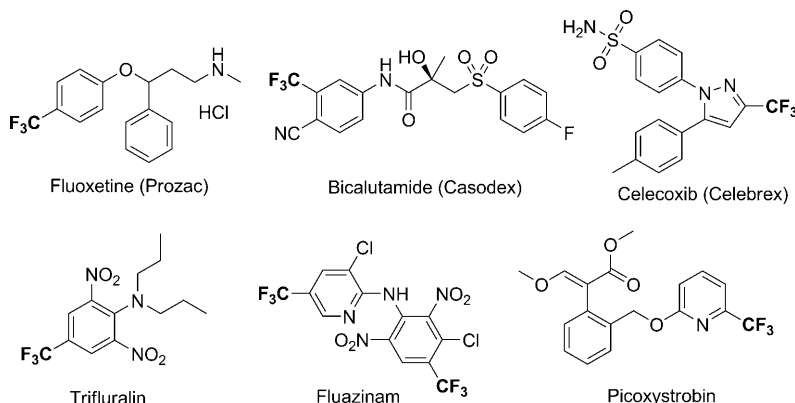


Simple, Stable, and Easily Accessible Well-Defined CuCF_3 Aromatic Trifluoromethylating Agents**

Olesya A. Tomashenko, Eduardo C. Escudero-Adán, Marta Martínez Belmonte, and Vladimir V. Grushin*

Trifluoromethylated aromatic compounds are widely used as active ingredients of numerous modern pharmaceuticals and agrochemicals (Scheme 1).^[1,2] Currently, CF_3 -bearing aro-

matic compounds are widely used as active ingredients of numerous modern pharmaceuticals and agrochemicals (Scheme 1).^[1,2] Currently, CF_3 -bearing aro-



Scheme 1. Active ingredients of selected pharmaceuticals and agrochemicals containing a trifluoromethylated aromatic moiety.

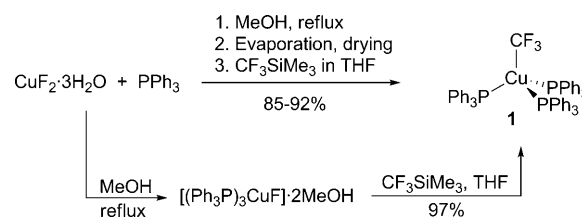
matic building blocks are made by a Swarts-type process involving exhaustive chlorination of a methyl group on the ring and subsequent Cl/F exchange on the resultant ArCCl_3 with HF .^[3] This process deals with hazardous materials and generates large quantities of chlorine waste.

An ecologically friendly alternative to the Swarts reaction is the direct introduction of a CF_3 group into the desired position on the ring. This has been achieved by copper-mediated^[4] or -catalyzed^[5] and palladium-mediated^[6] or -catalyzed^[7] trifluoromethylation of aromatic substrates. The most widely utilized are the $\text{Cu}-\text{CF}_3$ reagents, originally discovered by McLoughlin and Thrower^[8a,b] and further developed by Kobayashi and Kumadaki^[8c,d] for stoichiometric trifluoromethylation of haloarenes.^[2,4] These reagents, which have been known for over 40 years, are still poorly defined, and their structure and composition remain unknown. In their

classic report on the ^{19}F NMR spectroscopy studies of “ CuCF_3 ”, Wiemers and Burton^[9] identified these compounds as “elusive and complex species”. Understanding mechanisms of trifluoromethylation reactions with Cu^{I} reagents is important for further progress in the area. This understanding, however, is hardly conceivable without studies on well-defined CF_3 Cu^{I} complexes that can trifluoromethylate aromatic electrophiles. Such complexes are extremely rare, being limited to a few derivatives of only one type of ligand, N-heterocyclic carbenes (NHCs). Vicic and co-workers^[10] have recently prepared a handful of air-sensitive complexes of the type $[(\text{NHC})\text{Cu}(\text{CF}_3)]$ and demonstrated their ability to trifluoromethylate iodoarenes.^[10] Air-stable well-defined Cu^{I} trifluoromethylating reagents that are easy to make and handle are still unknown. Herein we report a high-yielding simple preparation, full characterization, and aromatic trifluoromethylation reactions of $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CF}_3)]$ (**1**), a remarkably air-

stable Cu^{I} trifluoromethyl complex. Complex **1** has been previously prepared by Komiya et al.^[11] by a multistep route requiring an organocopper reagent.^[12] Although microanalytical data and room-temperature NMR (^1H , ^{19}F , ^{31}P) and IR spectroscopic data for **1** have been provided,^[11] structural data, solution behavior, and reactivity studies for **1** have not been reported.

