Electrosynthesis of (trifluoromethyl)copper complexes from bromotrifluoromethane: reactivities with various organic halides

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Abstract

The synthesis of (trifluoromethyl)copper complexes is achieved easily by electroreduction of bromotrifluoromethane in N,N-dimethylformamide, in the presence of a sacrificial copper anode and various potential ligands. Three (trifluoromethyl)copper species are considered: two copper(II) and one copper(I). The mechanism of formation of the (trifluoromethyl)copper species is discussed and a study of their reactivities towards various organic halides is reported.

Keywords: Copper; Trifluoromethyl derivatives; Electroreduction; Mechanism; Bromotrifluoromethane; (Trifluoromethyl)copper complexes

1. Introduction

(Trifluoromethyl)copper compounds are good trifluoromethylation agents for aromatic and heteroaromatic halides [1]. However, their nature is not well defined [2] and their preparation still poses some difficulties although there are many methods that provide access to trifluoromethylcopper derivatives from various sources of the trifluoromethyl group [3]. The very few methods that use CF_3Br, a cheap and readily available source of the trifluoromethyl group, gave poor results [4] except with very activated aromatic iodide [5].

In a recent preliminary communication [6] we reported an efficient electrochemical trifluoromethylation of aromatic and heteroaromatic halides with CF_3Br and a sacrificial copper anode. We found that the "$CuCF_3$" species were formed in the presence of various complexing agents under mild conditions. Because of this success, we have extended our method to the trifluoromethylation of other organic halides and have carried out further studies of the "$CuCF_3$" complexes by ^{19}F NMR spectroscopy and electrochemistry. Recent results explain the nature and the electrochemical mechanism formation of "$CuCF_3$" complexes.

2. Results and discussion

2.1. Effects of the ligand on the formation of "$CuCF_3$" species

When CF_3Br was electroreduced in cold dimethylformamide (DMF) [7] in the presence of a potential ligand and a copper anode in a one-compartment cell, fitted with a stainless steel grid cathode, one, two or three "$CuCF_3$" species were detected (by ^{19}F NMR spectroscopy) depending upon the potential ligand. Tributylphosphine (PBu$_3$), triphenylphosphine (PPh$_3$), 1,2-bis(diphenylphosphino)ethane (dppe), 2,2'-bipyridine (bipy) and tetramethylenediamine (tmeda) were used [8]. [NBu$_4$]Br was the supporting electrolyte in a low concentration (3×10^{-2} M).

In the absence of a potential ligand no "$CuCF_3$" species were detected, but tetrafluoroethene was formed during the first hour of the electrolysis, and the potential of the cathode varied from -2.4 to -0.9 V before stabilizing at -0.85 V (vs. a saturated calomel electrode (SCE)). At this potential, only Cu^{2+} [9] from the oxidation of the anode is reduced to Cu(0), and no CF_3Br reacts [10]. These results indicate that the electroreduction of CF_3Br in the presence of Cu(II) (formed in situ) does not yield "$CuCF_3$" species under these experimental conditions. Likewise, Cu(0) formed in situ by the electroreduction of Cu^{2+} and the electroscored copper metal do not react with CF_3Br.

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Table 1
^{19}F chemical shifts of "CuCF$_3$" species in the presence of various reagents in dimethylformamide–C$_6$D$_6$ (1 : 1) (dilution of the samples in C$_6$D$_6$ before analysis by NMR (Bruker 300 MHz spectrometer) was necessary to minimize paramagnetic perturbations)

Reagents		δ (ppm (CCl$_3$F external))				
		PBu$_3$	PPh$_3$	dppe	bipy	tmeda
"CuCF$_3$"	A	− 27.8	− 27.3	− 26.5	− 26.2	− 25.8
	B	− 31	− 31	− 31	− 31.2 [a]	− 30.8 [a]
	C [b]	− 34	− 34	− 34	− 34.4 [a]	−

[a] B and 'C' are formed in very small amounts.

[b] Paramagnetic perturbations appeared with C.

Table 2
Relative ratios of "CuCF$_3$" species formed in the presence of various reagents after a 3240 C electrolysis (3 h) and a 6480 C electrolysis (6 h) (with a current density of 15 mA cm^2)

	3240 C electrolysis				6480 C electrolysis			
	A (%)	B (%)	C (%)	yield [a] (%)	A (%)	B (%)	C (%)	Yield [a] (%)
PBu$_3$ (0.5)	43	33	24	61	43	35	22	25
PPh$_3$ (0.5)	13	44	43	28	29	39	32	31
dppe (0.3)	34	58	8	16	Trace	77	23	18
bipy (0.75)	100	Trace	–	24	93	7	Trace	30
tmeda (2.5)	100	–	–	3	100	Trace	–	4.5

[a] Yield based on a two-electron reduction of CF$_3$Br.

