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Electrochemical synthesis of trifluoromethylcadmium and trifluoromethylzinc species using bromotrifluoromethane and sacrificial anodes

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Abstract

Trifluoromethylcadmium and trifluoromethylzinc species are easily prepared by electrolysis of bromotrifluoromethane in dimethylformamide using a one-compartment cell fitted with a cadmium or zinc anode. Both CF_3CdBr and $(CF_3)_2Cd$ result from the chemical reaction of CF_3Br with cadmium electrodeposited on the cathode. The formation of trifluoromethylzinc species involves a much more complex mechanism. Chemical corrosion of the electroscored zinc anode occurs; if the zinc anode is afterwards used as the cathode, the formation of CF_3ZnBr and $(CF_3)_2Zn$ increases significantly.

Keywords: Zinc; Cadmium; Electrochemical synthesis; Trifluoromethyl compounds

1. Introduction

Trifluoromethylcadmium and trifluoromethylzinc species are usually prepared by reaction of CF_3I [1] or CF_2X_2 (X=Cl or Br) [2] with the corresponding activated metals, or with dialkylcadmium [3] and dialkylzinc [4] respectively. Metathesis from $(CF_3)_2Hg$ [5] also provides access to trifluoromethylcadmium and trifluoromethylzinc species, but the toxicity of the mercury reagent makes this route less attractive. CF_3Br, a cheap and attractive source of trifluoromethyl, has been less used because of its low reactivity.

In the course of our work on the electrochemical activation of CF_3Br using sacrificial anodes [6], we have performed a simple and efficient electrosynthesis of trifluoromethylcadmium and trifluoromethylzinc species, $(CF_3)_2M$ and CF_3MBr (M=Cd or Zn). Electrolyses were carried out in a one-compartment cell, from a cold mixture of *N,N*-dimethylformamide (DMF) – CF_3Br in the presence of a cadmium or zinc anode and a stainless steel grid as the cathode, connected to a constant-current power supply. $(NBu_4)Br$ was used as supporting electrolyte in low concentration (3×10^{-2} mol l^{-1}). ^{19}F NMR analyses and cathodic potential measurements, performed during the electrolyses, have provided explanations for the formation of the organometallic species.

2. Results and discussion

2.1. *Trifluoromethylcadmium bromide and bis(trifluoromethyl)cadmium*

When CF_3Br is electroreduced in DMF in the presence of a cadmium anode, two trifluoromethylcadmium species are detected by ^{19}F NMR spectroscopy (−35 and −35.4 ppm referenced to $CFCl_3$ in DMF) corresponding to bis(trifluoromethyl)cadmium and (trifluoromethyl)cadmium bromide. The addition of $CdBr_2$ to a solution of trifluoromethylcadmium species results in an increase in the intensity of the peak at −35.4 ppm to the detriment of the peak at −35 ppm. We assume the occurrence of a Schlenk equilibrium:

$$2BrCdCF_3 \rightleftharpoons Cd(CF_3)_2 + CdBr_2$$

The signal at −35.4 ppm can be assigned to $BrCdCF_3$ and that at −35 ppm to $Cd(CF_3)_2$. These results are consistent with the literature [2].

The occurrence of a Schlenk equilibrium is corroborated by the following experiment. When iodine is added to a solution containing a mixture of $BrCdCF_3$ and $Cd(CF_3)_2$, there is slow formation of CF_3I, and a much more significant decrease in the amount of $Cd(CF_3)_2$ than of $BrCdCF_3$. The addition of iodine

