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ARTICLE

A Class of Effective of Decarboxylative Perfluoroalkylating Reagents: $[(\text{phen})_2\text{Cu}](\text{O}_2\text{CR}_\text{F})^\dagger$

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This article describes the invention of a class of effective reagents [(phen)₂Cu](O₂CR_F) (**1**) for the decarboxylative perfluoroalkylation of aryl and heteroaryl halides. Treatment of the copper *tert*-butoxide with phenanthroline ligands, with subsequent addition of perfluorocarboxylic acids afforded the 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 the 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 lead to widespread use of fluorine-containing compounds in the fields of medicinal chemistry^{8-10,11, 12} and material sciences.¹³ For instance, pentafluoroethyl groups are featured in many bioactive compounds and drugs, such as the angiotensin II receptor antagonist (DuP 532),¹⁴ antihypertensive K⁺ channel opener (KC-515),¹⁵ perfluoroalkyl substituted aniline insecticides¹⁶ and nucleobases¹⁷ (Scheme 1). The exploration of efficient perfluoroalkylation reactions, is therefore of great urgency.

Scheme 1 Bioactive compounds containing perfluoroalkyl groups.

Transition meta-mediated or -catalyzed trifluoromethylation has emerged as an attractive new strategy for C–CF₃ bond formation from arenes, aryl halides, arenediazonium salts, and the corresponding boronic acids.^{18–25, 26–35} There is, however, few examples for the introduction of the longer-chain perfluoroalkyl moieties, such as the C₂F₅ group, into organic molecules (Scheme 2).^{36, 37, 38} For instance, Hartwig and co-workers successfully employed stable (phen)Cu(C₂F₅), prepared from reaction of CuOt-Bu with C₂F₅SiMe₃, for pentafluoroethylation of arylboronate esters and heteroaryl bromides.^{39–41} Grushin's groups reported the ligandless Cu(C₂F₅) *in situ* prepared by the direct cupration of economical C₂F₅H⁴² and Mikami's groups later reported the same reagent synthesized from ethyl pentafluoropropionate.⁴³ The CuC₂F₅ reagent was demonstrated as an exceedingly versatile pentafluoroethylating reagent for a variety of substrates, including arylboronic acids and aryl bromides. Despite the

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popularity of these methods, some of them suffered from the use of expensive perfluoroalkylsilane sources such as $\text{C}_2\text{F}_5\text{SiMe}_3$ or gaseous $\text{C}_2\text{F}_5\text{H}$ (boiling point: -48.5°C), or the requirement of the addition of $\text{Et}_3\text{N} \cdot 3\text{HF}$ to enhance the reaction efficiency. An alternative approach to CuC_2F_5 is the decarboxylation of low-cost and easy-to-handled alkali metal pentafluoropropionates or methyl pentafluoropropionate.^{44–47} Unfortunately, these reactions have a number of limitations, such as the requirement for high temperature ($150\text{--}180^\circ\text{C}$), lack of practicability, and poor substrate scope, despite their economical nature.⁴⁸

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

Besides the C_2F_5 group, the incorporation of other higher fluorinated functional groups on an aromatic core structure has also gained exceptional attention.^{49, 50, 51, 52, 53, 54} Transition metal-catalyzed perfluoroalkylation of arenes and heteroarenes has proven to be useful and versatile methods 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 $\text{C}_n\text{F}_{2n+1}\text{I}$ ($n = 2, 4, 6, 8, 10$) species, and expensive reagents are typically needed. Therefore, the development of general and economic reagent for perfluoroalkylation is highly desirable.

In this context, we recently reported a copper(I) trifluoroacetate complex $(\text{phen})\text{Cu}(\text{O}_2\text{CCF}_3)$ 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 $[(\text{phen})_2\text{Cu}](\text{O}_2\text{CR}_\text{F})$, and demonstrate their applications on the perfluoroalkylation of (hetero)aryl halides to furnish the perfluoroalkylarenes in good yields.

Results and discussion

We started our studies by the synthesis of copper(I)- $\text{O}_2\text{CR}_\text{F}$ complexes. The copper species **1a** was generated by the reaction of the CuOt-Bu (prepared *in situ* from reaction of CuCl with NaOt-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 chain 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 .

Crystallization of **1a** by vapor diffusion of diethyl ether into a solution of CH_3CN afforded a dark red crystal 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 Figure 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.

