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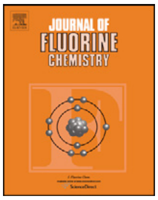

$Me_3SiCF_3/AgF/Cu$—A new reagents combination for selective trifluoromethylation of various organic halides by trifluoromethylcopper, $CuCF_3$[☆]

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ABSTRACT

An alternative copper halide-free route to obtain highly reactive trifluoromethylcopper species has been developed via the reaction of silver fluoride and trimethyl(trifluoromethyl)silane followed by a redox transmetallation with elemental copper. The composition of the reactive intermediate was investigated by means of UV/Vis/NIR, ESR, ^{19}F NMR spectroscopy and ESI mass spectrometry. "Trifluoromethylcopper" prepared by the oxidative transmetallation route exhibits excellent reactivity and selectivity in substitutions of iodine or bromine bond to aromatic or heterocyclic compounds for trifluoromethyl groups without any additional catalyst.

1. Introduction

It is well-known that pharmaceutical and agricultural chemicals containing trifluoromethyl groups often exhibit unique biological activities [1]. Therefore, the introduction of trifluoromethyl groups into organic molecules – designed for the development of model systems – has recently emerged as one of the most attractive research areas in synthesis and reactivity studies.

"Trifluoromethylcopper", although the real reactive species and the reaction mechanisms are not yet fully understood, can be generated by various methods. For example, Kobayashi et al. directly prepared it by the reaction of trifluoroiodomethane with "activated" copper in DMF [2] or HMPA [3]. Yagupolskii et al. [4] generated it using $Hg(CF_3)_2$ as a trifluoromethyl source by transmetallation to copper. Trifluoromethylcopper has also been prepared through in situ metathesis of (trifluoromethyl)cadmium or zinc reagents with copper(I) salts [5]. In a previous publication, we demonstrated that $Zn(CF_3)Br$ and derivatives are suitable reagents to prepare both $CuCF_3$ and CuC_2F_5 species [6]. The latter have been proved to act as excellent reagents for the introduction of perfluoroalkyl groups into organic molecules. Further innovative approaches target the trifluoromethylation of organic halides under mild conditions by using trialkyl(trifluoromethyl) silanes and copper(I) iodide in the presence of a suitable fluoride anion source (e.g. CsF, KF, $[NMe_4]F$) [7] even allowing multiple extensive trifluoromethyl group transfer [8]. The very first methods used expensive or toxic reagents such as CF_3I and $Hg(CF_3)_2$ or have been carried out in autoclaves. The latter appear to be more convenient and environmentally more friendly using $Zn(CF_3)Br$ – a reagent easily prepared from CF_3Br [9], a gas formerly used in fire extinguishers – and Me_3SiCF_3 [10] in the meantime the widely used compound, as recently demonstrated in reactions with a copper alkoxide–carbene complex [11]. Surveys on metal-mediated trifluoromethylation reactions in general [12] and on trifluorometylations of aryl and heteroaryl halides with copper reagents were recently presented [13]. While preparing this manuscript, we became aware of a closely related work dealing with silver-supported copper catalyzed trifluoromethylation of iodoarenes with $CuCF_3$ generated from $AgCF_3$ and copper iodide [14].

The oxidative properties of trifluoromethyl silver [15] encouraged us to investigate its reactions with copper starting from commercially available trimethyl (trifluoromethyl) silane, silver(I) fluoride and copper powder. A comparative and more general route to perfluoroorganocopper reagents, CuR_f (R_f = n-C_3F_7, n-C_4F_9, C_6F_5), generated via the corresponding perfluoroorganosilver reagents,

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AgR_f, and elemental copper through redox transmetallations will be presented in a forthcoming publication.

The great attention and importance of catalytic trifluoromethylation of organic substrates with copper reagents is best expressed by the fact that numerous publications [6,14,16] were released within the last one and a half year.