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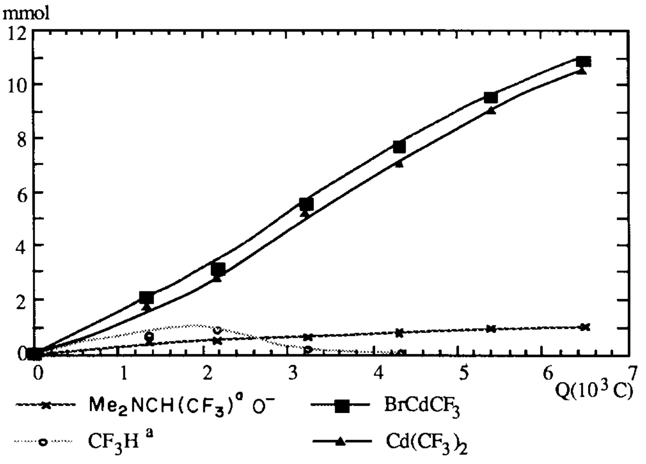

a ^{19}F NMR (in DMF, *vs.* CFCl$_3$): δ (Me$_2$NCH(O$^-$)CF$_3$) = -75.3 (large peak), δ (CF$_3$H) = -80 (d, J = 84 Hz).

Fig. 1.

gives BrCdI and less BrCdCF$_3$ via a Schlenk equilibrium, since (CF$_3$)$_2$Cd is consumed first when iodine is added.

Analysis of the formation of trifluoromethyl cadmium species during the electrolysis (Fig. 1) indicated that BrCdCF$_3$ and Cd(CF$_3$)$_2$ were formed in equal amounts, and that CF$_3$Br and the cadmium anode were reduced (Fig. 2) and oxidized respectively [7] in a two-electron process. No chemical corrosion of the cadmium anode by CF$_3$Br was detected. Faradaic yields, calculated on the basis of a two-electron reduction of CF$_3$Br, were 33% for BrCdCF$_3$ and 62% for Cd(CF$_3$)$_2$, i.e. 95% overall.

After an electrolysis involving a charge of 1080 C, the cathodic potential became stabilized at −0.8 V with respect to a saturated calomel electrode (SCE), much higher than the reduction potential of CF$_3$Br at a stainless steel electrode (−1.9 V (SCE)) [8] but very close to the reduction potential of Cd(II) salts to cadmium at gold or nickel electrodes (−1 V (SCE)).

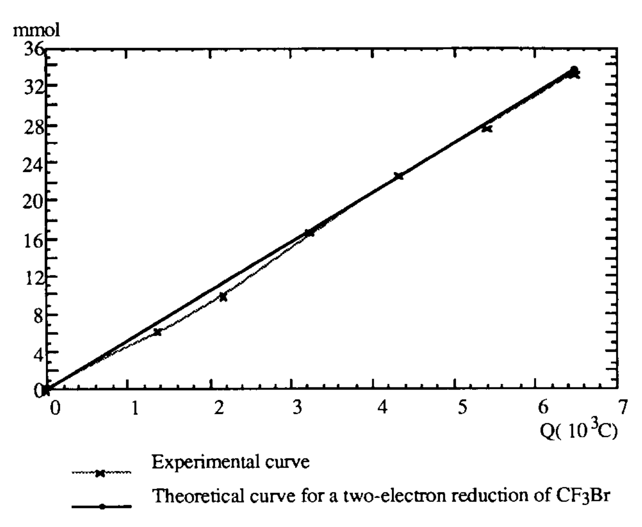

Fig. 2.

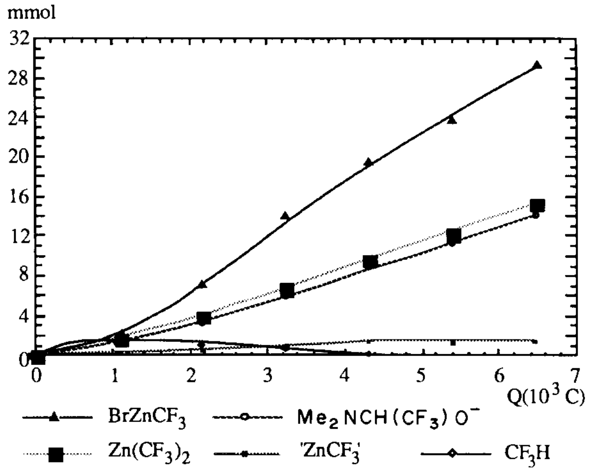

Fig. 3.

