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Formation of trifluoromethyl cadmates: ^{19}F and ^{113}Cd NMR spectroscopic investigations *

Dieter Naumann * **and Wieland Tyrra**

Fachbereich Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50 (F.R.G.)

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Abstract

The reactions of $Cd(CF_3)_2$ complexes with MX (M = alkali metal, X = halogen) in polar solvents yield initially the complex anions $[Cd(CF_3)_2X \cdot D]^-$ and $[Cd(CF_3)_3 \cdot D]^-$ (D = donor molecule). After some days $[Cd(CF_3)_4]^{2-}$ is also formed. The anions have been identified by ^{19}F and ^{113}Cd NMR spectroscopy. The chemical shifts, and especially the coupling constants $^2J(^{111,113}Cd, ^{19}F)$, are strongly dependent on the number of CF_3 groups bound to Cd.

Introduction

Although halogenocadmates have been known for a long time, only few organohalogeno and perfluoroorganohalogeno cadmates have been reported [1]. Osman and Tuck [2] described the syntheses of $[(n\text{-}C_3H_7)_4N][Cd(CF_3)I_2]$ and $[(n\text{-}C_3H_7)_4N][CdBr_2(C_6F_5)]$, as well as a number of non-fluorinated compounds formed by electrochemical reactions in acetonitrile:

$$CF_3I + Cd + [(n\text{-}C_3H_7)_4N]I \rightarrow [(n\text{-}C_3H_7)_4N][Cd(CF_3)I_2]$$

$$C_6F_5Br + Cd + [(n\text{-}C_3H_7)_4N]Br \rightarrow [(n\text{-}C_3H_7)_4N][CdBr_2(C_6F_5)]$$

$Cd(CF_3)_2$ complexes have been recently shown to act as excellent polar trifluoromethylation reagents [3]. Thus, we succeeded in preparing $[Ag(CF_3)_4]^-$, the first trifluoromethylargentate, by the reaction of $AgNO_3$ with $Cd(CF_3)_2 \cdot 2CH_3CN$ in CH_3CN [4]. It was therefore of interest to investigate whether the neutral complex ligands in $Cd(CF_3)_2$ complexes could undergo exchange with anionic complex ligands to form the corresponding trifluoromethylcadmates. For this purpose we investigated the reactions of some $Cd(CF_3)_2$ complexes with mainly alkali metal halides.

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* Dedicated to Professor Friedo Huber on the occasion of his 60th birthday.

Results and discussion

We obtained the first indications of the formation of trifluoromethyl cadmates in NMR spectroscopic investigations of the reaction mixtures obtained from $Cd(CF_3)_2$ complexes and Et_4NCl, Ph_4PCl, Ph_4AsCl, and Ph_4SbOSO_2R, when we observed unexpectedly small absolute values of the spin–spin coupling constants $^2J(^{111,113}Cd, {}^{19}F)$ (see Table 1).

Whereas by electrochemical preparative methods only $[CdCF_3I_2]^-$ could be obtained [2], we were able to identify the first bis-, tris- and tetrakis-(trifluoromethyl)cadmates when we treated $Cd(CF_3)_2$ complexes with alkali metal halides. All the reactions gave product mixtures containing trifluoromethyl cadmates. The resulting compounds are extremely sensitive to moisture and almost insoluble in most of the common organic solvents (e.g. CH_3CN, pyridine, DMSO). The product mixtures could be separated, but the isolation of pure compounds was not possible.

