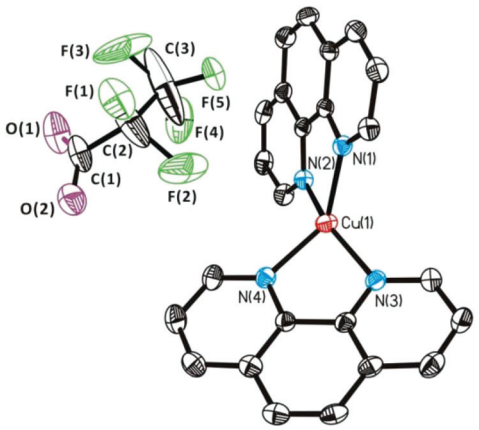


Fig. 1 ORTEP structure of complex **1a** with thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.071(2), Cu(1)–N(2) 2.007(7), Cu(1)–N(3) 2.012(4), Cu(1)–N(4) 2.062(2), C(1)–O(1) 1.221(4), C(1)–O(2) 1.209(4), C(1)–C(2) 1.599(6), N(1)–Cu(1)–N(2) 82.24(7), N(1)–Cu(1)–N(3) 109.23(7), N(2)–Cu(1)–N(4) 110.62(7), N(3)–Cu(1)–N(4) 82.20(7), O(1)–C(1)–O(2) 130.9(3), O(1)–C(1)–C(2) 104.2(3), O(2)–C(1)–C(2) 123.8(3).

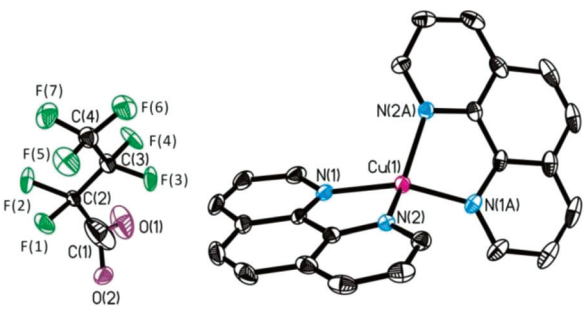


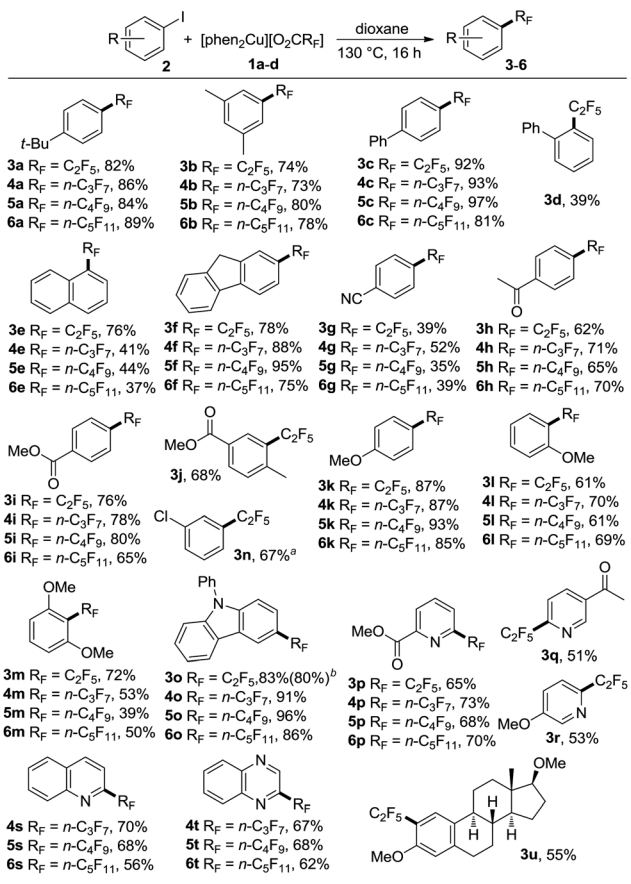
Fig. 2 ORTEP structure of complex **1b** with thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity.