2. Results and discussion

Trifluoromethylsilver is conveniently accessible from room temperature reactions of silver(I) fluoride and trimethyl(trifluoromethyl)silane in an appropriate solvent, such as acetonitrile, propionitrile or DMF [15] (Eq. (1)); the properties of $AgCF_3$ as an effective oxidative trifluormethylating reagent has been demonstrated in several examples [15]. However, effective trifluoromethylation of organic substrates by $AgCF_3$ is limited to reactions with acyl chlorides [17] and dithiuram disulfides; for the latter reactions, different reaction mechanisms may be considered [18].

$$AgF + (CH_3)_3SiCF_3 \rightarrow AgCF_3 + (CH_3)_3SiF \tag{1}$$

After 2 h, mixtures of $AgCF_3$ and elemental copper yielded reactive "trifluoromethylcopper" species which were used for further transformations (Eq. (2)).

$$AgCF_3 + Cu \rightarrow CuCF_3 + Ag \tag{2}$$

We suggest, in analogy to equilibria of AgR_f and $Ag[Ag(R_f)_2]$ [15,19], similar species of general composition "$Ag(CF_3)_2Cu$" as reactive intermediates, with Ag^+ acting as the halide interceptor and "Cu" as the reactive center. ^{19}F NMR spectroscopic investigations prove the most reactive derivative in the reaction mixtures being the trifluoromethylcopper species **1**.

Time dependent ^{19}F NMR spectra reveal, the signals of $AgCF_3$ (−23.9 ppm), the argentate $[Ag(CF_3)_2]^-$ (−26.4 ppm) and the less reactive $[Ag^{III}(CF_3)_4]^-$ (−33.0 ppm) (minor intensity) were dominant after addition of Me_3SiCF_3 to a well stirred solution of AgF in EtCN. These signals decreased more and more in intensity after addition of copper powder to the reaction mixture in favor of the broad signals of $CuCF_3$ (−28 ppm), $[Cu(CF_3)_2]^-$ (−32 ppm), and $[Cu^{III}(CF_3)_4]^-$ (−35 ppm) [5,20].

For better understanding, trifluoromethylcopper was prepared from copper(I) bromide, trimethyl(trifluoromethyl)silane and cesium fluoride in propionitrile with the aim to compare the intermediately formed trifluoromethylcopper obtained via both routes (Eq. (3)).

$$Me_3SiCF_3 + CsF + CuBr \underset{EtCN}{\longrightarrow} CuCF_3 + Me_3SiF + CsBr \tag{3}$$

However, ^{19}F NMR spectra of copper species generated by both methods were identical.

Storage of trifluoromethylcopper obtained from trifluoromethylsilver and copper powder in propionitrile or DMF at ambient temperature for 12 h led to the formation of a precipitate with the anion $[Cu^{III}(CF_3)_4]^-$ which was insoluble in most organic solvents without any definite knowledge of the cation (Ag^+ is involved anyhow). The formation of this anion is not yet understood. Time-dependent UV/Vis/NIR measurements of $Cu^{II}(CF_3)_2$ in DMF show the asymmetric absorbance band around 650–700 nm characteristic for d–d transitions (Cu^{2+}). We note that within 12 h the concentration of Cu^{II} (monitored via the relative absorbance maxima) is reduced by a factor of 2. Overall all spectra become slightly red-shifted and loose the distinct shoulder at higher energies. Slower reaction times indicating a further mechanistic step follow and a plateau is reached after 30 h. However, the speculation that the intermediate $Cu^{II}(CF_3)_2$ (d^9) undergoes dimerization to "$(CF_3)_2Cu^{II}Cu^{II}(CF_3)_2$" is only supported by the fact that the ESR signals are very weak and broad. Furthermore, the ESR resonance positions are not typical for monomeric Cu^{II} species. These observations guide us to formulate a mechanistic approach as outlined in Scheme 1. A final, very rapid rearrangement would lead to the non-magnetic mixed-valent species $Cu^I[Cu^{III}(CF_3)_4]$ (d^{10}/d^8).