Figure 1 shows a typical ^{19}F NMR spectrum of a product mixture. An increase in the number of CF_3 groups bound to Cd leads to a low-field shift as well as a decrease in the absolute value of the coupling constant $^2J(^{111,113}Cd, {}^{19}F)$. The number of CF_3 groups bound to Cd can be determined from the splitting of the ^{13}C

Table 1

^{19}F NMR data of trifluoromethyl cadmium compounds

Compound	$\delta(^{19}F)$ [a]	$^2J(^{111,113}Cd, {}^{19}F)$ (Hz)
$Cd(CF_3)_2 \cdot$ Glyme	−37.20	448/469
$Cd(CF_3)_2 \cdot 2CH_3CN$	−36.22	446/466
$Cd(CF_3)_2 \cdot 2DMSO\text{-}d_6$	−31.66	369/382
$Cd(CF_3)_2 \cdot 2Py$	−32.10	356/372
$Cd(CF_3)_2 \cdot$ Glyme/CsX/CH_3CN		
$[Cd(CF_3)_2Cl \cdot Glyme]^-$	−36.80	431/448
$[Cd(CF_3)_2Br \cdot Glyme]^-$	−36.16	408/426
$[Cd(CF_3)_2I \cdot Glyme]^-$	−36.40	398/416 [b]
$[Cd(CF_3)_3 \cdot Glyme]^-$	−32.80	268/281 [c]
$Cd(CF_3)_2$ in CH_2Cl_2/MX (M = Rb, Cs)/DMSO-d_6		
$Cs^+ [Cd(CF_3)_2Cl \cdot DMSO]^-$	−31.53	305/318
$Rb^+ [Cd(CF_3)_2I \cdot DMSO]^-$	−32.58	317/332
$Rb^+ [Cd(CF_3)_3 \cdot DMSO]^-$	−30.16	250/261
$Cs^+ [Cd(CF_3)_3 \cdot DMSO]^-$	−29.77	250/261
$[Cd(CF_3)_3 \cdot D]^-$ [d]		
$[Cd(CF_3)_3 \cdot Glyme]^-$ in CH_3CN	−32.80	268/281 [e]
$[Cd(CF_3)_3 \cdot CH_3CN]^-$ in CH_3CN	−30.98	240/251 [f]
$[Cd(CF_3)_3 \cdot DMSO]^-$ in DMSO	−30.85	259/270
$[Cd(CF_3)_3 \cdot Py]^-$ in pyridine	−30.95	252/264
$[Cd(CF_3)_4]^{2-}$		
in CH_3CN	−28.08	189/197
in Glyme/CH_3CN	−28.18	190/199

[a] In ppm, relative to CCl_3F. [b] $^1J(F,C)$ 375 Hz, quart, $^4J(F,F)$ 1.4 Hz. [c] $^1J(F,C)$ 378 Hz, d, sept, $^4J(F,F)$ 1.7 Hz. [d] With the cations Rb^+, Cs^+, Et_4N^+, Ph_4P^+, Ph_4As^+, Ph_4Sb^+. [e] $^1J(F,C)$ 377.9 Hz, d, sept, $\Delta\delta = 0.1441$ ppm [6], $^4J(F,F)$ 4.0 Hz. [f] $^1J(F,C)$ 383.5 Hz, d, sept, $\Delta\delta = 0.1447$ ppm [6], $^4J(F,F)$ 4.1 Hz.