We have developed the first organocopper-free, exceedingly simple and efficient synthesis of **1** (Scheme 2). It was found that $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{F})]\cdot 2\text{MeOH}$ ^[13] (**2**) smoothly reacted



Scheme 2. Synthesis of **1**.

with Ruppert’s reagent (CF_3SiMe_3) in THF to give **1**, which was isolated in 97% yield. The *p*-tolyl analogue of **1**, $[(p\text{-Tol}_3\text{P})_3\text{Cu}(\text{CF}_3)]$, was made similarly. As **2** is prepared by the reaction of CuF_2 hydrate with PPh_3 in MeOH under reflux, it was reasoned that the reported^[13] low-yielding (39%) iso-

[*] Dr. O. A. Tomashenko, E. C. Escudero-Adán, Dr. M. Martínez Belmonte, Dr. V. V. Grushin
The Institute of Chemical Research of Catalonia
Avgda. Països Catalans 16, 43007 Tarragona (Spain)
Fax: (+34) 977-920-825
E-mail: vgrushin@icrq.es

[**] We thank the ICIQ Foundation and Consolider Ingenio 2010 (Grant CSD2006-0003) for financial support.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201101577>.

lation step could be skipped. This was indeed accomplished by running the reaction leading to **2**, evaporating the solution, drying the residue, and treating it with CF_3SiMe_3 in THF. As a result, spectroscopically pure, white **1** precipitated out and was collected by filtration in 85–92 % yield, as calculated from the amount of $\text{CuF}_2 \cdot 3\text{H}_2\text{O}$ used (Scheme 2). The thus-prepared **1** was not contaminated with the Ph_3PO by-product (co-formed along with **2** in the first step) which stayed completely in the filtrate (as determined by ^{31}P NMR spectroscopy). The procedure is simple and efficient, allowing for easy preparation of pure **1** on a multigram scale. Although in solution the complex is oxygen- and moisture-sensitive, solid **1** can be stored and handled in air for at least a month without decomposition.

The structure of **1** was determined by single-crystal X-ray diffraction. One of the three independent tetrahedral molecules A, B, and C is shown in Figure 1.^[14] Selected geometry

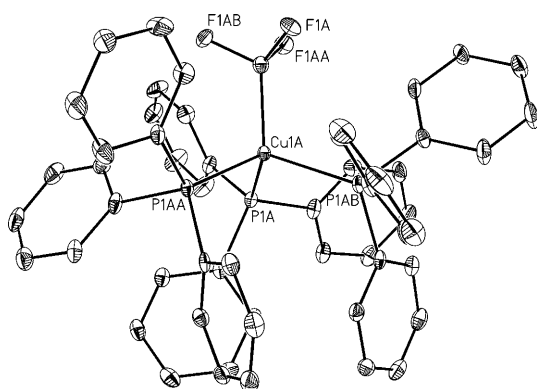


Figure 1. ORTEP drawing of one of the three molecules of **1** with thermal ellipsoids drawn at the 50 % probability level and all H atoms omitted for clarity.

parameters for **1** and its nonfluorinated analogue $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ (THF solvate),^[15] are presented in Table 1. The Cu–C bonds in molecules A, B, and C (2.018(7), 2.025(7), and 2.031(10) Å) are of similar length to the C–Cu bond (2.043(12) Å) found in $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$.^[15] The Cu–P bonds in **1** are only slightly longer (by 0.03–0.04 Å) than in $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$. The C–Cu–P bond angles in **1** are roughly 2–4° larger and the P–Cu–P bond angles for A and B up to 7°

Table 1: Selected bond lengths (Å) and angles (deg) for **1** and $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)] \cdot \text{THF}$.