$$2\,AgCF_3 + Cu \longrightarrow Cu^{II}(CF_3)_2 + 2\,Ag$$

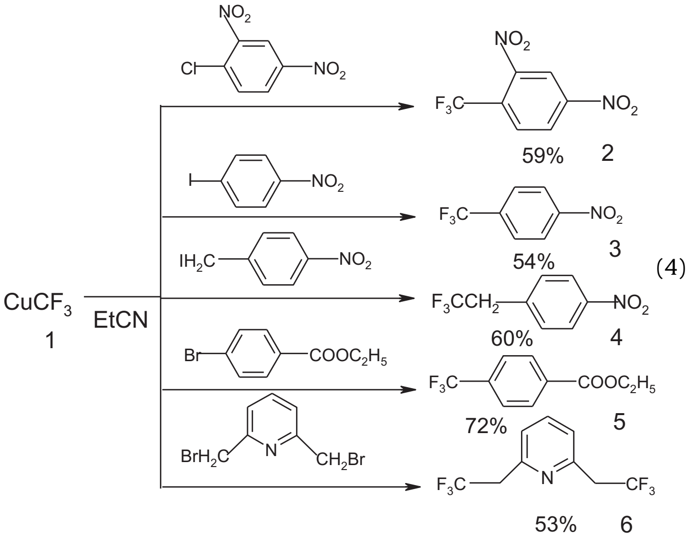
$$2\,Cu^{II}(CF_3)_2 \longrightarrow \text{"}(CF_3)_2Cu^{II}Cu^{II}(CF_3)_2\text{"}$$

$$\text{"}(CF_3)_2Cu^{II}Cu^{II}(CF_3)_2\text{"} \longrightarrow Cu^I[Cu^{III}(CF_3)_4]$$

Scheme 1.

In ESI mass spectra of the "Cu(III) precipitate" prepared in propionitrile and (for measurements purposes) diluted with acetonitrile, the following ions were detected (*m/z*): negative mode: 339.07 $[Cu(CF_3)_4]^-$ (100%); 658.97 $[Cu(EtCN)CH_2CNCu(CF_3)_4CH_2CNCu(EtCN)]^-$ (40%); 719.00 $K[Cu(CF_3)_4]_2^-$ (16%) (It has to be noted that potassium and sodium ions are often incorporated in such ions for lack of inertness in performing such experiments.); positive mode: 145.07 $[Cu(MeCN)_2]^+$ (24%); 159.00 $[Cu(EtCN)\text{-}MeCN\text{–}H]^+$ (92%); 161.05 $[Cu(EtCN)MeCN]^+$ (36%); 173.08 $[Cu(EtCN)_2]^+$ (88%); 338.87 $[Cu_3(MeCN)(EtCN)_2\text{–}5H]^+$ (100%); 340.87 $[Cu_3(MeCN)(EtCN)_2\text{–}3H]^+$ (44%); 441.79 $[Cu_4(MeCN)_2(EtCN)_2\text{–}6H]^+$ (48%); 539.20 $[Cu_5(MeCN)_4EtCN]^+$ (4%).

"Trifluoromethylcopper" **1** prepared in propionitrile reacts with 1-chloro-2,4-dinitrobenzene, 4-iodonitrobenzene, 4-nitrobenzyliodide, ethyl-4-bromobenzoate and 2,6-di(bromomethyl)pyridine to give the corresponding trifluormethylated products **2**–**6** in good yields (Eq. (4)).



It should be pointed out that reactions leading to compounds **4** and **6** occur at sp^3 hybridized carbon atoms, while all the other occur at carbon atoms of the aromatic ring systems.