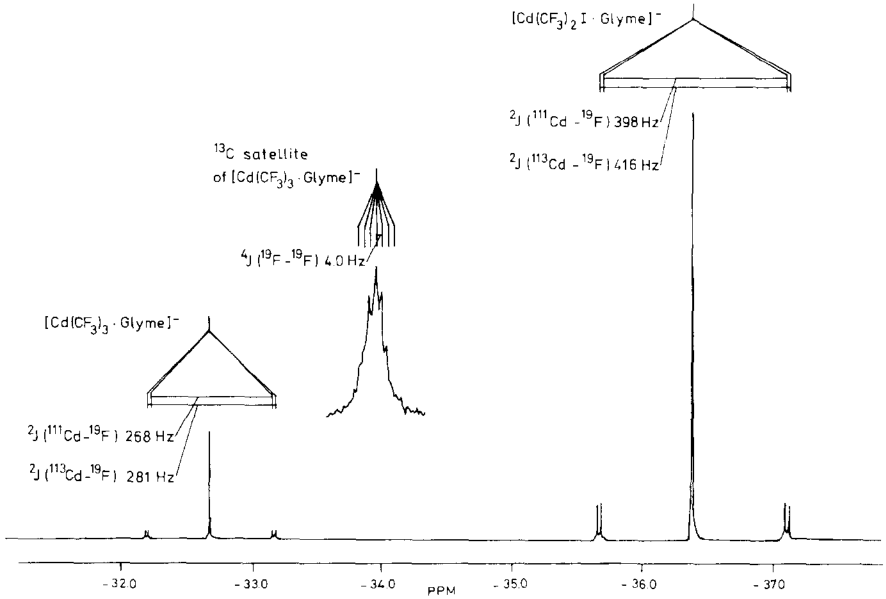

Fig. 1. ^{19}F NMR spectrum of [Cd(CF$_3$)$_2$I · Glyme]$^-$ and [Cd(CF$_3$)$_3$ · Glyme]$^-$ (CH$_3$CN; standard CCl$_3$F, ext.).

satellites in the ^{19}F NMR spectra and from the ^{113}Cd resonances; these splittings make possible unambiguous identification of the trifluoromethyl cadmates.

The primary products of the reactions of Cd(CF$_3$)$_2$ compounds with alkali metal halides are bis- and tris-(trifluoromethyl)cadmates, which show a significant low-field shift in the ^{19}F NMR spectra relative to that of the starting material as well as a decrease in the coupling constant ^2J(Cd, F). Only trace amounts of [Cd(CF$_3$)$_4$]$^{2-}$ are formed when the suspensions are stirred for several days.

The spectra of the trifluoromethyl cadmates are discussed in detail below.

Bis(trifluoromethyl)halogeno cadmates [Cd(CF$_3$)$_2$X · D]$^-$

The^{19}F and ^{113}Cd NMR spectra are shown in Figs. 1 and 2, and the NMR data are summarized in Tables 1, 2 and 3. The splitting of the ^{13}C satellites into quartets in the ^{19}F NMR spectrum (A$_3$A$'_3$X system) and the splitting of the ^{113}Cd signal into a septet shows the presence of two equivalent CF$_3$ groups bound to Cd. The decrease of the coupling constants ^2J(Cd, F) in the series Cl > Br > I indicates that in addition to the two CF$_3$ groups there is also a halogen atom bound to Cd.

This change is comparable to that observed in the NMR spectra of trifluoromethylmercury halides [5] (Table 4).

The dependence of the chemical shifts δ(^{19}F) and the coupling constants (^2J(Cd, F)) on the nature of the solvent permits the conclusion that a solvent molecule is also coordinated to the cadmium atom; the anion can therefore be formulated as [Cd(CF$_3$)$_2$X · D]$^-$.

Tris(trifluoromethyl)cadmates [Cd(CF$_3$)$_3$ · D]$^-$

NMR spectra and data are given in Figs. 1 and 2 and Tables 1 and 2, respectively. That the compound is a tris(trifluoromethyl)cadmium species is proved