Depending on the nature of the potential ligand, the ^{19}F NMR analysis of the solution after electrolysis of CF$_3$Br indicates one, two or three CuCF$_3$ species (denoted A, B and C in Table 1). With phosphines, the three species are formed whereas, with amines, only A is obtained. However, when a large amount of electricity is consumed (more than 3000 C), very small amounts of B and traces of C are detected in the case of 2,2′-bipyridine. With tmeda, C is not observed.

From the ^{19}F chemical shifts of these species, A is more influenced by the nature of the proligand than are B and C. When bipyridine is added to the solution of "CuCF$_3$", which had been prepared in the presence of PBu$_3$, the signal at δ = − 27.3 ppm moved to δ = − 26.2 ppm whereas the signals assigned to B and C do not change. Likewise, when tmeda is added to such a solution, the signal at δ = − 27.3 ppm moves to δ = − 26 ppm. A is thus more easily complexed by potential ligands.

The variations on the chemical shifts of B and C are so small that interaction with the potential ligand cannot be confirmed although the relative proportion and the overall yields of CuCF$_3$ are influenced by (Table 2). As 1–2 F are needed to oxidize 1 mol of copper (Table 3), the faradaic yields of CuCF$_3$ and the nature of the species must also be influenced by the nature of the

ions generated at the copper anode (i.e. Cu$^+$, Cu^{2+} or a mixture of Cu$^+$ and Cu^{2+}).

The effects of bipy and PBu$_3$ on the oxidation of a copper anode have been investigated in a divided cell. The electro-oxidation of the anode under a current density of 26 mC cm^{-2} occurred at about 1 V (SCE) in DMF with 2,2′ = bipyridine (0.1 M) and [NBu$_4$][BF$_4$] (0.1 M) as the supporting electrolyte. At this very positive potential the anode is expected to be oxidized to Cu^{2+}. Nevertheless, rotating-disk voltammetric analysis at a gold electrode of the anodic solution showed a quasi-reversible redox system (Fig. 1) comparable with the Cu(I)–Cu(II) system obtained from cyclic voltammetry at a gold electrode of the [CuBr · (3bipy)] (Fig. 2). The voltammogram exhibited a reduction wave of an intensity equal to the sum of the waves attributable to the reduction of Cu(II) to Cu(I) and to the oxidation
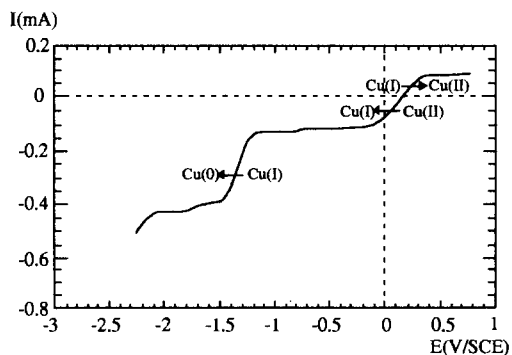
Table 3
Influence of reagent on the number of Faradays consumed per mole of copper oxidized

Reagent	PBu$_3$	PPh$_3$	dppe	bipy	tmeda
F (mole Cu)$^{-1}$	1.4	1.5	1.5	2	1

Fig. 1. Rotating-disk voltammetry at a gold electrode of the anodic solution (0.1 M of [NBu$_4$][BF$_4$] and 3 mmol of 2,2′-bipyridine in 30 ml of DMF) after the oxidation (193 C) of the copper rod.
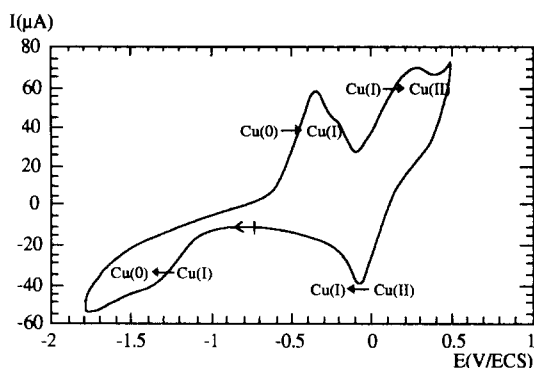
Fig. 2. Cyclic voltammetry with a gold electrode (disk of 0.03 cm² surface area; $v = 0.2$ V s^{-1}) of a solution of 2,2'-bipyridine (3 mmol), CuBr (1 mmol) and 0.1 M of [NBu$_4$][BF$_4$] in DMF (30 ml).