Furthermore, trifluoromethylcopper **1** directly prepared in DMF exhibited enhanced reactivity in comparison with similar derivatives prepared in propionitrile. For example, trifluoromethylcopper in propionitrile did not allow any bromine substitution in 2-bromopyridine by a trifluoromethyl group. In contrast, treatment of trifluoromethylcopper prepared in DMF reacts with 2-bromopyridine and even 2-bromopyrimidine

Table 1
Reaction temperatures and times (^{19}F NMR control) of "trifluoromethylcopper" (**1**, DMF) with selected organic substrates until complete consumption of "$CuCF_3$".

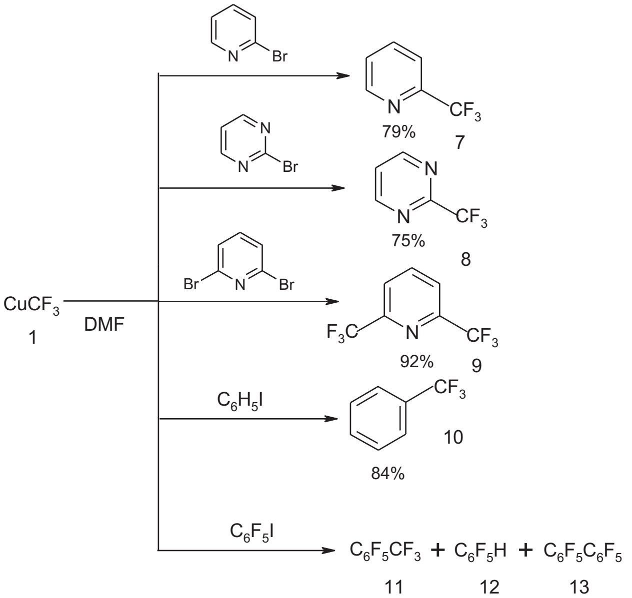
Product numbers	Starting compound	Temperature (°C)	Time (h)
7	2-Bromopyridine	90	5
8	2-Bromopyrimidine	20	12
9	2,6-Dibromopyridine	75	4
10	Iodobenzene	20	6
11–13	Iodopentafluorobenzene	50	3

under formation of 2-trifluoromethylpyridine **7** and 2-trifluoromethylpyrimidine **8** in 79% and 75% yield, respectively. Under similar conditions, $CuCF_3$ (**1**, DMF) reacted with 2,6-dibromopyridine in an 1:1 molar ratio to give a mixture of di- and mono-trifluoromethyl substituted compounds whereas upon treatment in a 2:1 molar ratio, 2,6-bis(trifluoromethyl)pyridine **9** was isolated in 92% yield.

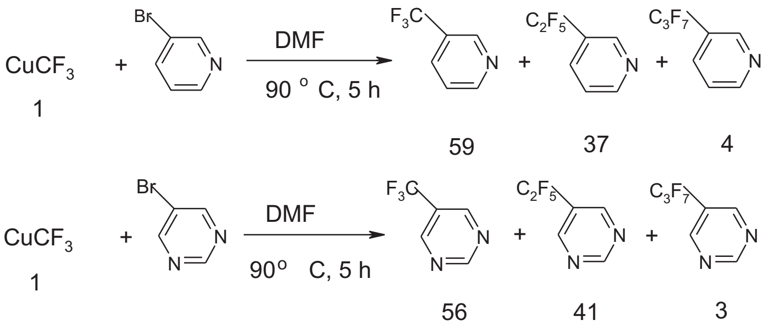
It is noteworthy that in the contrast to reactions of trifluoromethylcopper in EtCN (**1**, EtCN), reactions of trifluoromethylcopper in DMF (**1**, DMF) with organic substrates decrease selectivity resulting in considerable amounts of pentafluoroethyl- and heptafluoropropyl-derivatives.