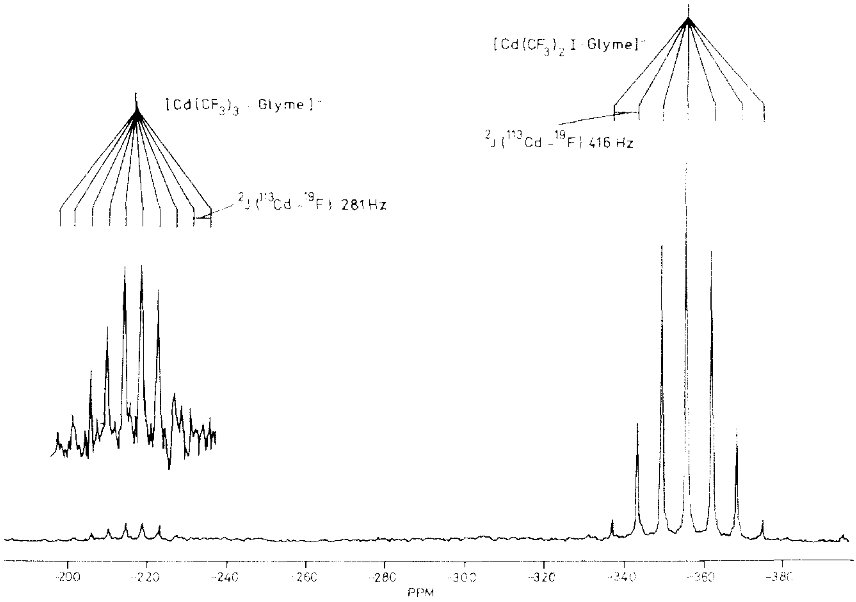

Fig. 2. ^{113}Cd NMR spectrum of [Cd(CF$_3$)$_2$I·Glyme]$^-$ and [Cd(CF$_3$)$_3$·Glyme]$^-$ (CH$_3$CN; standard 50% (CH$_3$)$_2$Cd in CDCl$_3$, ext.).

by the splitting of the ^{13}C satellites into septets in the ^{19}F NMR spectrum ($A_3A_6'X$ system) and that of the ^{113}Cd signal into a decet. The Cd atom is thus surrounded by three equivalent trifluoromethyl groups. The multiplicity of the signals does not

Table 2

^{113}Cd NMR data for trifluoromethyl cadmium compounds from the reactions of Cd(CF$_3$)$_2$·Glyme with CsX (X = Cl, I) in CH$_3$CN solutions

Compound	$\delta(^{113}\text{Cd})$ [a]	$^2J(^{113}\text{Cd}, ^{19}\text{F})$ (Hz)
Cd(CF$_3$)$_2$·Glyme	−465 sept	469
[Cd(CF$_3$)$_2$Cl·Glyme]$^-$	−449 sept	448
[Cd(CF$_3$)$_2$I·Glyme]$^-$	−356 sept	416
[Cd(CF$_3$)$_3$·Glyme]$^-$	−216 dec	281

[a] In ppm, relative to 50% (CH$_3$)$_2$Cd in CDCl$_3$; external, lock cyclohexane-d_{12}.

Table 3

Comparison of ^{113}Cd NMR data [a] for CdCl and CdCF$_3$ compounds

Compound	X = Cl/DMSO [b]	X = CF$_3$/CH$_3$CN
Cd^{2+}	−671.9	−655.5
CdX$^+$	−613.9	−593.1 [c]
CdX$_2$	−440.9	−482.0
[CdX$_3$]$^-$	−246.9	−216.0

[a] In ppm, relative to 50% (CH$_3$)$_2$Cd in CDCl$_3$; external, lock cyclohexane-d_{12}. [b] Ref. 7. [c] Product from reaction of Cd(CF$_3$)$_2$·Diglyme with TaF$_5$ in CH$_3$CN.

Table 4

Comparison of the coupling constants $^2J(^x\mathrm{E}, ^{19}\mathrm{F})$ ($^x\mathrm{E} = ^{199}\mathrm{Hg}, ^{113}\mathrm{Cd}$) of $HgCF_3X$ [5] and $CdCF_3X$ compounds