Fig. 4. Rotating-disk voltammetry at a gold electrode of the anodic solution (0.1 M of [NBu$_4$][BF$_4$] and PBu$_3$ 0.5 M in 30 ml of DMF) after the anodic oxidation (180 C) of a copper rod.

of Cu(I) to Cu(II). Cu(I) and Cu(II) are formed in a ratio 2:3. However, when the copper anode is oxidized under a lower current density (13 mC cm^{-2}) in the presence of 2,2'-bipyridine (0.75 M) in DMF, a Cu(I):Cu(II) ratio of 9:1 is revealed by linear voltammetric analysis (Fig. 3).

In the case of the electro-oxidation of the anode in a solution of PBu$_3$ (0.5 M in DMF), only a Cu(I) complex is revealed by the linear voltammetric analysis (Fig. 4). The latter is oxidized at almost 0.8 V (SCE) and is at once followed by the oxidation of PBu$_3$ at around 0.9 V (SCE). The voltammogram also indicated three reduction waves between -1.7 and -2.4 V, not well defined, at least for the two first waves, and difficult to reproduce. The total intensity of the processes is almost equal to the oxidation step.

The Cu(I) in the solution is present because, close to proximity of the anode, the electrodissolution of the copper causes such an increase in Cu(II) that a conproportionation reaction with the metal becomes possible:

$$Cu(II) + Cu_{metal} \longrightarrow 2Cu(I)$$
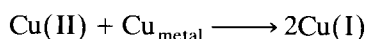
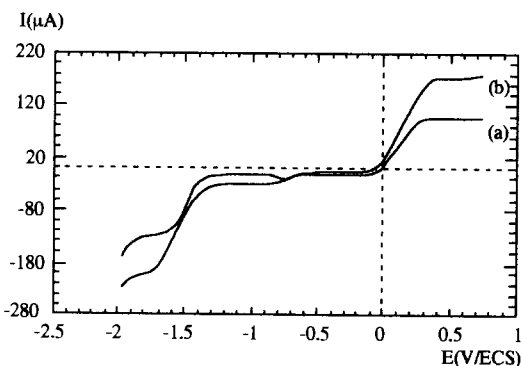Such a phenomenon is observed in the hydrometallurgy of copper [11].

Fig. 3. Rotating-disk voltammetry at a gold electrode of the anodic solution (0.1 M of [NBu$_4$][BF$_4$] and 0.75 M 2,2'-bipyridine in 30 ml of DMF) after the oxidation of a copper rod: curve (a), 50 C; curve (b), 100 C.
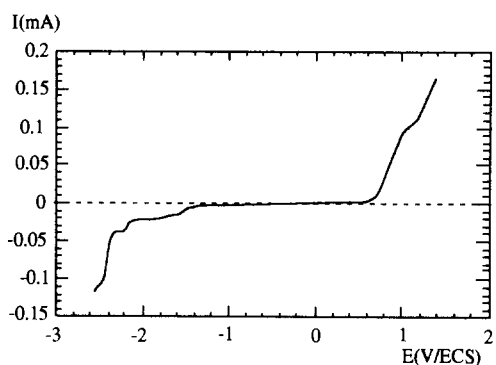
The relative stability of Cu$^+$ and Cu^{2+} in the presence of copper metal is very sensitive to the solvent. Either Cu(I) or Cu(II) can be formed alone, depending on the solvent. This is due to the difference between their relative free energies of solvation [12].

Under our electrochemical conditions, 2,2'-bipyridine stabilizes Cu(I) more strongly than Cu(II) in the presence of copper metal. This stabilization is favoured, since the applied charge density at the anode is low. With PBu$_3$, Cu(I) is stabilized even more with respect to Cu(II).

2.2. Oxidation states of "CuCF$_3$" species and mechanism of formation

When a solution of "CuCF$_3$", prepared in the presence of PBu$_3$ is oxidized with iodine under argon, A and B disappear whereas C is unaffected. These results suggest that A and B are Cu(I) species, and C may be a Cu(II) or a Cu(I) species strongly complexed.

To determine the nature of "CuCF$_3$" species and their mechanisms of formation, we examined the phenomena that occurred during the electroreduction of CF$_3$Br in the presence of a copper anode and different potential ligands.