For example, treatment of trifluoromethylcopper (**1**, DMF) with 3-bromopyridine at 90 °C for 5 h gave a mixture of 3-(trifluoromethyl)pyridine, 3-(pentafluoroethyl)pyridine and 3-(heptafluoropropyl)pyridine in a 59:37:4 ratio (^{19}F NMR). The reaction of trifluoromethylcopper in DMF (**1**, DMF) with 5-bromopyrimidine under similar conditions led to formation of a mixture of trifluoromethyl-, pentafluoroethyl- and perfluoropropyl-derivatives in a ratio 56:41:3, respectively. (Eq. (5))

We investigated the interactions of trifluoromethylcopper **1** in DMF with unactivated iodo-containing aromatics, namely, iodobenzene and iodopentafluoro-benzene. α,α,α-trifluorotoluene **10** was obtained in 83% yield upon treatment of trifluoromethylcopper with iodobenzene. A mixture of perfluorotoluene **11**, pentafluorobenzene **12** and perfluorobiphenyl **13** in a 48:32:20 ratio was isolated from the reaction of trifluoromethylcopper with iodopentafluorobenzene in DMF. The latter reaction demonstrated that trifluoromethylcopper can also react with organic compounds containing positively charged iodine. Probably due to the ion-radical character of trifluoromethylcopper in DMF, as well as the fact that also copper species in the oxidation states II and even III [6] are likely to be involved, may account for the reduced selectivity here. Reaction temperatures and times are summarized in Table 1.



(6)



(5)

Formation of pentafluoroethylcopper during the reaction of bromine containing organic compounds with trifluoromethylcopper (**1**, DMF) may be explained by the catalytic influence of copper(I) bromide continuously formed during the reactions. The ability of Ag^+ ions as halides interceptors appeared to be reduced in these cases. A targeted experiment with addition of copper(I) bromide to trifluoromethylcopper (**1**, DMF) led only to the formation of bromotrifluoromethane. However, heating of trifluoromethylcopper (**1**, DMF) to 80 °C after adding a small quantity (about 10%) of copper(I) bromide and stirring for 3.5 h allowed its quantitative conversion into pentafluoroethylcopper.

The reaction of trifluoromethylcopper (**1**, DMF) with an aliphatic 1-iodododecane proceeded more or less unselective with conversion of the CF_3 group into a C_2F_5 moiety or dehydrohalogenation finally giving a mixture of CF_3-, C_2F_5-, CH_2F- and fluorocontaining aliphates and olefins, beside minor quantities of CF_3H, C_2F_5H, and n-C_3F_7H.

3. Conclusion

"Trifluoromethyl copper" prepared by a copper halide-free route via redox transmetallation from trifluoromethyl silver and elemental copper exhibits excellent reactivity and selectivity in the substitution of iodine and bromine atoms bonded to aromatic or heterocyclic compounds even at sp^3 hybridized carbon atoms without any necessity of an additional catalyst. All observations indicate an interplay of copper compounds in oxidation states I, II and III as reactive intermediates with copper and silver halides being finally the halide interceptors. Further, intensive research is necessary to come up to a comprehensive understanding of these reactions.

4. Experimental

4.1. General

Schlenk techniques were used throughout all manipulations. Purifications were carried out in ambient atmosphere. NMR spectra of unprecedented, isolated compounds were recorded on a Bruker Avance II 300 (^{1}H, 300.1 MHz; ^{19}F, 282.4 MHz; ^{13}C, 75.4 MHz) spectrometer in $CDCl_3$ solutions unless quoted. External standards were used in all cases (^{1}H, ^{13}C: Me_4Si; ^{19}F: CCl_3F). Chemical shifts (δ) are given in ppm; couplings (J) in Hz. Visible melting points were determined using a Stuart melting point apparatus SMP10. All compounds are characterized by melting or boiling points, elemental analyses and NMR spectroscopic data. For known compounds, only melting or boiling points as well as ^{1}H and ^{19}F NMR data are listed, while values of elemental analyses are not given here. Copper(I) bromide was prepared using the method reported in [6]. AgF was purchased from Apollo, Me_3SiCF_3 from ABCR. All organic reagents were obtained from Aldrich or Acros and used without any further purification after NMR spectroscopic measurements to validate the quality. UV/Vis/NIR spectra were recorded on a CARY05E (Varian) spectrophotometer in absorbance mode using quartz glass sample holders. ESR measurements were carried out on an x-Band Biospin Spectrometer (Bruker).