Parameter	1 (A)	1 (B)	1 (C)	$[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)] \cdot \text{THF}$ ^[15]
Cu–C	2.018(7)	2.025(7)	2.031(10)	2.043(12)
Cu–P	2.353(1)	2.341(1)	2.347(1)	2.313(3) 2.313(3) 2.311(3)
C–Cu–P	111.32(3)	112.53(3)	109.57(4)	106.9(4) 106.7(4) 106.9(4)
P–Cu–P	107.56(3)	106.24(3)	109.37(4)	113.10(12) 113.17(12) 109.64(11)

smaller than in the Cu–CH₃ complex. At the same time, the P–Cu–P bond angle in molecule C (109.37(4)°) is virtually identical to one of those in the nonfluorinated complex (109.6(1)°). We therefore conclude that the crystal structures of **1** and $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ display very similar geometric parameters. This situation might be due to nearly equal electron donation from the CH₃ and the CF₃ ligands,^[2] as is the case for the $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CF}_3)]/[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CH}_3)]$ pair.^[16]

Room-temperature ^{31}P and ^{19}F NMR spectra of **1** (CD_2Cl_2) displayed singlets at $\delta = -0.8$ and -26.2 ppm, respectively, in accord with the literature data.^[11] These patterns did not change considerably in the temperature range of +25 to -90°C . In the presence of extra PPh_3 (3 equiv), still only one singlet in the ^{31}P NMR spectrum was observed at ambient temperature, pointing to phosphine exchange that is fast on the NMR time scale. Freezing out this exchange resulted in coalescence at -40°C and then in the appearance of two separate signals from **1** ($\delta = 3.4$ ppm) and from PPh_3 ($\delta = -5.5$ ppm) at -60°C and below. A ^{31}P NMR EXSY experiment allowed for the determination of the exchange rate at approximately 1 s^{-1} at -90°C . This ligand exchange occurring via PPh_3 dissociation is apparently slower for **1** than for its nonfluorinated analogue $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$. At -90°C , $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ displays two broad resonances, a large peak at $\delta = 2.8$ ppm, and a small peak at -7 ppm, which were assigned to $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ and PPh_3 , respectively.^[15] In the presence of three equivalents of PPh_3 , however, the ^{31}P NMR spectrum of $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ at -90°C shows only one broad resonance indicating that ligand exchange is still fast on the NMR time scale, whereas for **1** it becomes slow already at -60°C . However, solvent effects should not be neglected: the literature study on $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CH}_3)]$ was carried out in toluene, whereas our data were obtained in CD_2Cl_2 because of insufficient solubility of **1** in toluene (and also in THF).

In line with the NMR spectroscopy data, phosphine lability in **1** is manifested by its facile ligand exchange reactions. Treatment of **1** with 1,10-phenanthroline (phen) cleanly produced dark orange-red $[(\text{phen})\text{Cu}(\text{PPh}_3)(\text{CF}_3)]$ (**3**) that was isolated pure in 75–80 % yield and fully characterized, including by single-crystal X-ray diffraction (Figure 2).^[14] The molecule of **3** displays a distorted tetrahedral geometry with the Cu–C bond (1.985(1) Å) being only slightly shorter than in **1** (Table 1) by ca. 0.03–0.04 Å. In contrast, the Cu–P bond in **3** (2.2228(3) Å) is shorter than in **1** by 0.12–0.13 Å, a significant difference that is likely due to weaker electron donation to Cu from phen than from two PPh_3 ligands.