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

Fig. 1 ORTEP structure of complex **1a** with thermal ellipsoids set at 40% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): 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 omitted for clarity.

To evaluate the potential of these perfluorocarboxylate complexes to be reactive reagents in the decarboxylative perfluoroalkylation, we examined their reactions with aryl iodides in dioxane at 130 °C for 16 h (See supporting information). 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-9H-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 byproducts were detected. The electron-rich aryl iodides underwent smoothly to give the desired products **3k-m** in 61–87% yields. 1-Chloro-3-iodobenzene underwent the pentafluoroethylation smoothly to give the corresponding product **3n** in 67% yield with the chloro substituent intact. The ability to incorporate 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, estradiol derivative reacted to form the pentafluoroethylated product **3u** in modest yield.

Scheme 4 Perfluoroalkylation of aryl iodides with **1a-d**.^a

^a Conditions: **1a-d** (0.75 mmol), **2** (0.50 mmol), dioxane (5.0 mL), 16 h, N₂, 130 °C. Yields of isolated products are shown. ^b ¹⁹F NMR yield. ^c Conducted in a 2.7 mmol scale reaction.

To expand the scope of the transformation, we next embarked on an exploration of the incorporation of longer chain perfluoroalkyl groups with 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 the 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 the phthalic acid diamide derivatives following the reported procedures.⁷⁰

Scheme 5 Formal synthesis of perfluoroalkyl substituted aniline insecticides.

To gain a better understanding of the reaction mechanism, density functional theory (DFT) was employed using 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 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 LANL2DZ basis set. In order to account for missing London dispersion effects and basis set superposition error, dispersion (D3) corrections including Becke Johnson damping function (BJ) 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.

The mechanism can be considered to begin with the copper(I) perfluorocarboxylate complex as the starting complex (**a**) (Figure 3). 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 CO₂) was found to be 27.6 kcal/mol with two coordinating phen ligands (via TS₁). 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) in the activation barrier for the decarboxylation to 35.3 kcal/mol (via TS₁'). The metal center of TS₁ appears to be more electron rich (Mulliken charge = 0.142) compared to that of TS₁' (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). In the case of ethyl carboxylate, the activation barrier was 34.8 kcal/mol, in agreement with the less reactivity of Cu(I) ethylacetate. After the decarboxylation, the dissociation of one of the phen ligands resulted in more stable tricoordinate intermediate complex **c** ($\Delta G_{\text{rel}} = -6.2$ kcal/mol) and underwent the oxidative addition of the Ph-I bond to Cu with an overall activation barrier of 33.5 kcal/mol via TS₂ (rate determining step). A less stable pentacoordinate intermediate **e** was formed followed by an almost barrierless C–C bond coupling (via TS₃) to reductively release the product **f**. Overall, the reaction is exergonic by 38.2 kcal/mol.

Fig. 3 Free energy profile for the decarboxylation pentafluoroethylation of 4-iodobenzonitrile (Arl) with [phen₂Cu][O₂CC₂F₅]. Bond distances are given in Å.

Conclusions

In summary, we have invented an effective reagent $[(\text{phen})_2\text{Cu}](\text{O}_2\text{CR}_\text{F})$ from readily available and inexpensive starting materials. A series of copper(I) perfluorocarboxylate complexes supported by phenanthroline ligands have been prepared by treating CuOt-Bu and 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 the perfluoroalkylation.

Experimental

General information

^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^1H 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 and low field is positive. Coupling constants (J) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^1H 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 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 $[(\text{phen})_2\text{Cu}](\text{O}_2\text{CC}_2\text{F}_5)$ (1a**).** A solution of NaOt-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 $\text{C}_2\text{F}_5\text{CO}_2\text{H}$ (810 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 were washed with 2×2 mL of diethyl ether and dried under vacuum to obtain 1.38 g (79%) of **1a**. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) 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, $\text{DMSO}-d_6$) 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, $\text{DMSO}-d_6$) 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, $J_{\text{CF}} = 286.4$,

36.4 Hz, CF_3), 107.6 (tq, $J_{\text{CF}} = 266.6$, 35.4 Hz, CF_2). Elemental Analysis(%) calculated for $\text{C}_{27}\text{H}_{16}\text{CuF}_5\text{N}_4\text{O}_2$: C 55.25, H 2.75, N 9.54. Found: C 55.47, H 2.89, N 9.77.