	$^2J(^{199}\mathrm{Hg}, ^{19}\mathrm{F})$ (Hz) $HgCF_3X/THF$	$^2J(^{113}\mathrm{Cd}, ^{19}\mathrm{F})$ (Hz)	
		$CdCF_3X \cdot Glyme/CH_3CN$	$[Cd(CF_3)_2X \cdot Glyme]^-/CH_3CN$
X = Cl	1912.6	525	448
Br	1862.2	506	426
I	1744.1	501	416
CF_3	1317.7	469	281

allow us to decide whether Cd in the $[Cd(CF_3)_3]^-$ anions has a threefold or fourfold (involving a solvent molecule) coordination. In both cases the CF_3 groups are magnetically equivalent and therefore the same multiplicities would be expected. But the chemical shifts and especially the coupling constants ^2J(Cd, F) depend on the nature of the solvent used, and so we can conclude that the complex anions have the formula $[Cd(CF_3)_3 \cdot D]^-$. The formation of tris(trifluoromethyl)halogeno cadmates $[Cd(CF_3)_3X]^-$ can be excluded since no dependence of the NMR data on the nature of the halogen is observed.

Tetrakis(trifluoromethyl)cadmate $[Cd(CF_3)_4]^{2-}$

When the mixture from reactions of $Cd(CF_3)_2 \cdot Glyme$ with CsI in CH_3CN is kept for some days a further signal, at −28.18 ppm, with $^2J(^{111,113}\mathrm{Cd}, ^{19}\mathrm{F}) = 190/199$ Hz, is present in the ^{19}F NMR spectrum. The absolute values of ^2J(Cd, F) are even smaller than those for the trifluoromethyl cadmates described above. Unfortunately neither further coupling information nor a ^{113}Cd NMR spectrum could be obtained because of the very low concentration of the compound. But a comparison with the coupling constants of the trifluoromethyl cadmates described above leads us to conclude that $[Cd(CF_3)_4]^{2-}$ has been formed (Table 5).

Summary

The account above shows that a careful interpretation of all available data from the NMR spectra, especially the hetero spin–spin coupling constants, can lead to

Table 5

Comparison of the coupling constants $^2J(^x\mathrm{E}, ^{19}\mathrm{F})$ ($^x\mathrm{E} = ^{111,113}\mathrm{Cd}, ^{107,109}\mathrm{Ag}$) of $CdCF_3$ and $AgCF_3$ compounds in CH_3CN solutions

Compound	$^2J(^{111,113}\mathrm{Cd}, ^{19}\mathrm{F})$ (Hz)	$^2J(^{107,109}\mathrm{Ag}, ^{19}\mathrm{F})$ (Hz)	Compound [a]
$CdCF_3^+$ [b]	534/559		
$CdCF_3I \cdot Glyme$	478/501	112/129	$AgCF_3 \cdot Glyme$ [c]
$Cd(CF_3)_2 \cdot Glyme$	448/469	88/101	$[Ag(CF_3)_2]^-$
$[Cd(CF_3)_2I \cdot Glyme]^-$	398/416	19.8/22.6 (*cis*) 79.1/91.6 (*trans*)	$Ag(CF_3)_3 \cdot NCCH_3$
$[Cd(CF_3)_3 \cdot Glyme]^-$	268/281	26.1/30.4 (*cis*) 62.8/72.4 (*trans*)	$[Ag(CF_3)_3Cl]^-$
$[Cd(CF_3)_4]^{2-}$	190/199	35.3/40.7	$[Ag(CF_3)_4]^-$

[a] From ref. 4. [b] NMR data from the reaction product of $Cd(CF_3)_2 \cdot Diglyme$ with TaF_5 in CH_3CN. [c] In pyridine solution.

unambiguous conclusions regarding the composition of new compounds of the types concerned even though they are not isolable. We always observe a distinct dependence of the hetero coupling constants on the number of CF_3 groups bound to Cd and on the chemical environment. A comparison with a series of trifluoromethylsilver compounds we prepared previously [4] indicates that this behaviour is not limited to the $CdCF_3$ compounds (Table 5).