2.2.1. Tetramethylethylenediamine

A small quantity of A (1.5 mmol) and traces of B were formed in a 4:1 mixture of DMF and tmeda after a 7560 C electrolysis. Very little fluoroform and a fine suspension of Cu(0) in the solution were also observed [13]. As 1 F is consumed per mole of copper lost by the anode [14], obviously only Cu(I) is released by the anodic process. Therefore the suspension of Cu(0) resulted from the reduction of Cu(I) and the two "CuCF$_3$" species are copper(I) complexes, formed as follows: at the anode,
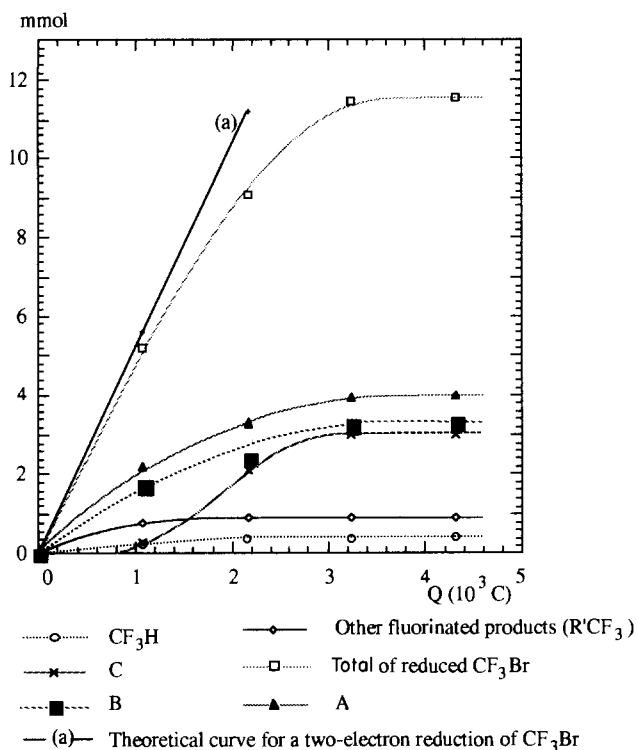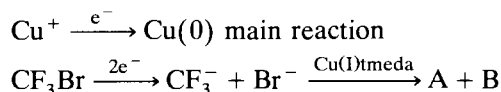
$$Cu \xrightarrow{-2e^-} Cu^{2+}$$

$$Cu^{2+} + Cu_{metal} \rightarrow 2Cu^+ \quad \text{complete conproportionation}$$
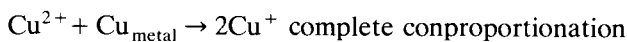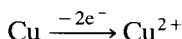
Fig. 5. Formation of trifluoromethyl products followed by ^{19}F NMR spectroscopy (4,4'-bifluorobiphenyl is used for ^{19}F NMR internal calibration) during the electrolysis of CF_3Br in the presence of PBu_3 (0.5 M) and a copper anode: O······O, CF_3H; ◇———◇, other fluorinated products ($R'CF_3$); ×———×, C; □······□, total of reduced CF_3Br; ▲------▲, B; ▼------▼, A; ———, curve (a), theoretical curve for a two-electron reduction of CF_3Br.
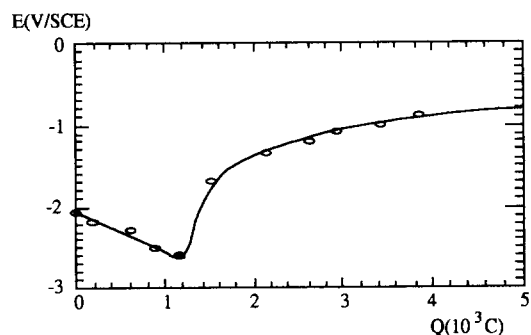

Fig. 6. Variation in the cathodic potential during the electrolysis.

It is interesting to correlate the variations in the cathodic potential (Fig. 6) with the evolution of the trifluoromethylated species during the electrolysis. As long as the potential is sufficiently negative (-1.3 V or less), i.e. during the first 2.5 h. CF_3Br is reduced with a good yield, and 95% of the CF_3Br is reduced within the first hour assuming a two-electron reduction. The yield of "$CuCF_3$" as A and B is also good, 41% 34% respectively, with only 5% in C form [15]. We assume that the oxidation of Cu to Cu(I) is the main anodic reaction during this period and that the cathodic reaction is the reduction of CF_3Br to "CF_3^-". In the solution, Cu(I) would combine with "CF_3^-" to yield "$CuCF_3$" as A and B.