The room-temperature ^{19}F NMR spectrum of analytically pure **3** in CD_2Cl_2 shows a singlet at $\delta = -23.6$ ppm but also a weak (<5 % total integral intensity) resonance at $\delta = -31.0$ ppm that is assigned to $[\text{Cu}(\text{CF}_3)_2]^-$ on the basis of the literature data for other bis(trifluoromethyl)cuprate salts.^[10b,17] The presence of this minor peak points to a slow (on the NMR time scale) equilibrium between **3** and $[\text{Cu}(\text{phen})_2]^+[\text{Cu}(\text{CF}_3)_2]^- + \text{PPh}_3$. The phosphine thus released is involved in fast exchange with **3**, the still-present major Cu species, as manifested by a broad signal at 2.0 ppm ($\Delta\nu_{1/2} \approx 100 \text{ Hz}$) in the ^{31}P NMR spectrum of **3** at the same

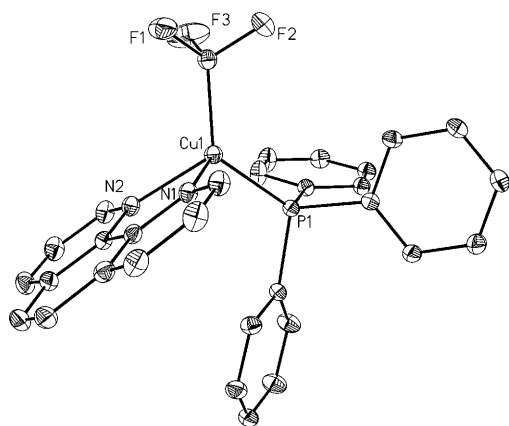


Figure 2. ORTEP drawing of **3** with thermal ellipsoids drawn at the 50% probability level and all H atoms omitted for clarity.

temperature (25 °C). The spontaneous generation of $[\text{Cu}(\text{CF}_3)_2]^-$ from **3** is similar to the formation of $[(\text{SiMe}_3)_2\text{Cu}]^+[\text{Cu}(\text{CF}_3)_2]^-$ from $[(\text{SiMe}_3)\text{Cu}(\text{CF}_3)]^{[10b]}$ ($\text{SiMe}_3 = 1,3\text{-dimesitylimidazolidin-2-ylidene}$).

Addition of 2,2'-bipyridyl (bpy) or 4,4'-di-*tert*-butyl-2,2'-bipyridyl (*t*Bu-bpy) to solutions of **1** also resulted in immediate color change to orange-red, suggesting formation of $[(\text{L-L})\text{Cu}(\text{PPh}_3)(\text{CF}_3)]$, where $\text{L-L} = \text{bpy}$ and *t*Bu-bpy, respectively. However, attempts to isolate the bpy and *t*Bu-bpy analogues of **3** resulted only in recovery of **1**. Apparently, bpy-type ligands bind to Cu more weakly than phen. As a result, $[(\text{L-L})\text{Cu}(\text{PPh}_3)(\text{CF}_3)]$ and **1** equilibrate in solution to produce only more stable and/or less soluble **1** upon crystallization.

Both **1** and **3** were found to readily trifluoromethylate aryl and heteroaryl halides. Trifluoromethylation of PhI (neat) with **1** slowly occurred even at room temperature, and after 24 h at 70 °C full conversion of **1** at 91% selectivity to PhCF_3 was observed (as determined by ^{19}F NMR spectroscopy). The reaction was then optimized for use without excess of the aromatic substrate. Herein we present only a succinct summary of the optimization work, which is described in detail in Supporting Information. In all cases the reactions were monitored by ^{19}F NMR spectroscopy with 4,4'-difluorobiphenyl or PhF as internal standards.

First, trifluoromethylation of PhI present in a large excess (11 equiv) with **1** was carried out at 70 °C in various solvents. Better yields were obtained in dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), diglyme, and toluene, whereas in MeCN, 1,2-dichloroethane, dimethylsulfoxide, and THF either the conversion of **1** was low or large quantities of CHF_3 as a side product were produced. The amount of PhI was then reduced to nearly stoichiometric (1.1 equiv), and the reaction was run in DMF, NMP, diglyme, and toluene at 100 °C. Full conversion (as determined by ^{19}F NMR spectroscopy) was observed after 2 h, with the yield of PhCF_3 ranging from 45 to 60% in diglyme, DMF, and NMP, and being 35% in toluene. The formation of PhC_2F_5 and CHF_3 side products was observed in all cases, as is quite common for Cu-promoted aromatic trifluoromethylation reactions.^[2,4] In DMF, NMP, and diglyme, CHF_3 was the main by-product, whereas in