Synthesis of $[(\text{phen})_2\text{Cu}][n\text{-C}_3\text{F}_7\text{CO}_2]$ (1b**).** A solution of NaOt-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 $n\text{-C}_3\text{F}_7\text{CO}_2\text{H}$ (960 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 were washed with 2×2 mL of diethyl ether and dried under vacuum to obtain 1.14 g (60%) of **1b**. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) 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, $\text{DMSO}-d_6$) 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, $\text{DMSO}-d_6$) 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, $\text{CF}_2\text{CF}_2\text{CF}_3$). Elemental Analysis(%) calculated for $\text{C}_{28}\text{H}_{16}\text{CuF}_7\text{N}_4\text{O}_2 \cdot \text{C}_6\text{H}_6$: C 57.11, H 3.10, N 7.83. Found: C 57.32, H 3.19, N 8.06.

General procedure for perfluoroalkylation of aryl iodides. In a dry box, $[(\text{phen})_2\text{Cu}](\text{O}_2\text{CR}_\text{F})$ (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 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 by ethyl ether (20 mL $\times$ 3), and the combined organic layers was washed with water (60 mL $\times$ 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 .

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Notes and references

1. T. Hiyama, *Organofluorine Compounds: Chemistry and Properties*, Springer, Berlin, 2000.
2. P. Kirsch, *Modern fluoroorganic chemistry : synthesis, reactivity, applications*, Wiley-VCH, Weinheim, 2004.
3. V. A. Petrov, *Fluorinated Heterocyclic Compounds: Synthesis, Chemistry, and Applications*, Wiley, Hoboken, 2009.
4. J. Nie, H.-C. Guo, D. Cahard and J.-A. Ma, *Chem. Rev.*, 2011, **111**, 455-529.
5. S. Roy, B. T. Gregg, G. W. Gribble, V.-D. Le and S. Roy, *Tetrahedron*, 2011, **67**, 2161-2195.
6. S. Barata-Vallejo, B. Lantaño and A. Postigo, *Chem.-Eur. J.*, 2014, **20**, 16806-16829.
7. X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683-730.
8. J.-P. Begue and D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, Wiley, Hoboken, 2008.
9. I. Ojima and Editor, *Fluorine In Medicinal Chemistry And Chemical Biology*, John Wiley & Sons Ltd., 2009.
10. T. Yamazaki, T. Taguchi and I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, Wiley-Blackwell, Chichester, 2009.
11. J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432-2506.
12. W. Zhu, J. Wang, S. Wang, Z. Gu, J. L. Aceña, K. Izawa, H. Liu and V. A. Soloshonok, *J. Fluorine Chem.*, 2014, **167**, 37-54.
13. T. Nakajima and H. Groult, *Fluorinated Materials for Energy Conversion*, Elsevier, London, 2005.
14. R. H. Chiou and M. W. Lo, *J. Chromatogr.*, 1992, **581**, 165-170.
15. N. Taka, H. Koga, H. Sato, T. Ishizawa, T. Takahashi and J.-i. Imagawa, *Bioorg. Med. Chem.*, 2000, **8**, 1393-1405.
16. M. Onishi, A. Yoshiura, E. Kohno, K. Tsubata, EP1380568A2, 2004.
17. M. Mâlebielle, S. Fujii and K. Kato, *Tetrahedron*, 2000, **56**, 2655-2664.
18. R. J. Lundgren and M. Stradiotto, *Angew. Chem. Int. Ed.*, 2010, **49**, 9322-9324.
19. T. Besset, C. Schneider and D. Cahard, *Angew. Chem. Int. Ed.*, 2012, **51**, 5048-5050.
20. D. L. Browne, *Angew. Chem. Int. Ed.*, 2014, **53**, 1482-1484.
21. O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475-4521.
22. L. Chu and F.-L. Qing, *Acc. Chem. Res.*, 2014, **47**, 1513-1522.
23. T. Furuya, A. S. Kamlet and T. Ritter, *Nature*, 2011, **473**, 470-477.
24. T. Liu and Q. Shen, *Eur. J. Org. Chem.*, 2012, 6679-6687.