we examined their reactions with aryl iodides in dioxane at 130 °C for 16 h (see the ESI†). The reagent proved to be broadly applicable and the desired products were generated in moderate to high yields. 4-*tert*-Butyl-, 3,5-dimethyl-, or 4-phenyl-substituted phenyl iodides reacted readily with **1a** to give the desired pentafluoroethylated products **3a–c** in 82%, 74%, and 92% yields, respectively (Scheme 4). The sterically hindered 2-iodobiphenyl provided the product **3d** in 39% yield. 1-Iodonaphthalene and 2-iodo-9*H*-fluorene underwent the reaction to furnish **3e** and **3f** in good yields. Reactions with electron-withdrawing aryl iodides also gave the desired products **3g** and **3h**, in 39% and 62% yields, respectively. Additionally, aryl iodides containing an ester group were also tolerated in this reaction to give the desired products (**3i** and **3j**, respectively) in good yields, and no transesterified by-products were detected. The electron-rich aryl iodides reacted smoothly to give the desired products **3k–m** in 61–87% yields. 1-Chloro-3-iodobenzene underwent pentafluoroethylation smoothly to give the corresponding product **3n** in 67% yield with the chloro substituent intact. The ability to incorporate a chloro substituent into the products provides opportunities for further functional manipulations through transition-metal-catalyzed cross-coupling reactions. Furthermore, the use of 3-iodo-*N*-phenylcarbazole gave the corresponding pentafluoroethylated product **3o** in good yield (83%). It should be emphasized that heteroaromatic substrates, such as 2-iodopyridines, 2-iodoquinoline, and 2-iodoquinoxaline, were also suitable reaction partners, affording the corresponding products **3p–t** in 51–80% yields. Furthermore, an estradiol derivative reacted to form the pentafluoroethylated product **3u** in modest yield.

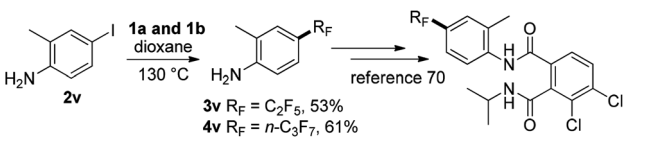
To expand the scope of the transformation, we next embarked on an exploration of the incorporation of longer chain perfluoroalkyl groups into complexes **1b–d**. A wide range of aryl iodides exhibited excellent reactivity, including those with electron-neutral, electron-donating, electron-withdrawing and *para*, *meta*, or *ortho* substituents (Scheme 4). For substrates with electron donating substituents, a higher reaction temperature (140 °C) was required to reach full conversion. In fact, the decarboxylative perfluoropropylation, perfluorobutylation, and perfluoropentylation provided the corresponding arene products **4a–4o**, **5a–5o**, and **6a–6o** in similar yields to those of pentafluoroethylation. Heteroarenes proved to be suitable substrates as well, delivering the synthetically useful products **4p–4t**, **5p–5t**, and **6p–6t**.

The synthetic utility of the developed methodology was also demonstrated by the synthesis of perfluoroalkyl substituted aniline insecticides. The perfluoroalkylation of 4-iodo-2-methylaniline **2v** with **1a** and **1b** provided **3v** and **4v** in 53% and 61% yields, respectively (Scheme 5). Compounds **3–4v** could readily be transformed into phthalic acid diamide derivatives following the reported procedures.[70]