toluene only minute quantities of CHF_3 were formed. The yield of PhC_2F_5 , however, was higher in toluene (up to 15%) than in the other solvents that provide stronger stabilization of $\text{Cu}-\text{CF}_3$ compounds toward decomposition to difluorocarbene.^[2] The latter is known^[2,4] to easily insert into the $\text{Cu}-\text{CF}_3$ bond to give CuC_2F_5 species, which can then pentafluoroethylate aromatic electrophiles.

To avoid or minimize the side processes, a number of ligands were tested as additives for the reaction of **1** with PhI in DMF and toluene. Tertiary phosphines such as PPh_3 , *n*Bu₃P, and *t*Bu₃P inhibited the trifluoromethylation and decreased the yield of PhCF_3 . This observation is consistent with a mechanism that involves PPh_3 dissociation (see above) from coordinatively saturated, 18-electron **1** prior to PhI coordination to the Cu center, finally leading to the $\text{Ph}-\text{CF}_3$ coupling. On the contrary, nitrogen ligands (phen, bpy, and *t*Bu-bpy) gave much better results: the pentafluoroethylation was totally suppressed in DMF and diminished to only a few percent in toluene. Further optimization allowed for the identification of conditions for trifluoromethylation of a series of iodoarenes in 55–90% yield (Table 2). Under these

Table 2: Aromatic trifluoromethylation with **1**.^[a]
 $[(\text{Ph}_3\text{P})_3\text{Cu}(\text{CF}_3)]$ **1** $\xrightarrow[\text{toluene, 80 °C}]{\text{Arl (1.1 equiv), } t\text{Bu-bpy (1.1 equiv)}}$ ArCF_3

Entry	Starting material	Product	Yield [%] ^[b]
1			60–65
2			55
3			70–75
4			60
5			50 (60 ^[c])
6			90
7			60 (70 ^[c])
8			65 (75 ^[c])
9			75

[a] Reaction conditions: **1** (0.05 mmol; $[\textbf{1}] = 0.09 \text{ M}$), ArI (1.1 equiv), *t*Bu-bpy (1.1 equiv), toluene, 80 °C, 2–22 h (see text). [b] Yields determined by ^{19}F NMR spectroscopy with 4,4'-difluorobiphenyl as an internal standard. [c] Yields in parenthesis were obtained in silylated tubes.

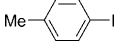
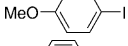
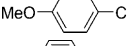
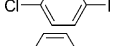
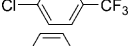
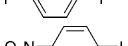
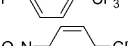
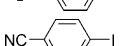
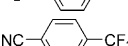
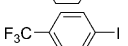
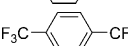
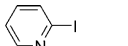
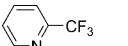
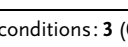
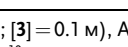
conditions, it took the reaction up to 22 h to go to completion for less reactive iodoarenes (Table 2, entries 1–4), whereas full conversion was observed after only 2–7 h for the more electron-deficient substrates (Table 2, entries 5–9). The only side product clearly observable by ^{19}F NMR spectroscopy was easily removable CHF_3 (b.p. = -82°C), and the pentafluoroethyl derivatives were detected in only minute amounts.

In order to understand the origin of the fluoroform side product, a series of labeling experiments were carried out. Reactions of **1** or $[(\text{C}_6\text{D}_5)_3\text{P}]_3\text{Cu}(\text{CF}_3)$ with PhI were found to produce only CHF_3 and never CDF_3 , regardless if run in