After 3 h electrolysis the cathodic potential stabilized at the reduction potential of Cu(II), around -0.8 V. CF_3Br is not reduced at this potential and the anode is probably oxidized to Cu(II). During the second hour of electrolysis the anode would be oxidized to a mixture of Cu(I) and Cu(II). Clearly, C is formed mainly during this period, when the potential varied from -2.5 to -1 V. It also arises from the reduction of CF_3Br because no more is formed when CF_3Br is not consumed, and it forms only when a mixture of Cu(I) and Cu(II) results from the anodic process. Therefore we propose that C is a copper(II) complex. Moreover, C does not arise from the oxidation of A and B since its concentration increases with increasing

and, at the cathode,

$$Cu^+ \xrightarrow{e^-} Cu(0) \text{ main reaction}$$

$$CF_3Br \xrightarrow{2e^-} CF_3^- + Br^- \xrightarrow{Cu(I)tmeda} A + B$$

2.2.2. PBu_3

Fig. 5 shows the evolution of different fluorinated species in the case of PBu_3 (0.5 M) during the electrolysis. After about 3500 C have passed, no more "$CuCF_3$" species are formed.

Table 4
Proposed mechanism

| | Free PBu_3 in solution | | |
	High	Low	Approximately zero
At the anode	$Cu \xrightarrow{-2e^-} Cu^{2+}$	$Cu \xrightarrow{-2e^-} Cu^{2+}$	$Cu \xrightarrow{-2e^-} Cu^{2+}$
	$Cu^{2+} + Cu_{metal} \rightleftharpoons 2Cu^+$ (mainly Cu^+)	$Cu^{2+} + Cu_{metal} \rightleftharpoons 2Cu^+$ (Cu^+-Cu^{2+} mixture)	(mainly Cu^{2+})
At the cathode	$CF_3Br \xrightarrow{2e^-} CF_3^- + Br^-$	$Cu^{2+} \xrightarrow{2e^-} Cu(0)$	$Cu^{2+} \xrightarrow{2e^-} Cu(0)$
	$\downarrow Cu(I)$	$CF_3Br \xrightarrow{2e^-}_{Cu(II)} CF_3^- + Br^-$	(no "$CuCF_3$")
	$A + B$	C ↙ ↘ Cu(I) $A + B$	

concentrations of A and B. It is formed only as long as CF_3Br is reduced in the presence of Cu(II).

A and B are not formed after some time because Cu(II) is formed instead of Cu(I), which is no longer stabilized. This change in the stabilization of the copper ions is attributable to the decreasing amount of free PBu_3 in the solution. Originally Bu_3 was introduced in an amount of 20 mmol and it complexes "$CuCF_3$" and CuBr. However, as its concentration drops, it becomes insufficient to stabilize the copper(I). The yield of "$CuCF_3$" is inevitably restricted by the concentration of PBu_3 which cannot exceed 0.5 M, the limit of solubility in DMF.

In short, the proposed mechanism is as given in Table 4.

2.2.3. 2,2'-bipyridine

^{19}NMR analyses during the electrosynthesis of "$CuCF_3$" in the presence of 2,2'-bipyridine (0.75 M) show that A is formed all the time. B appeared after about 2000 C in low quantity, and traces of C after 3000 C (Fig. 7). However, the total amount of "$CuCF_3$" is limited by the concentration of bipy [16].

2 F are consumed per mole of copper lost by the anode [17], and the anode is oxidized to Cu(II). Nevertheless, rotating-disk voltammetric analysis at a gold electrode of a solution containing 1 mmol of A reveals no complex of Cu(II) with bipy (Fig. 8). The voltammogramm shows an oxidation wave with $E_{1/2} = 0.16$ V (SCE) and a reduction wave of the same intensity with $E_{1/2} = -1.65$ V (SCE).