To gain a better understanding of the reaction mechanism, density functional theory (DFT) was employed using the Gaussian 09 suite of quantum chemistry packages.[71] All the geometries were optimized at the standard B3LYP level of density functional theory with the 6-31G(d) basis set for C, H, O, N and F atoms and the LANL2DZ (Los Alamos National Laboratory 2 double ζ) basis set for Cu and I atoms.[72,73] The energies were further refined with the 6-311+G(d,p) basis set for all atoms except Cu and I which were treated with the LANL2DZ basis set. In order to account for missing London dispersion effects and basis set superposition error, dispersion (D3) corrections including the Becke–Johnson (BJ) damping function and geometrical counterpoise corrections (gCP) were also added.[74,75] The effect of dioxane solvent was considered using the solvation model based on density (SMD).[76] The free energy values obtained at the B3LYP-SMD-gCP-D3(BJ)/6-311+G(d,p)//B3LYP/6-31G(d) level of theory were used to discuss the energetics in the reaction profile.



Scheme 4 Perfluoroalkylation of aryl iodides with **1a–d**. Conditions: **1a–d** (0.75 mmol), **2** (0.50 mmol), dioxane (5.0 mL), 16 h, N_2, 130 °C. Yields of isolated products are shown. [a] ^{19}F NMR yield. [b] Conducted in a 2.7 mmol scale reaction.



Scheme 5 Formal synthesis of perfluoroalkyl substituted aniline insecticides.

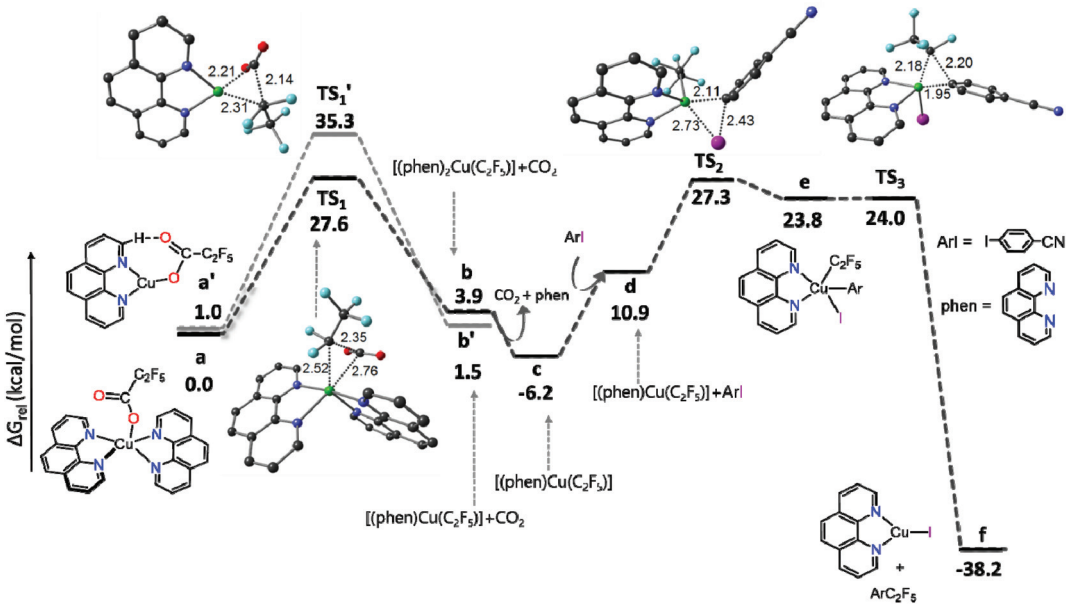


Fig. 3 Free energy profile for the decarboxylation pentafluoroethylation of 4-iodobenzonitrile (ArI) with $[phen_2Cu][O_2CC_2F_5]$. Bond distances are given in Å.