Reaction process

Though we have no evidence for the reaction mechanism, the products identified suggest the following sequence of reactions (D = singly coordinating ligand):

$$CsX + Cd(CF_3)_2 \cdot 2D \rightleftarrows Cs^+[Cd(CF_3)_2X \cdot D]^- + D$$

$$[Cd(CF_3)_2X \cdot D]^- + Cd(CF_3)_2 \cdot 2D \rightleftarrows [Cd(CF_3)_3 \cdot D]^- + CdCF_3X \cdot 2D$$

$$2[Cd(CF_3)_3 \cdot D]^- \rightleftarrows [Cd(CF_3)_4]^{2-} + Cd(CF_3)_2 \cdot 2D$$

It is possible that $CsCF_3$ is formed as an intermediate according to

$$CsX + Cd(CF_3)_2 \cdot 2D \rightleftarrows \text{“}CsCF_3\text{”} + CdCF_3X \cdot 2D,$$

and then reacts with $Cd(CF_3)_2 \cdot 2D$ as follows

$$\text{“}CsCF_3\text{”} + Cd(CF_3)_2 \cdot 2D \rightarrow Cs^+[Cd(CF_3)_3 \cdot D]^- + D$$

This can neither be proved nor disproved from the NMR spectra.

Experimental

NMR spectra

Bruker FT NMR spectrometer AM 300; ^{19}F NMR: 282.4 MHz; ^{113}Cd NMR: 66.5 MHz; standards: CCl_3F (ext., ^{19}F), $(CH_3)_2Cd$ (50 Vol. % in $CDCl_3$, ext., ^{113}Cd).

Preparations

All reactions were carried out under dry nitrogen. Solvents and alkali metal halides were carefully dried by standard methods. Compounds $Cd(CF_3)_2 \cdot D$ (D = $2CH_3CN$, 2 pyridine, glyme) were prepared as previously described [3c].

Preparation of $Cd(CF_3)_2 \cdot 2(CH_3)_2SO$

A 2.5-fold molar excess of CF_3I was condensed on to a solution of 2 ml $(CH_3)_2Cd$ in 10 ml of CH_2Cl_2 at −196 °C. The solution was cautiously warmed to −78 °C and stirred at this temperature for about 1 h and then at −30 °C for about 48 h. Residual CF_3I and CH_3I were distilled off at −40 °C in vacuo. The stoichiometric amount of $(CH_3)_2SO$ was added to the colourless solution at −30 °C and the mixture was stirred until precipitation set in. Evaporation of the solvent under reduced pressure left $Cd(CF_3)_2 \cdot 2(CH_3)_2SO$ as a colourless solid.

General procedure for the preparations of trifluoromethyl cadmates

The $Cd(CF_3)_2$ complex was dissolved in an aprotic solvent at room temperature and an equimolar amount of the alkali metal halide was added. The mixture was stirred at room temperature for some hours, during which a white solid separated. The suspensions were investigated by ^{19}F and ^{113}Cd NMR spectroscopy.

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References

1 e.g. Gmelins Handbuch der Anorganischen Chemie, System-Nr. 33, 8. Aufl., Verlag Chemie, Weinheim, 1959.
2 A. Osman and D.G. Tuck, J. Organomet. Chem., 169 (1979) 255.
3 (a) E.K.S. Liu and L.B. Asprey, J. Organomet. Chem., 169 (1979) 249; (b) L.J. Krause and J.A. Morrison, J. Am. Chem. Soc., 103 (1981) 2995; (c) H. Lange and D. Naumann, J. Fluor. Chem., 26 (1985) 1; (d) L. Heinze and D.J. Burton, J. Fluor. Chem., 29 (1985) 359.
4 W. Dukat and D. Naumann, Rev. Chim. Min., 23 (1986) 589.
5 P.J. Goggin, R.J. Goodfellow, D.M. McEvan, A.J. Griffiths and V. Kessler, J. Chem. Res. (S), (1979) 194; J. Chem. Res. (M), (1979) 2315.
6 R.W. Harris, J. Mol. Spectr., 10 (1963) 301.
7 T. Drakenberg, N.D. Björk and R. Portanova, J. Phys. Chem., 82 (1978) 2423.