We assume that A, a copper(I) complex, results from the simultaneous electroreduction of CF_3Br and a complex of Cu(II) with bipy formed at the anode.
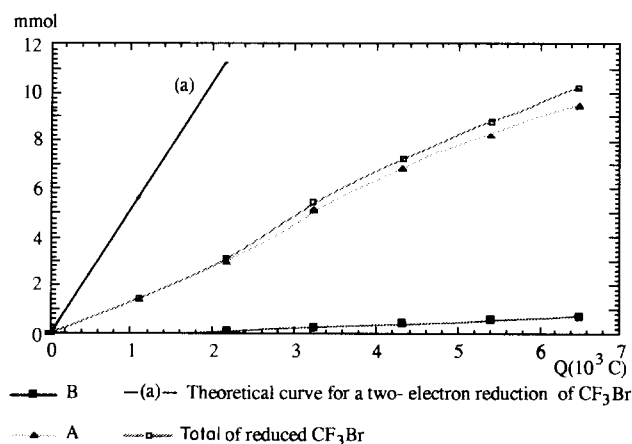
Fig. 7. ^{19}F NMR analysis (4,4'-bifluorobiphenyl is used for ^{19}F NMR internal calibration) of the electrosynthesis of "$CuCF_3$" in the presence of 2,2'-bipyridine (0.75 M): ■———■, B; ▲———▲, A; □———□, total of reduced CF_3Br; ———, curve (a), theoretical curve for a two-electron reduction of CF_3Br. Traces of C are also detected after almost 300°C.
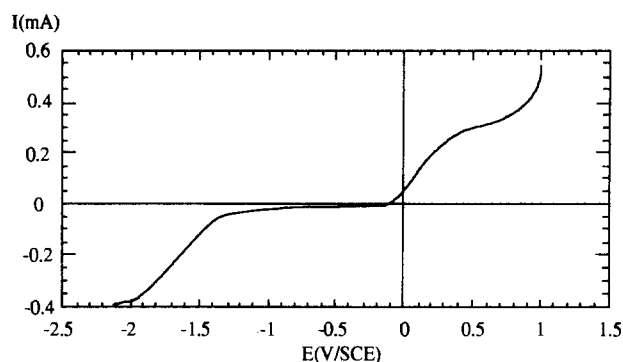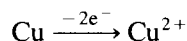
Fig. 8. Rotating-disk voltammetry at a gold electrode of a solution of DMF containing 0.1 M [NBu$_4$][BF$_4$] and 1 mmol of a solution of "$CuCF_3$"-bipy.

The cathodic potential varied progressively from -1.7 to -1 V (SCE) during the electrolysis. Presumably in this range of potentials, CF_3Br and the copper(II) complex are reduced, to "CF_3^-" and a copper(I) complex of bipy.
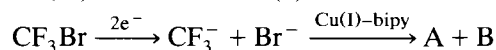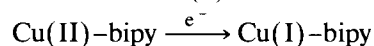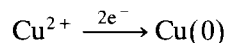
In the case of a solution of DMF-bipy (0.5 M), the cathodic potential reached a maximum of -0.8 V, corresponding to the reduction potential of uncomplexed copper(II) after nearly 6000 C electrolysis. No more more "$CuCF_3$" was then formed.

In conclusion, the proposed mechanism is as follows:

at the anode,

$$Cu \xrightarrow{-2e^-} Cu^{2+}$$

and, at the cathode,

$$Cu^{2+} \xrightarrow{2e^-} Cu(0)$$

$$Cu(II)-bipy \xrightarrow{e^-} Cu(I)-bipy$$

$$CF_3Br \xrightarrow{2e^-} CF_3^- + Br^- \xrightarrow{Cu(I)-bipy} A + B$$

2.3. Reactivities of "$CuCF_3$" with organic halides

The "$CuCF_3$" complexes prepared from the electroreduction of CF_3Br in the presence of a copper anode and different L were coupled with various organic halides RX at 80-100°C under argon:

$$CF_3Br \xrightarrow[e^-, DMF, L, [NBu_4]Br \, (1 \, mmol), \, -15°C]{Cu \, anode, \, stainless \, steel \, cathode} \text{"}CuCF_3\text{"}L$$

$$\xrightarrow[\Delta]{RX} RCF_3$$
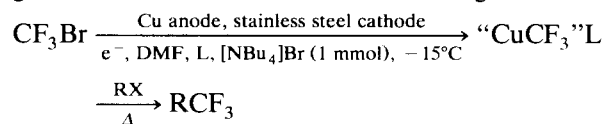
where $L=PBu_3$ or bipy.

The results with aromatic and heteroaromatic halides, summarized in Table 5 (entries 1-14), complete those published in a previous paper (see [6]). The effects of substituents on the aromatic rings on the coupling reaction and the formation of perfluoroalkylated side products has been discussed already by others (see Ref. [3] and references cited therein).

"CuCF$_3$" complexed by bipy was used to trifluoromethylate some vinylic, benzylic and allylic halides. Very good yields of trifluoromethylated products were obtained with the vinylic halide α-bromocinnamaldehyde (86%) and β-bromostyrene (98%) (Table 5, entries 15–17). Lower yields (68%) was obtained with α-bromostyrene. In this case, the coupling reaction was carried out only at 70°C because of the thermal lability of the halide.

The coupling reaction is found to be stereoselective: a mixture of Z/E-β-trifluoromethylstyrene in a ratio 13:87 was obtained from a mixture of Z/E β-bromostyrene of ratio 15:85.