The mechanism can be considered to begin with the copper(I) perfluorocarboxylate complex as the starting complex (**a**) (Fig. 3). The previous DFT studies mainly focused on distorted tetrahedral transition states with one phen ligand for the Cu-catalyzed decarboxylation reaction,[77–80] but we observed that an octahedral transition state with two phen ligands is much more favored. The activation barrier for the decarboxylation (extrusion of CO_2) was found to be 27.6 kcal mol^{-1} with two coordinating phen ligands (*via* $\mathbf{TS_1}$). In contrast, the dissociation of one of the ligands from the Cu(I) complex resulted in a significant increase ($\Delta\Delta G^{\ddagger}$ = 7.7 kcal mol^{-1}) in the activation barrier for the decarboxylation to 35.3 kcal mol^{-1} (*via* $\mathbf{TS_1}'$). The metal center of $\mathbf{TS_1}$ appears to be more electron rich (Mulliken charge = 0.142) compared to that of $\mathbf{TS_1}'$ (Mulliken charge = 0.246). The initial ArI bond breaking before the decarboxylation was also modeled but a much higher activation barrier was computed (46.8 kcal mol^{-1}). In the case of ethyl carboxylate, the activation barrier was 34.8 kcal mol^{-1}, in agreement with the less reactivity of Cu(I) ethylacetate. After the decarboxylation, the dissociation of one of the phen ligands resulted in a more stable tricoordinate intermediate complex **c** (ΔG_{rel} = −6.2 kcal mol^{-1}) which underwent the oxidative addition of the Ar–I bond to Cu with an overall activation barrier of 33.5 kcal mol^{-1} *via* $\mathbf{TS_2}$ (rate determining step). A less stable pentacoordinate intermediate **e** was formed followed by an almost barrierless C–C bond coupling (*via* $\mathbf{TS_3}$) to reductively release the product **f**. Overall, the reaction is exergonic by 38.2 kcal mol^{-1}.

Conclusions

In summary, we have invented an effective reagent $[(phen)_2Cu](O_2CR_F)$ from readily available and inexpensive starting materials. A series of copper(I) perfluorocarboxylato complexes supported by phenanthroline ligands have been prepared by treating CuO*t*-Bu and the phen ligand with perfluorocarboxylic acids. The molecular structures of these complexes have been determined by X-ray diffraction. These air-stable complexes can serve as an efficient reagent for the decarboxylative perfluoroalkylation of aryl and heteroaryl halides to form perfluoroalkyl (hetero)arenes of high value. DFT methods indicate that the coordination of the second phen ligand may reduce the energy barrier for the decarboxylation of perfluorocarboxylate to facilitate perfluoroalkylation.

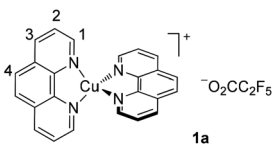
Experimental

General information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard (0.00 ppm). Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on a Waters GCT-TOF at the Shanghai Institute of Organic Chemistry. 2-Iodo-3,17-dimethoxy-β-estra-1,3,5(10)-triene was prepared according to the published procedures.[81] Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published

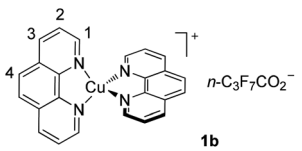
procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

Synthesis of [(phen)$_2$Cu][$O_2CC_2F_5$] (1a). A solution of NaO*t*-Bu (345 mg, 3.6 mmol) in 10.0 mL of THF was added to a suspension of CuCl (297 mg, 3.0 mmol) in 60 mL of THF, and the resulting mixture was stirred at room temperature for 120 min. The resulting light yellow mixture was filtered through a layer of Celite. To this filtrate was added a solution of 1,10-phenanthroline (1080 mg, 6.0 mmol) in 10 mL of THF. The resulting solution turned reddish brown immediately and was stirred at room temperature for an additional 5 min. A THF solution (1 mL) of $C_2F_5CO_2H$ (492 mg, 3.0 mmol) was added dropwise and the mixture was further stirred at room temperature for 20 min. The solution was filtered, and the filtrate was dried under vacuum to yield a dark red solid. The resulting solid was washed with 2 × 2 mL of diethyl ether and dried under vacuum to obtain 1.38 g (79%) of **1a**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (d, J = 3.7 Hz, 4H, H_1), 8.82 (dd, J = 8.1, 1.1 Hz, 4H, H_3), 8.27 (s, 4H, H_4), 7.99 (dd, J = 8.1, 4.7 Hz, 4H, H_2). ^{19}F NMR (376 MHz, DMSO-d_6) δ −81.5 (t, J = 1.4 Hz, 3F, CF_3), −118.1 (d, J = 1.4 Hz, 2F, CF_2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.3 (t, J = 21.9 Hz), 149.8 (s), 143.5 (s), 137.7 (s), 129.4 (s), 127.5 (s), 126.2 (s), 120.0 (qt, J_{CF} = 286.4, 36.4 Hz, CF_3), 107.6 (tq, J_{CF} = 266.6, 35.4 Hz, CF_2). Elemental Analysis (%) calculated for $C_{27}H_{16}CuF_5N_4O_2$: C 55.25, H 2.75, N 9.54. Found: C 55.47, H 2.89, N 9.77.