4.2. General procedure for the preparation of "trifluoromethylcopper" and its reactions

4.2.1. Method A

To a well stirred mixture of AgF (0.51 g, 4 mmol) in 5 ml of propionitrile Me_3SiCF_3 (0.57 g, 4 mmol) was added at room temperature. The mixture was stirred for 20 min and copper powder (0.51 g, 8 mmol) was added. After stirring for 4 h, the formation of "$CuCF_3$" was complete. The corresponding halogen containing aromatic derivative (4 mmol) was added and the reaction mixture was stirred for up to 6 h at ambient temperature and for additional 12 h at 75–80 °C. The reaction was terminated after signals of $CuCF_3$ were no longer detected in the ^{19}F NMR spectra. The mixture was filtered from precipitates and 15 ml of diethyl ether were added. The mixture was washed with water and dried over $MgSO_4$. The solvent was evaporated and the remainder was crystallized or distilled from the organic phase under reduced pressure.

*4.2.1.1. 2,4-Dinitro(trifluoromethyl)benzene (**2**).* Colourless crystals. Yield 0.56 g (59%), m.p. 46–48 °C (pentane), lit. m.p. 48 °C [4]. ^{19}F NMR, δ (ppm): −60.3 (s, CF_3, $^1J_{F,C}$ = 275 Hz,); ^{1}H NMR, δ (ppm): 8.13 (m, 1H, H-6), 8.61 (m, 1H, H-5), 8.76 (m, 1H, H-3). ^{13}C NMR, δ (ppm): 121.0 (q, CF_3, $^1J_{F,C}$ = 275), 128.8 (q, C-1, $^2J_{F,C}$ = 35 Hz), 148.7 (s, C-2), 120.6 (s, C-3), 150.1 (s, C-4), 127.0 (s, C-5), 129.9 (q, C-6, $^3J_{F,C}$ = 5 Hz).

*4.2.1.2. 4-Nitro(trifluoromethyl)benzene (**3**).* Colourless crystals. Yield 0.41 g (54%), m.p. 40–41 °C (pentane), lit. m.p. 40–41 °C [4]. ^{19}F NMR, δ (ppm): −63.2 (q, CF_3, $^1J_{F,C}$ = 273 Hz, $^2J_{F,C}$ = 33 Hz, $^4J_{F,H}$ = 0.8 Hz, $^5J_{F,H}$ = 0.8 Hz); ^{1}H NMR, δ (ppm): 7.86 (m, 2H, H-2,6), 8.38 (m, 2H, H-2,6). ^{13}C NMR, δ (ppm): 123.0 (q, CF_3, $^1J_{F,C}$ = 273, $^2J_{F,C}$ = 33 Hz), 136.2 (q, C-1, $^2J_{F,C}$ = 33 Hz), 126.8 (q, C-2,6, $^3J_{F,C}$ = 4 Hz), 124.1 (s, C-3,5) 150.0 (s, C-4).

*4.2.1.3. 4-Nitro-(2,2,2-trifluoroethyl)benzene (**4**).* Colourless crystals. Yield 0.49 g (60%), m.p. 63–65 °C (pentane), lit. m.p. 65 °C [4]. ^{19}F NMR, δ (ppm): −65.3 (t, CF_3, $^3J_{F,H}$ = 10.7 Hz); ^{1}H NMR, δ (ppm): 3.50 (q, 2H, CH_2, $^3J_{H,F}$ = 10.7 Hz), 7.50 (d, 2H, H-3,5, $^3J_{H,H}$ = 8.7 Hz), 8.20 (d, 2H, H-2,6, $^3J_{H,H}$ = 8.7 Hz).