25. C. Ni, M. Hu and J. Hu, *Chem. Rev.*, 2015, **115**, 765-825.
26. M. Oishi, H. Kondo and H. Amii, *Chem. Commun.*, 2009, 1909-1911.
27. L. Chu and F.-L. Qing, *Org. Lett.*, 2010, **12**, 5060-5063.
28. T. F. Liu and Q. L. Shen, *Org. Lett.*, 2011, **13**, 2342-2345.
29. T. D. Senecal, A. T. Parsons and S. L. Buchwald, *J. Org. Chem.*, 2011, **76**, 1174-1176.
30. I. Popov, S. Lindeman and O. Daugulis, *J. Am. Chem. Soc.*, 2011, **133**, 9286-9289.
31. T. Knauber, F. Arian, G.-V. Roeschenthaler and L. J. Goossen, *Chem.-Eur. J.*, 2011, **17**, 2689-2697.
32. H. Kondo, M. Oishi, K. Fujikawa and H. Amii, *Adv. Synth. Catal.*, 2011, **353**, 1247-1252.
33. L. Chu and F.-L. Qing, *J. Am. Chem. Soc.*, 2011, **134**, 1298-1304.
34. Y. Nakamura, M. Fujiu, T. Murase, Y. Itoh, H. Serizawa, K. Aikawa and K. Mikami, *Beilstein J. Org. Chem.*, 2013, **9**, 2404-2409.
35. T. Ogawa, N. Kumagai and M. Shibasaki, *Angew. Chem. Int. Ed.*, 2013, **52**, 6196-6201.
36. M. M. Kremlev, W. Tyrra, A. I. Mushta, D. Naumann and Y. L. Yagupolskii, *J. Fluorine Chem.*, 2010, **131**, 212-216.
37. P. K. Mykhailiuk, *Chem.-Eur. J.*, 2014, **20**, 4942-4947.
38. F. Sladojevich, E. McNeill, J. Börgel, S.-L. Zheng and T. Ritter, *Angew. Chem. Int. Ed.*, 2015, **54**, 3712-3716.
39. H. Morimoto, T. Tsubogo, N. D. Litvinas and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2011, **50**, 3793-3798.
40. N. D. Litvinas, P. S. Fier and J. F. Hartwig, *Angew. Chem. Int. Ed.*, 2012, **51**, 536-539.
41. M. G. Mormino, P. S. Fier and J. F. Hartwig, *Org. Lett.*, 2014, **16**, 1744-1747.
42. A. Lishchynskiy and V. V. Grushin, *J. Am. Chem. Soc.*, 2013, **135**, 12584-12587.
43. H. Serizawa, K. Aikawa and K. Mikami, *Org. Lett.*, 2014, **16**, 3456-3459.
44. J. N. Freskos, *Synth. Commun.*, 1988, **18**, 965-972.
45. G. E. Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, *J. Chem. Soc. Perkin Trans. 1*, 1988, 921-926.
46. B. R. Langlois and N. Roques, *J. Fluorine Chem.*, 2007, **128**, 1318-1325.
47. T. Schareina, X.-F. Wu, A. Zapf, A. Cotté, M. Gotta and M. Beller, *Top. Catal.*, 2012, **55**, 426-431.
48. K. A. McReynolds, R. S. Lewis, L. K. G. Ackerman, G. G. Dubinina, W. W. Brennessel and D. A. Vicic, *J. Fluorine Chem.*, 2010, **131**, 1108-1112.
49. J. Burdon, P. L. Coe, C. R. Marsh and J. C. Tatlow, *Chemical Communications (London)*, 1967, 1259-1260.
50. P. M. Murphy, C. S. Baldwin and R. C. Buck, *J. Fluorine Chem.*, 2012, **138**, 3-23.
51. A. Bravo, H.-R. Bjørsvik, F. Fontana, L. Liguori, A. Mele and F. Minisci, *J. Org. Chem.*, 1997, **62**, 7128-7136.
52. M. Iizuka and M. Yoshida, *J. Fluorine Chem.*, 2009, **130**, 926-932.
53. V. M. Fernández-Alvarez, M. Nappi, P. Melchiorre and F. Maseras, *Org. Lett.*, 2015, **17**, 2676-2679.
54. S. Barata-Vallejo, S. M. Bonesi and A. Postigo, *RSC Advances*, 2015, **5**, 62498-62518.
55. T. Sugiishi, H. Amii, K. Aikawa and K. Mikami, *Beilstein J. Org. Chem.*, 2015, **11**, 2661-2670.
56. N. Kamigata, T. Ohtsuka, T. Fukushima, M. Yoshida and T. Shimizu, *J. Chem. Soc. Perkin Trans. 1*, 1994, 1339-1346.
57. X.-T. Huang and Q.-Y. Chen, *J. Org. Chem.*, 2001, **66**, 4651-4656.
58. L. He, K. Natte, J. Rabeah, C. Taeschler, H. Neumann, A. Brückner and M. Beller, *Angew. Chem. Int. Ed.*, 2015, **54**, 4320-4324.
59. R. N. Loy and M. S. Sanford, *Org. Lett.*, 2011, **13**, 2548-2551.
60. Y. B. Dudkina, D. Y. Mikhaylov, T. V. Gryaznova, O. G. Sinyashin, D. A. Vicic and Y. H. Budnikova, *Eur. J. Org. Chem.*, 2012, 2114-2117.