Substituted benzylic bromides gave also very good yields of substituted products and even the chlorine homologue gave quite good yields. However, the coupling reaction is strongly influenced by steric hindrance (Table 6, entries 1–7). When the aromatic ring bears a substituent in the 2-position or the methylene group is substituted, the yield drops to 32% and about 0% respectively. Electron-withdrawing substituents at the 4-position of the aromatic rings do not favour the coupling reaction.

As regards the allylic halides (Table 6, entries 8–12), reactions were carried out between 30 and 60°C in order to minimize dimerization reactions and the ther-

Table 5
Coupling reaction of electrogenerated "CuCF$_3$" with aromatic, heteroaromatic and vinylic halides

Entry	ArX (10 mmol)	Ligand	T (°C)	t (h)	ArCF$_3$ [a] isolated yield (%)
1	3,5-Dichlorobromobenzene	PBu$_3$	90	12	20
2	2'-Bromoacetophenone	bipy	90	5	60 [b]
3	3'-Bromoacetophenone	bipy	100	12	17
4	4'-Bromoacetophenone	bipy	90	5	56
5	Methyl 2-iodobenzoate	bipy	80	3	90
6	Methyl 2-bromobenzoate	PBu$_3$	80	5	77
7	Methyl 3-bromobenzoate	bipy	100	12	25
8	Methyl 4-chlorobenzoate	bipy	100	12	15
9	3-Bromobenzonitrile	bipy	100	12	28
10	2-Bromobenzonitrile	bipy	90	12	51 [c]
11	2-Bromonitrobenzene	bipy	80	5	90
12	2-iodothiophene	bipy	80	3	60 (95) [d]
13	2-Bromothiophene	bipy	80	12	(30) [d]
14	3-Bromothiophene	bipy	80	12	Trace
15	α-bromostyrene	bipy	70	12	60
16	β-bromostyrene (Z/E-15/85)	bipy	80	5	90 Z/E-13/87
17	α-bromocinnamaldehyde	bipy	80	5	80

[a] Mainly starting halide and traces (gas chromatography (GC) yield) of hydrogenation and pentafluoroethylated byproducts were recovered.
[b] 17% (GC yield) of acetophenone were also formed.
[c] 10% (GC yield) of benzonitrile were also formed.
[d] GC yield in parentheses.

Table 6
Coupling reaction of electrogenerated CuCF$_3$–bipy complex with benzylic and allylic halides

Entry	Substrate (10 mmol)	T (°C)	t (h)	RCF$_3$ [a] isolated yield (%)
1	α-Bromotoluene	80	5	83
2	α-Chlorotoluene	85	5	50
3	α-Bromo-o-xylene	80	12	20
4	α-Bromo-α'-(methyl)toluene	80	12	trace
5	α-Bromo-3-cyanotoluene	80	12	50
6	α-Bromo-3-bromotoluene	70	3	18
7	α-Bromo-4-nitrotoluene	90	1N	(1) [b]
8	Crotyl bromide (Z + E)	35	2	(73) [c] 30: Z+E
9	3,3-Dimethylallyl bromide	30	3	(72) [c] 30
10	1-phenyl-4-bromobutene	60	3	85
11	β-Methallyl chloride	30	5	(50) [c] 32
12	3-Bromocyclohexene	60	1N	–

[a] Mainly dimers were formed as the byproduct, except for entries 5, 7 and 12 where the starting material were recovered.
[b] GC yield.
[c] Yield calculated by ^{19}F NMR spectroscopy with 4,4'-bifluorobiphenyl added as a standard.

mal degradation of the halides. The yields of trifluoromethylated products, as determined by ^{19}F NMR spectroscopy vary from good to excellent. The low isolated yields are due to the great volatility of the trifluoromethylated products, except for 1-phenyl-4,4,4,-trifluorobutene.

Attempts to couple "CuCF$_3$"–bipy with alkyl halides (C$_7$H$_{15}$Br, C$_9$H$_{19}$Br and C$_9$H$_{19}$I) were unsuccessful.

3. Conclusion

(Trifluoromethyl)copper complexes have been prepared with reasonable yields from the cheap reagent CF$_3$Br in the presence of a sacrificial copper anode and a phosphine or a diamine under mild conditions. The part played by the proligand in determining the number, proportions and yields in the electrochemical formation of the "CuCF$_3$" species - is discussed. In the anodic oxidation process conproportionation can occur. Three "CuCF$_3$" species (A, B and C) can be obtained. With diamines (tmeda and bipy), A is formed selectively, and with phosphines (PBu$_3$, PPh$_3$ and dppe), A, B and C are formed. A and B are copper(I) complexes and C a cupric copper(II) complex. Coupling with various organic halides other than alkyl halides, is achieved with reasonable yields.