1a

Synthesis of [(phen)$_2$Cu][n-$C_3F_7CO_2$] (1b). A solution of NaO*t*-Bu (345 mg, 3.6 mmol) in 10 mL of THF was added to a suspension of CuCl (297 mg, 3.0 mmol) in 60 mL of THF, and the resulting mixture was stirred at room temperature for 120 min. The resulting light yellow mixture was filtered through a layer of Celite. To this filtrate was added a solution of 1,10-phenanthroline (1080 mg, 6.0 mmol) in 10 mL of THF. The resulting solution turned reddish brown immediately and was stirred at room temperature for an additional 5 min. A THF solution (1 mL) of n-$C_3F_7CO_2H$ (642 mg, 3.0 mmol) was added dropwise and the mixture was further stirred at room temperature for 20 min. The solution was filtered, and the filtrate was dried under vacuum to yield a dark red solid. The resulting solid was washed with 2 × 2 mL of diethyl ether and dried under vacuum to obtain 1.14 g (60%) of **1b**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (d, J = 3.7 Hz, 4H, H_1), 8.82 (dd, J = 8.1, 1.0 Hz, 4H, H_3), 8.27 (s, 4H, H_4), 7.99 (dd, J = 8.1, 4.7 Hz, 4H, H_2). ^{19}F NMR (376 MHz, DMSO-d_6) δ −80.2 (t, J = 8.5 Hz, 3F, CF_3), −115.6 (q, J = 8.4 Hz, 2F, CF_2), −126.1 (s, 2F, CF_2). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.0 (t, J = 22.2 Hz), 149.8 (s), 143.5 (s), 137.7 (s), 129.4 (s), 127.5 (s), 126.2 (s), 125.0–104.4 (m, $CF_2CF_2CF_3$). Elemental Analysis (%) calculated for $C_{28}H_{16}CuF_7N_4O_2{\cdot}C_6H_6$: C 57.11, H 3.10, N 7.83. Found: C 57.32, H 3.19, N 8.06.



1b

General procedure for perfluoroalkylation of aryl iodides

In a dry box, [phen$_2$Cu][O_2CR_F] (0.75 mmol), aryl or heteroaryl halides (0.50 mmol), and 5 mL dioxane were added to a oven dried 25 mL test tube with a Teflon screw cap. The tube was sealed and the solution was stirred at 130 °C for 16 h. Then the reaction mixture was filtered through a layer of Celite, eluted with diethyl ether. The resulting mixture was extracted with ethyl ether (20 mL × 3), and the combined organic layers were washed with water (60 mL × 3), and then dried over magnesium sulfate. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane/Et_2O.

Acknowledgements

Financial support from the National Natural Science Foundation of China (NSFC) (grant number 21372044), the Research Fund for the Doctoral Program of Higher Education of China (grant number 20123514110003), and Fuzhou University (grant number 022494) is gratefully acknowledged.

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