*4.2.1.4. 4-Trifluoromethylbenzoic acid ethyl ester (**5**).* Colourless liquid. Yield 0.63 g (72%), b.p. 90–92 °C (13.33 mbar). lit. b.p. 78–80 °C (5.0 Torr) [21]. ^{19}F NMR, δ (ppm): −63.6 (s, CF_3); ^{1}H NMR, δ (ppm): 1.40 (t, 3H, CH_3, $^3J_{H,H}$ = 7.2 Hz), 4.38 (q, 2H, CH_2, $^3J_{H,H}$ = 7.2 Hz), 7.58 (d, 2H, H-3,5, $^3J_{H,H}$ = 9.0 Hz), 7.90 (d, 2H, H-2,6, $^3J_{H,H}$ = 9.0 Hz).

*4.2.1.5. Bis-2,6-(2,2,2-trifluoroethyl)pyridine (**6**).* Colourless liquid. Yield 0.51 g (53%), b.p. 65–67 °C (1.6×10^{-2} mbar). ^{19}F NMR, δ (ppm): −64.8 (t, $2CF_3$, $^1J_{F,C}$ = 278 Hz, $^3J_{F,H}$ = 11 Hz); ^{1}H NMR, δ (ppm): 3.63 (q, 4H, $^3J_{F,H}$ = 11 Hz); 7.33 (d, 2H, H-3,5); 7.72 (t, 1H, H-4). ^{13}C NMR, δ (ppm): 125.4 (q, 2C (CF_3), $^1J_{F,C}$ 278 = Hz), 42.7 (q, 2C (CH_2), $^2J_{F,C}$ = 29 Hz), 150.9 (q, 2C, C-2,6, $^3J_{F,C}$ = 3 Hz), 123.6 (q, 2C, C-3,5, $^4J_{F,C} \approx 1$ Hz), 137.4 (s, C-4). MS (20 eV, m/e): 243 (100%, M^+); 223 (32%, M^+–HF); 203 (20%, M^+–2HF); 174 (12%, M^+–CF_3).

4.2.2. Method B

To a well stirred mixture of AgF (1.27 g, 10 mmol) in 10 ml of DMF, Me_3SiCF_3 (1.7 g, 12 mmol) was added at room temperature. The mixture was stirred for 20 min and copper powder (1.0 g, 15 mmol) was added. After stirring for 4 h, the formation of $CuCF_3$ was complete. The corresponding halogen containing compound (9 mmol) (in the case of 2,6-dibromopyridine, 4.5 mmol) was added and the reaction mixture was stirred under conditions surveyed in Table 1. The reaction was terminated unless signals of $CuCF_3$ were no longer detected in the ^{19}F NMR spectra. The mixture was filtered from the solid precipitate and poured into 50 ml of water. The organic layer was extracted with diethyl ether and dried over $MgSO_4$. Ether was evaporated and the remainder was distilled under reduced pressure or crystallized.

*4.2.2.1. 2-(Trifluoromethyl)pyridine (**7**).* Colourless liquid. Yield 1.15 g (79%), b.p. 138–139 °C, lit. b.p. 138–140 °C [22]. ^{19}F NMR, δ (ppm) ($CDCl_3$): −68.2 (s, CF_3, $^1J_{F,C}$ = 274 Hz, $^2J_{F,C}$ = 34 Hz); ^{1}H NMR, δ (ppm): 7.68 (d, 1H, H-3); 7.89 (t, 1H, H-4); 7.51 (t, 1H, H-5); 8.74 (d, 1H, H-6). ^{13}C NMR, δ (ppm): 121.5 (q, CF_3); 148.3 (s, C-2); 120.2 (q, C-3, $^3J_{F,C}$ = 3 Hz); 137.4 (s, C-4); 126.4 (s, C-5); 150.0 (s, C-6).