[D₈]toluene, [D₇]DMF, [H₈]toluene, or [H₇]DMF. The iodoarene substrate could not be the source of H, as the original trifluoromethylation in neat PhI (see above) produced only trace amounts of HCF₃. However, after **1** was heated with D₂O in [H₈]toluene (50 °C, 1 h), a characteristic signal from CDF₃ appeared in the ¹⁹F NMR spectrum as a 1:1:1 triplet at $\delta = -79.7$ ppm with $J(\text{F,D}) = 12.2$ Hz. Although this result suggested that hydrolysis of **1** could be responsible for the side-formation of CHF₃, the residual water alone in the solvents used (< 2 ppm for toluene and < 20 ppm in DMF) could not account for the amounts of CHF₃ produced in the reactions. It was therefore presumed that Cu–CF₃ bond hydrolysis might have been caused by traces of water and Si–OH moieties on the surface of the glass tubes used for the reactions. Indeed, repeating some of the experiments in presilylated (ClSiMe₃/toluene) tubes did minimize the production of CHF₃, leading to improved yields of the desired products by approximately 10 % (Table 2, entries 5, 7, and 8). As fully expected,^[2,4] organic bromides were less reactive under similar conditions. Trifluoromethylated products were formed upon treatment of 4-bromonitrobenzene, benzyl bromide, and 2-bromonaphthalene with **1**/tBu-bpy in only 25, 10, and 5 % yield, respectively.

Complex **3** was also found to efficiently trifluoromethylate iodoarenes in DMF at 80 °C in 60–85 % yield (Table 3). The choice of the solvent was determined by good solubility of **3** in DMF. Improved yields were obtained in certain cases, for example, for 4-trifluoromethylchlorobenzene (80 %), 4-trifluoromethylbenzonitrile (85 %), and 2-trifluoromethylpyridine (85 %). Importantly, there is no need to use iodoarene substrates in excess for efficient trifluoromethylation with **1** and **3** (Table 2 and Table 3). In contrast, the trifluoromethylation of ArI with the only other reported well-defined CuCF₃ complexes (NHC-stabilized) can be high-yielding only when the aromatic substrate is present in a large (fivefold) excess.^[10]

Table 3: Trifluoromethylation with **3**.^[a]

$[(\text{phen})\text{Cu}(\text{PPh}_3)(\text{CF}_3)] \xrightarrow[\text{DMF, 80 } ^\circ\text{C}]{\text{ArI (1.1 equiv)}} \text{ArCF}_3$			
Entry	Starting material	Product	Yield [%] ^[b]
1			65
2			60
3			65
4			80
5			60
6			70
7			85
8			60
9			85

[a] Reaction conditions: **3** (0.06 mmol); [**3**] = 0.1 M, ArI (1.1 equiv), DMF, 80 °C, 16 h. [b] Yields determined by ¹⁹F NMR spectroscopy with 4,4'-difluorobiphenyl as an internal standard.

In conclusion, the first efficient, exceptionally simple procedure has been developed for the synthesis of [(Ph₃P)₃Cu(CF₃)] (**1**). This complex has been fully characterized in the solid state and in solution.^[18] Complex **1** is not only the first NHC-free well-defined CF₃Cu^I complex that can trifluoromethylate haloarenes, but it may also serve as a starting material for the synthesis of other new Cu–CF₃ compounds such as **3**. We believe that being easily accessible, air-stable in the solid state, and having a long shelf life, **1** will find further applications in synthetic and mechanistic studies.

Experimental Section

1: A mixture of CuF₂·3H₂O (0.33 g, 2.14 mmol) and PPh₃ (2.24 g, 8.56 mmol) in MeOH (50 mL) was stirred under reflux in air until most of the copper salt had dissolved (overnight). After the minute amounts of residual solids were filtered off, the filtrate containing **2** and Ph₃PO^[13] was evaporated to dryness on a rotary evaporator. The pale yellow solid residue was dried under vacuum (ca. 0.1 mm Hg) overnight and treated with dry THF (4 mL) and CF₃SiMe₃ (1.27 mL, 4 equiv)^[19] in a glove box. After the mixture was stirred for 2 h under argon (HCF₃ evolution observed), the white solid was quickly separated by filtration in air, washed with dry THF (3 × 1 mL), then with excess hexane, and dried under vacuum. The yield of **1** as a white crystalline solid was 1.8 g (92 %). NMR (CH₂Cl₂, 25 °C): ³¹P{¹H} $\delta = -0.8$ ppm (br. s); ¹⁹F $\delta = -26.2$ ppm (s).