The simplicity of the electrolysis procedure makes this route an attractive alternative for the trifluoromethylation of a large variety of organic halides compared with the usual organometallic methods. An one-step procedure has been developed [18]. Work is in progress to valorize other chlorofluorocarbons by this method.

4. Experimental section

N,N-dimethylformamide (Prolabo) was distilled over anhydrous copper sulfate under reduced pressure and then dried over molecular sieve (4Å). The supporting electrolytes [NBu$_4$]Br (Fluka) and [NBu$_4$][BF$_4$] were dried under vacuum before used. The tmeda (Janssen) was distilled over BaO. Other reagents were obtained from Janssen, Fluka or Aldrich and generally used as received. Copper rods (diameter, 1.5, 1 and 0.6 cm) as anodes are available commercially (Ventron or Johnson Matthey), as is the stainless steel grid used as cathode.

The one-compartment electrolysis cell was a cylindrical glass vessel [19]. The two-compartment cell was two cylindrical glass vessels separated by a sintered glass (No. 4). An SCE was used as reference. Electrolyses were carried out using a stabilized constant current supply (Sodilec EDL 36-07) and the cathodic potentials were followed with a millivoltmeter (Minisis 5000). Electrochemical analyses were performed with an EGG-PARC 275A electrochemical set. ^{19}F NMR spectra were recorded on a Bruker (200 and 300 MHz) or a Varian T60 spectrometer. Mass spectra were recorded with an ITD 800 Finnigan spectrometer coupled to a gas chromatograph. Chemical shifts were referenced to tetramethylsilane and CFCl$_3$.

4.1. General procedure for electrosynthesis

Freshly distilled DMF (40 ml), [NBu$_4$]Br (1 mmol) and the proligand (2,2′-bipyridine (30 mmol) PBu$_3$ (20 mmol) or PPh$_3$ (20 mmol)) were introduced under argon into the electrolysis cell fitted with a copper anode (immersed to 2 cm) and a stainless steel grid as the cathode (20 cm^2 area). The cell was immersed in a cold bath ($-$15°C) and CF$_3$Br was bubbled through the solution. A constant current of 0.3 A was passed for 6 h (6500 C) with bipy or for 3.5 h (3800 C) with PBu$_3$ or PPh$_3$. The cell was then flushed with argon, fitted with a condenser and 10 mmol of organic halide were introduced in the solution. The cell was heated in an oil bath at 30–100°C for 3–5 h or overnight (for the very less reactive halides).

The solution was hydrolyzed (50 cm^3; 2 mol dm^{-1}), decanted, extracted with pentane or pentane–ether

(3 × 50 ml) and then dried over MgSO$_4$. The solvent was distilled off. The crude products were then purified by column chromatography (silica gel; 70–230 mesh) with pentane or pentane–ether as eluent. Trifluoromethylthiophen (Table 5, entry 12) and allylic (Table 5, entries 8, 9, 11 and 12) solutions were purified by distillation. All compounds had correct spectroscopic and analytical data.

References and notes

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[7] When the electrolysis was carried out in other complexing solvents (tetramethylurea or pyridine) without any other reagent or in a mixture with DMF, no "CuCF$_3$" species were formed except for pyridine where a trace of "CuCF$_3$" were detected. We found that only amide solvents such as DMF, dimethylacetamide and N-methylpyrrolidine suited to the preparation of "CuCF$_3$" species in the presence of a complexing agent.
[8] Other simple donors such as R$_2$S (R = Me or Et), 2,3-toluidine and EtNMe$_2$ were tried without any success. Only traces of "CuCF$_3$" species were detected for the last two.
[9] 13.2 mmol of the copper rod were oxidized after a 2520 C electrolysis, i.e. 2 F mol^{-1} of Cu.
[10] CF$_3$Br is reduced at $-$1.9 V (SCE) at a stainless steel electrode; see G.P. Andrieux, L. Gélis, M. Medebielle, J. Pinson and J.M. Savéant, *J. Am. Chem. Soc.*, 112 (1990) 3509.
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[13] No copper deposit is observed at the cathode.
[14] 78.3±10% mmol of electrons and 74 mmol of copper are consumed during a 7 h electrolysis at 300 mA.
[15] The rest of the reduced CF$_3$Br is protonated or reacts with the proligand.
[16] When the electrolysis is carried out in a solution of DMF containing 0.5 M bipy, the formation of "CuCF$_3$" stopped after almost 6000 C.
[17] 37.3 mmol of copper are oxidized in a 7560 C electrolysis.
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