*4.2.2.2. 2-Trifluoromethylpyrimidine (**8**).* Colourless liquid. Yield 1.0 g (75%), b.p. 42 °C (1.1×10^{-1} mbar), lit. b.p. 60 °C (10 mm Hg) [23]. ^{19}F NMR, δ (ppm) ($CDCl_3$): −70.6 (s, CF_3, $^1J_{F,C}$ = 275 Hz, $^2J_{F,C}$ = 37 Hz); ^{1}H NMR, δ (ppm): 8.95 (d, 2H, H-4,6, $^3J_{H,H}$ = 5 Hz); 7.55 (t, 1H, H-5). ^{13}C NMR, δ (ppm): 119.4 (q, CF_3); 156.7 (s, C-2); 123.1 (s, C-5); 158.0 (s, C-4,6).

*4.2.2.3. 2,6-Bis(trifluoromethyl)pyridine (**9**).* Colourless crystals. Yield 0.99 g (92%), m.p. 56–57 °C (hexane), lit. m.p. 55–56 °C [24]. ^{19}F NMR, δ (ppm) ($CDCl_3$): −68.1 (s, $2CF_3$, $^1J_{F,C}$ = 275 Hz, $^2J_{F,C}$ = 36 Hz); ^{1}H NMR, δ (ppm): 7.92 (d, 2H, $^3J_{H,H}$ = 7.5 Hz, H-3,5); 8.13 (t, 1H, $^3J_{H,H}$ = 7.5 Hz, H-4). ^{13}C NMR, δ (ppm): 121.9 (q, $2CF_3$); 148.8 (q, 2C, C-2,6); 123.1 (2C, C-3,5); 139.3 (1C, C-4).

*4.2.2.4. α, α, α-Trifluoromethylbenzene (**10**).* Colourless liquid. Yield 1.8 g (84%), b.p. 101–102 °C, lit. b.p. 101–103 °C [25]. ^{19}F NMR, δ (ppm) ($CDCl_3$): −62.8 (s, CF_3, $^1J_{F,C}$ = 272 Hz, $^2J_{F,C}$ = 32 Hz); ^{1}H NMR, δ (ppm): 7.67 (s, 2H, H-2,6); 7.52 (s, 2H, H-3,5); 7.57 (s, 1H, H-4). ^{13}C NMR, δ (ppm): 124.1 (q, CF_3); 130.7 (s, C-1); 125.2 (q, C-2,6, $^3J_{F,C}$ = 4 Hz); 128.7 (s, C-3,5); 131.7 (s, C-4).

*4.2.2.5. Mixture of perfluorotoluene (**11**) and pentafluorobenzene (**12**).* Colourless liquid. Yield 1.6 g, b.p. of the mixture 96–100 °C.

Perfluorotoluene (**11**). ^{19}F NMR, δ (ppm) ($CDCl_3$): −56.1 (m, 3F, CF_3), −139.5 (m, 2F, F-2,6), −153.6 (m, 2F, F-3,5), −146.8 (m, 1F, F-4).

Pentafluorobenzene (**12**). ^{19}F NMR, δ (ppm) ($CDCl_3$): −138.6 (m, 2F. F-2,6), −159.5 (m, 2F, F-3,5), −162.0 (m, 1F, F-4). ^{1}H NMR, δ (ppm): 6.9 (m, 1H, H-1).

4.2.2.6. Decafluorobiphenyl (**13**). Colourless crystals. Yield 0.41 g, m.p. 68–70 °C (hexane), lit. m.p. 69 °C [26]. All analytic data are in full agreement with earlier published material.

4.3. Trifluoromethylcopper prepared from Me_3SiCF_3, cesium fluoride and copper(I) bromide

A well stirred mixture of trimethyltrifluoromethylsilane (0.29 g, 2 mmol), CuBr (0.14 g, 1 mmol), 15-crown-5 (0.88 g, 4 mmol) and propionitrile (10 ml) was cooled to −60 °C and then CsF (0.30 g, 2 mmol) was added. The reaction mixture was slowly warmed to ambient temperature with stirring for 4 h. The ^{19}F NMR spectrum was identical with that of $CuCF_3$ prepared via trifluoromethylsilver.

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