3: A solution of phen (0.20 g, 1.09 mmol) in dry CH₂Cl₂ (2 mL) was added to a solution of **1** (1.0 g, 1.09 mmol) in dry CH₂Cl₂ (8 mL). All solids quickly dissolved to produce a red-orange solution. After 30 min, Et₂O (5 mL) was added to prompt crystallization of **3**, with subsequent addition of another 5 mL portion of Et₂O. The solid was separated by decantation, washed with Et₂O (3 × 3 mL), and dried under vacuum. The yield of **3** as orange-red crystals was 0.48 g (77 %). NMR (CD₂Cl₂, 25 °C): ¹H $\delta = 7.2$ –7.4 (m, 15H, PPh₃), 7.6 (dd, $J = 5$ and 9 Hz, 2H, phen), 7.8 (br. s, 2H, phen), 8.3 (d, $J = 7$ Hz, 2H, phen), 9.0 ppm (br. s, 2H, phen); ¹⁹F $\delta = -23.6$ (major, s, CuCF₃), -31.0 ppm (minor, s, [Cu(CF₃)₂][−]); ³¹P $\delta = 2.0$ ppm (br. s). Calcd. for C₃₁H₂₃CuF₃N₂P: C 64.8, H 4.0, N 4.9; found: C 65.0, H 4.0, N 4.7.

General procedure for aromatic trifluoromethylation with **1**: In a glovebox, a 5 mm NMR tube was charged with **1** (50 mg, 0.054 mmol), ArI (0.060 mmol, 1.1 equiv), tBu-bpy (16 mg, 0.060 mmol, 1.1 equiv), dry toluene (0.55 mL), and a stock solution of 4,4'-difluorobiphenyl (internal standard) in toluene (0.05 mL). The tube was sealed with a rubber septum and heated in an oil bath at 80 °C (Table 2). The reaction was monitored by ¹⁹F NMR spectroscopy.

General procedure for aromatic trifluoromethylation with **3**: In a glovebox, a 5 mm NMR tube was charged with **3** (36 mg, 0.063 mmol), ArI (0.070 mmol, 1.1 equiv), 4,4'-difluorobiphenyl (internal standard, 4–8 mg), and dry DMF (0.6 mL). The tube was sealed and heated in an oil bath at 80 °C for 16 h. The mixture was analyzed by ¹⁹F NMR spectroscopy.

Received: March 3, 2011

Revised: April 5, 2011

Published online: June 22, 2011

Keywords: copper · fluorine · haloarenes · aromatic trifluoromethylation · organometallic compounds

- [1] a) J. H. Clark, D. Wails, T. W. Bastock, *Aromatic Fluorination*, CRC, Boca Raton, FL, **1996**; b) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**; c) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**; d) I. Ojima,