We propose that Cd(II), generated by the electrooxidation of the anode, is reduced at −0.8 V (SCE) at the cathode, forming Cd(0) in a form more reactive than massive cadmium, even when electrochemically scored. The CF$_3$Br should then react with Cd(0), leading to BrCdCF$_3$ and to Cd(CF$_3$)$_2$ via a Schlenk equilibrium (Scheme 1).

2.2. *Trifluoromethylzinc bromide and bis(trifluoromethyl)zinc*

In a previous paper [6b] we reported that unreactive side products BrZnCF$_3$ and Zn(CF$_3$)$_2$ were formed during the electrosynthesis of α-trifluoromethyl alcohols from the corresponding carbonyl compounds, CF$_3$Br and a sacrificial zinc anode in a mixture of DMF-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine used as solvent. The trifluoromethylzinc species can be prepared simply by electroreducing CF$_3$Br in the presence of a zinc anode, under the same conditions as for the electrosynthesis of trifluoromethylcadmium species. ^{19}F NMR analyses revealed the formation of two principal organozinc species with resonances at −42.0 and −42.8 ppm vs. CFCl$_3$ [10] (Fig. 3).

Unlike trifluoromethylcadmium species, the trifluoromethylzinc species do not react with I$_2$ or ZnBr$_2$ even if the latter is added in a large excess. Thus, in the absence of a Schlenk equilibrium between ZnBr$_2$, Zn(CF$_3$)$_2$ and BrZnCF$_3$, we cannot differentiate be-

anodic reaction: $\mathrm{Cd} \xrightarrow{-2e^-} \mathrm{Cd(II)}$
cathodic reaction: $\mathrm{Cd(II)} \xrightarrow{2e^-} \mathrm{Cd(0)}$
oxidative addition: $\mathrm{Cd(0)} + \mathrm{CF_3Br} \longrightarrow \mathrm{BrCdCF_3}$
Schlenck equilibrium:
$$2\mathrm{BrCdCF_3} \xrightleftharpoons[\text{equilibrium constant } K = 0.8\ [9]]{} \mathrm{Cd(CF_3)_2} + \mathrm{CdBr_2}$$

Scheme 1.

tween the mixed and the symmetrical organozinc species, as we did in the case of cadmium. However, these two species do not have the same reactivity towards dilute aqueous HCl. The compound giving the low field signal decomposes more rapidly than the other. We assume that this species is $Zn(CF_3)_2$ ($\delta = -42$ ppm) and that the other is $BrZnCF_3$ ($\delta = -42.8$ ppm). Moreover, if the intensities of both NMR signals are correlated with the loss of mass of the zinc rod, this assignment is more consistent with the overall expected trifluoromethylzinc species than the reverse assignment.

The aminoalcohol $Me_2NCH(CF_3)O^-$ was formed in almost the same amount as $BrZnCF_3$. Fluoroform, as well as a third trifluoromethylzinc species that we designated "$ZnCF_3$" [10], were also detected, but in small amounts.

Judged by the total amount of electricity passed, trifluoromethyl products are obtained in an overall faradaic yield of 220%, on the basis of a two-electron reduction of CF_3Br. Similarly, the loss of mass of the zinc rod is twice that expected for a two-electron oxidation [11]. Since it is unlikely that these trifluoromethyl products are formed via a one-electron electrochemical process, chemical reactions between the zinc anode and CF_3Br should occur while electrolysis proceeds. This phenomenon is enhanced if the applied current density is decreased. Thus, when the solution is electrolysed at 5 mA cm^{-2} instead of 15 mA cm^{-2}, trifluoromethyl products are obtained in a faradaic yield greater than 300%, with the proportions of products being unchanged.

We therefore conclude that in addition to the electrochemical anodic process

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

CF_3Br attacks the electroscored anodic zinc to yield trifluoromethylzinc species:

$$Zn + CF_3Br \longrightarrow BrZnCF_3 + Zn(CF_3)_2 + \cdots$$

The lower the current density, the greater is the chemical attack of the anode compared with its faradaic oxidation. However, this only takes place during the electrolysis and is not discernible when the current is off.