61. K. Aikawa, Y. Nakamura, Y. Yokota, W. Toya and K. Mikami, *Chem.-Eur. J.*, 2015, **21**, 96-100.
62. J.-C. Xiao, C. Ye and J. n. M. Shreeve, *Org. Lett.*, 2005, **7**, 1963-1965.
63. Q. Qi, Q. Shen and L. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 6548-6551.
64. H. Kato, K. Hirano, D. Kurauchi, N. Toriumi and M. Uchiyama, *Chem.-Eur. J.*, 2015, **21**, 3895-3900.
65. X. Lin, C. Hou, H. Li and Z. Weng, *Chem.-Eur. J.*, 2016, **22**, 2075-2084.
66. Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K.-W. Huang, *Angew. Chem. Int. Ed.*, 2013, **52**, 1548-1552.
67. Y. Liu, C. Chen, H. Li, K.-W. Huang, J. Tan and Z. Weng, *Organometallics*, 2013, **32**, 6587-6592.
68. C. Chen, L. Ouyang, Q. Lin, Y. Liu, C. Hou, Y. Yuan and Z. Weng, *Chem.-Eur. J.*, 2014, **20**, 657-661.
69. R. Huang, Y. Huang, X. Lin, M. Rong and Z. Weng, *Angew. Chem. Int. Ed.*, 2015, **54**, 5736-5739. Corrigendum: 2015, 54, 8022.
70. M. Tohnishi, H. Nakao, E. Kohno, T. Nishida, T. Furuya, T. Shimizu, A. Seo, K. Sakata, S. Fujioka, H. Kanno, US20010041814A1, 2001.
71. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2013.
72. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
73. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785-789.
74. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
75. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
76. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
77. L. J. Gooßen, W. R. Thiel, N. Rodríguez, C. Linder and B. Melzer, *Adv. Synth. Catal.*, 2007, **349**, 2241-2246.
78. L. Xue, W. Su and Z. Lin, *Dalton Trans.*, 2011, **40**, 11926-11936.
79. K. Vikse, G. N. Khairallah, J. S. McIndoe and R. A. J. O'Hair, *Dalton Trans.*, 2013, **42**, 6440-6449.
80. A. Fromm, C. van Wuelen, D. Hackenberger and L. J. Goossen, *J. Am. Chem. Soc.*, 2014, **136**, 10007-10023.
81. X. Lu, J. Yi, Z.-Q. Zhang, J.-J. Dai, J.-H. Liu, B. Xiao, Y. Fu and L. Liu, *Chem.-Eur. J.*, 2014, **20**, 15339-15343.

Figure 1 illustrates the synthesis of Cu(I) complexes. (a) ORTEP diagram of the Cu(I) complex $[Cu(1,10-phen)(2,2,6,6-tetramethyl-1,10-phenanthroline)]PF_6$, showing the coordination of the copper center by the 1,10-phenanthroline and 2,2,6,6-tetramethyl-1,10-phenanthroline ligands. Thermal ellipsoids are drawn at the 50% probability level. (b) Reaction scheme for the synthesis of Cu(I) complexes: $[Cu(1,10-phen)(2,2,6,6-tetramethyl-1,10-phenanthroline)]PF_6 + R-I \rightarrow [Cu(1,10-phen)(2,2,6,6-tetramethyl-1,10-phenanthroline)(R)]PF_6 + HI$, where $R = C_2F_5, n-C_3F_7, n-C_4F_9, n-C_5F_{11}$.