- Fluorine in Medicinal Chemistry and Chemical Biology*, Wiley-Blackwell, Chichester, UK, **2009**.
- [2] O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, DOI: 10.1021/cr1004293.
- [3] R. Filler, *Adv. Fluorine Chem.* **1970**, 6, 1.
- [4] a) D. J. Burton, Z. Y. Yang, *Tetrahedron* **1992**, 48, 189; b) M. A. McClinton, D. A. McClinton, *Tetrahedron* **1992**, 48, 6555; c) D. J. Burton, L. Lu, *Top. Curr. Chem.* **1997**, 193, 45; d) M. Schlosser, *Angew. Chem.* **2006**, 118, 5558; *Angew. Chem. Int. Ed.* **2006**, 45, 5432; e) S. Roy, B. T. Gregg, G. W. Gribble, V.-D. Le, S. Roy, *Tetrahedron* **2011**, 67, 2161.
- [5] a) M. Inoue, K. Araki, Jpn. Patent JP 2009-234921, **2009**; b) M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909; c) T. Knauber, F. Arian, G.-V. Roeschenthaler, L. J. Gooßen, *Chem. Eur. J.* **2011**, 17, 2689.
- [6] a) V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2006**, 128, 4632; b) V. V. Grushin, *Acc. Chem. Res.* **2010**, 43, 160; c) N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2010**, 132, 2878; d) Y. Ye, N. D. Ball, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2010**, 132, 14682.
- [7] a) X. Wang, L. Truesdale, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, 132, 3648; b) E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, *Science* **2010**, 328, 1679.
- [8] a) V. C. R. McLoughlin, J. Thrower, U. S. Patent 3408411, **1968**; b) V. C. R. McLoughlin, J. Thrower, *Tetrahedron* **1969**, 25, 5921; c) Y. Kobayashi, I. Kumadaki, *Tetrahedron Lett.* **1969**, 10, 4095; d) K. Sato, A. Tarui, M. Omote, A. Ando, I. Kumadaki, *Synthesis* **2010**, 1865.
- [9] D. M. Wiemers, D. J. Burton, *J. Am. Chem. Soc.* **1986**, 108, 832.
- [10] a) G. G. Dubinina, H. Furutachi, D. A. Vicić, *J. Am. Chem. Soc.* **2008**, 130, 8600; b) G. G. Dubinina, J. Ogikubo, D. A. Vicić, *Organometallics* **2008**, 27, 6233; c) I. Kietlsch, G. G. Dubinina, C. Hamacher, A. Kaiser, J. Torres-Nieto, J. M. Hutchison, A. Klein, Yu. Budnikova, D. A. Vicić, *Organometallics* **2010**, 29, 1451.
- [11] Y. Usui, J. Noma, M. Hirano, S. Komiya, *Inorg. Chim. Acta* **2000**, 309, 151.
- [12] M. Kubota, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1978**, 51, 2909.
- [13] D. J. Gulliver, W. Levason, M. Webster, *Inorg. Chim. Acta* **1981**, 52, 153.
- [14] CCDC 814545 (**1**) and 814538 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [15] P. S. Coan, K. Folting, J. C. Huffman, K. G. Caulton, *Organometallics* **1989**, 8, 2724.
- [16] a) J. Goodman, V. V. Grushin, R. B. Larichev, S. A. Macgregor, W. J. Marshall, D. C. Roe, *J. Am. Chem. Soc.* **2009**, 131, 4236; b) J. Goodman, V. V. Grushin, R. B. Larichev, S. A. Macgregor, W. J. Marshall, D. C. Roe, *J. Am. Chem. Soc.* **2010**, 132, 12013.
- [17] a) M. A. Willert-Porada, D. J. Burton, N. C. Baenziger, *J. Chem. Soc. Chem. Commun.* **1989**, 1633; b) A. Kütt, V. Movchun, T. Rodima, T. Dansauer, E. B. Rusanov, I. Leito, I. Kaljurand, J. Koppel, V. Pihl, I. Koppel, G. Ovsjannikov, L. Toom, M. Mishima, M. Medebielle, E. Lork, G.-V. Roeschenthaler, I. A. Koppel, A. A. Kolomeitsev, *J. Org. Chem.* **2008**, 73, 2607.
- [18] After our work was submitted for publication, a report appeared on aromatic trifluoromethylation with [(phen)CuCF₃] that was isolated and characterized in solution: H. Morimoto, T. Tsubogo, N. D. Litvinas, J. F. Hartwig, *Angew. Chem.* **2011**, 123, 3877; *Angew. Chem. Int. Ed.* **2011**, 50, 3793.
- [19] The presence of two MeOH molecules H-bonded to the F ligand in **2** necessitates the use of excess of CF₃SiMe₃, which is decomposed by the H-bonded methanol. To avoid the use of excess CF₃SiMe₃, we attempted the reported preparation of alcohol-free [(Ph₃P)₃Cu(F)] by drying **2** or its EtOH analogue at 70 °C and 0.01 torr.^[13] It was found, however, that during the drying the ROH adducts were losing not only the alcohol but also PPh₃, as was established by ¹H and ³¹P NMR spectroscopic analysis of the trapped volatiles.