The cathodic potential (stainless steel or nickel cathode) during the electrolysis (Fig. 4) becomes constant after a period of induction at about −1.4 V (SCE), which is the formal reduction potential of Zn(II) into Zn(0) in DMF.

At the cathode, the main electrochemical reaction is

$$Zn^{2+} + 2e^- \xrightarrow[DMF]{-1.4\ V} Zn(0)$$

Since no metal deposit is observed on the cathode or in solution, Zn(0) must react rapidly with CF_3Br, leading to the trifluoromethylzinc species.

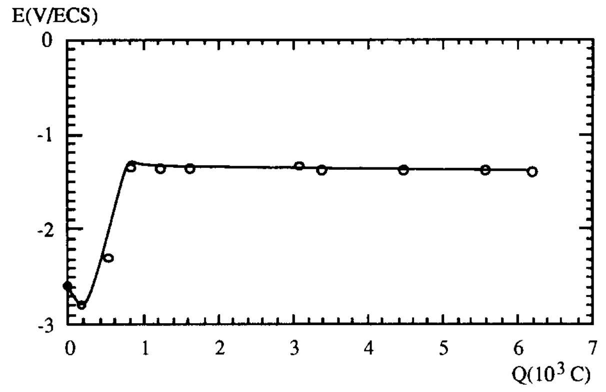

Fig. 4.

To confirm these inferences, we have carried out the electrolysis in a divided cell. Each compartment was fitted with an identical rod of zinc as electrode and contained the same solution (DMF, 30 ml; NBu_4BF_4, 0.2 M; CF_3Br). After a first electrolysis of the solution (total charge, 200 C), corresponding to a two-electron reduction of 1 mmol of CF_3Br (and to the oxidation of the zinc anode to form 1 mmol of Zn^{2+}), CF_3H and a few $Me_2NCH(CF_3)O^-$ are formed in the cathodic compartment, amounting to about 1 mmol. The formation of trifluoromethyl products is ascribed to electrolytic reduction of CF_3Br to CF_3^-, which reacts mainly with residual water to give CF_3H. In the anodic compartment, $BrZnCF_3$ and $Zn(CF_3)_2$ are formed in a 2:1 ratio. Traces of "$ZnCF_3$" and $Me_2NCH(CF_3)O^-$ are also detected. Almost 5 mmol of trifluoromethylzinc compounds are obtained. These trifluoromethylzinc species can result only from chemical attack on the electroscored anodic zinc by CF_3Br. The anodic solution also contains 1 mmol of Zn^{2+}. The polarity of the cell was then reversed and a new 200 C electrolysis carried out to reduce the 1 mmol of Zn(II) to Zn(0), with the expectation that the Zn(0) thus formed in the new cathodic compartment (ex-anodic compartment) would react with CF_3Br to yield at least 1 mmol of trifluoromethylzinc species. Much to our surprise, almost 5 mmol of trifluoromethylzinc species, mainly $BrZnCF_3$ and $Zn(CF_3)_2$, are formed. Undoubtedly the zinc cathode has been corroded.

Moreover, when the same electrolysis is carried out in a divided cell with $ZnBr_2$ added to the cathodic compartment, which is fitted with a stainless steel, a nickel or even a zinc cathode, no trifluoromethylzinc species are formed there. Clearly, the formation of trifluoromethylzinc species in the cathodic compartment fitted with a zinc electrode is related to the initial presence of zinc salts formed by oxidation of the zinc anode contact with CF_3Br.

3. Conclusion

Excellent yields of trifluoromethylcadmium ($BrCdCF_3$ and $Cd(CF_3)_2$) and trifluoromethylzinc ($BrZnCF_3$ and $Zn(CF_3)_2$) species were obtained from CF_3Br using the sacrificial anode process under mild and simple conditions. The mechanism of formation of $BrCdCF_3$ and $Cd(CF_3)_2$ has been elucidated. Electrochemical processes intervene only in the formation of an active Cd(0), which then reacts in a classical organometallic way with CF_3Br to form $BrCdCF_3$ and $Cd(CF_3)_2$ via a Schlenk equilibrium. The formation of $BrZnCF_3$ and $Zn(CF_3)_2$, is much more complex. In a single-compartment cell, $BrZnCF_3$ and $Zn(CF_3)_2$ result mainly from the chemical attack by CF_3Br on the electroscored zinc anode during the electrolysis. In a divided cell, trifluoromethylzinc species can also be formed in the cathodic compartment in the presence of a zinc electrode, CF_3Br and zinc salts formed by electro-oxidation of the electrode. In this case, an intermediate zinc species, chemically regenerated, probably intervenes in the corrosion of the cathode.

Trifluoromethylcadmium or trifluoromethylzinc species are inert towards most organic halides except allylic halides, with which trifluoromethylcadmium species react slowly to yield the corresponding trifluoromethylated products with a low yield (around 30%). Investigation of the electrochemical activation of trifluoromethylcadmium and trifluoromethylzinc species is currently under way.

4. Experimental section

DMF (Prolabo) was distilled over anhydrous copper sulphate, under reduced pressure, and then dried over molecular sieves (4 Å). The supporting electrolytes $(NBu_4)Br$ (Fluka) and $(NBu_4)BF_4$ were dried under vacuum before use. Zinc and cadmium rods (diameter, 1.2 or 0.8 cm), used as anodes, were commercially available (Ventron or Johnson Matthew) as well as the stainless steel grid and nickel sponge used as cathodes.

The one-compartment electrolysis cell was a cylindrical glass vessel [12]. The two-compartment cell was made of two cylindrical glass vessels separated by a sintered glass (No. 4). An SCE was used as the reference electrode. Electrolyses were carried out using a stabilized constant current power supply (Sodilec EDL 36-07) and the cathodic potential was monitored using a millivoltmeter (Minisis 5000). ^{19}F NMR spectra were recorded on a Varian T60 spectrometer. Chemical shifts are referenced to $CFCl_3$.

4.1. General procedure for electrosynthesis

Freshly distilled DMF (35 ml), $(NBu_4)Br$ (1 mmol) and 4,4′-bifluorobiphenyl (2 mmol) for ^{19}F NMR internal calibration were introduced into the electrolysis cell fitted with a cadmium or zinc anode and a stainless steel grid as the cathode (area, 20 cm^2). The cell was immersed in a cold bath (−15°C) and CF_3Br was bubbled through the solution. Electrolysis was performed at constant current of 0.3 A.

The formation of trifluoromethyl compounds was monitored by ^{19}F NMR analysis of aliquots from the electrolysed solution. All operations were carried out under argon or CF_3Br.

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[7] 37.9 mmol of the cadmium rod were oxidized after 6 h of electrolysis at 0.3 A, i.e. about 2 F mol^{-1} of Cd.

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[9] Calculation of K at 15–20°C: $[CdBr_2] = [Cd(CF_3)_2]$ and $[Cd(CF_3)_2]/[BrCdCF_3] = 0.91$; thus $K = [Cd(CF_3)_2][CdBr_2]/[BrCdCF_3]^2 = 0.8$.

[10] ^{19}F NMR (in DMF vs. $CFCl_3$): δ $(Zn(CF_3)_2) = -42.8$; δ $(BrZnCF_3) = -42$; δ ("$ZnCF_3$") $= -40.2$; δ $(Me_2NCHCF_3(O^-)) = -75.3$ (broad peak).

[11] After 6 h of electrolysis at 0.3 A, 73.8 mmol of trifluoromethyl compounds were formed (i.e. about 1 F mol^{-1} of CF_3Br) and 73 mmol of the zinc rod were oxidized (i.e. about 1 F mol^{-1} of Zn).

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